

MEASUREMENT OF FUMIGANTS IN THE FOOD STORAGE INDUSTRY

INTRODUCTION

Various fumigants including phosphine (PH₃), methyl bromide (MeBr or CH₃Br) and Vikane (sulfuryl fluoride, or SO₂F₂) are used as pesticides in such applications as food storage, customs shipment quarantines, and building pest control. This Application note focuses on methyl bromide and phosphine in the food storage industry. RAE Systems currently does not have a sensor for Vikane.

Methyl Bromide

MeBr is a fumigant for plant product storage (food, furniture, etc.) and is commonly used in customs quarantines. It is due to be phased out in the US in January 2005 under the Montreal Protocol because of its ozone-depleting properties, but will continue to be used for some time in developing countries and in the US for critical needs. MeBr has a low 8-hour TWA of 1 ppm and a ceiling of 20 ppm. MeBr can be measured by PID using 10.6 eV or 11.7 eV lamps:

MeBr Correction Factors for RAE PIDs

9.8 eV	10.6 eV	11.7 eV
Not Detectable	1.7	1.3

The standard 10.6 eV lamp is preferred because it lasts longer than the 11.7 eV lamp, and the sensitivity is about the same.

For high-concentration initial doses, it may be desirable to use a dilution fitting (see Technical Note TN-167). At low ppm levels, interferences can become an issue, and some of them can be removed using the UltraRAE with a Butadiene RAE-Sep tube (p/n 012-3024-005). The UltraRAE should be fitted with a 10.6 eV lamp and run with a 60-second measure wait time. The detection limit is about 0.2 ppm. See TN-147 for more details on UltraRAE use.



Figure 1. MiniRAE 2000 PID (left) and UltraRAE (right).

Gas detection tubes are also available if a low-cost method is needed:

Gas Detection Tubes for MeBr

Part No.	Standard Range	Extended Range
10-131-10	1-18 ppm	0.5-36 ppm



Figure 2. Gas detection tubes for MeBr and PH₃ with hand pump.

Phosphine Gas and Solid Forms (Phostoxin)

Phosphine gas is used as a pesticide in food storage units, especially in the agriculture and marine shipping industries. To ensure adequate pest control, several hundred ppm are typically applied and the concentration verified by a detector. Phostoxin (55% aluminum phosphide) is a convenient solid source (pellets or beads) that slowly releases gaseous PH₃ on contact with moisture in the air. Other common trade names for solid forms include Celphos, Quickphos, Gastowin, Delitia, Detia gas, Magtoxin, and Agtoxin. PH₃ has low exposure limits: 8-hour TWA of 0.3 ppm and STEL of 1 ppm. After treatment, PH₃ must be measured at low levels before workers can safely enter the storage vessels.

PH₃ can be measured by PID using all three available lamps:

Phosphine Correction Factors for RAE Systems PIDs

9.8 eV	10.6 eV	11.7 eV
28	3.9	1.1

In most cases the 10.6 eV lamp is chosen because of its good sensitivity and durability. At high concentrations, the 9.8 eV lamp may be useful if cross-interferences are present. The advantage of a PID over tubes or electrochemical sensors is its fast response

time of just a few seconds, compared to minutes. A PID also offers a strong sampling pump that allows measurements to be made remotely using extension tubing and to check for leaks in shipping containers or in tight spaces.

PH₃ Lamp Fogging Phenomenon

Phosphine is unique in its behavior with PIDs in that it reacts photochemically to form products that can coat a PID lamp. This occurs with all lamps and becomes more severe as concentration and exposure time increase. The situation is most obvious at a few hundred ppm, but even 20 ppm can cause a noticeable response drop within minutes. Short, intermittent exposures help minimize the build up of such coatings. The coatings are easily removed by cleaning the lamp crystal with anhydrous methanol. At the TWA level, the coating deposits are negligible.

PH₃ Measurement Recommendations for PID

1. Calibrate using isobutylene gas instead of a PH₃ standard.
2. Use as short an exposure duration as possible (e.g., 10 seconds, with a MiniRAE 2000).
3. Expose to the lowest concentration possible; i.e., use a dilution probe if available and still allows enough gas to measure accurately.
4. On the MiniRAE 2000 or above, turn the lamp drive down to 150 (or use an old lamp).
5. Recalibrate frequently, possibly after every few measurements.
6. Clean the lamp frequently. For MiniRAE 2000, leave the unit on the charger overnight.
7. Leave the pump on between measurements to help flush out the coating.

PH₃ Tubes and Electrochemical Sensors

It is also possible to measure PH₃ using colorimetric gas detection tubes and electrochemical (EC) sensors. RAE Systems currently offers three tube ranges:

Gas Detection Tubes for PH₃

Part No.	Standard Range	Extended Range
10-116-10	5-50 ppm	2.5-100 ppm
10-116-20	25-500 ppm	12.5-1000 ppm
10-116-25	50-1000 ppm	25-2000 ppm

The electrochemical sensor can be used in single-gas and multi-gas meters and has the following specifications:

- Range: 0.1-5 ppm
- Maximum overload: 20 ppm
- Resolution: 0.1 ppm
- Response time (t₉₀): 60 seconds



Figure 3. ToxiRAE II single gas-monitor with electrochemical PH₃ sensor.

PH₃ SUMMARY

A useful combination might be to use tubes to measure the high concentrations used for initial doses and a PID or electrochemical sensor to monitor TWA-level exposures. Again, the advantages of a PID are the fast response time and strong pump, allowing remote measurements and searching for leaks. The advantages of tubes are their low cost and ability to measure high concentrations, while the advantages of EC sensors are the moderate cost and ability to measure low concentrations.