SGX SENSORTECH

Linearity Corrections to Pellistor Responses at High Gas Levels

Introduction

The response of a pellistor sensor to flammable gases is essentially linear with concentration at gas levels up to typically 60% of the lower explosive limit (LEL). At gas levels approaching the LEL there is observed a deviation from linearity in the form of a reduction in signal when expressed in terms of signal per %LEL. Performance tests often require the linearity of an instrument to be tested over the operating range and therefore, for those instruments designed to be used up to the LEL, this non-linearity at high gas levels may cause problems during the performance testing. The mechanism for this non-linearity can include the following effects:

a) Diffusion Considerations

Pellistors are usually housed in a flameproof enclosure that normally contains a sintered metal flame arrester that also acts as a primary diffusion barrier through which the gas must pass before reaching the sensing element. Having passed through this initial barrier, there is a second (less critical) barrier at the entrance to the sensor can before the gas reaches the vicinity of the sensor beads. Once near the catalytic detector bead, there is a third barrier that is formed by diffusion of combustion products away from the detector that produces a depletion layer around the surface of the detector. This depletion layer changes the rate of diffusion of fuel to the catalyst surface. Under normal operating conditions, the response of a pellistor is rate determined by the rate of arrival of fuel to the catalytic surface and therefore by the rate of diffusion of fuel to the catalyst. This rate determining step, r_d, can be expressed by:

$$r_d = D_{12} A \frac{dC}{dx} \quad \cdots\cdots\cdots\cdots \quad (1)$$

where D_{12} is the binary diffusion coefficient, A is the cross-sectional area through which the gas diffuses, C is the bulk gas concentration and x is the distance from the diffusion barrier.

It can be considered that, for a fixed ambient pressure with the sintered metal and sensor can entrance remaining unchanged, the size of the depletion layer surrounding the sensor increases with increasing gas concentration. As such, the diffusion time of fuel to the catalyst surface increases non-linearly with concentration of fuel. The concentration of fuel as a function of distance diffused through the depletion layer can be expressed by:

$$C = \frac{N}{2(\pi D_{12} t)^{1/2}} \exp\left(\frac{-x^2}{4D_{12}t}\right) \quad \cdots\cdots\cdots\cdots \quad (2)$$

where C is the concentration at a distance x from the diffusion barrier after a time t from an initial number of molecules N at time zero. This results in an apparent decrease in the diffusive flux of molecules close to the catalyst surface as the size of the depletion layer increases and therefore a corresponding deviation in the value of r_d from equation 1. It is also apparent that an increase in the effect of external diffusion controlling elements (such as reducing the opening of the pellistor can) will lead to a reduction in the effect of diffusion through the depletion layer and a consequent improvement in the linearity of the signal at high gas levels. e2v technologies' range of pellistors includes many closed can devices which illustrate this improvement of linearity at the expense of reduced output when compared with the same pellistor in an open can housing.

b) Adsorption Considerations

The rate of reaction of fuel on a pellistor under normal operating conditions is diffusion controlled, since the rate determining step is the rate of diffusion of fuel to the catalyst surface. At the catalyst surface, the reaction is therefore not normally rate determining and follows a heterogeneous mechanism largely dependent on the surface coverage of the reactants. At low operating temperatures (i.e. temperatures achieved by running the pellistor at voltages below those recommended for normal operation), the rate determining step can change from diffusion of reactants to the rate of reaction on the catalyst surface. Indeed, Arrhenius plots have been published by Firth (Trans. Faraday Soc., 62, 2571 (1966)) on different catalyst compositions, with the discussion relating the rate to be determined by reaction of adsorbed intermediates. Surface catalysis can usually be divided into the following basic steps:

1. Diffusion of reactants to the surface
2. Adsorption of reactants at the surface
3. Chemical reaction on the surface
4. Desorption of products from the surface
5. Diffusion of products from the surface

Under cool running conditions, the rate determining step is no longer the diffusion of reactants. The kinetics of such surface reactions can often be successfully treated on the basis that the rate determining step is reaction of adsorbed molecules, the reaction rate per unit surface area is proportional to the fraction of surface covered and this fraction can be described by a Langmuir isotherm. The associated reaction rate can then be described by:

$$r_a = \frac{kbP}{(1+bP)} \quad \ldots\ldots\ldots\ldots \quad (3)$$

where k is the rate constant, b is the adsorption coefficient and P is the partial pressure of fuel. The term $(1+bP)$ introduces non-linearity with increasing fuel concentration.

c) Constant Voltage Responses

The out-of-balance voltage from a sensor bridge arrangement powered by a constant voltage supply can be described in terms of the resistances of the detector and compensator as follows:

$$\Delta V = \frac{i\Delta R_d}{(1+R_d/R_c)} \quad \ldots\ldots\ldots\ldots \quad (4)$$

where ΔV is the voltage signal, i is the current through the detector, ΔR_d is the change in the detector resistance, R_d, and R_c is the compensator resistance. For small changes in R_d, this produces a linear relationship with fuel concentration, but for larger changes in fuel concentration, the increase in voltage drop across the detector and associated decrease in voltage drop across the compensator leads to an increase in the value of $(1+R_d/R_c)$ and subsequent non-linearity of the voltage signal.

d) Non-linearity Estimation

Both equations 3 and 4 above have a similar form that also approximates to the effect of an increase in the depletion layer thickness as discussed in section a) above. In general, the non-linearity may be expressed by:

$$R = \frac{K[F]}{(1+KK_2[F])} \quad \ldots\ldots\ldots\ldots \quad (5)$$

where R is the overall response, K is the normal linear slope of response against fuel concentration [F] and K_2 is the non-linear slope contribution. This relationship can also be expressed in a reciprocal form as:

$$\frac{1}{R} = \frac{1}{K[F]} + K_2 \quad \cdots\cdots\cdots \quad (6)$$

Non-linear correction may then be applied by inserting a value for K_2 in the above expressions. Note that, should K_2 be zero, a linear response results and the effect of the non-linear contribution is small at low fuel concentrations. The value of K_2 can be estimated by measuring the response at two fuel calibration points.

For example:
A batch of VQ542R miniature sensing heads was exposed to 100%LEL and 50%LEL methane and the ratio of the responses varied from 1.75 to 1.95 (a linear relationship gives a factor of 2.0). From this, the following can be deduced:

The mean signal ratio is approximately 1.85, i.e. $R_{100} = 1.85 \times R_{50}$, therefore:

$$\frac{1}{R_{100}} = \frac{1}{(1.85)(R_{50})} = \frac{1}{(100)(K)} + K_2 = \frac{1}{(1.85)(50)(K)} + \frac{K_2}{1.85} \quad \cdots\cdots\cdots \quad (7)$$

This results in the expression:

$$K_2 = \frac{1}{(566.7)(K)} \quad \cdots\cdots\cdots \quad (8)$$

Thereby calibrating at, for example, 50%LEL would automatically incorporate changes to both K and K_2 to provide linearisation at higher gas levels. Rearranging the response equation (6) and incorporating the relationship between constants in (8) gives:

$$[F] = \frac{R}{\left(K - \frac{R}{566.7}\right)} \quad \cdots\cdots\cdots \quad (9)$$

where [F] is the fuel concentration to be displayed, R is the sensor response signal and K is the slope required to calibrate the signal at a single gas concentration.

The effect of using equation (9) above for the VQ542R sensor can be tabulated as follows:

Gas Conc. (%LEL)	R (1.75) (mV)	Linear (1.75) (%LEL)	[F] calc. (%LEL)	R (1.85) (mV)	Linear (1.85) (%LEL)	[F] calc. (%LEL)	R (1.95) (mV)	Linear (1.95) (%LEL)	[F] calc. (%LEL)
0	0	0	**0**	0	0	**0**	0	0	**0**
10	17	11	**11**	16	11	**10**	15	10	**9**
20	33	22	**21**	32	21	**20**	30	20	**19**
30	48	32	**31**	47	31	**30**	45	30	**29**
40	62	41	**41**	61	41	**40**	60	40	**39**
50	75	50	**50**	75	50	**50**	75	50	**50**
60	87	58	**59**	89	59	**60**	89	59	**60**
70	99	66	**68**	102	68	**70**	103	69	**71**
80	110	73	**77**	114	76	**80**	117	78	**82**
90	121	81	**85**	127	85	**90**	132	88	**94**
100	131	87	**94**	139	93	**100**	146	97	**106**

Refer to the notes overleaf.

Notes:

'R (1.75)' is the sensor response for a ratio of R_{100}/R_{50} of 1.75 and 'Linear (1.75)' is the indicated %LEL from a linear calibration based on the use of 50%LEL calibration gas for a ratio of R_{100}/R_{50} of 1.75.

'R (1.85)' is the sensor response for a ratio of R_{100}/R_{50} of 1.85 and 'Linear (1.85)' is the indicated %LEL from a linear calibration based on the use of 50%LEL calibration gas for a ratio of R_{100}/R_{50} of 1.85.

'R (1.95)' is the sensor response for a ratio of R_{100}/R_{50} of 1.95 and 'Linear (1.95)' is the indicated %LEL from a linear calibration based on the use of 50%LEL calibration gas for a ratio of R_{100}/R_{50} of 1.95.

Each data set is normalised to a sensor response of 75 mV when exposed to 50%LEL.

'[F] calc.' is the concentration as calculated from equation 9 for each set of response ratio data.

The limits for linearity testing at CSA are ±5% fsd for readings above 50% fsd and for Cenelec are ±5% fsd or ±10% reading, whichever is the greater. On this basis, a linear expression would be insufficient to meet the CSA requirement at 100% LEL for response ratios of 1.75 and 1.85, but expression (9) does improve the situation significantly. The Cenelec requirement can also be met from the above data using equation (9), particularly in the case of $R_{100}/R_{50} = 1.75$ where a linear expression would not be sufficient.

The range of response ratios R_{100}/R_{50} from 1.75 to 1.95 may be sufficient to enable equation (9) to be applied to several different e2v technologies sensor types. However, it should be noted that the user's sensor housing may have an effect on the linearity aspects of the sensor response, which may lead to smaller response ratios and therefore require a different K_2 value. The above example for the VQ542R miniature sensing head includes the effects of the complete housing assembly.