Data Processing for CONTROS HydroC® CO_2

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Introduction

General Information

This document provides information on how to process the sensor data of a CONTROS HydroC® CO_2 and is based on Fietzek, 2016. The aim is to correct the sensor data with respect to a baseline drift as well as for the change of the sensors sensitivity over the entire working range (span).

Due to technical reasons, the sensor itself is calculating the CO_2 gas concentration differently, resulting in slightly different sensor data than calculated using the present instructions. However, the sensor-generated data will initially be within the given specifications, but ignoring a potential drift of the baseline or of the sensitivity during the course of the sensor usage.

To perform a manual data processing, the following parameters should be requested from Contros. Those parameters are generated during the individual calibration procedure for your specific sensor and will be provided in a separate "Data Processing Sheet".

Calibration Data

S_{raw}	Sensor raw signal
S_{ref}	Sensor reference signal
T_{gas}	Gas temperature
p_{NDIR}	Cell pressure
S_{proc}	Final processed NDIR signal
$x_{CO_2,reference}$	CO_2 mole fraction from the reference system transferred to the condition within the HydroC's gas stream.

k_i	Coefficients of the calibration polynomial with forced zero crossing. The maximum index i states the degree of the used polynomial.

Sensor Specific Parameters

$T_0 = 273.15 \text{ K}$	Normal temperature
$p_0 = 1013.25 \, m\text{bar}$	Normal pressure
F	NDIR unit specific scale factor.
T_{sensor}	Temperature of the internal CO_2 sensor.
$f(T_{sensor})$	NDIR unit specific temperature compensation factor.
$S'_{2beam,Z}$	Two-beam signal during the regular zeroings.
Regression error	Estimate error of the polynomial regression found during calibration.

Sensor Signal

The dual-beam NDIR detector provides a raw and a reference signal, S_{raw} and S_{ref}, that are combined to a continuously referenced two-beam signal through

$$S_{\text{2beam}} = \frac{S_{\text{raw}}}{S_{\text{ref}}}.$$

The thermal response characteristics of every NDIR detector are determined with a zero-gas once during an initial, post-production gas calibration. Since every NDIR sensor features a temperature probe next to its detector, T_{sensor}, these characteristics can be included at this stage by means of a T_{sensor}-dependent factor, $f(T_{\text{sensor}})$. This step happens for backup reasons, since typically the NDIR detector within the underwater sensor is operated at a stabilized temperature. Including the temperature compensation the two-beam signal becomes

$$S'_{\text{2beam}} = \frac{S_{\text{raw}}}{S_{\text{ref}}} f(T_{\text{sensor}}).$$

Accordingly, the detector also provides a two-beam signal during the regular zeroings (Z) at discrete points in time,

$$S'_{\text{2beam,Z}} = \frac{S_{\text{raw,Z}}}{S_{\text{ref,Z}}} f(T_{\text{sensor}}).$$

The drift corrected (DC) NDIR signal by means of continuous two-beam referencing and time-dependent zero signals, is given by

$$S'_{\text{DC}}(t) = \frac{S'_{\text{2beam}}(t)}{S'_{\text{2beam,Z}}(t)}.$$

Due to the continuous zero signal referencing the $S'_{\text{DC}}(t)$ can be interpreted as a $\frac{I}{I_0}$ from Beer-Lambert Law and a processed (proc) and final NDIR sensor signal, which is proportional to the gas concentration, is

$$S_{\text{proc}} = F\left(1 - \frac{I}{I_0}\right)$$

$$S_{\text{proc}}(t) = F\left(1 - S'_{\text{DC}}(t)\right)$$

$$S_{\text{proc}}(t) \sim x_{\text{CO}_2,\text{wet}}(t).$$

With F being a NDIR-unit specific scale factor for a more convenient calculation and calibration and $x_{\text{CO}_2,\text{wet}}$ being the mole fraction in wet air present in the NDIR cuvette.

Realistically, the $S_{\text{proc}}(t)$ is directly proportional to the number of target molecules, n, in the beam path, which motivates the introduction of a density correction derived from the ideal gas law (with p, V and T being the pressure, volume and temperature of the gas respectively, n denoting the moles of gas and R meaning the ideal gas constant:

$$pV = nRT.$$

Rearrangement of those equations after Fietzek, 2016 yields

$$S_{\text{proc}} \sim x_{\text{CO}_2,\text{wet}} \frac{T_0 p}{p_0 T}.$$

Calibration Polynomial

The processed sensor signal is calibrated against a reference system using the following equation:

$$k_3 S_{\text{proc}}^3 + k_2 S_{\text{proc}}^2 + k_1 S_{\text{proc}}^1 = x_{\text{CO}_2,\text{wet}} \frac{T_0 p}{p_0 T}$$

$$x_{\text{CO}_2,\text{wet}} = \left(k_3 S_{\text{proc}}^3 + k_2 S_{\text{proc}}^2 + k_1 S_{\text{proc}}^1\right) \frac{p_0 T}{T_0 p}.$$

The parameter $x_{\text{CO}_2,\text{wet}}$ is given in units µmol mol⁻¹ or ppm. The factors of the calibration polynomial are k_1, k_2 and k_3. T is the gas temperature, T_{gas}, converted to Kelvin and p the cell pressure, p_{NDIR}, which is both provided by the sensor. The reference gas temperature and cell pressure, T_0 and p_0, are standard values. If two calibration polynomials are compared both polynomials must have been obtained by using the same T_0 and p_0.

The desired p_{CO_2} output parameter of the sensor is derived by multiplying $x_{\text{CO}_2,\text{wet}}$ with the pressure measured behind the membrane in the sensor's gas stream, p_{in},

$$p_{\text{CO}_2} = x_{\text{CO}_2,\text{wet}} \frac{p_{\text{in}}}{1013.25}.$$

Baseline (Zero) Drift Correction

If a baseline drift of the sensor is observed, the "zero signals", i.e. the $S'_{2beam,Z}$ should be calculated over the entire course of the sensor deployment time prior to the calculation of the CO_2 mole fraction. The zero signals are provided best by regular zero measurement intervals during the sensor deployment.

The duration of a zeroing by the HydroC® is typically 2 min and for successful data processing clear "zero signals", i.e. the $S'_{2beam,Z}$, are required. Therfore typically the first 30 seconds from every zeroing interval data are discarded due to the fact that they contain the signal drop from ambient CO_2 to zero concentration. The remaining data points recorded during the zeroing interval including their time stamps are averaged to obtain smooth zero measurements at discrete points in time.

In between two adjacent zeroings the $S'_{2beam,Z}$ are linearly interpolated in time. This provides a zero signal for every measuring point of the sensor: $S'_{2beam,Z}(t)$. If there are data points obtained with a properly wamed-up sensor before the first or after the last zeroing, the course of the following or preceding two $S'_{2beam,Z}$ is linearly extrapolated backward or forward in time respectively. If sensor data recorded between a pre- and post-calibration show gaps, because it e.g. originates from two different deployments or the measurements was interrupted for other reasons, the same extrapolation procedure is applied to data directly before or after these gaps.

Span Drift Correction

Changes in the sensor's concentration dependent characteristics are considered by transforming the polynomial of the pre-deployment calibration into the polynomial of the post-deployment calibration (cf. Fietzek et al. 2014). In the case of single continuous deployments or applications in which the sensor shows a continuous drift pattern the transformation between the polynomials is carried out best according to the pattern in the zero signals, $S'_{2beam,Z}$. As written in Fietzek et al. (2014) "this approach assumes a causal relationship between the temporally often nonlinear change in the zero signal and the change in concentration-dependent sensor response." Concretely, the calibration factors k_i of the polynomial then become $S'_{2beam,Z}(t)$-dependent through the following relationship:

$$k_i(t) = k_{i,\mathrm{pre}} +$$

$$\left(\frac{S'_{2beam,Z}(t_{\mathrm{first}}) - S'_{2beam,Z}(t)}{S'_{2beam,Z}(t_{\mathrm{first}}) - S'_{2beam,Z}(t_{\mathrm{last}})} \right) (k_{i,\mathrm{post}} - k_{i,\mathrm{pre}}),$$

with $k_{i,\mathrm{pre}}$ and $k_{i,\mathrm{post}}$ denoting the calibration coefficients of the pre- and the post-deployment calibration polynomial, respectively and t_{first} and t_{last} referring to the first and last measuring point of the data set, respectively.

In the case of a discontinuous course of the $S'_{2beam,Z}(t)$ within a dataset as caused by e.g. deployments with several interruptions or in different areas, the transformation of the pre- into the post-deployment coefficients should happen according to the runtime of the sensor, t_{run}. The runtime is set to zero at the beginning of the pre-deployment calibration and counts the actual sensor runtime in seconds, whenever the sensor is powered. This transformation approach assumes a linear drift of the concentration-dependent sensor response with the actual runtime of the unit. If the runtime is used for transformation, $t_{\mathrm{run,first}}$, $t_{\mathrm{run,last}}$ and t_{run} are to replace the $S'_{2beam,Z}$-equivalents in the above equation for the determination of $k_i(t)$. Before the runtime was introduced as a parameter, the less-than-ideal solution for processing data sets with a discontinuous drift pattern was a linear transformation between the first and the last timestamp of a deployment or data set.

Data Processing Summary

In short, the processing steps are:

1. Extraction of the zeroing data from a data set and calculation of the $S'_{2\text{beam,Z}}(t)$.

2. Calculation of the drift-corrected $S_{\text{proc}}(t)$ using the information obtained from zeroings,

$$S_{\text{proc}}(t) = F\left(1 - \frac{S'_{2\text{beam}}(t)}{S'_{2\text{beam,Z}}(t)}\right).$$

3. Calculation of the drift-corrected polynomial coefficients from the pre- and the post-deployment calibration as described in section Span Drift Correction.

4. Calculation of $x_{\text{CO}_2,\text{wet}}$ using the baseline drift-corrected $S_{\text{proc}}(t)$ and the drift-corrected polynomial coefficients $k_i(t)$:

$$x_{\text{CO}_2,\text{wet}}(t) = \left(k_3(t)S_{\text{proc}}^3(t) + k_2(t)S_{\text{proc}}^2(t) + k_1(t)S_{\text{proc}}^1(t)\right)\frac{p_0 T_{\text{gas}}(t)}{T_0 p_{\text{NDIR}}(t)}.$$

5. Calculation of p_{CO_2} in µatm using the pressure sensor behind the membrane, p_{in}:

$$p_{\text{CO}_2} = x_{\text{CO}_2,\text{wet}}\frac{p_{\text{in}}}{1013.25}.$$

Finally, it makes sense to extract the flush interval data from the processed p_{CO_2} series. The term "flush interval" is used to describe the data after a zeroing, which is characterized by the signal recovery from the zero reading to ambient p_{CO_2}. The duration of the flush interval should be set to sufficiently cover the equilibration phase of the sensor and is typically set as 10 to 15 min. The flush interval data can either be solely filtered or
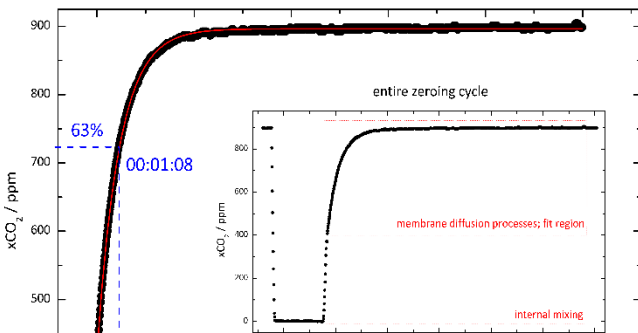

Figure 1: Zeroing cycle including zero CO₂ gas measurement and the subsequent flush of the zero gas by the sample gas.

used for in situ response time determination as further elaborated in e.g. Fiedler et al. (2013). Figure 1 visualizes the zeroing interval and

depicts the related signal course for better comprehensibility.

References

Fiedler, Björn et al. "In Situ CO2 and O2 Measurements on a Profiling Float." *Journal of Atmospheric and Oceanic Technology* 30.1 (2013): 112–126. Web. 24 Jan. 2013.

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