Application Note	Use of “Equivalent” Calibration Gas Mixtures	Date	August 8, 2001
		Nº	AN20010808
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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.

There are two important factors to consider when selecting the right calibration gas mixture for combustible gas sensors.

1. Scale of calibration for proper sensitivity of the LEL sensor.
2. Type of calibration gas mixture for protection against selective loss of sensitivity due to sensor poisoning.

Scale Of Calibration

Biosystems 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.

The amount of heat produced by the combustion of a particular gas on the active bead reflects the “Heat of Combustion” for that gas. The heat of combustion may vary from one combustible gas to another. The heat of combustion affects the “output” of the sensor, which in turn is used by the detector to display an LEL reading.

A combustible gas sensor may be calibrated to any number of different gases. The gas used to calibrate the instrument is known as the “Calibration Standard”. If an instrument is only going to be used for a single type of gas it should be calibrated to that gas. As long as the gas that is encountered is the same gas that was used during calibration, the readings will be exact (within the tolerances of the instrument design). Figure 1 illustrates that a reading of 50% LEL will be obtained when the sensor is exposed to an actual concentration of 50% LEL of the same type of LEL gas.

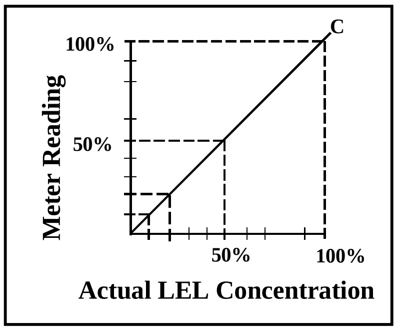

Figure 1 Linear response to the gas used in the calibration

Figure 2 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.

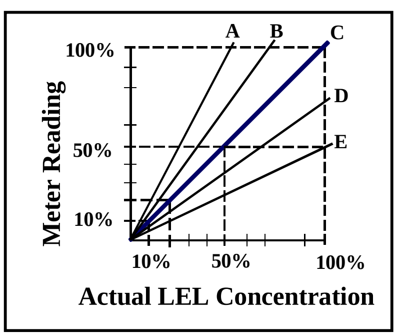

Figure 2 Relative response curves

Note that the instrument response to the gas to which the instrument was calibrated is still accurate. For the other gases the instrument responses are either higher or lower than the response to the gas to which it was calibrated.

Some gases may produce higher readings than the calibration standard. This results in the instrument going into alarm early. This type of error is usually not dangerous, since it simply results in workers exiting the affected area sooner than they otherwise would have.

Other gases may produce lower readings than the calibration standard. This can potentially result in a more 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% LEL, the differences due to relative the response of the combustible sensor are minimal.

Choosing the Right Scale of Calibration Gas Mixture

The other method for reducing the effects of this sort of error is in the choice of the 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. It may not be possible to calibrate directly to the gas measured or the gas encountered may be unknown. In these cases a mixture which provides an appropriate sensor response should be selected.

Relative response may be expressed as a ratio between the gas encountered and the calibration standard. Table 1 lists the expected response of a sensor that has been calibrated to pentane, propane or methane to a variety of other combustible gases. The closer the relative response is to 1.0, the more accurate the reading. For instance, if the sensor is calibrated to propane, then exposed to acetone, the response ratio is so close (1.05 to 1) that for all intents and purposes any error is trivial.

Combustible Gas / Vapor Exposure	Relative response when sensor is calibrated on …		
	Pentane	Propane	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 Relative response ratios

As may be seen from this table, when the instrument is calibrated to methane, readings for most gases on the list are dangerously low. On the other hand, when calibrated to pentane, for many gases readings are excessively high. When the instrument is calibrated to propane however, most of the gases on the list will produce readings which are quite close to or only a little higher than actual.

For many applications propane (or a mixture that provides a similar level of sensitivity) is the gas that's "just right" for combustible sensor calibration.

Poisoning Of Combustible Gas Sensors

The combustible sensor may be affected by the atmosphere in which it is being used. Age and usage can also have a serious effect on sensitivity. Chronic exposure to substances containing silicone (found in many lubricants), the tetra-ethyl-lead found in "leaded" gasoline, halogenated hydrocarbons (Freons®, or solvents such as trichloroethylene and ethylene 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. Once again, verifying the accuracy of the sensors on a regular basis is essential to assuring worker safety.

If a combustible gas sensor is poisoned by exposure to silicone, sensitivity tends to be lost first with regards to methane. This means the sensor may exhibit reduced sensitivity to methane while not exhibiting any loss of sensitivity to other gases. In extreme cases the sensor may not respond at all to methane while it is still responds appropriately to other gases. It may even be possible to perform a calibration with these other gases. This condition can be very dangerous when the calibration gas used is based on any other combustible gas than methane.

This means that while methane does not typically provide an appropriate calibration scale, it is still important that the instrument be challenged with methane in order to recognize desensitized LEL sensors.

For many users it is not practical to obtain one calibration gas to establish a scale of calibration and then additionally use a methane gas to ensure that the LEL sensor has not been poisoned.

"Equivalent" Calibration Gases

Figure 3 shows the relative response to propane and methane using a combustible gas sensor that has been calibrated to propane.

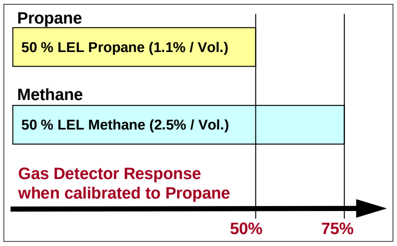

Figure 3 Propane and methane response on a propane calibrated detector

When exposed to 50% LEL propane the gas detector reading will be 50% LEL. When exposed to 50% LEL methane the same detector will display a reading of 75% LEL.

If the concentration of methane were to be gradually reduced, the sensor response and consequently the instrument readings will be reduced as well. At some point the methane will be reduced to a concentration that will result in a display reading of 50% LEL. This level is 32% LEL methane or 1.62% methane by volume. In other words if a combustible gas sensor that has been calibrated to propane is exposed to 32% LEL methane the response will be equal to that of 50% LEL propane. This means that a mixture of 1.62% methane by volume generates the same sensor response as 50% LEL propane gas and may therefore be considered "Propane Equivalent". This relationship is shown in figure 4.

A gas detector calibrated to 50% LEL propane equivalent gas will also provide additional adjustments if the sensor is poisoned by silicone.
The same calculation can be done to establish a "Pentane Equivalent" calibration gas. In this case, the concentration needed to generate the same sensor response as 50% LEL pentane is1.25% methane by volume.

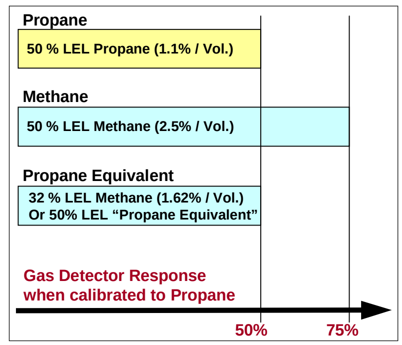

Figure 4 Propane Equivalent response

Summation

Biosystems offers both Propane "Equivalent" and Pentane "Equivalent" calibration gas mixtures that are based on methane to provide additional adjustments for LEL sensors, which have been poisoned by silicone. Biosystems also offers methane calibration gas mixtures based on the actual percentage of LEL methane.

Remember that in actual practice, the relative response varies somewhat from sensor to sensor. Response ratios may also shift over the life of a particular sensor. Most importantly, if sensitivity is lost due to poisoning, it is frequently lost first with regards to methane.

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 reputable gas detector manufacturers place so much emphasis on verification of accuracy, and why use of Biosystems' brand "equivalent" mixtures is such a good idea.

Failure to recognize the fact that an LEL sensor can selectively lose sensitivity to methane can lead to a condition where a calibrated instrument will fail to detect natural gas (a.k.a. methane).

Biosystems recommends that the accuracy of any gas detector be verified before each day's use. Please read also Biosystems' application note*: AN20010807 "Frequency for Verifying Sensor Accuracy"*. This application note provides recommendations for the frequency of sensor accuracy verification as well as procedures for lengthening the intervals between verification of sensor accuracy.

When purchasing Biosystems brand equivalent calibration gas mixtures you are assured that you calibration gas has been formulated to provide maximum protection against LEL sensor poisoning.

Always use Biosystems brand calibration gas to verify the accuracy of your instruments. Your life is too important to take a chance.