AAN 803-01 CORRECTING FOR BACKGROUND CURRENTS IN FOUR ELECTRODE TOXIC GAS SENSORS

Introduction

Electrochemical amperometric gas sensors have a background current in addition to the current from oxidation or reduction of the sampled gas. This background current is commonly called the **zero current.** These zero currents can be significant and can frustrate attempts to make measurements at low gas concentrations. Sources of these zero currents can include anodisation or cathodic reduction of the working electrode (WE), electrochemical oxidation or reduction of the sensor electrolyte or electrolyte contaminants by the WE and reduction of oxygen in the sampled air.

This Application Note explains how to correct for the zero current over the entire temperature range of the sensor without making extra measurements at temperatures other than the ambient calibration temperature.

If you have purchased Alphasense ISB or AFE circuits, the offsets will be calibrated in mV because the measured signal was converted to mV through a trans-impedance amplifier, so although sensor electrochemistry is based on current, each current equation is followed by the mV equivalent equation.

Sources of the zero current

In order to correct for zero currents, the Alphasense A4 and B4 sensor families include an additional electrode, an auxiliary electrode (AE), buried within the sensor. The AE has the same catalyst structure as the working electrode (WE) so, in principle, since it is not in contact with the sampled gas, any background current arising from solid electrode processes or from electrochemistry involving the electrolyte will be measured on both the WE and the AE. This AE current could then be subtracted from the WE total current to give a corrected WE current corresponding solely to the electrochemical reaction of the sampled gas.

There is also frequently a contribution to the background current from oxygen reduction at the WE. However, the AE is buried in the sensor electrolyte, limiting oxygen access to the AE by the solubility and diffusion rate of oxygen in the electrolyte. The result is the electrolyte strongly decreases oxygen access to the AE. This must be considered when understanding the correction for the sources of the background/zero current.

Electronic offset currents and offset voltages will also add to the measured signal and must be corrected, as explained in the next section. If you have purchased sensors with the Alphasense ISB or AFE circuits, you will have been provided with both the the electronics offsets and (electronics plus sensor) zero offsets (in mV).

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Simple correction at ambient temperature by subtraction

If we set a required Limit of Detection as between 5 and 20 ppb. The allowed error is between 10 and 40 ppb, depending on national air quality standards. Since the sensitivity for most A4/ B4 sensors is between 200 and 600 nA/ ppm, then the error of the residual zero current that is acceptable at ambient temperature is between ±5 and ±25 nA. This error nulling can be achieved at ambient temperature by:

Either:

1 Programming into your software the zero voltage of both the WE and AE as provided by Alphasense and include separately the electronic and sensor offsets, correcting only the sensor offset. for temperature

Or:

2 If you are using your own electronics, then supply a flow of good quality zero (clean) air over the sensor for at least 20 minutes and measure the WE and AE currents (or voltages). But first measure the open circuit offset to determine your electronic offset error, which is a separate correction.

Whichever approach you use:

3 First subtract the two electronic offsets from the WE and AE signals. Then multiply the AE sensor zero signal by n (which is dependent on temperature), as described below, and subtract this from the WE signal to obtain the corrected WE current/ voltage.

The electronic error, which is not normally temperature dependent, should be measured separately and subtracted from all measurements before correcting for the temperature dependence of the zero current, as discussed below. A good potentiostat circuit should not contribute significantly to the temperature dependence of the zero correction; Alphasense circuits have been tested and their zero offset change with temperature is negligible and can be ignored.

Zero current correction including temperature

The simplest correction algorithm to correct for the effect of temperature on background currents is to subtract the AE current from the WE current. Since the WE and AE do not have the same surface area, a scaling constant must be included to correct for this geometric difference. For B4–type sensors the WE area is 1.16 times the area of the AE, so it would be expected that the AE currents would have to be adjusted by a factor of 1.16. If we represent the currents at the two electrodes as I_{WE} and I_{AE} then the following relationship would be expected to hold in zero air, ignoring any oxygen reduction current differences:

$$I_{WE} - 1.16\, I_{AE} = 0 \qquad (1a)$$

$$V_{WE} - 1.16\, V_{AE} = 0 \qquad (1b)$$

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In practice, though, the adjustment will not be as simple as that because the structures of the electrodes are by no means planar. Fig. 1 illustrates schematically the structure for the membrane WE in gas sensors.

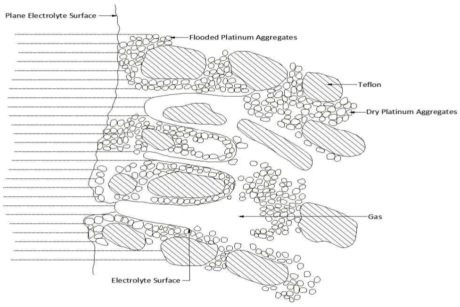

Fig 1. Schematic drawing of a PTFE bonded Platinum WE

Clearly, the active electrode area for a given electrode will be different from the geometric area of that electrode. Also, since the AE is completely submersed in the electrolyte there will be liquid on both sides of the electrode membrane with possibly bubbles of trapped gas in the membrane pores or with complete flooding of the pores - Fig. 2.

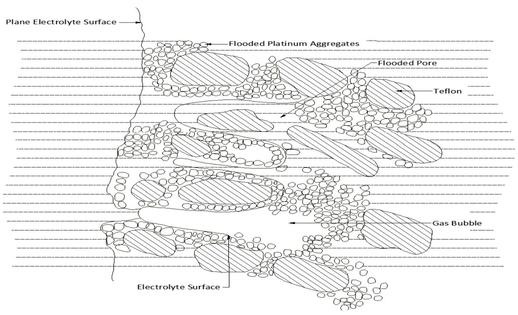

Fig. 2. Schematic drawing of a PTFE bonded Platinum AE

Thus, the ratio of the active areas of a WE and an AE will not be the same as the ratio of the geometric areas. In addition, the active area may vary with temperature because of gas and liquid expansion in the membrane pores. Finally, the electrochemistry could be different because of the different environments. Therefore the required multiplying factor for I_{AE} in eqn. (1) could even be negative if the current at one electrode is anodic and at the other it is cathodic. We now designate the multiplier as *n* and eqn. (1) becomes

$$I_{WE} - n\, I_{AE} = 0 \qquad (2a)$$
$$V_{WE} - n\, V_{AE} = 0 \qquad (2b)$$

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So although you can zero the current at ambient temperature easily by just adjusting until the reading is zero, correcting for baseline using equation 2 over the entire temperature range is not as simple.

If we include the electronic offset error for both the WE and AE amplifiers, which is independent of temperature, and designate it as I_{PCBWE} and I_{PCBAE}, eqn. (2) becomes

$$(I_{WE} - I_{PCBWE}) - n\,(I_{AE} - I_{PCBAE}) = 0 \qquad (3a)$$
$$(V_{WE} - V_{PCBWE}) - n\,(V_{AE} - V_{PCBAE}) = 0 \qquad (3b)$$

Electronics engineers will note that in the commonly used trans-impedance amplifier configuration, the electronic offset error is not just the offset current. The offset voltage will be multiplied by the gain factor for that stage and will add to the output voltage as an offset error. This offset voltage is normally the dominant factor in the electronic offset error.

The next step

This Application Note will now explain the correction algorithm for each sensor type, using test results from the B family sensors; the A family sensors follow the same rules and a summary table of the correction terms for both A and B family sensors can be found in **Annex 1**.

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NO_2 Sensors

Figs. 3 and 4 show typical plots of zero currents for the WEs and AEs, respectively, as a function of temperature. To correct for WE background currents using eqn. (3) the multiplying factors for the AE zero currents have to be determined and electronic offset errors subtracted.

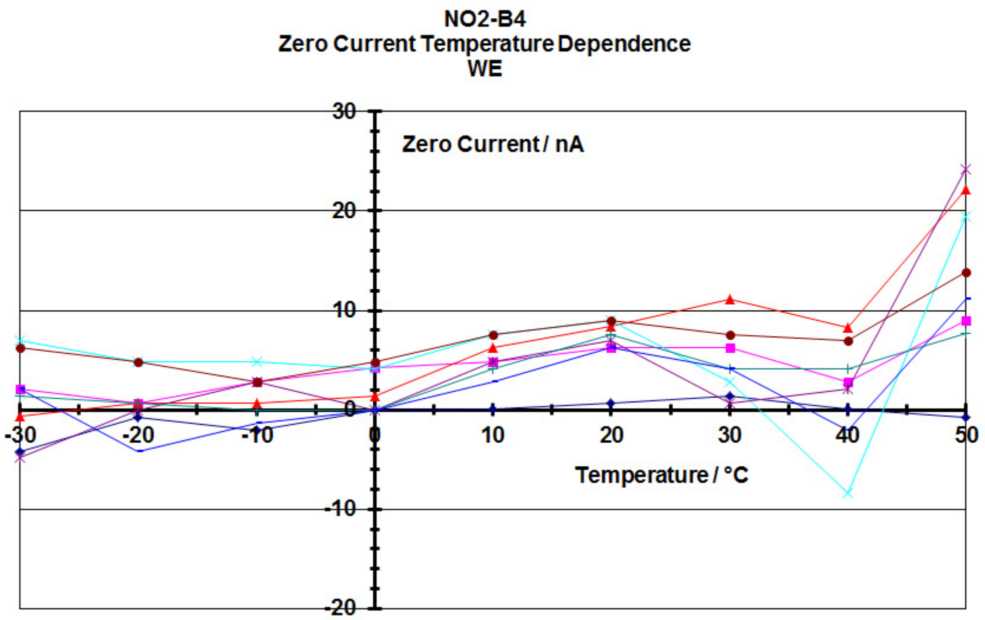

Fig. 3 Plots of zero currents for the WEs in NO2-B4 sensors as a function of temperature

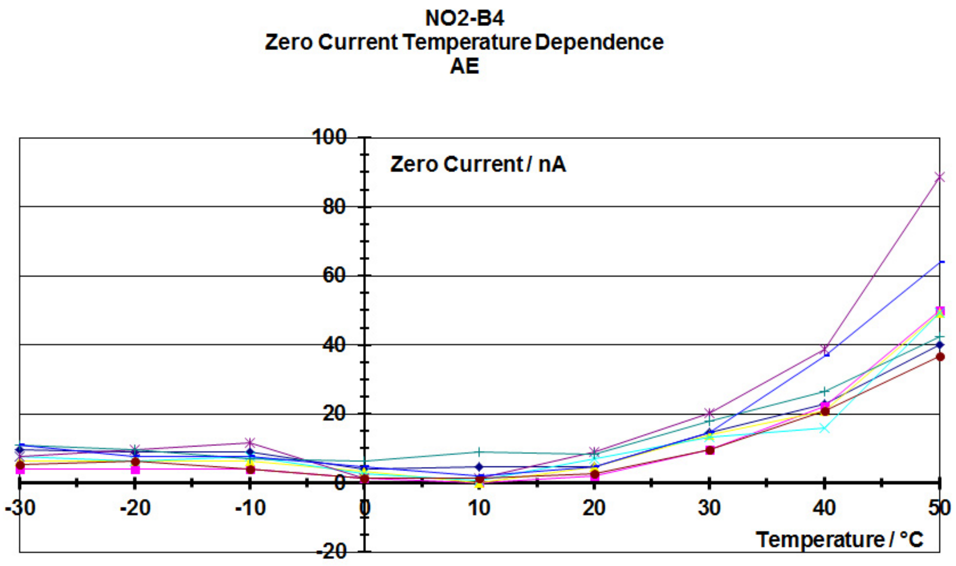

Fig. 4 Plots of zero currents for the AEs in NO2-B4 sensors as a function of temperature

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Table 1 shows the ratio of WE/ AE currents for NO2-B4 sensors as a function of temperature.

Table 1 WE/AE current ratios as a function of temperature for NO2-B4 and NO2-A4 sensors

Temperature range/°C	-30 to +10	+20	+30 to +50
WE/AE current ratios B4 sensors	0.76	0.68	0.23
WE/AE current ratios A4 sensors	1.09	1.35	3.00

Eqn. (3a) is then applied with the measured PCB currents (I_{PCBWE} *and* I_{PCBAE}) for the sensors used in this illustration being subtracted from the measured values of I_{WE} and I_{AE} according to the equation. When this is done the corrected WE currents as a function of temperature are as shown in Fig. 5 for 77 measurements with eight different NO2-B4 sensors.

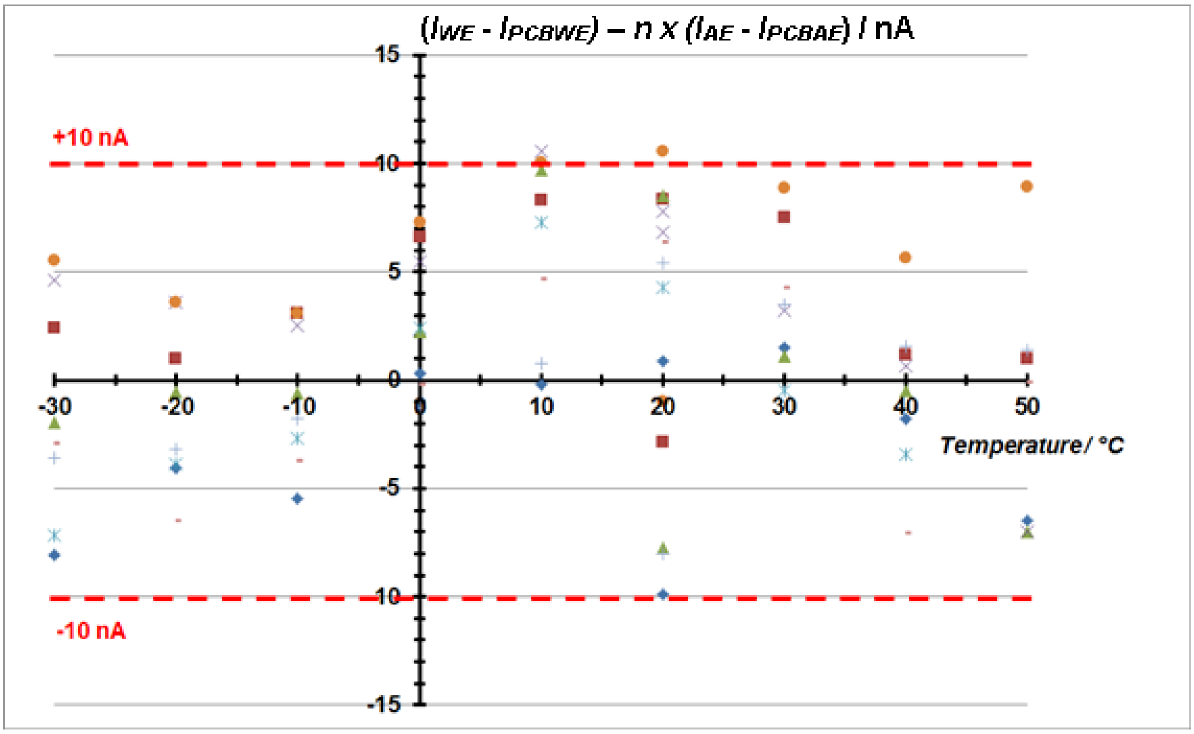

Fig. 5 Plots of $(I_{WE} - I_{PCBWE}) - n \times (I_{AE} - I_{PCBAE})$ for NO2-B4 sensors as a function of temperature after applying current ratios for three temperature zones

All but three of the 77 measurements for the corrected WE zero currents lie in the ± 10 nA range, and even those three outliers are within 1 nA of the range. A similar plot is obtained for NO2-A4 sensors with the current ratios given in Table 1.

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SO_2 Sensors

Figs. 6 and 7 show typical plots of zero currents for the WEs and AEs, respectively, as a function of temperature. To correct for WE zero currents using eqn. (3) the multiplying factors for the AE zero currents have to be determined and electronic offset errors subtracted.

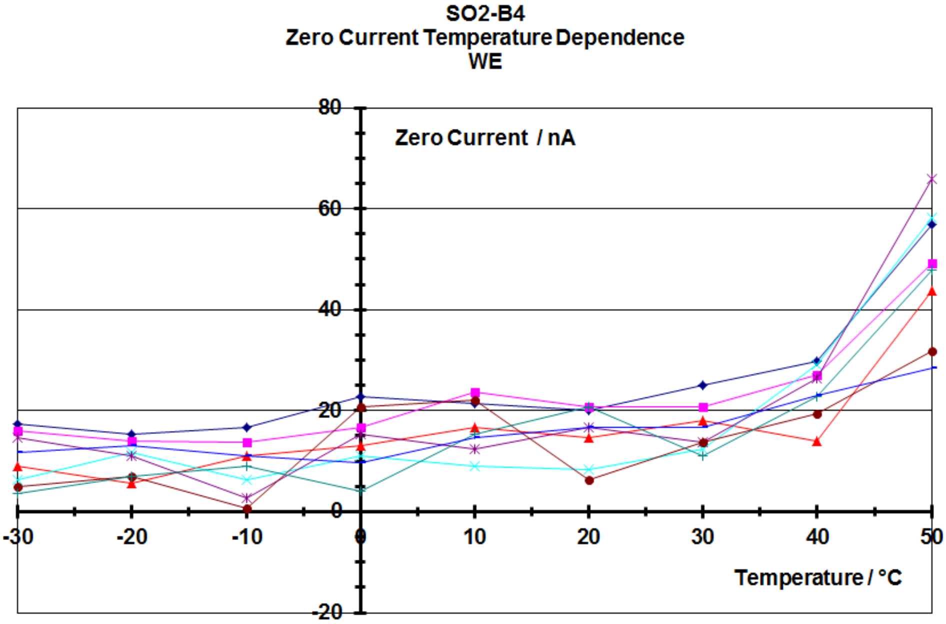

Fig. 6 **Plots of zero currents for the WEs in SO2-B4 sensors as a function of temperature**

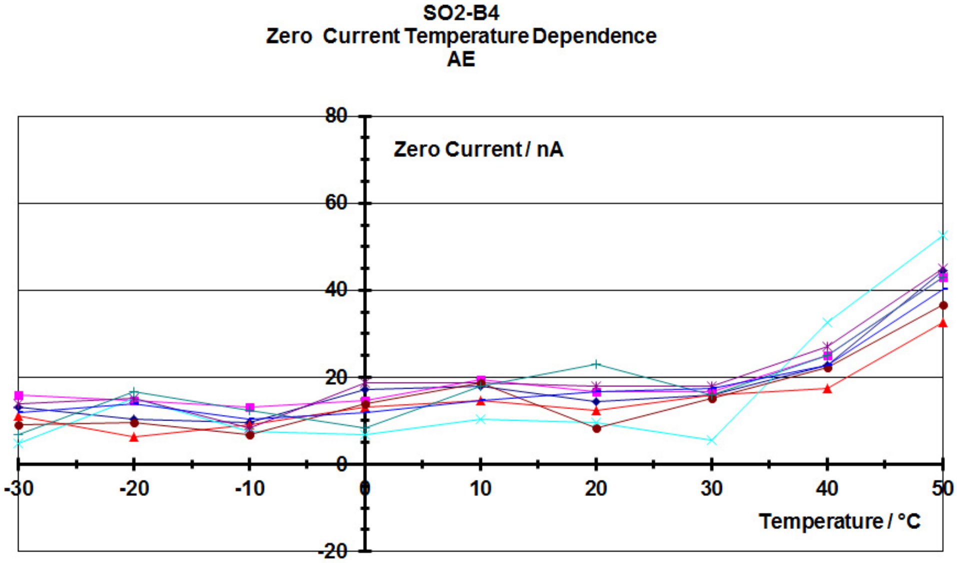

Fig. 7 **Plots of zero currents for the AEs in SO2-B4 sensors as a function of temperature**

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Table 2 shows the ratio of WE/ AE currents for SO2-B4 sensors as a function of temperature.

Table 2 WE/AE current ratios as a function of temperature for SO2-B4 and SO2-A4 sensors

Temperature range/°C	-30 to +10	+20	+30 to +50
WE/AE current ratios B4 sensors	0.96	1.34	1.10
WE/AE current ratios A4 sensors	1.15	1.82	3.93

Again eqn. (3a) is then applied with the measured PCB currents (I_{PCBWE} and I_{PCBAE}) for the sensors used in this illustration being subtracted from the measured values of I_{WE} and I_{AE} according to the equation. When this is done the corrected WE currents as a function of temperature are as shown in Fig. 8 for 85 measurements with eight different sensors.

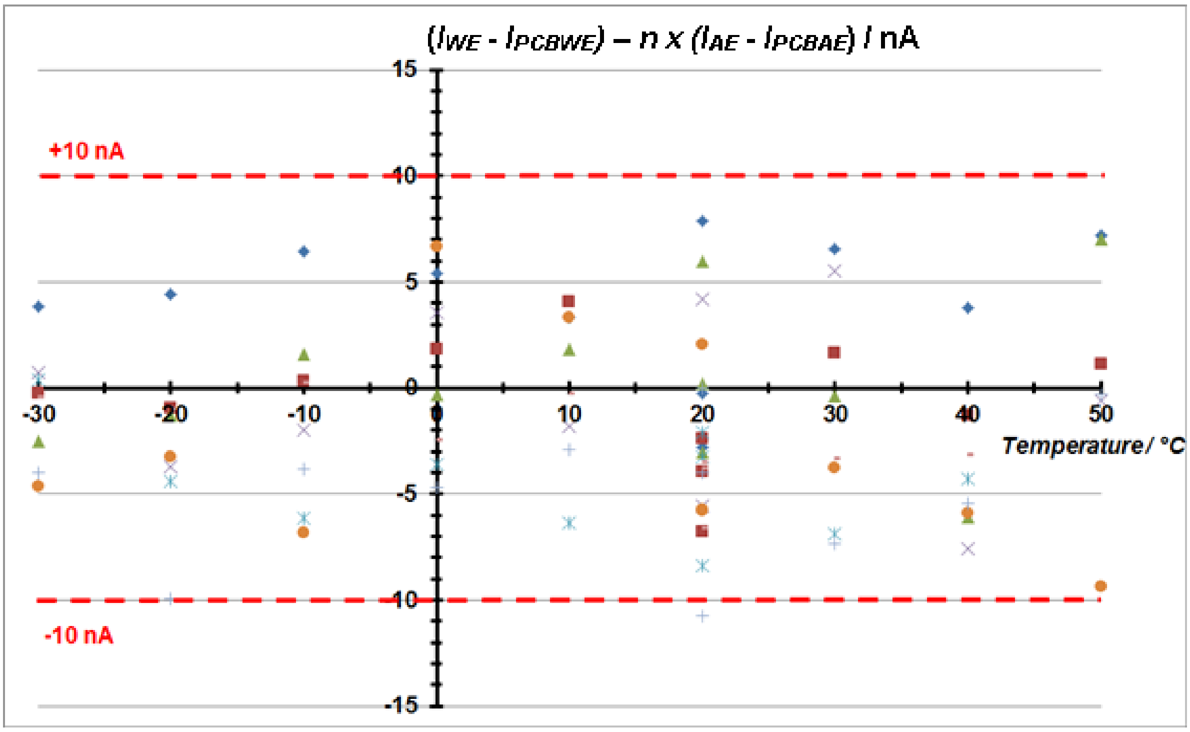

Fig. 8 Plots of (I_{WE} - I_{PCBWE}) – *n x* (I_{AE} - I_{PCBAE}) for SO2-B4 sensors as a function of temperature after applying current ratios for three temperature zones

All but one of the 85 measurements for the corrected WE zero currents lie in the range ±10 nA and that one outlier is within 1 nA of the range. A similar plot is obtained for SO2-A4 sensors with the current ratios shown in Table 2.

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NO Sensors

Figs. 9 and 10 show typical plots of zero currents for the WEs and AEs, respectively, as a function of temperature. To correct for WE zero currents using eqn. (3) the multiplying factors for the AE zero currents have to be determined and electronic offset errors subtracted.

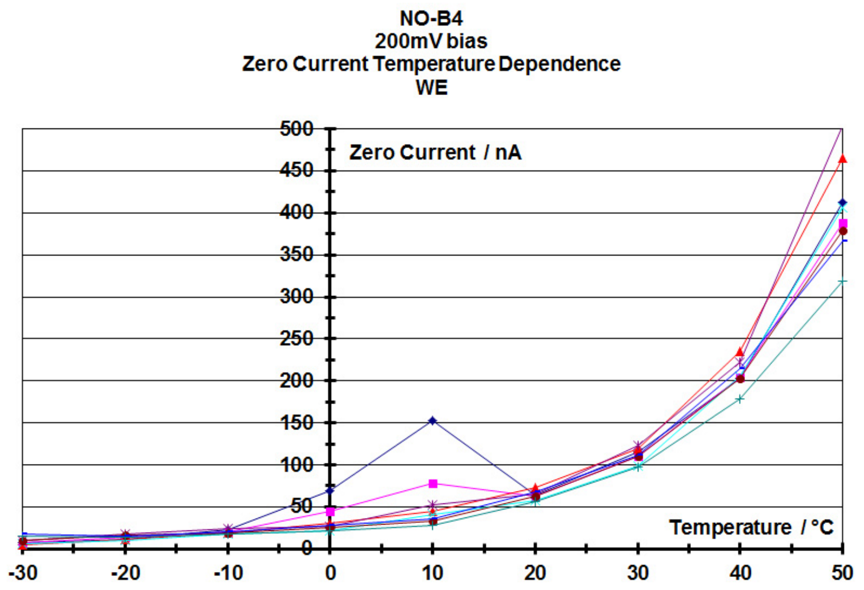

Fig. 9 **Plots of zero currents for the WEs in NO-B4 sensors as a function of temperature**

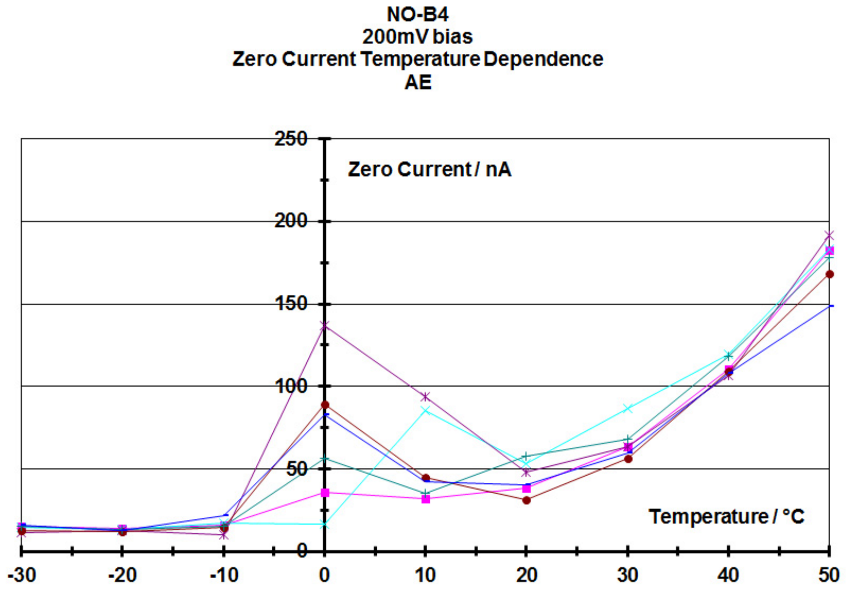

Fig. 10 **Plots of zero currents for the AEs in NO-B4 sensors as a function of temperature**

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Table 3 shows the ratio of WE/AE currents for NO-B4 sensors as a function of temperature.

Table 3 WE/AE current ratios as a function of temperature for NO-B4 and NO-A4 sensors

Temperature range/°C	-30 to +10	+20	+30 to +50
WE/AE current ratios B4 sensors	1.04	1.82	2.00
WE/AE current ratios A4 sensors	1.48	2.02	1.72

Eqn. (3a) is applied as previously, and when this is done the corrected WE currents as a function of temperature are as shown in Fig. 11 for 55 measurements with eight different sensors.

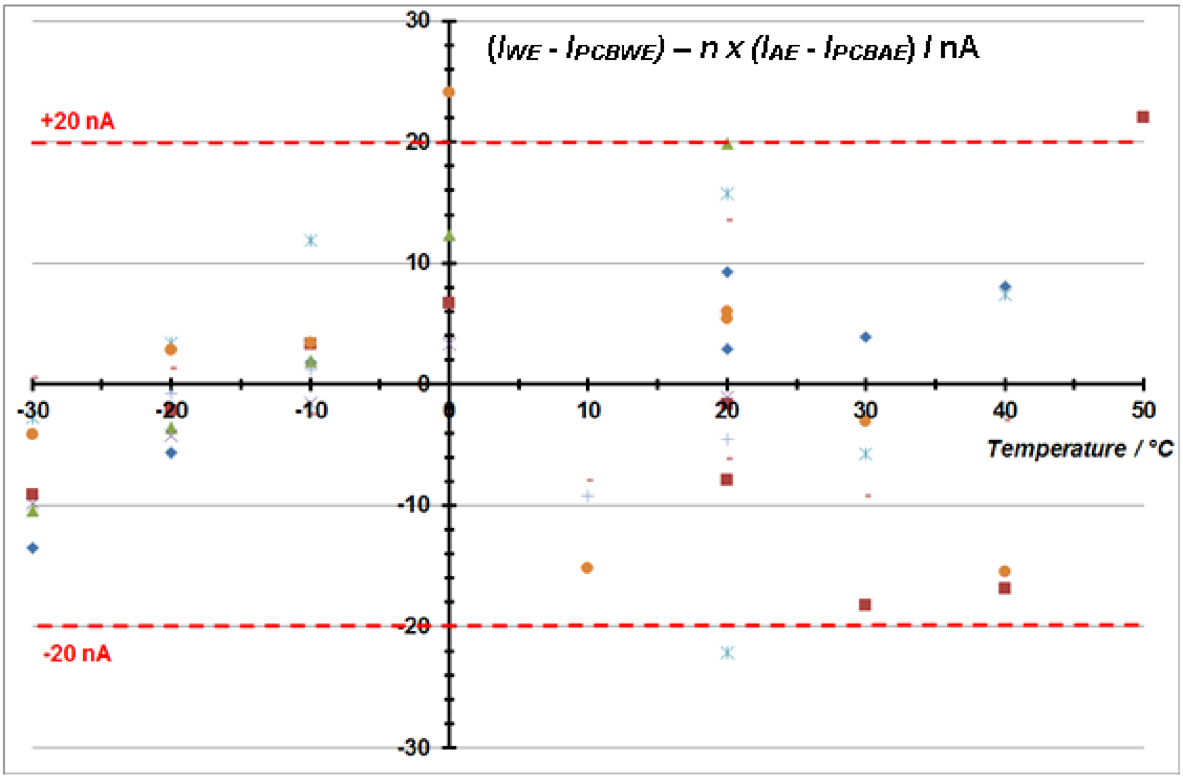

Fig. 11 Plots of $(I_{WE} - I_{PCBWE}) - n \times (I_{AE} - I_{PCBAE})$ for NO-B4 sensors as a function of temperature after applying current ratios for three temperature zones

The majority of the 55 measurements for the corrected WE zero currents lie in the range ±20 nA with the few outlying points still falling within ~ ±30 nA. There is only one measurement at 50°C which indicates that correction at that temperature is not very reliable. A similar plot is obtained for NO-A4 sensors using the current ratios from Table 3.

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O_3 Sensors

Figs. 12 and 13 show typical plots of zero currents for the WEs and AEs, respectively, as a function of temperature. To correct for WE zero currents using eqn. (3) the multiplying factors for the AE zero currents have to be determined and electronic offset errors subtracted.

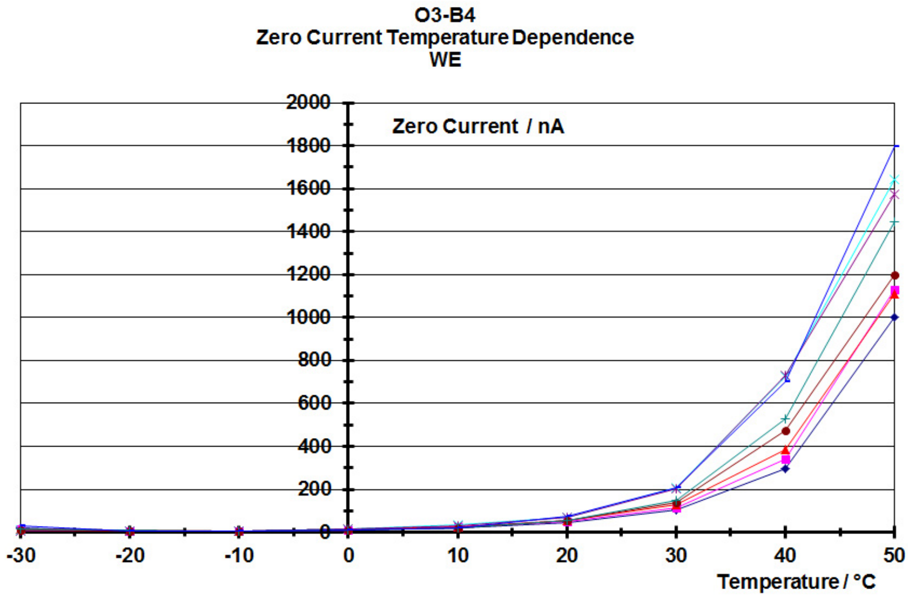

Fig. 12 Plots of zero currents for the WEs in O3-B4 sensors as a function of temperature

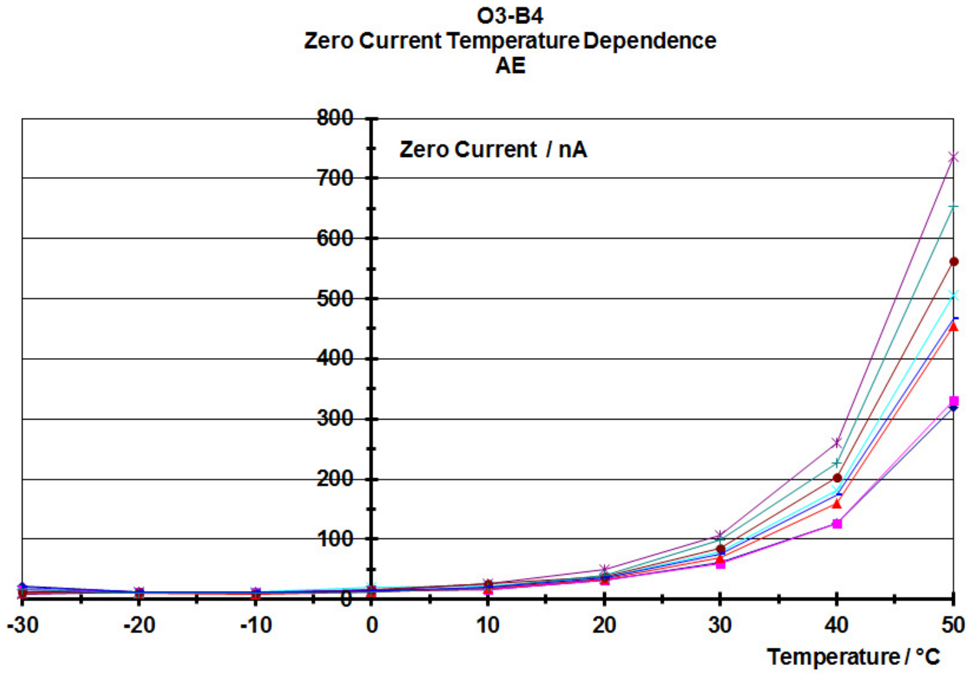

Fig. 13 Plots of zero currents for the AEs in O3-B4 sensors as a function of temperature

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Table 4 shows the ratio of WE/AE currents for O3-B4 sensors as a function of temperature.

Table 4 WE / AE current ratios as a function of temperature for O3-B4 and O3-A4 sensors

Temperature range/°C	-30 to 0	+10 to +30	+40
WE/AE current ratios B4 sensors	0.77	1.56	2.85
WE/AE current ratios A4 sensors	0.75	1.28	1.36

The O3-B4 sensors have different characteristics from the other sensors discussed in this Application Note and this is reflected in the slightly different temperature ranges for the multiplying factor, *n*. Also at the higher temperatures there is a wide variability in zero currents and at present it is not possible to correct for the zero currents at +50°C to a good accuracy. For +40°C correction is limited.

For the temperature range -30°C to +30°C and 40°C eqn. (3a) has been applied. When this is done the corrected WE currents as a function of temperature are as shown in Fig. 14.

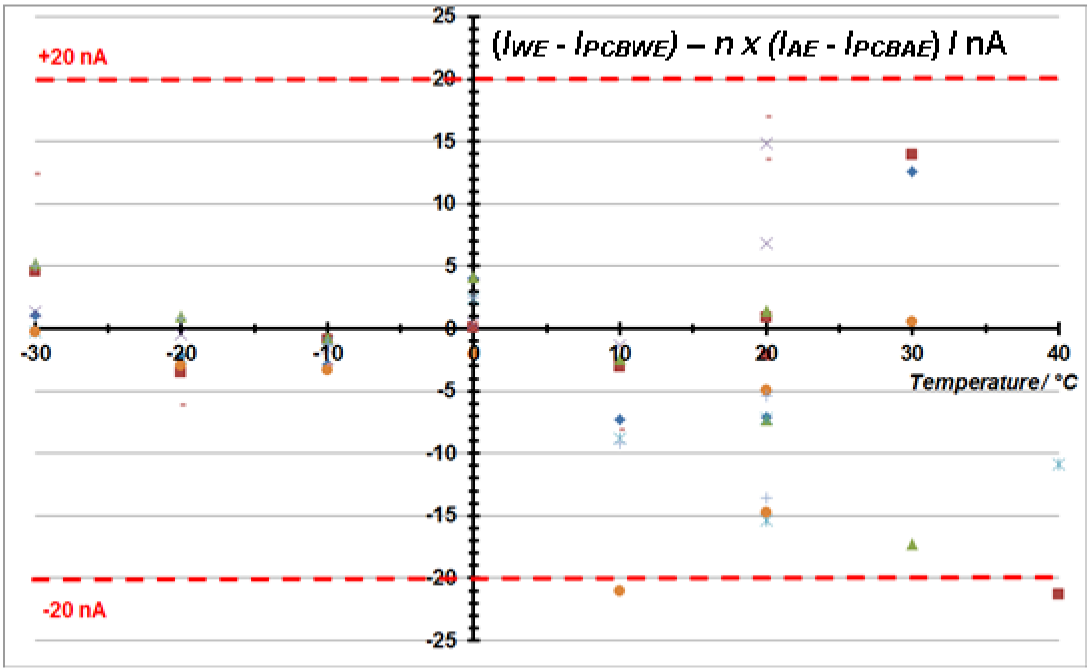

Fig. 14 Plots of (I_{WE} - I_{PCBWE}) – n x (I_{AE} - I_{PCBAE}) for O3-B4 sensors as a function of temperature after applying current ratios for three temperature zones

The majority of the 62 measurements for the corrected WE zero currents lie in the range ±20 nA. The two outlying points still fall within ~ ±25 nA. A similar plot is obtained for O3-A4 sensors employing the current ratios from Table 4.

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CO Sensors

Figs. 15 and 16 show typical plots of zero currents for the WEs and AEs, respectively, for CO-B4 sensors as a function of temperature. To correct for WE zero currents using eqn. (3) the multiplying factors for the AE zero currents have to be determined and electronic offset errors subtracted.

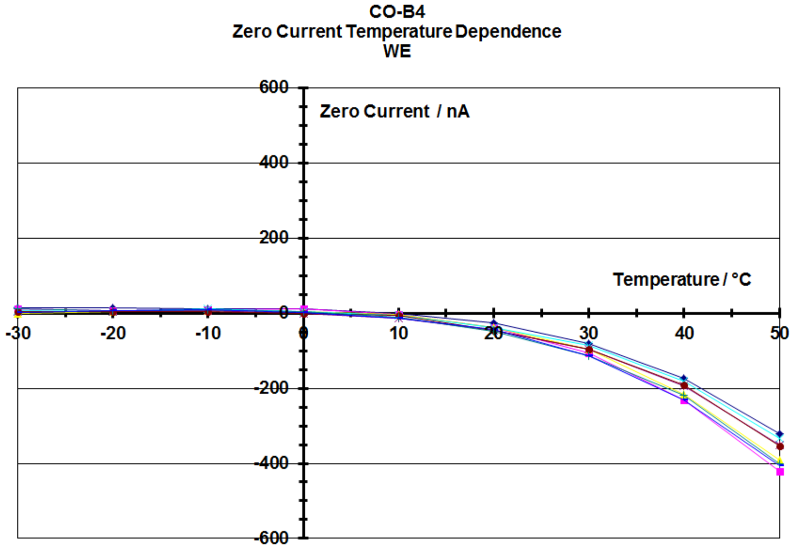

Fig. 15 Plots of zero currents for the WEs in CO-B4 sensors as a function of temperature

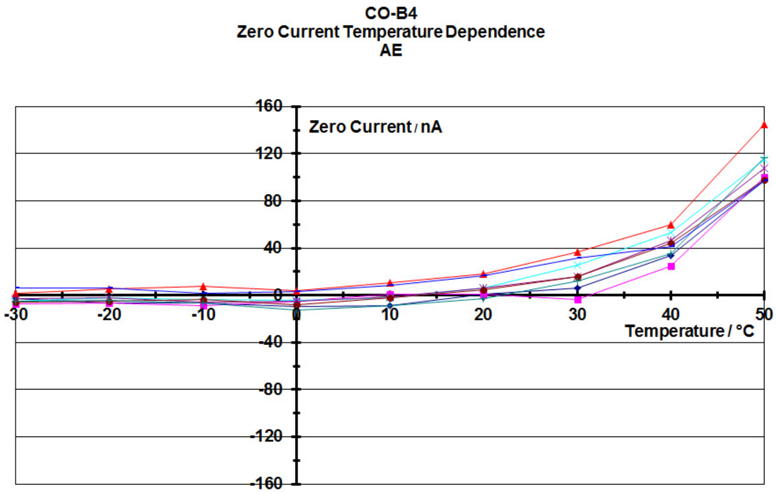

Fig. 16 Plots of zero currents for the AEs in CO-B4 sensors as a function of temperature

Table 5 shows the ratio of WE/AE currents for CO-B4 sensors as a function of temperature.

Table 5 WE / AE current ratios as a function of temperature for CO-B4 and CO-A4 sensors

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Temperature range/°C	-30 to +10	+20	+30 to +50
WE/AE current ratios B4 sensors	-1.0	-1.0	-3.8
WE/AE current ratios A4 sensors	+1.0	-1.0	-0.76

As can be seen from Figs. 15 and 16 the CO-B4 sensors have different characteristics from the other sensors discussed in this Application Note and this is reflected in the negative values of *n*. Also because of the nature of the electrocatalyst, the correction is less precise than for other sensors, particularly at higher temperatures. At the higher temperatures there is a wide variability in zero currents and hence the current limits are rather larger than for other sensors.

When eqn. (3a) is applied as previously the corrected WE currents as a function of temperature are as shown in Fig. 17 for 76 measurements with eight different sensors. A similar plot is obtained for CO-A4 sensors with the current ratios from Table 5.

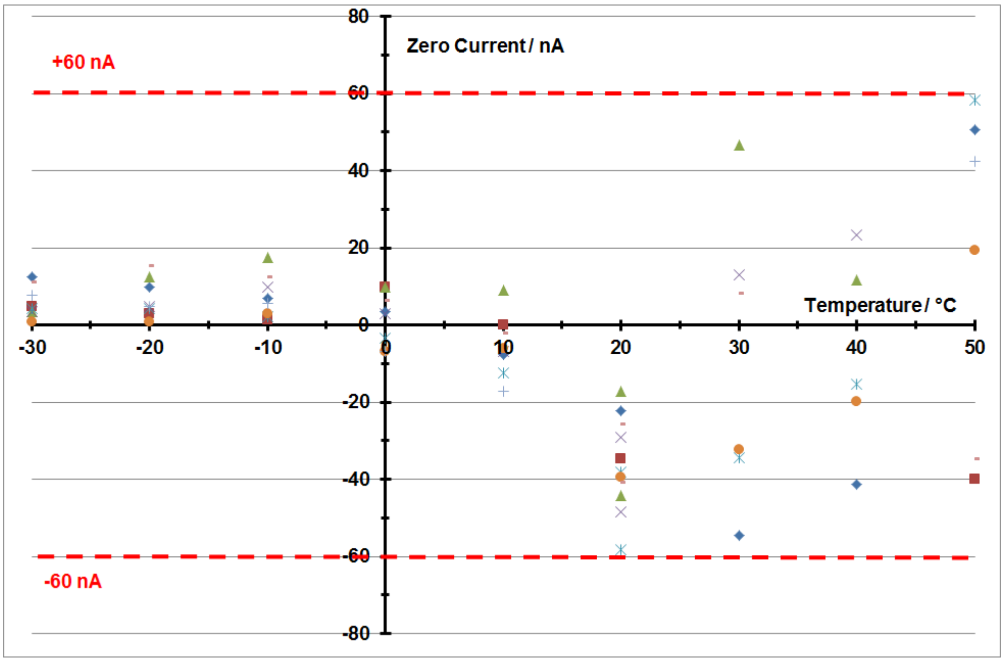

Fig. 17 Plots of (I_{WE} - I_{PCBWE}) – n x (I_{AE} - I_{PCBAE}) for CO-B4 sensors as a function of temperature after applying current ratios for three temperature zones

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Conclusions

Background/ zero currents for electrochemical gas sensors can often be significant, frustrating attempts to make measurements of low levels of the sampled gas. This background error can be corrected for by making use of an additional electrode, the auxiliary electrode (AE), buried within the sensor.

To correctly subtract the zero current from the measured current, follow the instructions below. These instructions are written for systems where the output is volts, which are linearly scaled with the sensor current.

Initial calibration

1 If you have purchased Alphasense AFE or ISB electronics, then program into your software the zero voltage of both the WE and AE as provided by Alphasense. Include separately in your software the electronic offset.

If you are using your own electronics, then supply a flow of good quality zero air over the sensor for at least 20 minutes and measure the WE and AE currents (or voltages). But first measure the open circuit offset to determine your electronic offset errors, which are a separate correction.

2 Create a look-up table or other method in your software for determining the correct value of n for your sensor at the measured sensor temperature. Ensure that the temperature that you record as the sensor temperature is the temperature at the top of the sensor. This measured temperature does not need to be very accurate, but it must be sufficiently accurate to select the correct value of n from the look-up table.

Correcting measurements

1 Measure the WE and AE current or voltage in your application.

2 Determine the temperature of operation, and from this temperature determine the correct value of n.

3 Multiply the AE current/ voltage by n.

4 Subtract the two separate electronic offsets from both the WE and AE.

5 Subtract this scaled AE current/ voltage from the WE current/ voltage. The corrected WE will be linearly dependent on gas concentration, so divide this by the sensitivity (nA/ ppm or mV/ ppm) to obtain the gas concentration.

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Appendix 1

Look-up table for *n* from -30°C to +50°C

	-30°C	-20°C	-10°C	0°C	10°C	20°C	30°C	40°C	50°C
CO-A4	+1.0	+1.0	+1.0	+1.0	+1.0	-1.0	-0.76	-0.76	-0.76
CO-B4	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-3.8	-3.8	-3.8
NO-A4	1.48	1.48	1.48	1.48	1.48	2.02	1.72	1.72	1.72
NO-B4	1.04	1.04	1.04	1.04	1.04	1.82	2.00	2.00	2.00
NO2-A4	1.09	1.09	1.09	1.09	1.09	1.35	3.00	3.00	3.00
NO2-B4	0.76	0.76	0.76	0.76	0.76	0.68	0.23	0.23	0.23
SO2-A4	1.15	1.15	1.15	1.15	1.15	1.82	3.93	3.93	3.93
SO2-B4	0.96	0.96	0.96	0.96	0.96	1.34	1.10	1.10	1.10
O3-A4	0.75	0.75	0.75	0.75	1.28	1.28	1.28	1.28	-
O3-B4	0.77	0.77	0.77	0.77	1.56	1.56	1.56	2.85	-
H2S-A4									
H2S-B4									

Note that n is constant over wide temperature range and you need only decide from the ambient temperature to select from two or three values to determine n.

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