Intrinsic Safety Information for Approvals

Introduction

Alphasense toxic sensors are three electrode electrochemical cells that produce small currents at low voltages when exposed to gases. The purpose of this Application Note is to explain sensor output during normal use and sensor output during a system fault or when changing sensors. This Note applies to all four families of Alphasense toxic gas sensors: A, B, C and D.

Three conditions are reviewed:

i) Current and output generated under ambient conditions during normal use

ii) Maximum open circuit voltage

iii) Transient current generated when short-circuiting from an open circuit condition

It is useful to compare these worse case results with a definition of a "Simple Apparatus" as stated in BS EN 50014 Section 1 Clause 1.3. The section titled "General Requirements" states that:

"Devices in which according to the manufacturer's specifications, none of the values 1.2V, 0.1A, 20µJ or 25mW is exceeded need not be certified or marked".

Current generated during normal use

Alphasense carbon monoxide, hydrogen sulfide, nitrogen dioxide, chlorine, nitric oxide, sulfur dioxide, hydrogen cyanide, ozone, phosphine and other hydrides, hydrogen chloride and hydrogen bromide electrochemical cells use a three electrode sensing structure. For many applications the working ("sensing") electrode is held at zero bias with respect to the reference electrode by using high impedance operational amplifier that provides current through the counter electrode whose potential is allowed to float. This current is generated in order to maintain the reference electrode at a controlled bias, normally zero volts. This current from the op amp balances the current generated at the working electrode, which increases linearly with the gas concentration; this current is measured as the sensor output:

Gas concentration (ppm) x sensor sensitivity (µA/ppm) = sensor output (µA)

This linear relationship breaks down when either of the following conditions occurs:

(a) When the concentration of gas is greater than the sensor range then the limited solubility of gas in the electrolyte and possible saturation of the catalyst will lead to non-linear behaviour.

(b) When the operational amplifier (which is used to both measure the current going into the working electrode and to maintain its potential close to the reference electrode potential) output current saturates. This saturation current will depend on the op amp selected and the instrument manufacturer; many low power op amps offer only 1 to 5mA current capability but high output op amps can supply up to 60 mA. The manufacturer of the op amp specifies the saturation current for that op amp, but typically for portable instrumentation; the saturation current is 1 to 3 mA, depending on the op amp selected. This second condition of the op amp limits the maximum output current.

The output current in normal use can be calculated from the above equation, knowing the gas concentration and the sensitivity. This is true as long as the gas concentration is within the sensor's linear range and the op amp has not saturated.

Voltage generated during normal use

In normal amperometric operation the maximum sensor voltage generated is a combination of the potential difference between the working and reference electrodes and the potential difference between the reference and counter electrodes.

For a sensor with zero voltage bias applied to the working electrode, the potential difference between the working and reference electrodes will be zero or very close to zero (less than a few mV). For biased sensors the potential will be equal to the bias voltage. The reference electrode potential is determined by the reference couple, which is generally taken as the equilibrium based on O2, H+ and H2O, and this is discussed further below. The counter electrode potential is not controlled and will float depending on gas concentration at the working electrode (which will set the current demand) and other factors, including adequate access to of oxygen to the counter if a reduction is occurring there. In the absence of any target gas the counter electrode potential will be very close to the working electrode potential. However, it is reasonable to say that the potential difference between the working and counter electrodes (i.e. the overall sensor voltage) will under normal operation be at least a few hundred milli-volts.

For an anodic process at the working electrode in the presence of air the counter electrode process is likely to be the reduction of oxygen:

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\quad$ E = +1.25V

The potential has been calculated on the basis of E0 of +1.23V for the equilibrium and adjustment for a partial pressure of oxygen of 0.2 atm and an acid solution of ~5M, which is a common electrolyte for a number of gas sensors. For a cathodic process at the working electrode a likely counter electrode reaction is the oxidation of water, which is the reverse of the reaction given above. So the same potential considerations will apply whether the sensing electrode is carrying out an oxidation or reduction.

Under normal use, an Alphasense three electrode sensor with an anodic working electrode reaction and a zero bias will show a maximum sensor potential of 1.25 volts; this will rarely be achieved and in normal use a value closer to a few hundred mV at full scale gas concentration is more typical.

Maximum open circuit voltage

The maximum sensor open circuit voltage is calculated as the sum of the working-counter electrode potentials using the Nernst equation. The equations below assume a gas concentration of 1000 ppm.

Although the controlling reaction of the reference and counter electrodes is not agreed by all, as indicated above it is usually modelled on the oxygen reduction reaction:

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\quad$ $E^0 = 1.227V$

This reaction at the reference and counter electrodes is not reversible but the theoretical potential for this reaction, correcting for the non-standard conditions, is, as already mentioned, about 1.25V on the Standard Hydrogen Electrode (SHE) scale at 25°C. This is true for the Alphasense CO, H_2S and SO_2 sensors, but is not true for other sensors as discussed below.

Typical electrode reactions are given below and in each case the first reaction being that occurring at the working electrode, the second is that at the counter electrode, and the third is the overall sensor reaction. The cell voltage is taken as the WE potential minus the CE potential; all potentials below are referenced to the SHE. Relevant sensors are listed below, but are not exclusive.

Other sensors using the same electrochemistry also apply.

For CO sensors (CO-A1/F/X/E, CO-B1/F/X/E, CO-C1/F/X, CO-D1, CO-D4, D2):

$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O$	E = -0.09V
$1/2\ O_2 + 2H^+ + 2e- \rightleftharpoons H_2O$	E = +1.25V
$CO_2 \rightleftharpoons CO + 1/2O_2$	**E = -1.34V**

For SO_2 sensors (SO2-AF, SO2-BF, SO2-CF, SO2-DF, SO2-D4):

$SO_3 + 2H^+ + 2e^- \rightleftharpoons SO_2 + H_2O$	E = +0.35V
$1/2\ O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	E = +1.25V
$SO_3 \rightleftharpoons SO_2 + 1/2\ O_2$	**E = -0.90V**

For H_2S sensors (H2S-A1, H2S-AH, H2S-AE, H2S-B1, H2S-BE, H2S-BH,H2S-D1, H2S-D4, D2):

$SO_3 + 8H^+ + 8e^- \rightleftharpoons H_2S + 3H_2O$	E = +0.85V
$2\ O_2 + 8H^+ + 8e^- \rightleftharpoons 4H_2O$	E = +1.25V
$H_2SO_4 \rightleftharpoons H_2S + 2O_2$	**E = -0.40V**

For NO sensors (NO-A1, NO-AE, NO-B1, NO-BE, NO-C1, NO-D1, NO-D4):

$NO_2 + 2H^+ + 2e^- \rightleftharpoons NO + H_2O$	E = +0.94V
$1/2\ O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	E = +1.25V
$NO + 1/2\ O_2 \rightleftharpoons NO_2$	**E = -0.31V**

For ClO_2 sensors (CLO2-A1, CLO2-B1, CLO2-D1, CLO2-D4):

$ClO_3- + 2H^+ + e^- \rightleftharpoons ClO_2 + H_2O$	E = +1.06V
$½\ O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	E = +1.25V
$2ClO_3^- + 2H^+ \rightleftharpoons 2ClO_2 + H_2O + ½\ O_2$	**E = -0.19V**

For PH_3 sensors (PH3-A1, PH3-AE, PH3-B1, PH3-BE, PH3-D4):

$H_3PO_3 + 6H^+ + 6e^- \rightleftharpoons PH_3 + 3H_2O$	E = + 0.40V
$½\ O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	E = +1.25V
$H_3PO_3 \rightleftharpoons PH_3 + {}^3/2\ O_2$	**E = -0.85V**

For HCl/HBr sensors (HCL-A1, HCL-AH, HCL-B1, HCL-BH):

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	E = +1.52V
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	E = +1.22V
$½\ O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	E = +1.25V
$Cl_2 + H_2O \rightleftharpoons 2Cl^- + ½\ O_2 + 2H^+$	**E = +0.27V**
$Br_2 + H_2O \rightleftharpoons 2Br^- + ½\ O_2 + 2H^+$	**E = -0.03V**

Note that HBr/HCl and NO sensors have the WE with a positive bias of ~0.3V with respect to the reference electrode. Therefore, if this bias is applied when measuring the open circuit sensor voltage the maximum voltage will be more positive by the amount of bias.

All of the above involve oxidative processes at the working electrode and all are based on the use of H_2SO_4.

The following systems have reductions at the sensing electrode.

For NO_2 sensors (NO2-A1, NO2-AE, NO2-B1, NO2-BE, NO2-D1, NO2-D4, NO2-C1):

$NO_2 + 2H+ + 2e- \leftrightharpoons NO + H_2O$	E = +1.15V
$½ O_2 + 2H+ + 2e- \leftrightharpoons H_2O$	E = +1.25V
$NO_2 \leftrightharpoons NO + ½ O_2$	**E = -0.10V**

For Cl_2 sensors (CL2-A1, CL2-AE, CL2-B1, CL2-BE, CL2-D4):

$Cl_2 + 2e^- \leftrightharpoons 2Cl^-$	E = +1.67V
$½ O_2 + 2H^+ + 2e^- \leftrightharpoons H_2O$	E = +1.25V
$Cl_2 + H_2O \leftrightharpoons 2Cl^- + ½ O_2 + 2H^+$	**E = +0.42V**

For O_3 sensors (O3-A1, O3-B1, O3-D4):

$O_3 + 2H^+ + 2e^- \leftrightharpoons O_2 + H_2O$	E = +1.99V
$½ O_2 + 2H^+ + 2e^- \leftrightharpoons H_2O$	E = +1.20V
$O_3 \leftrightharpoons O_2 + ½ O_2$	**E = +0.79V**

For HCN sensors (HCN-A1, HCN-B1, HCN-D4):

$Ag(CN)_2^- + e^- \leftrightharpoons Ag + 2CN-$	E = -0.17V
$½ O_2 + 2H^+ + 2e- \leftrightharpoons H_2O$	E = +0.51V
$Ag(CN)_2^- + H_2O\ Ag + 2HCN + ½ O_2$	**E = -0.68V**

For O2 sensors (LFO2-A4)

$½ O_2 + 2H^+ + 2e^- \leftrightharpoons H_2O$	E = +1.25V
$H_2O \leftrightharpoons 2e- + 2H+ + ½ O_2$	E = +1.25V
	E = 0V

The maximum theoretical sensor open circuit voltage between the working electrode and counter electrode is summarised in Table 1 below. The table also shows the effect of gas concentration on the theoretical open circuit voltage at 25°C.

Target Gas	Gas Concentration	
	10 ppm	1000 ppm
CO	- 1.28	- 1.34
SO_2	- 0.84	- 0.90
H_2S	- 0.39	- 0.40
NO	- 0.27	- 0.31
ClO_2	- 0.12	- 0.19
PH_3	- 0.83	- 0.85
HCl	+0.39	+ 0.27
HBr	+ 0.09	- 0.03
NO_2	- 0.16	- 0.10
Cl_2	+ 0.36	+ 0.42
O_3	+ 0.73	+ 0.79
HCN	- 0.44	- 0.68
Target Gas	Gas Concentration	
	20.9%	90%
O_2	0	0

Table 1: Theoretical open circuit sensor voltages.

The calculated voltages would never be achieved in normal use for several reasons:

1. The theoretical Nernst potentials are never achieved because when the sensor is operating the electrochemical processes, such as described above, are well removed from equilibrium and, hence, are at some distance from the theoretical thermodynamic potentials.
2. Should the potentiostat circuit fail so that a sensor becomes on open circuit then the electrochemical processes will move towards equilibrium and the appropriate Nernst potentials will be achieved. The time taken for this to occur will depend on the reversibility of the reactions involved, with very reversible electrochemical systems reaching equilibrium in a matter of minutes, or less. For very irreversible systems the time will be much longer, and in some cases equilibrium may never be attained.
3. In the open circuit condition toxic gas sensors are susceptible to gaseous diffusion of the test gas to both the reference and the counter electrodes, and this will lead to an equalisation of the electrode potentials and a decrease of the open circuit potentials.
4. The calculated voltages assume ideal gaseous and solution behaviour, but this assumption will only affect the final voltage by a few milli-volts or tens of milli-volts at most.

Tests at Alphasense have shown that open circuit voltages achieve typically half their theoretical potential voltage (see table above).

Transient current generated when short-circuiting from an open circuit condition

The maximum transient current can be determined from the open circuit voltage and impedance of the sensor. This transient current will be further limited by the value of the load resistor, but for a worse case discussion we assume the load resistor is a short circuit. The decay rate will depend on the impedance of the sensor, but typically the transient current decays in less than a few seconds. The measured internal resistance of sensors is between 4 and 8 ohms.

Table 2 gives for each sensor peak transient current when short-circuiting at 1000 ppm gas concentration. This value will increase with higher gas concentrations, but by only a few percent.

Sensor Gas	mA (@ 1000 ppm)
CO	170
SO_2	220
H_2S	100
NO	150
ClO_2	120
PH_3	150
HCl	100
HBr	100
NO_2	100
Cl_2	120
O_3	100
HCN	100
Target Gas	mA (@20.9%)
O_2	100

Table 2: Transient currents for short-circuited sensors

In summary, the transient current when short-circuiting an Alphasense toxic gas sensor is considerably less than 0.5 A.

Measurement	Condition	CO	SO_2	H_2S	NO
Maximum current (mA)	normal use	<0.15	<0.25	<0.15	<0.15
Maximum voltage (V)	normal use	1.25	1.25	1.25	1.25
Maximum voltage (V)	open circuit(100%)	1.34	0.90	0.40	0.31
Max transient current (mA)	short circuit (100%)	<200	<250	<120	<120

Measurement	Condition	ClO_2	PH_3	HCl	HBr
Maximum current (mA)	normal use	<0.08	<0.25	<0.15	<0.15
Maximum voltage (V)	normal use	1.25	1.25	1.25	1.25
Maximum voltage (V)	open circuit(100%)	0.19	0.85	0.17	0.03
Max transient current (mA)	short circuit (100%)	<120	<250	<100	<100

Measurement	Condition	NO_2	Cl_2	O_3	HCN	O_2
Maximum current (mA)	normal use	<0.08	<0.08	<0.15	<0.15	<0.5
Maximum voltage (V)	normal use	1.25	1.25	1.20	0.51	0.6
Maximum voltage (V)	open circuit(100%)	0.10	0.42	0.79	0.68	0.1
Max transient current (mA)	short circuit (100%)	<120	<120	<150	<200	<200

Table 3: Summary of intrinsic safety information for Alphasense toxic sensors

Table 4 lists both the required bias voltages and minimum acceptable voltage supply required for the counter electrode.

Sensor Gas	Bias voltage (mV)	mA (@ 1000 ppm)
CO	0	-300
SO_2	0	-250
H_2S	0	-75
NO	+300	-450
ClO_2	0	+650
PH_3	0	-400
HCl	0	-400
HBr	0	-400
NO_2	0	+650
Cl_2	0	+650
O_3	0	-1650
HCN	0	-400
O_2	-600	-600

Table 4: Required bias voltage for the WE and minimum voltage supply for the CE

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