July 10, 2003

Applications Note: Use of "pentane equivalent" calibration gas mixtures

Introduction

The gas that is used to verify accuracy is every bit as important as the detector itself when it comes to worker safety. Choosing (and using) the right mixture is critical to the success of your atmospheric monitoring program.

BW understands the importance of calibration, and we are always on the lookout for ways to improve the process. To that end, BW is pleased to announce the introduction of a new series of "pentane equivalent" calibration gas mixtures. These mixtures are designed to provide an even more dependable (and easy) means for the verification of accuracy of instruments that include a sensor for the detection of combustible gas.

What are "pentane equivalent" mixtures and why are they better?

Using BW’s new "equivalent" mixtures is *exactly* like using our older mixtures. In the case of the GasAlertMicro and GasAlertMax, all you have to do is press the "cal" button, attach the adaptor, and flow gas to the sensors. All the adjustments are made automatically.

The difference comes from what's in the cylinder of gas. In the past, BW has usually recommended using mixtures that include 50% LEL methane as the combustible gas used for general purpose calibration. BW's new equivalent mixtures are still based on methane, but in concentrations that are designed to produce a level of sensitivity "equivalent" to that provided by a mixture that contains a 50% LEL concentration of pentane.

The reasoning behind the development of these new formulations has to do with how combustible sensors detect gas, and what happens to sensitivity in the event that a combustible sensor ever becomes "poisoned". *If sensitivity is lost due to poisoning, it tends to be lost first with regards to methane.* A partially poisoned sensor might still respond accurately to pentane, while showing a dangerously reduced response to methane. BW’s equivalent mixtures eliminate this potentially dangerous source of calibration error. Because BW’s equivalent mixtures are based on methane, any loss of sensitivity to methane is detected (and can be corrected) immediately.

Environmental conditions can have an effect on sensor accuracy

There are three types of sensors which are commonly used in confined space monitors; oxygen, combustible gas (LEL), and toxic gas sensors. Each type of sensor uses a slightly different detection principle. The kinds of conditions that can affect accuracy vary from one type of sensor to the next. The type of sensor that is most prone to being affected by the atmosphere in which it is being used tends to be the combustible sensor. Age and usage can have a serious effect on sensitivity. Chronic exposure to silicone containing substances (found in many lubricants), the tetra-ethyl-lead found in "leaded" gasoline, halogenated hydrocarbons (Freons®, or solvents such as trichloroethylene and methylene chloride), high concentrations of hydrogen sulfide or even very high concentrations of combustible gas may all lead to degraded combustible sensor performance. In most cases all this means is that the sensitivity is adjusted upwards at the time the instrument is calibrated. In the worst case, the sensor may need to be replaced. Verifying the accuracy of the sensors on a regular basis is *essential* to assuring worker safety.

How combustible sensors work

The minimum amount of a combustible gas or vapor in air that will explosively burn if a source of ignition is present is the Lower Explosive Limit (LEL) concentration. Combustible gas readings are given in percent LEL, with a range of zero to 100 percent explosive.

Combustible sensors contain two coils of fine wire coated with a ceramic material to form beads. The "active" bead is coated with a palladium-based material that allows catalyzed combustion to occur on the surface of the bead. The "reference" bead lacks the catalyst coating, but in other respects exactly resembles the active bead. Any combustible vapors that are present will be subject to catalytic combustion on the surface of the active bead, heating this bead to a higher temperature. The temperature of the untreated reference bead is unaffected by the presence of gas. The difference between the temperatures of the two beads is proportional to the amount of combustible gas present. Since the beads are strung on the opposite arms of a Wheatstone Bridge electrical circuit, the instrument perceives this as a change in the electrical resistance in the circuit. It is this change in resistance due to differential heating that is used by the instrument to provide a reading.

Relative response

BW combustible gas sensors are non-specific and respond to all combustible gases and vapors. It is not necessary for the combustible vapor to be present in LEL concentrations. Even trace amounts of combustible gas can be detected by this method.

Catalytic hot bead sensors respond to a wide range of ignitable gases and vapors. The amount of heat produced by the combustion of a particular gas/vapor on the active bead will reflect the heat of combustion for that substance. Heat of combustion varies from one substance to another. For this reason readings vary between equivalent concentrations of different combustible gases. The amount of heat provided by oxidation of the molecule on the active bead surface actually is inversely proportional to the heat of combustion for that gas. This occurs because of differences in molecular interaction with the catalytic surface. In general, the larger the size of the molecule, the greater the heat of combustion. On the other hand, the smaller the molecule, the more readily it is able to penetrate the sintered surface of the bead, and interact with the catalyst in the oxidation reaction.

A combustible gas and vapor reading instrument may be calibrated to any number of different gases or vapors. If an instrument is only going to be used for a single type of gas over and over again, it is usually best to calibrate the instrument to that particular hazard. As long as the gas that is encountered is the same gas that was used during calibration, the readings will be exactly accurate (to the tolerances of the instrument design). This is what is illustrated in Figure 1.0:

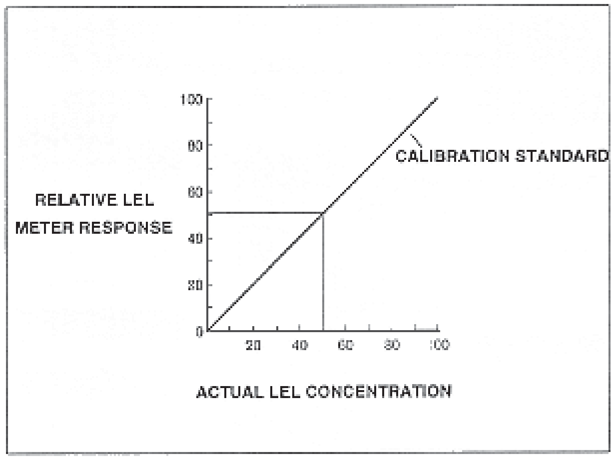

Figure 1.0: Linear response to the gas used in calibration

Note that in a properly calibrated instrument, a concentration of 50 percent LEL produces a meter response (reading) of 50 percent LEL.

Figure 2.0 illustrates what may be seen when a combustible sensor is used to monitor gases other than the one to which it was calibrated. The chart shows the "relative response curves" of the instrument to several different gases.

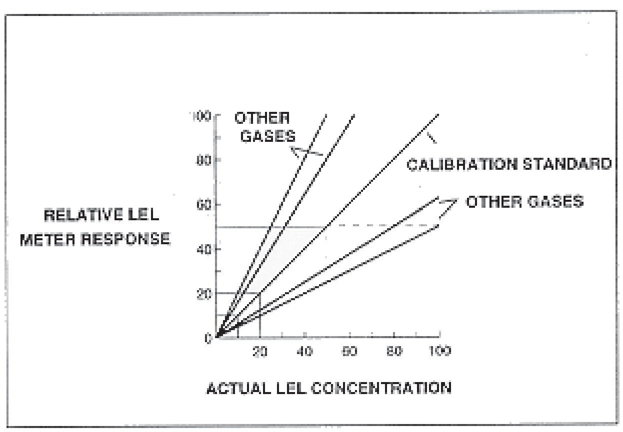

Figure 2.0: Relative response curves

Note that the response to the gas to which the instrument was calibrated, the "calibration standard", is still precisely accurate. For the other gases the responses are a little off.
In the case of some gases the readings are a little high. This results in the instrument going into alarm a little bit early. This type of error is not usually dangerous, since it simply results in workers exiting the affected area sooner than they otherwise would have.

Gases that produce lower relative readings than the calibration standard can result in a more potentially dangerous sort of error. One way to reduce the potential for this type of error is to use a lower alarm setting. It may be seen from the graph that the amount of relative error decreases the lower the alarm point is set. If the alarm point is set at 10 percent LEL, the differences due to relative response of the combustible sensor are minimal.

Choosing the right calibration mixture

The other method for reducing the effects of this sort of error is in the choice of the calibration gas used to calibrate the combustible sensor. The best results are obtained when calibration is done using the same gas that is expected to be encountered while actually using the instrument. When it is not possible to calibrate directly to the gas to be measured, or when the combustible gas is an unknown, a mixture which provides a sensor response that is more typical of the range of combustible gases and vapors that will be encountered should be selected.

Relative response may be expressed as a ratio and presented in the form of a table. Table 1.0 lists the expected response of a sensor that has been calibrated to pentane, pentane or methane to a selection of other combustible gases. The closer the relative response comes to 1.0, the more accurate the reading. For instance, if the sensor is calibrated to pentane, then exposed to hexane, the response ratio is so close, (0.9 to 1), that for all intents and purposes any error is trivial.

Combustible Gas / Vapor	**Relative response when sensor is calibrated on pentane**	**Relative response when sensor is calibrated on propane**	**Relative response when sensor is calibrated on methane**
Hydrogen	2.2	1.7	1.1
Methane	2.0	1.5	1.0
Propane	1.3	1.0	0.65
n-Butane	1.2	0.9	0.6
n-Pentane	1.0	0.75	0.5
n-Hexane	0.9	0.7	0.45
n-Octane	0.8	0.6	0.4
Methanol	2.3	1.75	1.15
Ethanol	1.6	1.2	0.8
Isopropyl Alcohol	1.4	1.05	0.7
Acetone	1.4	1.05	0.7
Ammonia	2.6	2.0	1.3
Toluene	0.7	0.5	0.35
Gasoline (Unleaded)	1.2	0.9	0.6

Table 1.0. Relative response ratios

As may be seen from Table 1.0, when the instrument is calibrated to methane, readings for many gases on the list are somewhat low. On the other hand, when calibrated to pentane, most of the gases on the list will produce readings that are quite close to, or a little bit higher than actual. For many applications pentane, or a mixture which provides a similar level of sensitivity, is the gas that's "just right" for combustible sensor calibration.

Table 2.0 lists examples of the equivalent methane concentration that provides the same level of sensitivity as direct calibration to the listed combustible gases and vapors. By varying the concentration of methane in the calibration gas mixture, it is possible to simulate the characteristics of any desired combustible gas.

Combustible Gas / Vapor	**Relative response when sensor is calibrated to 2.5% (50% LEL) methane**	**Concentration of methane used for equivalent 50% LEL response**
Hydrogen	1.1	2.75% CH4
Methane	1.0	2.5% Vol CH4
Ethanol	0.8	2.0% Vol CH4
Acetone	0.7	1.75% Vol CH4
Propane	0.65	1.62% Vol CH4
n-Pentane	0.5	1.25% Vol CH4
n-Hexane	0.45	1.12% Vol CH4
n-Octane	0.4	1.0% Vol CH4
Toluene	0.35	0.88% Vol CH4

This technique is particularly useful for target gases and vapors (such as toluene) that are not available packaged in field portable cylinders in LEL range concentrations.

Summation

The catalytic "hot bead" sensors used in BW instruments are resistant to poisoning, stable, and have proven to be an exceptionally dependable sensor design. But it's still important to verify accuracy on a regular basis. Most importantly, if sensitivity is lost due to poisoning, it is frequently lost first with regards to methane. The safest approach is to verify the function of the sensor by testing it by exposure to methane, or a methane based calibration gas mixture.

In most cases the loss of sensitivity is incremental, that is, it occurs a little at a time. In some cases, however, the loss of sensitivity can be almost immediate. This is the reason that gas detector manufacturers stress the importance of periodically testing their instruments by exposing them to known concentration calibration gas, and why use of methane based "pentane equivalent" calibration gas is such a good idea.