Correcting For Background Currents In Four-Electrode Toxic Gas Sensors

Introduction

This application note provides some guidance on the correction of the zero background current within the temperature range from -30°C to +50°C using only the ambient sensor temperature and knowledge of the reference ambient calibration temperature.

Correction of the zero background is complex and the results obtained from these simple algorithms should be considered as the first step in a process to correlate sensor results to the gas concentration measured by a reference analyser. Secondary corrections are usually required to further correct for any residual offsets and gain changes to obtain an acceptably accurate gas concentration. This application note describes only the primary correction to the zero background current for the effects of temperature. Further residual corrections are only discussed below.

Electrochemical amperometric gas sensors generate a background current in addition to the current from oxidation or reduction of the sampled gas. This background current is commonly called the **zero background current**. Zero background currents can be significant and can frustrate attempts to make measurements at low gas concentrations. Sources of these zero currents can include anodic or cathodic reactions on the working electrode (**WE**), electrochemical oxidation or reduction of the sensor electrolyte or electrolyte contaminants, and reduction of oxygen in the sampled air. The auxiliary electrode (**AE**) will also generate a current which mostly tracks the WE current.

If you have purchased the Alphasense Individual Sensor Boards (ISB) or Analogue Front End (AFE) boards, the calibrated offsets and sensor outputs will be expressed in voltage (mV) rather than current (nA). You will also have been provided with values for the electronic offsets for the WE (mV) and AE (mV) channels, and the Total Zero Offsets (mV) as a sum of the electronic offsets and the sensor offsets as determined in zero air at a temperature of 20 - 25°C. These values will be required when calculating the corrected WE output.

Term definitions

WE_u = uncorrected raw WE output
AE_u = uncorrected raw AE output
WE_c = corrected WE output
WE_e = WE electronic offset on the AFE or ISB
AE_e = AE electronic offset on the AFE or ISB
WE_o = WE sensor zero, i.e. the sensor WE output in zero air
AE_o = AE sensor zero, i.e. the sensor AE output in zero air
WE_T = Total WE zero offset
AE_T = Total AE zero offset

n_T = temperature dependent correction factor for algorithm 1, refer to Table 3 for values
k_T = temperature dependent correction factor for algorithm 2, refer to Table 3 for values
k'_T = temperature dependent correction factor for algorithm 3, refer to Table 3 for values
k''_T = temperature dependent correction factor for algorithm 4, refer to Table 3 for values

Initial calibration

1 If the sensors have been purchased on Alphasense AFE (Analog Front End) or ISB (Individual Sensor Board) electronics, then the following parameters will have been provided:

WE electronic offset, WE_e (mV)
AE electronic offset, AE_e (mV)
Total WE zero offset, WE_T, (mV)
Total AE zero offset, AE_T, (mV)
WE sensor zero (WE_o)
AE sensor zero (AE_o)
WE sensitivity in units of nA/ppb and mV/ppb. The latter will allow you to directly convert the mV output into ppb of gas.

Program your software with the supplied values. Remember to subtract the electronic offsets WE_e and AE_e from the raw WE_u and AE_u readings before correcting.

If you are using your own electronics, then first measure the open circuit voltage to determine your own board's WE and AE electronic offsets By default, Alphasense sets the electronic offsets on the AFE boards and ISBs to within the range 200 to 300 mV so that any zero sensor currents, either positive or negative about zero current can be measured as positive voltages.

Fit the sensor(s) to your board, apply power and allow several hours for the sensor to stabilise in ambient, clean air. Measure the outputs from the WE and AE channels, this will be your 'Total WE zero offset (WE_T)' and 'Total AE zero offset (AE_T)'. Note that the sensor will respond to any gases and VOCs in your ambient air. Alphasense calibrates zero current using filtered, scrubbed and dehumidified air.

2 Create a look-up table or other method in your software for determining the correction factor for your sensor at the measured sensor temperature (see table 3 for the complete list of temperature compensation factors). Correction factors are typically linearly interpolated between the temperatures listed in the Table.

3 Ensure that the temperature recorded as the sensor temperature is the temperature at the top of the sensor to within ±1°C to ensure using the correct temperature compensation factor.

Initial temperature corrections and calculating the gas concentration

1 Measure the WE and AE current (or voltage from your ISB or AFE) in your application.

2 If using Alphasense AFE boards or ISBs, subtract the working electrode and auxiliary electrode electronic offsets (WE_e and AE_e) from both the uncorrected WE and AE total outputs (WE_u and AE_u). On your own boards, determine the sensor output by subtracting any offsets to obtain the actual sensor output.

3 Determine the temperature of operation, and from this temperature select the appropriate correction factor of n_T, k_T, k'_T or k''_T depending on which algorithm is to be used (**Table 1**).

4 Table 1 illustrates how each equation uses a different approach for how the sensor parameters are combined. Table 2 is offered as a suggestion of which equation to use for a sensor type, but you are encouraged to explore the other equations in Table 1. Each model has their own limitations and you may find your own optimum choice to better suit the conditions in which the sensor is used.

5 Divide the final corrected WE result (WE_c) by the sensor's sensitivity to calculate the gas concentration. If desired, developers may wish to add a further refinement to the final gas concentration value by dividing the corrected WE output (WE_c) by a temperature corrected sensitivity instead of only the single ambient sensor sensitivity value provided. Each sensor type usually has a plot in its technical datasheet illustrating how the sensor sensitivity varies with temperature. Thus a complete temperature profile for the sensor type can be produced that corrects for background current changes (above) and sensitivity (or gain) changes due to temperature changes.

Compensation on the OX-A431 or OX-B431 sensor

This is a special case for this sensor since it responds to both O3 and NO2 gases but with different sensitivities. In the environment the two gases are usually present at the same time where air quality measurements are being made. If you received your OX sensor on an AFE or ISB then you will have been given a calibration certificate that provides the sensitivity for NO2 and O3 on the sensor. To determine the O3 concentration on the OX sensor you will require the NO2 concentration determined from an NO2 sensor (NO2-A43F or NO2-B43F). Use this value to calculate the output from the OX sensor by multiplying the NO2 concentration by the NO2 sensitivity of the OX sensor. The resulting mV value is equivalent to the WE_c result from any one of the algorithms, call this WE_c(NO2). Then take the total raw mV output from the OX sensor on an AFE or ISB and subtract WE_e and WE_c(NO2), treat the result as the equivalent of (WE_u – WE_e) in the compensation algorithms. Treat AE, (and WE_o and AE_o) as usual for the OX sensor in the algorithms and follow through the calculations to obtain WE_c(O3). Divide this value by the O3 sensitivity to give the O3 concentration.

Further residual corrections

After applying your chosen algorithm, you may find the results do not meet your expectations for accuracy when compared to reference values. You may find the gas concentrations are negative compared to reference values or appear to be much smaller or larger than the reference values but in general the sensor output is following the reference gas concentration. Respectively these are offset errors (which can also be in the positive direction) and gain errors.

Several factors may be skewing your results:

- thermal transients can temporarily destabilise the sensor signal
- humidity changes and humidity transients (usually due to temperature transients) can also destabilise temporarily the sensor signal, and
- diurnal and seasonal temperature/humidity patterns can shift calibration
- the difference between real environments where, amongst other things, humidity is present to varying levels compared to the lab testing environment where the correction factors were determined at controlled temperatures, dry gases, and no cross-sensitive gases.

These real but uncontrolled variations will affect the initial lab calibration. Although the sensors will adapt to the new environment the zero currents (WE_o and AE_o) will be different and sensitivity will change to a lesser degree. Cross-sensitivity to other gases and VOCs may also change to a lesser extent and contribute to the change of the WE_o zero current.

These residual errors can be corrected by empirically determining and applying a correction factor to the sensor sensitivity and applying a correction to minimise the offset error such that the sensor gas reading matches as closely as possible a set of reference gas values over a period of time, e.g. one week, although longer will provide more confidence in the corrections.

It should be noted that compensating the outputs of sensors for the effects of environmental effects, i.e. temperature, humidity, is complex.

These algorithms are provided as suggestions for attempting to correct for temperature changes only and should not be regarded as a complete solution for providing gas concentration results that meet an accuracy acceptable for your application.

For the calibration of a low cost air quality network, one suggested strategy would be to initially cluster your sensor nodes together around a reference station. Preferably they should be within about 1 m of the station to ensure as best as possible, the same gas sample is within this shared environmental volume. What follows will then be a process of sensor calibrations to your environment of your sensors as described above. Published papers, for example references 1,2,3, explain in much more detail air quality network deployment and the challenges on obtaining accurate results.

Alphasense follows a continual process improvement process and as such is working to refine the process of compensating sensor readings for the effects of the environment for our customers. Please contact us to follow our progress.

References

1. Mead et al., Atmos. Environ. 70 (2013) 186-203; https://doi.org/10.1016/j.atmosenv.2012.11.060
2. Popoola et al., Atmos. Environ. 147 (2016) 330-343; https://doi.org/10.1016/j.atmosenv.2016.10.024
3. Cross et al., Atmos. Meas. Tech., 10, 3575–3588, 2017; https://doi.org/10.5194/amt-10-3575-2017

Table 1: Algorithms to correct the WE output for the effects of temperature

Algorithm	Equation	Notes
1	$WE_c = (WE_u - WE_e) - n_T * (AE_u - AE_e)$	Subtraction of the electronic offsets from the raw WE_u and AE_u outputs then scales the net AE output with the n_T factor. Gross under or over compensation can occur if ($AE_u - AE_e$) is of opposite sign to n_T, or if ($AE_u - AE_e$) is significantly smaller or larger than (WE_u-WE_e). Over compensation could lead to the final gas concentration appearing negative, or much higher compared to a reference value.
2	$WE_c = (WE_u - WE_e) - k_T * \left(\frac{WE_o}{AE_o}\right) * (AE_u - AE_e)$	A refinement of Algorithm 1 where the AE scaling factor n_T is replaced with k_T*(WE_o/AE_o). An error or gross over compensation will result if AE_o is very small compared to WE_o or is zero. If WE_o and AE_o are of opposite signs then over compensation can also occur. Over compensation could lead to the final gas concentration appearing negative or much higher compared to a reference.
3	$WE_c = (WE_u - WE_e) - (WE_o - AE_o) - k'_T * (AE_u - AE_e)$	Avoids the problem of Algorithm 2 with a zero AE_o value. Gross over or under compensation can result if AE_o is of opposite sign to WE_o, or if AE_o is significantly smaller or larger than WE_o. Over compensation could lead to the final gas concentration appearing negative or much higher compared to a reference.
4	$WE_c = (WE_u - WE_e) - WE_o - k''_T$	Correction without using the outputs from the auxiliary electrode. Gross under or over compensation can occur if WE_o or k''_T are significantly smaller or larger than WE_u. Over compensation could lead to the final gas concentration appearing negative or much higher compared to a reference.

Table 2: Suggested algorithms for both A and B type sensors

Sensor	Suggested algorithm		Alternative algorithm	
	A	B	A	B
CO	1	1	4	2
H_2S	2	1	1	2
NO	3	2	4	3
NO_2	1	1	3	3
OX	3	1	1	3
SO_2	4	4	1 or 3	1 or 2

Table 3: Zero background current temperature compensation factors

Sensor	Algorithm	Factor	T / °C								
			-30	-20	-10	0	10	20	30	40	50
CO-A4	1	n_T	1	1	1	1	-0.2	-0.9	-1.5	-1.5	-1.5
	2	k_T	-1.1	-1.1	-1.1	-1.1	0.2	1	1.7	1.7	1.7
	3	k'_T	1.9	2.9	2.7	3.9	2.1	1	-0.6	-0.3	-0.5
	4	k''_T	13	12	16	11	4	0	-15	-18	-36
CO-B4	1	n_T	0.7	0.7	0.7	0.7	1	3	3.5	4	4.5
	2	k_T	0.2	0.2	0.2	0.2	0.3	1	1.2	1.3	1.5
	3	k'_T	-1	-0.5	0	0	0	1	1	1	1
	4	k''_T	55	55	55	50	31	0	-50	-150	-250
H2S-A4	1	n_T	3	3	3	1	-1	-2	-1.5	-1	-0.5
	2	k_T	-1.5	-1.5	-1.5	-0.5	0.5	1	0.8	0.5	0.3
	3	k'_T	9	9	9	9	3	1	0.3	0.3	0.3
	4	k''_T	50	46	43	37	25	0	-8	-16	-20
H2S-B4	1	n_T	-0.6	-0.6	0.1	0.8	-0.7	-2.5	-2.5	-2.2	-1.8
	2	k_T	0.2	0.2	0	-0.3	0.3	1	1	0.9	0.7
	3	k'_T	-14	-14	3	3	2	1	-1.2	-1.2	-1.2
	4	k''_T	52	51	48	45	26	0	-65	-125	-180
NO-A4	1	n_T	1.7	1.7	1.6	1.5	1.5	1.5	1.5	1.6	1.7
	2	k_T	1.1	1.1	1.1	1	1	1	1	1.1	1.1
	3	k'_T	0.7	0.7	0.7	0.7	0.8	1	1.2	1.4	1.6
	4	k''_T	-25	-25	-25	-25	-16	0	56	200	615
NO-B4	1	n_T	2.9	2.9	2.2	1.8	1.7	1.6	1.5	1.4	1.3
	2	k_T	1.8	1.8	1.4	1.1	1.1	1	0.9	0.9	0.8
	3	k'_T	0.8	0.8	0.8	0.8	0.9	1	1.1	1.2	1.3
	4	k''_T	-25	-25	-25	-25	-16	0	56	200	615
NO2-A43F	1	n_T	0.8	0.8	1	1.2	1.6	1.8	1.9	2.5	3.6
	2	k_T	0.4	0.4	0.6	0.7	0.9	1	1.1	1.4	2
	3	k'_T	0.2	0.2	0.2	0.2	0.7	1	1.3	2.1	3.5
	4	k''_T	-4	-4	-4	-4	-2	0	10	35	132
NO2-B43F	1	n_T	1.3	1.3	1.3	1.3	1	0.6	0.4	0.2	-1.5
	2	k_T	2.2	2.2	2.2	2.2	1.7	1	0.7	0.3	-2.5
	3	k'_T	1	1	1	1	1	1	0.4	-0.1	-4
	4	k''_T	7	7	7	7	4	0	0.5	5	67
OX-A431	1	n_T	1	1.2	1.2	1.6	1.7	2	2.1	3.4	4.6
	2	k_T	0.5	0.6	0.6	0.8	0.9	1	1.1	1.7	2.3
	3	k'_T	0.1	0.1	0.2	0.3	0.7	1	1.7	3	4
	4	k''_T	-5	-5	-4	-3	0.5	0	9	42	134
OX-B431	1	n_T	0.9	0.9	1	1.3	1.5	1.7	2	2.5	3.7
	2	k_T	0.5	0.5	0.6	0.8	0.9	1	1.2	1.5	2.2
	3	k'_T	0.5	0.5	0.5	0.6	0.6	1	2.8	5	5.3
	4	k''_T	1	1	1	1	1	1	8.5	23	103
SO2-A4	1	n_T	1.3	1.3	1.3	1.2	0.9	0.4	0.4	0.4	0.4
	2	k_T	3.3	3.3	3.3	3	2.3	1	1	1	1
	3	k'_T	1.5	1.5	1.5	1.5	1	1	1	1	1
	4	k''_T	0	0	0	0	0	0	5	25	45
SO2-B4	1	n_T	1.6	1.6	1.6	1.6	1.6	1.6	1.9	3	5.8
	2	k_T	1	1	1	1	1	1	1.2	1.9	3.6
	3	k'_T	1	1	1	1	1	1	2	3.5	7
	4	k''_T	-4	-4	-4	-4	-4	0	20	140	450