AUTOMATED REAL-TIME MONITORING OF PHOSPHINE CONCENTRATIONS OUTSIDE LARGE FUMIGATED TOBACCO WAREHOUSES USING GC/PFPD

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ABSTRACT
A Series 3000 Field MINICAMS Gas Chromatograph equipped with a Pulsed Flame-Photometric Detector (GC/PFPD) was used to detect phosphine in air outside tobacco storage warehouses containing high concentrations of phosphine (348–578 ppm). The lower limit of quantitation (LLOQ) for the GC/PFPD was 0.04 ppm. Phosphine concentrations during the study ranged from ≤0.04 ppm to 0.17 ppm. A Dräger Pac III personal gas monitor fitted with a DrägerSensor XS EC hydride sensor was used to confirm GC/PFPD data.

INTRODUCTION
Stored tobacco has been fumigated with phosphine for more than 30 years. The concentration of phosphine within a large fumigated warehouse is monitored to ensure successful elimination of all life stages of the cigarette beetle. Phosphine concentrations in air outside storage warehouses being fumigated with phosphine are monitored because phosphine is highly toxic. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values (TLVs) for phosphine are a time-weighted average (TWA) 0.3 ppm over an 8-hour period and a short-term exposure limit (STEL) of 1.0 ppm for 15 minutes. The immediately dangerous to life or health (IDLH) concentration for phosphine is 50 ppm.

Phosphine detector tubes, electrochemical cells, and portable gas chromatographs are among the current instruments used to monitor phosphine concentrations in and around structures being fumigated.

In the present work, a novel application of the Series 3000 Field MINICAMS GC/PFPD is discussed. The instrument was used for the near-real-time monitoring of phosphine concentrations in air outside large, sealed tobacco warehouses being fumigated with phosphine. Confirmatory data were collected comparing the GC/PFPD data with concurrent data from a Dräger Pac III personal gas monitor fitted with a DrägerSensor XS EC hydride sensor.

EXPERIMENTAL

Instrument Configuration
Phosphine concentrations were monitored using a Series 3000 Field MINICAMS Gas Chromatograph with a Pulsed Flame-Photometric Detector optimized for phosphorus detection (CMS Field Products, O.I. Analytical) equipped with an integral sampling loop. A 12-port stream selection system (CMS Field Products) was used to sample eleven different monitoring points established around four large tobacco storage warehouses (Figure 1). Various lengths of unheated, gas-tight polyethylene tubing were used to transfer samples from the monitoring points to the GC/PFPD with a 1/10 hp vacuum pump (CMS Field Products). Samples of ambient air at each monitoring location were collected and analyzed every five minutes. For each cycle, the sampling time was 100 seconds and the analysis time was 200 seconds. The flow rate was approximately 150 mL/minute.

The GC was fitted with a GS-Q PLOT column (0.32 mm ID x 15 meters) from J&W Scientific, Inc. The initial column temperature was 50°C for 50 seconds. The column was heated at 2.5°C/second for a total analysis time of 200 seconds. The retention time of phosphine was 58.0 seconds. Nitrogen (Air Products and Chemicals, Inc.) was used as the carrier gas at a flow rate of 5.0 mL/minute.

A Dräger Pac III Personal gas monitor fitted with a DrägerSensor XS EC Hydride Sensor (Pestcon Systems Inc.) was used to measure phosphine concentrations at various monitoring points (mounted at a height of 1 meter) concurrently with GC sampling. The phosphine LLOQ for the Dräger Pac III monitor used in this experiment was 0.04 ppm. The confirmatory data were collected by taking the highest concentration observed with the Pac III during the 100 second sampling period of the GC/PFPD. That Pac III concentration was then compared to the concentration measured using the GC/PFPD (Table I).
Analytical Standards

A certified 0.370 ppm phosphine standard (Air Liquide America Corp.) was diluted with nitrogen to give phosphine standard concentrations of 0.037 ppm and 0.185 ppm. The three standards were used to generate a concentration versus peak height (nanoamperes) linear regression calibration curve ($R^2 = 0.99$). The curve was used for determining unknown phosphine concentrations from monitoring samples collected during the study. Typical relative standard deviations for these standards were in the range of 0.50% to 6.7%.

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The 0.370 ppm standard was used daily to span the Dräger Pac III detector. It was also used as a check standard to monitor the performance of the GC/PFPD during the study. The check standard was introduced into the sampling lines from a 10 liter Tedlar bag at different sampling locations on six different occasions. The air samples fortified with the phosphine standard gave recovery values from 82-27%.

![Warehouse layout and sampling positions at the Danville, VA tobacco storage facility.](image)

Table I  Comparison of GC/PFPD and Dräger Pac III Data

<table>
<thead>
<tr>
<th>Sampling Location</th>
<th>GC-PFPD Concentration (ppm)</th>
<th>Pac III Concentration (ppm)*</th>
<th>Absolute Difference (ppm)***</th>
<th>GC-PFPD Concentration (ppm)</th>
<th>Pac III Concentration (ppm)*</th>
<th>Absolute Difference (ppm)***</th>
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Average Absolute Difference from Experiments 1 and 2: 0.01

*Maximum value observed over a 5 minute period

**Reported values below calibration range

*** $|x_1 - x_2|$, where $x_1$ = GC/PFPD concentration and $x_2$ = Pac III concentration.

**** No data collected.
The sensitivity of the GC/PFPD typically allows for a Lower Limit of Detection (LLOD) for phosphine between 0.01 and 0.02 ppm. In fact, the Series 3000 Field MINICAMS recorded phosphine concentrations below 0.01 ppm during the study. However, the LLOQ for the GC/PFPD for this study was 0.04 ppm. Therefore, data below the LLOQ is included to illustrate the capability of the instrument and should be considered as ≤0.04 ppm.

CONCLUSION

Near-real-time monitoring of ambient air around large structures being fumigated with phosphine using the Series 3000 Field MINICAMS GC/PFPD has been shown. This technology is very useful for multi-point phosphine monitoring around large structures being fumigated with phosphine-based fumigants.

While the GC/PFPD performed well sampling around the clock, similar conclusions about the ability of the Dräger Pac III personal monitor’s performance during continuous monitoring are beyond the scope of this study.

ACKNOWLEDGEMENTS

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REFERENCES