COMMUNICATIONS

A Portable Gas Chromatograph for Macro- and Microdetermination of Fumigants in the Field

A sensitive portable gas chromatograph, the Photovac 10A10, designed to analyze air samples for contaminants in the 0.001–100-ppm range was tested and found to be very suitable for analyzing fumigants, both at the low levels of concern for human health and at higher levels needed for pest control. By use of a Teflon column packed with Carbopack BHT, the conditions for analyzing phosphine, methyl bromide, and ethylene oxide at concentrations below 0.1 ppm were established. From the standpoint of precision, versatility, and ease of operation the instrument gave consistent and reliable data, even at very low concentrations.

When fumigants are used for pest control, rapid and precise methods of analysis are needed to measure the concentrations of gas that are present in the atmosphere. Usually two ranges of concentrations are of concern—the high levels that are used to kill the pest organism and the low concentrations that may remain after the treatment to contaminate the atmosphere of the work place and affect human health. An instrument capable of analyzing the several kinds of gases used for fumigation over this wide range of concentrations and one that can be used for rapid, on-the-spot determinations would be of great value to the pest-control industry. At the present time suitable techniques for analyzing some fumigants are not available, and also the threshold values set by health authorities are sometimes below the limits of the methods that are used.

A sensitive and versatile gas chromatograph that will detect and analyze both low and high levels of fumigant and can be used under field conditions has recently become available. It is sensitive enough to detect a wide range of gases at ppb levels, and it can also be used for the higher concentrations needed for pest control. This instrument is portable and can be operated with relative ease by semiskilled personnel.

DESCRIPTION OF THE INSTRUMENT

The gas chromatograph called the Photovac 10A10 is produced by Photovac, Inc., of Thornhill, Ontario, and is described more fully by Barker and Leveson (1980). It is packaged in a rugged anodized aluminum case (Figure 1) and the total weight is 11 kg. Rechargeable batteries for up to 8-h operation are built in, and a lecture bottle of high-purity air, supplying enough carried gas for up to 10 days, is mounted on the front panel (fittings are provided for external air and AC connection, if required).

Internal control functions are managed automatically wherever possible, and the front panel has been simplified to include only three controls and three switches. The chromatography column is easily changed within 10 min, and lengths up to 6 m (25 m for capillary columns) can be accommodated. The instrument is built to operate at ambient temperatures with good resolution of contaminants. The life of the column packing is greatly prolonged due to ambient temperature operation, and column inefficiences are overcome by the high detector sensitivity.

A highly skilled analyst is not needed to operate this instrument; inexperienced personnel can obtain accurate results in the ppb range after less than 3 h of instruction. The instrument may be taken to the sampling site or kept in a central location where samples are brought to it. Because it operates without a flame or glowing wire or heaters, and it is completely enclosed, this gas chromatograph can be used with relative safety in dust-laden, potentially explosive atmospheres.

For all air analyses the procedure is the same: the instrument is set up, a volume of the sample is taken with a conventional gas-tight syringe, the sample is injected into the chromatograph at the injection port, and the results are recorded as peaks on the chart of a recorder. Depending on the type of gas and the concentration, the injection volumes may be varied from 1 μL to 1 mL, and the overall dynamic concentration range is 10^6. A valve for automatic sampling of small quantities of an atmosphere can be obtained for use in place of sampling by syringe.

PROCEDURE FOR TESTING

The instrument was tested both in the laboratory and under field conditions. In the laboratory it was investigated for its ability to analyze high and low concentrations of six fumigants: phosphine, methyl bromide, ethylene oxide, ethylene dibromide, carbon tetrachloride, and 1,1,1-trichlorethane. In the field it was used for measuring the levels of phosphine present in treated bins and in the working area of a grain elevator.

A 1.2 m × 3 mm i.d. Teflon column packed with Carbopack BHT was used to separate the fumigants from other components of the atmosphere for subsequent detection by the photoionization detector with a UV lamp as described by Barker and Leveson. Carrier gas flow rates of 15–30 cm^3/min were tested mainly at a temperature of 25 °C. A 1-mV Hewlett-Packard Model 3380 A integrator was used in the laboratory to measure the detector response; for field work a 100-mV chart recorder was used. Sample sizes of 10 μL–1 mL were taken depending on concentration of the fumigant. For high concentrations the smaller sample sizes were taken, and the sensitivity of the instrument was reduced by attenuating up to 100 times. Because of the high sensitivity of the detector, air samples without fumigant were injected to determine if other compounds with similar retention times might interfere. Standards for calibration of the instrument were made by dilution of the appropriate fumigant in 12-L flasks.

RESULTS

The sensitivity of the instrument and retention times for phosphine, methyl bromide, and ethylene oxide are

0021-8561/82/1430-0986$01.25/0 Published 1982 by the American Chemical Society

Figure 1. Injecting sample of phosphine into Photovac 10A10 gas chromatograph.

shown in Table I. For a 1-mL phosphine–air sample a full-scale response of the recorder was obtained with 0.2 ppm at attenuation ×1 on a 100-mV recorder. Higher concentrations were analyzed by taking smaller samples. Although no components of the samples taken were found to interfere directly with the analysis of phosphine (retention time 1.6 min at 25 °C with a carrier gas flow rate of 10 cm^3/min), other materials were present and did have an effect on clearing of the column. When a large volume (1 mL) of sample was injected under laboratory conditions, peaks indicating the presence of an unknown compound were found at 5.62 and 31.46 min (Figure 2B). These compounds were present in samples of phosphine-free air, and although they did not interfere with the analysis of phosphine, they did delay further sampling until the column was cleared of all contaminants.

Table I. Concentrations of Fumigant Giving Full-Scale Response on Photovac 10A10 Using a 100-mV Recorder and a 1-mL Sample of Fumigant–Air Mixture at 25 °C (1.2-m Teflon Column of Carbopak BHT)

fumigant	ionization potential, eV	retention time, min	flow of carrier gas, cm^3/min	response full scale, ppm
PH_3	10.0	0.8	20	0.2
PH_3	10.0	1.6	10	0.3
CH_3Br	10.5	2.9	15	0.01
CH_3Br	10.5	2.5	20	0.01
CH_3Br	10.5	1.2	40	0.01
C_2H_4O	10.5	2.2	15	0.04

The instrument was also tested at a lower temperature in the laboratory, and it was found that the short retention time could be maintained by increasing the flow rate of the carrier gas.

The instrument was used in a field trial where elevator bins of corn were fumigated with phosphine. The concentrations found in the bins and on the bin floor were as follows:

bin no.	no. of days after fumigant applied	concn of phosphine, ppm
129	1	130
209	71[a]	0.02
103	18	0.15
bin floor		0[b]

[a] Corn was removed from bin 209 on the day previous to analysis. [b] None detectable.

When phosphine from elevator bins was analyzed at 21 °C, the retention time was 2.1 min (Figure 2A). With a 50-μL sample a large quantity of contaminant was found at 51.5-min retention time. Here again the contaminant created a problem in the frequency of sampling for phosphine.

Methyl bromide was tested at three carrier flow rates to determine the effect of flow rate on retention time and sensitivity. At a higher rate of 40 cm^3/min the retention time was reduced to 1.2 min, but full-scale response for

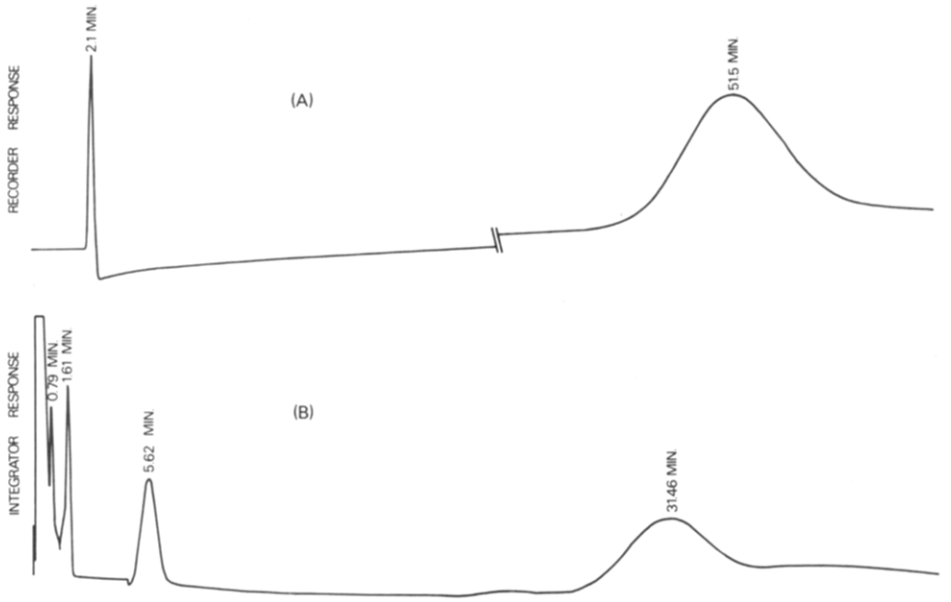

Figure 2. (A) PH_3–air sample (50 μL) from grain elevator bin, analyzed with 10 cm^3/min carrier gas at 21 °C, signal attenuated ×20, and PH_3 retention time = 2.1 min. (B) 0.2 ppm of PH_3 in air sample (1 mL), analyzed with 10 cm^3/min carrier gas at 25 °C, signal attenuation ×1, and PH_3 retention time = 1.61 min.

0.01 ppm was obtained for all three flow rates tested (Table I). High concentrations of 3000 ppm could also be analyzed by using a 10-μL sample size at 100× attenuation.

When ethylene oxide was analyzed, a 1-mL sample of 0.04 ppm gave a full-scale deflection on the recorder. Higher concentrations could be determined with smaller samples and by attenuation of up to 100 times. The retention time for ethylene oxide was 2.2 min at 15 cm^3/min carrier gas.

Analysis of the higher boiling fumigants ethylene dibromide, carbon tetrachloride, and 1,1,1-trichloroethane proved to be more difficult under the conditions tested here. The retention time of these materials on the Carbopak BHT column was more than 1 h, indicating the need for selection of more suitable column packings for workable retention times. Further investigation was done with the fumigant ethylene dibromide; however, as sorption factors and the establishment of precise standards were found to be somewhat complex, these results are being published separately.

The instrument performed satisfactorily for all three compounds (phosphine, methyl bromide, and ethylene oxide), even at very low concentrations. Fluctuations of the surrounding air temperature had no observable adverse effects on the performance of the instrument. The only problem that arose concerned interfering substances in the atmosphere. These contaminants had no effect on accuracy or reliability, but they did influence the number of samples that could be taken in any given period of time. According to the manufacturer a simple modification will be made in the instrument to overcome this problem. With such modification we expect that this instrument would be quite satisfactory for the detection and analysis of both high and low levels of phosphine and several other fumigants in commercial situations.

LITERATURE CITED

Barker, N. J.; Leveson, R. C. *Am. Lab. (Fairfield, Conn.)* **1980**, *12* (Dec), 76-83.

E. J. Bond
T. Dumas*

Research Centre
Agriculture Canada
London, Ontario, Canada N6A 5B7

Received for review December 28, 1982. Revised manuscript received May 18, 1982. Accepted June 2, 1982.

Helenin Inhibition of Liver Microsomal Enzymes

When helenin in the presence of NADPH was incubated with male rate liver microsomes prepared from the phenobarbital-pretreated animals, there occurred a significant loss of the microsomal cytochrome P-450 as well as the activity of benzphetamine *N*-demethylase. However, no inhibition of the hemoprotein was noted in the microsomal incubations with helenin minus NADPH, suggesting that the metabolic product(s) of the sesquiterpene lactone may have been responsible for the inhibition of the microsomal enzyme activities.

Several species of the *Helenium* (sneezeweed) and *Hymenoxys* (bitterweed, rubberweed) are well-known poisonous plants that are sometimes responsible for heavy losses of livestock (U.S. Department of Agriculture, 1968). A number of structurally related sesquiterpene lactones such as helenalin and hymenoxon have been isolated from these plants, and their toxicity in test animals has been confirmed (Kim, 1980). Although some of these lactones have been found to be useful in medicine as anthelmintic, bactericidal, fungicidal, and antitumor agents (Dalvi et al., 1971; Kim, 1980; Kupchan et al., 1971; Lee et al., 1971, 1977), they are highly toxic compounds, and the plants containing them may cause severe losses of food-producing animals, especially sheep and cattle (Kingsbury, 1964). Furthermore, a species of helenium has been reported to have caused poisoning of human beings who consumed bread made with flour that was contaminated with large quantities of seeds of the plant (Kingsbury, 1964). It is also interesting to note that consumption of even a small quantity of bitter sneezeweed by lactating cows makes the milk very bitter in taste and virtually unpalatable (Radeleff, 1970). Thus, in view of the economic importance of these plants in food and agriculture and since these lactones are toxic to liver and information with regard to their effect on hepatic microsomal enzymes is lacking, the following report on the toxicity of helenin as a representative of sesquiterpene lactones is presented.

EXPERIMENTAL SECTION

Chemicals. Helenin was purchased from Sigma Chemical Co. (St. Louis, MO). All other chemicals used were analytical or reagent grade.

Isolation and Incubation of Liver Microsomes. Male Sprague-Dawley rats weighing 150–200 g were given a daily ip dose of 50 mg/kg phenobarbital for 4 successive days to induce microsomal enzymes. Twenty-four hours after the last injection, the animals were sacrificed and liver microsomes isolated following the established procedure (Dalvi and Howell, 1977). These microsomes containing cytochrome P-450 as the terminal oxidase were resuspended in 0.05 M Hepes buffer, pH 7.8, and the suspensions were incubated with helenin dissolved in methanol (1 mM final concentration) in the presence or absence of the NADPH-generating system (Dalvi and Howell, 1977). At the end of the 15-min incubation period, reactions were stopped by placing the incubation flasks in ice-cold water. The contents of the flasks were transferred to corresponding centrifuge tubes and centrifuged, and the microsomal pellets after washing twice with the buffer were resuspended in a known amount of 0.1 M phosphate buffer, pH 7.4. An aliquot from each of the resuspended microsomal suspensions was removed to determine the

0021-8561/82/1430-0988$01.25/0