



Application Note 7

Phosphine Measurement Using 7E and 7SH CiTiceLs

Introduction

Phosphine 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 over the last 60 years. However another increasingly important application for the gas is in semiconductor manufacture. These two applications have vastly different requirements, and so require different sensors.

Phosphine - chemical data:

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

Toxicity:

> 2000ppm Lethal to man in a few minutes
 400-600ppm Dangerous to life after 30-60 minutes
 100-190ppm Maximum that can be tolerated for an hour
 7ppm Maximum that can be tolerated for several hours without symptoms
 0.3ppm { Short Term Exposure Limit (Source: HSE GN EH40/93)
 { Threshold Limit Value (Source: ACGIH 1983)

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 between 10 to 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 today 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.

Semiconductors

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.

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 an electrochemical carbon monoxide CiTiceL as a phosphine sensor was investigated^[1].

Theoretical calculations predict that complete oxidation of phosphine will readily occur in the acid medium of an electrochemical cell according to the following equation:



7E Carbon Monoxide CiTiceL

One sensor suitable for this reaction is the 7E uncompensated Carbon Monoxide CiTiceL. Inbuilt filters and other features used on other Carbon Monoxide CiTiceLs preclude their use as phosphine sensors. Tests have indicated that with a 1000ppm PH₃ the sensitivity of a batch of 7E sensors varied between 230 and 239µA. With a 10 Ohm load resistor connected a 90% response time of under 60 seconds was measured.

The conclusion drawn from our testing is the sensitivity of the 7E to phosphine is approximately 235nA/ppm ± 36nA, with the resolution at 20°C approximately 0.2ppm PH₃. As such it would not be feasible to use the 7E for determining regulatory health exposure limits, as the set level is commonly 0.3ppm PH₃ for a certain period of time. However the 7E would certainly indicate whether an area (such as a grain silo or tanker hold) had 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 most fumigation applications but not for semiconductor manufacture.

Cross sensitivities to other gases, recorded as a percentage of the reading for PH₃, at 100ppm and 20°C have been measured as:

	PH ₃	CO	H ₂	SO ₂	H ₂ S	CO ₂	NH ₃	CH ₄
%	100	33	<15	28	112	0	0	0

^[1] Initial Investigations: Ducom P., Bourges C. "Determination of phosphine concentrations with an electrochemical cell", Laboratoire Denrées Stockées, Ministère de l'Agriculture, 33152 Cenon, France



7SH Sulphur Dioxide CiTiceL

An alternative to the 7E capable of measuring phosphine down to TLV levels is also required. Of the sensors thought likely to respond, in tests the 7SH Sulphur Dioxide CiTiceL gave the best results. When subjected to the same tests as the 7E sensors, a batch of 7SH CiTiceLs showed a response to 5ppm of phosphine of approximately $4.75\mu\text{A/ppm}$. The 7SH sensors also showed a 90% response in under a minute with a 10W load resistor.

Clearly this gives a much higher response to phosphine than the 7E. The resolution at 20°C is better than 0.1ppm and hence very capable of detecting the TLV level of 0.3ppm. 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 far more suitable sensor for such applications where the prime concern is personnel safety.

Cross sensitivities to other gases, recorded as a percentage of the reading for PH_3 , at 100ppm and 20°C have been measured as:

	PH_3	CO	H_2	SO_2	H_2S	CO_2	NH_3	CH_4
%	100	0	0	25	35	0	0	0

Summary

Type 7E:		
Gas	CO	PH_3
Sensitivity	$0.075 \pm 0.010 \mu\text{A/ppm}$	$0.235 \pm 0.036 \mu\text{A/ppm}$
Minimum Range	0-20ppm	0-10ppm
Maximum Range	0-2000ppm	0-2000ppm
Resolution at 20°C	0.5ppm	0.2ppm
Type 7SH:		
Gas	SO_2	PH_3
Sensitivity	$1.25 \pm 0.25 \mu\text{A/ppm}$	$4.75 \pm 1.0 \mu\text{A/ppm}$
Minimum Range	0-3ppm	0-1ppm
Maximum Range	0-100ppm	0-25ppm
Resolution at 20°C	0.1ppm	<0.1ppm

See also 4PH phosphine sensor which is manufactured and tested with phosphine