Phosphine Measurement in Fumigation and Semiconductor Applications

Introduction

Phosphine (PH_3) is a colourless, flammable, toxic gas which smells like garlic or decaying fish. It is a volatile gas with a high vapour pressure, a specific weight comparable with that of air and a low molecular weight. All these properties favour the use of phosphine in fumigation applications, the major use of the gas for the last few decades.

More recently, another important application for phosphine has been in semiconductor manufacture.

These two applications have vastly different requirements, and so require different sensors.

Fumigation

Grain and other foodstuffs in storage have always been susceptible to attacks by pests. The FAO (Food and Agriculture Organisation of the United Nations) estimates that 10 - 20% of the world's harvest is destroyed by insects and rodents. Toxic gas fumigation provides an effective solution to the problems of foodstuff storage and transportation. First used in 1935, phosphine is one of the most widely used fumigants in the world.

For successful fumigations using phosphine, it is important that the concentration and flow of phosphine are carefully monitored and controlled; too low a concentration can lead to eggs and pupae surviving the fumigation; too high a concentration can lead to a phenomenon known as 'phosphine narcosis' whereby insects enter a torpid state in which they are resistant to phosphine gas.

Semiconductor Applications

Whereas the measurement of phosphine in fumigation applications provides a means of process control, its use in semiconductor manufacture is personnel protection. Unlike fumigation processes, which involve large, enclosed spaces which can be 'flooded' with gas, semiconductor manufacture requires 'hands on' supervision. Therefore, the legal requirement to protect the work force requires monitoring of TLV levels. Clearly the levels needed to exterminate a barn full of insects is going to be a lot higher.

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Chemical Data and Exposure Limits

Chemical Formula:	PH_3
Molecular Weight:	34.1
Lower Explosive Limit:	1.79 - 1.89% volume in air

Toxicity:

7 ppm	Maximum that can be tolerated for several hours without symptoms
100-190 ppm	Maximum that can be tolerated for an hour
400-600 ppm	Dangerous to life after 30-60 minutes
>2000 ppm	Lethal to man in a few minutes

Short Term Exposure Limit (STEL) & Threshold Limit Value (TLV) 0.3 ppm PH_3

Detection

In the past, phosphine concentrations have been traditionally determined by glass tube detectors. Although these can determine concentration, they suffer from poor accuracy and, when used in large scale or in-transit applications, high cost. In addition, the technique is unsuitable for continuous monitoring or control applications.

For these reasons the use of electrochemical sensors for phosphine measurement was investigated. Theoretical calculations predict that complete oxidisation of phosphine will readily occur in the acid medium of an electrochemical cell according to the following equation:

$$PH_3 + 4H_2O \rightarrow H_3PO_4 + 8H^+ + 8e^-$$

The PH3 3E 1 LT from City Technology's Sensoric range is a high performance phosphine sensor with a nominal range of 0 - 5 ppm and a resolution of 0.015 ppm. This makes the sensor ideal for phosphine measurements at the TLV levels required in semiconductor applications.

A filtered version, the PH3 3E 1 F LT is also available. This incorporates a filter to remove acid gases from the gas stream.

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7SH Sulfur Dioxide CiTiceL

Of the alternative sensors thought likely to respond to phosphine at TLV levels, the 7SH Sulfur Dioxide CiTiceL gave the best results.

When subjected to tests, a batch of 7SH CiTiceLs showed a response to 5 ppm PH_3 of approximately 4.75 µA/ppm. With a 10 Ω load resistor connected, a T90 response time of under 60 seconds was measured. The resolution (at 20°C) is better than 0.1 ppm, and hence the 7SH is deemed capable of detecting phosphine at the TLV level of 0.3 ppm.

In addition, the sensor shows virtually no cross-sensitivity to hydrogen or carbon monoxide, both of which are commonly present in semiconductor manufacture. Hence, the 7SH is a suitable sensor for such applications where the prime concern is personnel safety.

However, neither the PH3 3E 1 LT or the 7SH are suitable for the higher concentrations of phosphine typically seen in fumigation applications - for these applications, the unfiltered 7E carbon monoxide sensor may be a more suitable option.

7E Carbon Monoxide CiTiceL

In-built filters and other features used on many Carbon Monoxide CiTiceLs preclude their use as phosphine sensors. However, the 7E is an unfiltered Carbon Monoxide CiTiceL and readily responds to phosphine. Tests have indicated that with 1000 ppm PH_3, the sensitivity of a batch of 7E sensors varied between 230 and 239 µA. With a 10 Ω load resistor connected, a T90 response time of under 60 seconds was measured.

The conclusion drawn from this testing is that the sensitivity of the 7E to phosphine is approximately 235 ± 36 nA/ppm, with the resolution (at 20°C) approximately 0.2 ppm PH_3. As such it would not be feasible to use the 7E for determining regulatory health exposure limits (as the STEL is 0.3 ppm PH_3). However, the 7E would certainly indicate whether an area (such as a grain silo or tanker hold) contains a lethal amount of phosphine.

In addition, it should be possible to use the 7E in an actively controlled system whereby the build up of phosphine is accurately measured and controlled. The 7E, therefore, could be suitable for many fumigation applications but not for semiconductor manufacture.

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Cross sensitivities to Other Gases

Cross sensitivities to various gases, recorded as a percentage of the reading for PH_3, have been measured as:

	PH3 3E 5 LT	PH3 3E 5 F LT	7E	7SH
Phosphine (PH_3)	100%	100%	100%	100%
Carbon Monoxide (CO)	0%	0%	33%	0%
Hydrogen (H_2)	0%	0%	< 15%	0%
Sulfur Dioxide (SO_2)	18%	0%	28%	25%
Hydrogen Sulfide (H_2S)	7%	0%	112%	35%
Carbon Dioxide (CO_2)	0%	0%	0%	0%
Ammonia (NH_3)	0%	0%	0%	0%
Methane (CH_4)	0%	0%	0%	0%

Summary

The Sensoric PH3 3E 5 LT and PH3 3E 5 LT phosphine sensors are ideal for phosphine measurement at TLV levels. Specifications can be found on the product datasheets. Alternatively, the unfiltered 7E carbon monoxide sensor may be suitable.

For measurement of higher concentrations of phosphine, typically used in fumagation applications, the PH3 3E 5 LT and 7E do not have an adequate measurement range. A possible alternative is the7SH sulfur dioxide CiTiceL

	7E Carbon Monoxide CiTiceL		**7SH Sulfur Dioxide CiTiceL**	
	CO	**PH_3**	**SO_2**	**PH_3**
Sensitivity	0.075 ± 0.010 µA/ppm	0.235 ± 0.036 µA/ppm	1.25 ± 0.25 µA/ppm	4.75 ± 1.00 µA/ppm
Minimum Range	0 - 20 ppm	0 - 10 ppm	0 - 3 ppm	0 - 1 ppm
Maximum Range	0 - 2000 ppm	0 - 2000 ppm	0 - 100 ppm	0 - 25 ppm
Resolution at 20°C	0.5 ppm	0.2 ppm	0.1 ppm	< 0.1 ppm

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Performance characteristics on this data sheet outline the performance of newly supplied sensors. Output signal can drift below the lower limit over time.

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