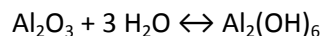# Measurement in CO2 with HTF™ Aluminum Oxide Technology
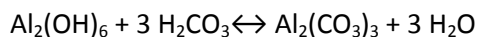
**The Basic Chemistry:**

Measurement of H2O in CO2 using the Xentaur HTF™ aluminum oxide sensor is straight forward if the proper precautions are taken. CO2 dissolves in water creating carbonic acid.

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

The carbonic acid then can react with water disassociating the water molecule. This process can also occur with hydrated aluminum oxide. Aluminum oxide reacts with water as noted below:

$$Al_2O_3 + 3\ H_2O \leftrightarrow Al_2(OH)_6$$

The carbonic acid has an affinity for water so the following reaction then occurs:

$$Al_2(OH)_6 + 3\ H_2CO_3 \leftrightarrow Al_2(CO_3)_3 + 3\ H_2O$$

Therefore, the net effect is that some of the water is displaced from the hydrated aluminum oxide which shifts the change in the dielectric constant of the aluminum oxide. The result is that the sensor reads dry. These chemical changes reach equilibrium without excess moisture present. In turn, this means a stable response which allows calibration to correct the shift.

Experiments have shown that this shift in sensor response is more pronounced with high moisture levels ( >100 ppmv) in the presence of high concentrations of CO2 (> 50%). The reaction can also reverse when the CO2 is removed therefore it is best to calibrate in the process stream if it suspected that a shift has occurred. However, it should be noted that continued use of the HTF™ is high CO2 applications with high moisture content will permanently shift the HTF™ response curve.

**The Application:**

There are several ways to approach this shift in response. The first approach would be to avoid exposing a sensor to high moisture levels in CO2. This can be done by installing a sensor into the sample system then purging the sample system with dry nitrogen or air until the dew point reading is well below -42 C for a sustained period of time. Then dry CO2 can be introduced into the sample system minimizing the shift.

However, in most cases, the end user will install a new transmitter with a sensor then immediately expose it to the CO2 stream. In most cases, a sintered metal filter has been specified which has approximately 11 ft$^2$ of surface area. Filters that have been exposed to ambient conditions absorb enough moisture that it helps drive the changes to the sensor surface when introduced into CO2. Therefore, most users will experience a shift in response of a sensor over the first few days of operation.

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However, as stated above, the shift becomes stable and can be calibrated once the sensor has reached equilibrium.
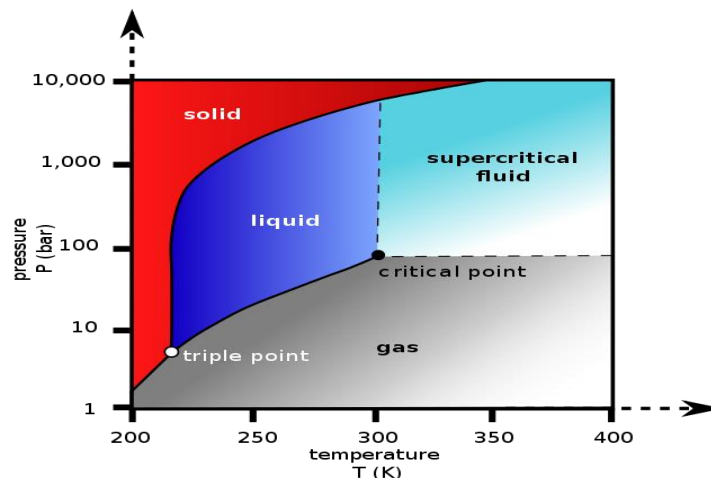
When calibrated in CO2, the sensor response will remain stable unless the sensor is exposed to ambient air conditions or excess water. As stated above, removing the sensor from pure CO2 can cause the chemical reactions to reverse and it also adds excess moisture back into the filter which will drive the reaction once CO2 is reintroduced. It is a normal response that end users experiencing a drier than expected reading will remove the sensor into ambient conditions to see if the sensor wets up. As just explained, this action just adds to instability of the measurement. End users can conclude that the sensor is "bad" then replace the sensor without changing the handling conditions. The same phenomena will be experienced again.

**Reference Measurements:**

It has been our experience that most on-line CO2 measurements are compared to a laboratory value. This should always evoke the question of what measurement method was used in the laboratory. In many cases, a condensation method is employed. There are issues with any condensation approach that must be considered.

For CO2 in a beverage application, the maximum allowable water concentration is 20 ppmv (-55 C dew point). Industrial CO2 specifications are in the 5 – 10 ppmv levels. Therefore most industrial CO2 processes target H2O values well below the specification values: dew points in the -80 C or less range.

CO2 has an approximate boiling point of -57 C and a melting point of -78 C.



Therefore any condensation method that cools gas phase CO2 to these levels cannot distinguish between CO2 condensate and H2O condensate. If the reported laboratory values for moisture in CO2 are between -60 C and -72 C the method of analysis should be questioned. Note that CO2 becomes solid at -78.5 C. As noted above, most of the process requirements are < 5 ppmv (-65 C dew point) and

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typically are in the area of 1 ppmv (-76 C dew point).  Mole sieve driers can achieve levels of < 100 ppb quite easily so dry numbers should be expected.

**Process Field Calibration:**

Because of the high repeatability and large response of the HTF™ sensor several methods of field calibration are  possible.  For this application, the simplest method is to use two known points with the SpanCheck™ function combined with a single point calibration.

Although the Al2O3 sensor is a capacitive sensor, it is used as a signal attenuator in most Xentaur dew point products.  A known signal is sent into the sensor and then the resulting signal coming out of the sensor is measured.  The actual response of the sensor is measured in db of attenuation of the reference signal.  Because the Xentaur HTF™ process is well characterized, the db of attenuation for dry and saturated (+20 C dew point) measurements stay within a very tight range.  However the slope of response at the extremes of the sensor range is less steep so a relatively small change in db can result in a large change in dew point.

Taking that into consideration, the empirical data shows that the effects of $CO_2$ in dry conditions shifts the sensor response by -.6 db.  This is actually relatively minor. The shift is consistent across the entire response curve and has been shown to be repeatable sensor to sensor.   Therefore to calibrate a sensor that is suspected to have shifted in a $CO_2$ stream, the low and wet db points can be shifted, a new curve calculated then if necessary, use a single point calibration to adjust the curve.  The process is as follows:

Equipment Requirements:

- A capacitance decade box with the output to a male BNC connector.
- For LPDT use, a pin to BNC female adapter.
- A Xentaur sensor base.
- XPDM Portable
- A Xentaur XDT manual for software instruction reference
- The initial factory settings of the installed sensor.  This can be found on the production sheet shipped with each transmitter.
    - Low Dew Point
    - Low db
    - Wet Dew Point (always +20 C)
    - Wet db

Note that this procedure does not detail all steps in the process covered in the XDT manual and by the flow charts in Appendix A of the manual.  It also assumes some familiarity with the function of Xentaur

dew point transmitters.  Also, the same software runs the XDT and the LPDT so only the XDT manual is required.

1. Record the instrument reading, line pressure,  and flow rate prior to implementing any changes. Normally, flow should be within 1-3 l/min and pressure should be at atmospheric.  If the pressure is greater than just a few psig, pressure correction needs to be used on the measurement.
2. With the transmitter active in the process, enter the Setup Mode.   Unlock the transmitter using the software functions.  Reset the unit to the Setup Mode.
3. From the Alternate Display option set the transmitter to flash db ($^{o}C^{o}F$) along with dew point.
4. Record low db and low dew point in the Setup Mode.  Make sure it matches the factory settings.
5. If the low db matches the factory settings, subtract -.6 db from the factory setting and enter the value in the low db field.
6. From the calibration option in the Setup mode, make sure that there is no single point calibration active.  The dew point set point in the Self Calibration setting will read zero if no single point calibration is active.  If a single point calibration is active, disable it via the instructions in the manual.
7. Exit the Setup Mode and return to Measurement Mode.
8. The display on the transmitter should now display the primary engineering units as well as $^{o}C^{o}F$ (db).
9. Remove the sensor from the process and allow it to wet up.  The sensor can be cupped in the users hand and blown on gently several times then held tightly for about 1 minute.
10. Observe the db value.  It should be in the range of -4 to + 4 db ($^{o}C^{o}F$).
11. Return the sensor to the process to start to dry. For LPDT's remove the sensor from the transmitter and install on a Xentaur sensor base then install the base into the sample cell.
12. Connect the transmitter to the capacitance box.  For LPDT's this will require using the pin to BNC adapter.
13. Vary the capacitance load on the box until the transmitter displays the following db value: Original factory wet db -.6 db.  Verify the db reading remains stable for at least 4 flash cycles.
14. Enter the CAL function and run SpanCheck™.
15. Once SpanCheck™ has completed the transmitter will return to Measurement Mode.  Reinstall the transmitter to the sensor.
16. Let the sensor equilibrate with the process for 24 hours.  However, attach the XPDM to the outlet of the sample cell.  Please note that the plunger of the XPDM must be kept in when initiating the flow through the XPDM. Make sure the XPDM plunger will stay in the dry position (in) during the dry down process.
17. At the end of 24 hours, compare the transmitter reading to the expected reading for the process. Please note the comments made about the source of the expected reading in the Reference Measurements section.

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18. Pull the sensor plunger out on the XPDM.  Allow the XPDM reading to stabilize for at least 1 hour.
19. Compare the reading of the XPDM to the transmitter reading, if the readings agree within 4-5 C, the transmitter is reading correctly.
20. If the XPDM and the transmitter do not agree, then use the XPDM reading to single point calibrate the transmitter.  Follow the procedure in the XDT manual.
21. After completing the process return the transmitter to Setup Mode. Disable the duel display and lock the software per the instructions in the manual

At this point, the proper measurement should be displayed .  If there is a discrepancy between the readings and the expected reading of the process, it will take more engineering evaluation as to the source of the expected value.  The transmitter reading should remain stable within the normal bounds of the process variations.