

## **PHOSPHINE MEASUREMENT AT ENVIRONMENTAL LEVELS BY GAS CHROMATOGRAPHY AND PORTABLE METHODS**

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### **ABSTRACT**

Effective methods for generating standard concentrations of phosphine in air in the ppb range have been developed. They have been used to evaluate modified commercial devices which may prove useful for field measurement of low levels of phosphine.

Our analyses are based on gas chromatography with phosphorus-specific flame photometric or nitrogen/phosphorus-specific thermionic detectors. These detectors have recorded detection limits in the picogram ( $\text{ng L}^{-1}$  or ppb) range for phosphine. Several auxiliary techniques for detecting low phosphine concentrations have, in our laboratory, been tested against the standard GC analyses. Some of these involve novel uses of sensors in which they function as GC detectors, and others involve the amplification of existing electrochemical and opto-chemical sensors.

### **INTRODUCTION**

As air pollution is taken more seriously as a threat to human health, industries which emit substances into the atmosphere are finding it in their own best interest to determine whether their activities contribute to the problem. Recent Australian guidelines on environmental levels of phosphine ( $\text{PH}_3$ ) are so low, from 4 to 20  $\mu\text{g m}^{-3}$ , or 3 to 13 parts per billion v/v (ppb), that sensitive analytical methods are required to make field measurements. The perceived threat of bans on using  $\text{PH}_3$  (Banks, 1994), unless it can be shown that concentrations near grain stores do not exceed levels about 100 times lower than those in work-places, has prompted our efforts to develop field measurement methods. Trace-level  $\text{PH}_3$  analysis is therefore becoming important for ensuring the continued use of this fumigant by the grain industry.

The proposed International Standards Organisation ISO 14000 series of Environmental Management Standards (Standards Australia, 1995) emphasises both pollution management on the part of industry and open communication with workers and the public, rather

than stressing regulatory prescriptions for detection and correction. This will encourage industry, in consultation with other parties, to participate in the management of emissions. The relationship among the regulatory authorities, the community and the  $\text{PH}_3$ -using industries hinges on realistic assessments of both the level of  $\text{PH}_3$  in the environment and the origin of the chemical. The grain industry is only one of several sources of  $\text{PH}_3$  in the environment (Vinsjansen and Thrane, 1978; Devai *et al.*, 1988; Gassmann and Glindemann, 1993; Devai and Delaune, 1995). Not only is trace analysis of  $\text{PH}_3$  difficult, but questions also arise concerning sample instability and interference from other substances. These problems have led to disagreement about non-industrial  $\text{PH}_3$  sources (Burford and Bremner, 1972).

$\text{PH}_3$  concentrations can be considered, from the point of view of measurement means and aims, under three broad categories: fumigation concentrations, work-place concentrations and environmental concentrations. Fumigation concentrations typically range from hundreds or thousands of parts per million by volume (ppm) (for metal phosphide applications, especially in sealed storages) to tens of ppm (for more modern methods such as SIROFLO®). The principal concern in monitoring fumigation concentrations within storages is how to achieve effective pest control at an economic price. Work-place concentrations, set by regulatory bodies, mandate levels ranging from about 1 ppm, which is the Short Term Exposure Limit (STEL), to the Threshold Limit Value (TLV) of 0.1 ppm in Germany and 0.3 ppm in other countries. Work-place concentrations are the concern of employers and employees within  $\text{PH}_3$ -using industries. The category of environmental concentrations can be defined in general terms as concentrations that occur outside the work-place. They are typically lower than work-place concentrations. A pragmatic lower bound is set by the effective limit of gas detection, in the order of 1 ppb or lower, depending on the technique used. Environmental levels are an issue which may affect the community as a whole; this means that the concerns, such as those arising from sources of  $\text{PH}_3$  and levels and durations of exposure, are not easily defined in a manner to which all involved parties can agree.

Australia's National Health and Medical Research Council (NHMRC) Standing Committee on Toxicity (SCoT) examined  $\text{PH}_3$ -toxicity data and recommended an environmental action level of  $4 \mu\text{g m}^{-3}$  ( $\approx 3$  ppb) (NHMRC, 1992). These levels were based on sub-acute animal studies which found a no-effect level of 0.3 ppm. This figure was divided by ten to allow for species differences and by a further factor of ten as an added safety margin to allow for variability in the human population. However, the SCoT recognised the difficulty of measuring 3 ppb with hand-held instruments and went on to recommend a short-term intervention level of  $20 \mu\text{g m}^{-3}$  ( $\approx 15$  ppb). These draft guidelines have not yet been put into practice but they serve as harbingers of the regulatory requirements which may be expected in the future.

Since the application of gas chromatography to  $\text{PH}_3$  analysis in the 1960's, detection limits have fallen from about  $1 \mu\text{g}$  of  $\text{PH}_3$  to 0.1–10 pg. It is notable that wide variations in the reported limits of detection remain and that the limits have not fallen consistently over the period.

### Laboratory analysis

It was essential to have a reliable laboratory analytical system for generating and quantifying standards and samples in the range from 1 to 100 ppb in order to evaluate tools which may be useful as field methods for detecting  $\text{PH}_3$  in this range. The packed columns used for analysis of higher concentrations gave unacceptable results when  $\text{PH}_3$  concentrations were low and sample sizes large due to failure to separate oxygen ( $\text{O}_2$ ) in the sample from  $\text{PH}_3$ . The use of a megabore capillary column at lower oven temperatures allowed the separation of  $\text{O}_2$  and  $\text{PH}_3$  without the penalty of peak broadening.

For environmental analyses, the gas chromatography systems which we have used are: carrier — nitrogen ( $\text{N}_2$ ); column — GSQ (J&W), DB Wax (J&W), length 30 m, i.d. 0.53 mm; oven temperature — 30–50°C; detector — Flame Photometric (FPD) (Tracor) or Thermionic specific (TSD or NPD) (Varian, and SRI Inc. stand-alone). Chromatographs were a Tracor MT150, a Varian 3400 and a Varian Aerograph.  $\text{PH}_3$  (ca. 85%) source determinations were carried out on a Gow-Mac Gas Density (GADE) detector fitted to a Tracor MT150 chromatograph. Reference gas cylinders (BOC Australia spectra seal b standard) were assayed, for comparison, on a GC/FPD, with quantitatively diluted samples of  $\text{PH}_3$  source which had been assayed by GC/GADE.

Our early investigations into establishing the linear range and detection limit of our GC detectors focused one of the problems of working with low concentrations of gas. A series of static  $\text{PH}_3$  concentrations were prepared by serial dilution and analysed by GC/NPD on a DB 624-megabore column. Excellent linearity of response over three orders of magnitude was observed, but at concentrations of the order of 10 ppb and below there was considerable deviation from a linear response (Fig. 1) due to the effect of  $\text{O}_2$  (in the sample) co-eluting with  $\text{PH}_3$ . At higher  $\text{PH}_3$  concentrations, the response caused by the  $\text{PH}_3$  masked the small contribution from the  $\text{O}_2$ .

The stability of  $\text{PH}_3$  samples at low concentrations is a matter of some debate. Some researchers (e.g. Vinsjansen and Thrane, 1978) found that samples in gastight bags were stable for days or weeks, but other reports (Frank and Rippen, 1987) agree with our experience that  $\text{PH}_3$  samples can degrade in a matter of hours or days.  $\text{PH}_3$  can also break down on surfaces such as brass or be absorbed into teflon and silicone rubber (Waterford and Winks, 1986). If one accepts that the stability of  $\text{PH}_3$  at low concentrations is not assured, the question of how to maintain reliable standards arises. These concerns became critical as measurement of lower concentrations was attempted. We solved this problem by using continuous flow standards.

First, a cylinder of a mixture of  $\text{PH}_3$  in  $\text{N}_2$  was accurately assayed as described above. The  $\text{PH}_3$  concentrations in these cylinders are typically in the range 1–50 ppm, and, in the experience of this laboratory, remain stable for periods of years.

Secondly, two electronic mass flow controllers (MFC's) were calibrated using either a certified bubble flowmeter or a certified digital flowmeter. Our experience with MFC's has been that they maintain excellent flow rate control and linearity between calibrations. Figure 2 is a calibration chart of a MFC. In this case, the maximum flow was 25 ml min<sup>-1</sup>. When calibrating a mass flow controller, particular attention was paid to the extremities of

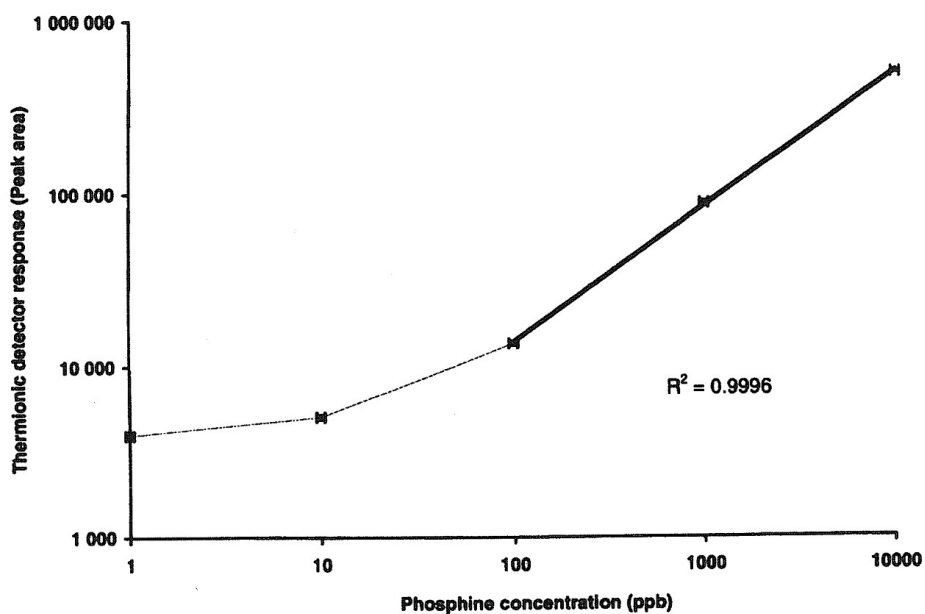


Fig. 1. An example of a linearity assessment (GC/NPD, DB 624 column). At lower concentrations the presence of oxygen in the samples gave spuriously high responses.

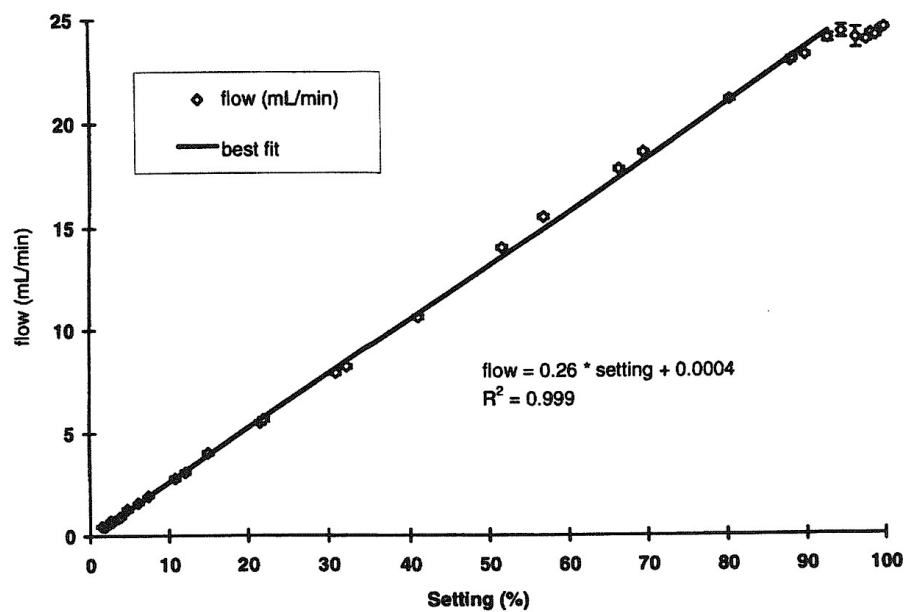


Fig. 2. Calibration chart of a mass flow controller (MFC) used for production of continuous flow standards by quantitative dilution.

the flow range (i.e. below 5% and above 90% of the maximum flow) because deviations from linearity most often occur in those ranges. In the example shown, readings above 92% were not used in the calculation of the line of best fit because they deviated from the line. Thus, in practice, this MFC could not be used at settings above 92%.

The next step involved blending a low flow from the  $\text{PH}_3$  standard cylinder with a higher flow of air which had been filtered to remove both hydrocarbons and any ambient  $\text{PH}_3$  and then humidified (Winks and Hyne, 1994) to about 55% r.h. In this manner dilution ratios between 5 (maximum  $\text{PH}_3$  flow, minimum air flow) and 10,000 (minimum  $\text{PH}_3$  flow, maximum air flow) were obtained using a  $25 \text{ ml min}^{-1}$  MFC for  $\text{PH}_3$  and a  $3,500 \text{ ml min}^{-1}$  MFC for air. With a standard cylinder containing 25 ppm  $\text{PH}_3$ , this equates to a concentration range of 5 ppm to 2.5 ppb.

Quantitative dilution by mass flow has several advantages. MFC's are pressure-independent and thus better than either regulators or mechanical diluters. The calibration of flow rates assures accurate dilution. Continuous flow avoids surface reaction/absorption problems and provides unlimited volume for testing cumulative (or long time period) field monitoring methods. Humidified air can be blended with  $\text{PH}_3/\text{N}_2$  for verisimilitude, i.e. the properties of the standard mixture are as close as possible to those of an actual environmental air sample. Concentrations can be set in seconds and become stable in minutes.

The linearity of the GC/FPD response to a range of  $\text{PH}_3$  blends produced by the method described above is shown in Fig. 3. Three manual injections of 2.0 ml were made at each

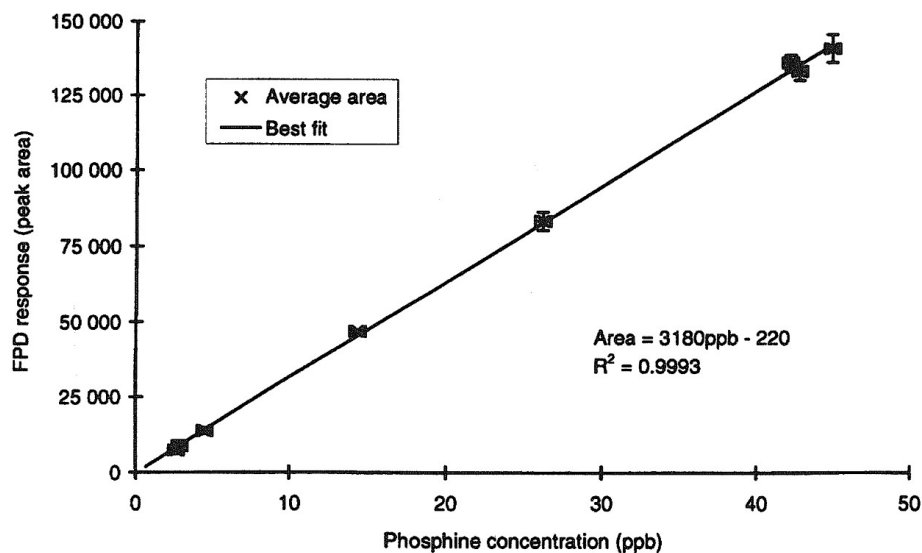


Fig. 3. Linearity of GC/FPD measurements of phosphine in air produced by quantitative dilution. The minimum resolvable peak under these conditions has an area of about 3000 mV sec, so the limit of detection in this case was about 1 ppb.

concentration, and the average peak area was plotted. The error bars show the standard deviations of the readings. Excellent results ( $R^2 = 0.9993$ ) were obtained over a range of 2.5–45 ppb. The linearity of the GC determinations validates the accuracy of the MFC-produced dilutions created by the blending of the  $\text{PH}_3/\text{N}_2$  and air streams. The small vertical error bars, even at the lowest concentration (2.6 ppb), indicate the reproducibility of the measurements.

The responses of the GC detectors to the size (volume) of the injected sample were also varied to determine at what point they began to deviate from linearity. In practice there is a maximum sample volume which may be introduced before the column becomes overloaded (leading to peak distortion) and pressure, flow or flame chemistry fluctuations affect the detector. Generally, injection volumes of more than 1 ml are not used for megabore (0.53-mm i.d.) columns, but in the interests of increasing sensitivity, even to the extent of exceeding the bounds of linearity, we investigated samples of the maximum size which could be injected.

In this experiment, we used a stream of 22 ppb  $\text{PH}_3$  in air and manually injected samples onto a J&W brand GSQ column with  $\text{N}_2$  carrier gas running at a head pressure of 18 psi. The FPD responses, in terms of peak height and peak area, are shown in Fig. 4. The relationship between peak area and injection volume was linear from 200  $\mu\text{l}$  to 3 ml, and occasionally even to 4 ml (not shown). However, the larger injections produced chromatographic anomalies such as split peaks. This is reflected by the lack of increase of

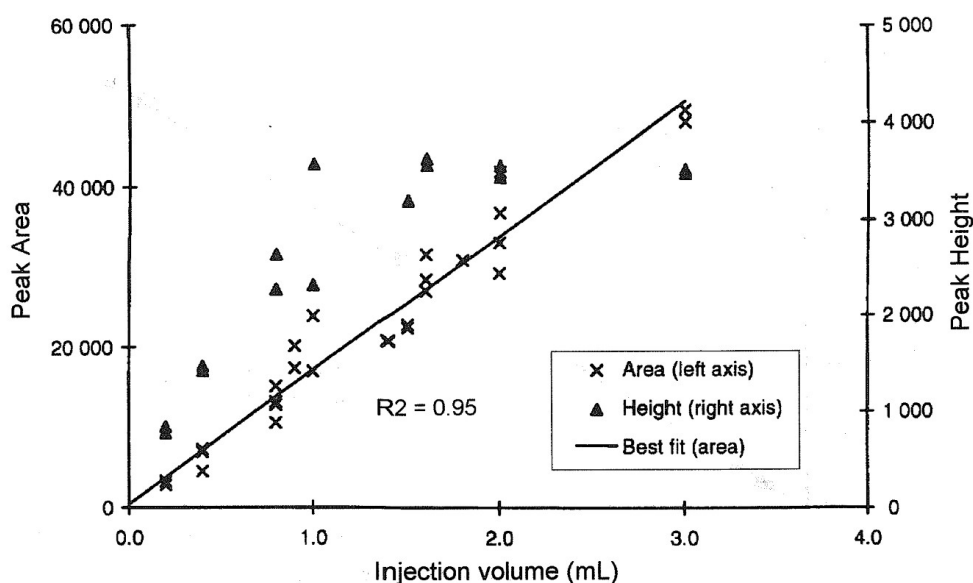


Fig. 4. Response of the GC/FPD to variations in the volume of sample. A linear response in peak area (crosses, left axis) was found in the range 200  $\mu\text{l}$ –3 ml, but the peak height (triangles, right axis) was not linear above about 1.25 ml, which indicates column overloading.

peak heights where injection volumes were larger than about 1.25 ml. The use of increased injection volumes is justified when concentrations near the limit of detection are encountered and detection, rather than quantitation, becomes the goal.

An example of a GC analysis near the limit of detection of our GC/FPD is shown in Fig. 5. In this case we used a GSQ column at 45°C and a manual injection of 3.0 ml of a MFC blend of 1.5 ppb  $\text{PH}_3$ . The trace shows a large response, due to  $\text{O}_2$ , followed by the small  $\text{PH}_3$  peak (marked). The second injection, of the same volume of laboratory air, shows no  $\text{PH}_3$  peak.

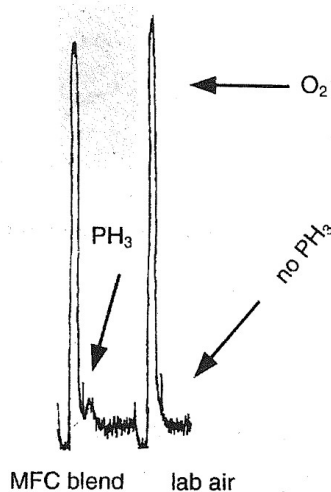


Fig. 5. Example of a GC/FPD analysis of a) 1.5 ppb phosphine in air, and b) lab air. Large peaks are due to oxygen and small peak (marked) is phosphine.

### Field methods

A paper-tape  $\text{PH}_3$  monitoring device, the Autostep, manufactured by the GMD Corp. of the USA, measures  $\text{PH}_3$  concentrations in the range 5–400 ppb. An internal pump draws sample air through a section of paper-tape chemically treated to discolour on contact with  $\text{PH}_3$ . A photosensor continuously monitors the darkness of the stain. A quantitative reading requires a sampling period of 4 min when concentrations are less than 100 ppb. Readings are expressed as graduated bars, with a resolution (or block size) of 5 ppb. At concentrations higher than 100 ppb, i.e. when the photosensor detects a fully-developed stain in less than 4 min, the device automatically steps the paper-tape to the next unused portion and begins again. We found that the device gave consistent readings, although it was less accurate at lower concentrations than at higher ones.

We modified the device by disconnecting its built-in pump and attaching a pump capable of drawing sample at ten times the normal rate, or  $1 \text{ L min}^{-1}$ . The expectation was that the device's sensitivity would be increased tenfold so, for example, a concentration of 10 ppb would be read as if it were 100 ppb, and 1 ppb would be read as 10 ppb. Figure 6

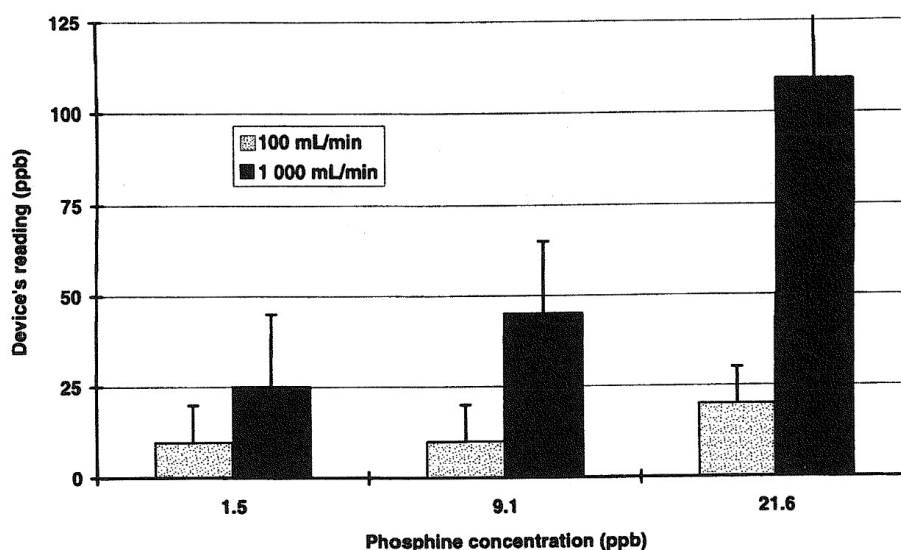


Fig. 6. Measurements of phosphine samples at three concentrations between 1.5 and 21.6 ppb using a GMD Autostep paper-tape phosphine monitor. The light bars show the readings of the unmodified device, and the darker bars show the readings obtained by increasing the sampling rate by a factor of ten.

shows the device's response to a range of concentrations from 1.5 ppb to approx 22 ppb. The device gave anomalously high responses to the 1.5 ppb sample at both flow rates, but at 9.1 and 21.6 ppb, it gave accurate readings with its own pump and higher readings by a factor of five (rather than the expected ten) at the higher sample flow rate. The attenuated response at the higher flow rate was possibly due to either air leakage around the paper strip or insufficient contact time. The paper-tape device holds promise as a fairly simple semi-quantitative method of field monitoring.

As one attempts to measure lower concentrations of  $\text{PH}_3$  in the air, the likelihood of false positive readings becomes more prevalent with most measuring techniques. The physical separation of sample components by chromatography circumvents many sources of false positive readings where it can be shown that the likely interfering species are separated from  $\text{PH}_3$ . The main drawbacks to the use of GCs in the field are the capital cost of the equipment, the bulkiness of the various carrier and detector gases and the power requirements.

We have been developing a solid state detector (SSD) system which is highly sensitive to  $\text{PH}_3$  but has no gas requirements (apart from compressed air generated on site) and very low power usage. It is based on a sensor that has been examined for use in fumigation monitors (Ryan *et al.*, 1994) and is presently in an early prototype stage attached to a laboratory GC; further work may see it become the basis of a compact, simple hybrid portable field "GC" monitor. The detector itself is not specific to  $\text{PH}_3$ , but by using a gas chromatography column to perform separation of the constituents of field samples, real-time quantitative  $\text{PH}_3$  measurements in the low ppb range appear to be feasible.



An example of the output of the GC/SSD is shown in Fig. 7. Retention time (i.e. time elapsed since the injection of the sample) is shown on the horizontal axis and the detector-amplified response (in volts) on the vertical axis. The dashed trace shows the detector's response to a few  $\mu\text{l}$  of 25 ppm  $\text{PH}_3$  in  $\text{N}_2$  standard which identifies the compound's retention time as about 1 min under these conditions. The solid traces show the detector's response to 1-ml injections of 95 ppb (black line) and 38 ppb (grey line). In each case there is a large negative peak, centred on 30-sec retention time, which is due to the  $\text{O}_2$  in the sample. In both cases a clear peak at the same retention time as the standard is present. Injections of  $\text{PH}_3$ -free air show no peak at this retention time (not shown in this diagram). It must be pointed out, however, that the baseline of the detector is not stable; there are several fluctuations of a similar magnitude to the  $\text{PH}_3$  peaks. Baseline stability must be improved before the detector's limit of detection can be lowered by the 1–2 orders of magnitude that are required to successfully monitor  $\text{PH}_3$  at the levels required by the NHMRC guidelines.

In earlier work (Pratt *et al.*, 1994) we found that some commercially available  $\text{PH}_3$  monitors based on electrochemical cells responded in a linear fashion to  $\text{PH}_3$  concentrations throughout the 'workspace' range (100 ppb–1 ppm). It was therefore thought that, with appropriate amplification, some of them could be used to monitor field concentrations in the 1–100 ppb range. However, the devices we tested (Amahsco 0–5 ppm GEM, MSTox 9001) were both too sensitive to fluctuations of humidity, air pressure and

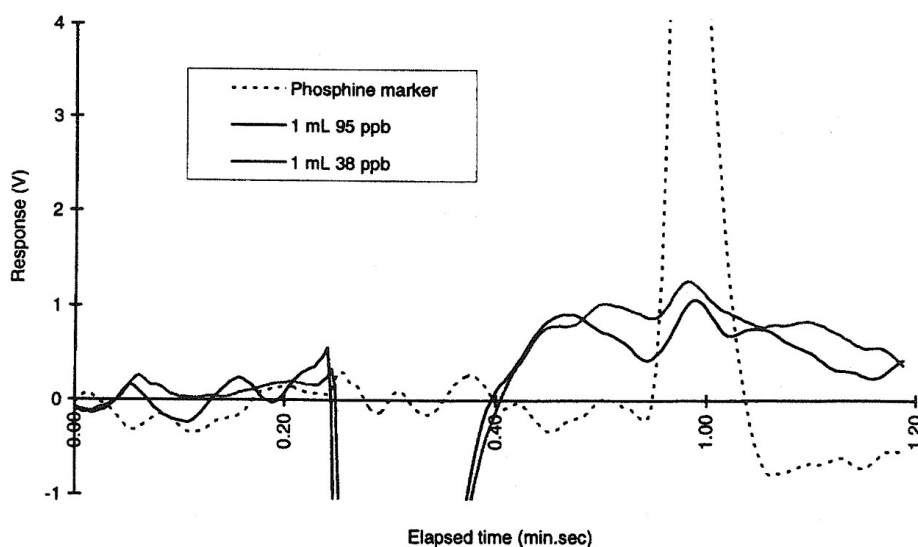


Fig. 7. Gas chromatograph/solid state detector traces of 95 and 38 ppb phosphine samples in air. Injections of 1 ml, large negative peak at 30 sec is oxygen, small peaks at 1 min are due to phosphine. Dashed trace is detector's response to 4 ml injection of 25 ppm phosphine in nitrogen (therefore no negative oxygen peak).

temperature, and too cross-sensitive to other gases such as  $\text{H}_2\text{S}$ ,  $\text{CO}$  and  $\text{SO}_2$ , for use in monitoring  $\text{PH}_3$  below 10 ppb. In addition, the long response time (in the order of 2 min for a 90% response) made it hard to distinguish between responses to gas concentrations and the other influences mentioned above. This is in no way a criticism of the suitability of these or other electrochemical monitors for work-place or fumigation monitoring, for which they are designed, where the  $\text{PH}_3$  concentrations of interest are high enough to produce a clear response.

### CONCLUSIONS

The grain industry's need to measure environmental levels of  $\text{PH}_3$  seems inevitable. Laboratory detection of parts per billion is feasible using standard apparatus, but scrupulous attention must be paid to the quality of gas standards at these levels. We have found that a continuous flow of freshly-diluted  $\text{PH}_3$  in air provides reliable gas concentrations of virtually unlimited volume and duration from which comparisons with unknown samples can be made. In view of the variability of the stability of  $\text{PH}_3$  in the laboratory environment, we feel that field measurements of  $\text{PH}_3$  must be made as soon as possible after sampling. This necessitates taking the laboratory to the site and will be the subject of further work.

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### REFERENCES

- Banks, H.J. (1994) Fumigation — an endangered technology? In: *Proc. 6th Int. Working Conf. on Stored-Product Protection* (Edited by Highley, E., Wright, E.J., Banks, H.J. and Champ, B.R.), Canberra, Australia, 17–23 April 1994, CAB International, Wallingford, Oxon, UK, 2–6.
- Burford, J.R. and Bremner, J.M. (1972) Is phosphate reduced to phosphine in waterlogged soils? *Soil Biol. Biochem.* **4**, 489–495.
- Devai, I., Felfody, L., Wittner, I. and Plosz, S. (1988) Detection of phosphine: new aspects of the phosphorus cycle in the hydrosphere. *Nature* **333**, 343–345.
- Devai, I. and Delaune, R.D. (1995) Evidence for phosphine production and emission from Louisiana and Florida marsh soils. *Organic Geochem.* **23**, 277–279.
- Frank, R. and Rippen, G. (1987) Verhalten von Phosphin in der Atmosphäre. [Fate of phosphine in the atmosphere]. *Lebensmitteltechnik*, July/August 1987, 409–411.
- Gassmann, G. and Glindemann, D. (1993) Phosphane ( $\text{PH}_3$ ) in the biosphere. *Angewandte Chemie (International English Edition)* **32**, 761–763.

- NHMRC (1992) Minutes of meetings of the NHMRC Standing Committee on Toxicity. Therapeutic Goods Administration, Commonwealth Department of Health and Family Services, Canberra, Australia.
- Pratt, S.J., Drury, L., Waterford, C.J. and Winks, R.J. (1994) *Evaluation of Fumigant Detection Equipment for Use in Grain Storage Facilities. Interim Report*. Consultative Report No. 21. CSIRO Division of Entomology, Canberra, Australia (unpublished but available on request).
- Ryan, R., Waddell, S., Alexander, P.W., Bowles, K., Cherkson, L., Morgan, J. and Hibbert, D.B. (1994) Low-cost detector for the continuous monitoring of phosphine fumigation. In: *Proc. 6th Int. Working Conf. on Stored-Product Protection* (Edited by Highley, E., Wright, E.J., Banks, H.J. and Champ, B.R.), Canberra, Australia, 17–23 April 1994, CAB International, Wallingford, Oxon, UK, 183–187.
- Standards Australia (1995) Environmental management systems — Specification with guidance for use. *AS/NZS ISO 14001 (Int): 1995*. and Environmental management systems — General guidelines on principles, systems and supporting techniques. *AS/NZS ISO 14004 (Int): 1995*.
- Vinsjansen, A. and Thrane, K.E. (1978) Gas-chromatographic determination of phosphine in ambient air. *Analyst* **103**, 1195–1198.
- Waterford, C.J. and Winks, R.G. (1986) Loss rates of phosphine associated with various materials used in laboratory fumigation apparatus. *J. Stored Prod. Res.* **22**, 25–27.
- Winks, R.G. and Hyne, E.A. (1994) Measurement of resistance to grain fumigants with particular reference to phosphine. In: *Proc. 6th Int. Working Conf. on Stored-Product Protection* (Edited by Highley, E., Wright, E.J., Banks, H.J. and Champ, B.R.), Canberra, Australia, 17–23 April 1994, CAB International, Wallingford, Oxon, UK, 244–250.