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Note

Rapid analysis and gas sampling of ethylene dibromide in the gaseous phase and as residues in citrus fruit

S. C. MORRIS* and L. E. RIPPON
Gosford Horticultural Postharvest Laboratory, N.S.W. Department of Agriculture, P.O. Box 355, Gosford 2250 (Australia)
and
R. HALAMEK
Biological and Chemical Research Institute, Rydalmere, Sydney (Australia)
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The decline of fumigant in the gaseous phase during fumigation has been reported by many workers. This decline is quite rapid for a fumigant of low volatility such as ethylene dibromide (EDB)[1–4]. However, no thorough investigations have been reported on the fate of EDB during fumigation.

To attempt such an investigation a rapid sampling and analytical technique is essential. This is because determining accurately EDB loss and concentration gradients requires sampling from various points within the fumigation chamber at each sampling time. As the standard EDB fumigation for citrus fruit is 2 h (ref. 5), following EDB losses necessitates a sampling time of 30 sec or less and total analysis time of less than 2 min for each sample.

Gaseous sampling techniques previously reported include the use of evacuated flasks[6–8], gas-sampling flasks through which the sample has been drawn[9,10], bubbling through solvents[11,12], trapping in absorbance tubes[13,14] and direct sampling by syringe for gas chromatographic (GC) analysis[15–17]. Of these methods the first four are much too slow and impractical for large numbers of samples. Direct sampling by syringe is unsatisfactory as considerable diffusion out of, and sorption onto the inside of the syringe occurs rapidly. This causes problems when the syringe has to be taken any distance to the gas chromatograph and/or held for several minutes or longer prior to injection.

Almost all EDB analytic techniques reported recently use GC, with the shortest retention time reported as 2.57 min[16]. Other retention times are 5.5 min[18,19], 6.0 min[20] and 7.9 min[21]. Some of these latter times are optimized for the separation of fumigation mixtures containing EDB and could be shortened if EDB was present alone. However, while retention time could be reduced, it is unlikely that a sufficiently rapid analysis with sufficient resolution from the solvent front could be obtained using these systems.

This paper describes techniques of gas sampling and GC analysis which met these exacting requirements. A modified extraction technique enabling EDB residues in fruit to be analysed with this method is also reported.

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EXPERIMENTAL

Gas sampling

In order to permit sampling at various locations in the fumigation chamber, lengths of stainless-steel tubing were connected through the side wall with screw fittings (Fig. 1a). The tubing was connected to a short length of Viton rubber tubing outside the chamber sealed with a clamp.

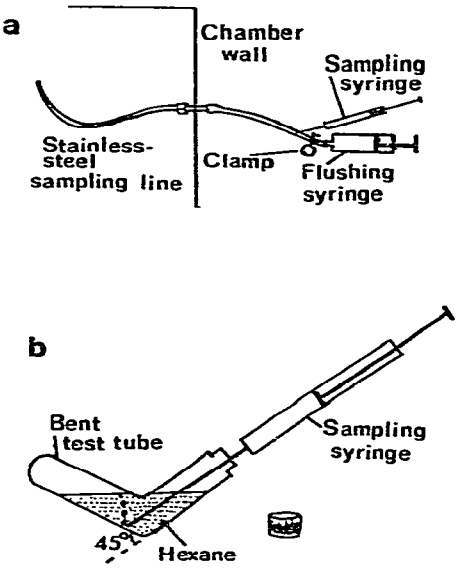

Fig. 1. Gas sampling apparatus. (a) Gas-sampling lines connected through the side of the fumigation chamber to permit samples to be taken from any position within chamber. Internal volume of sampling line was <3 ml. (b) Gas-sampling tubes made by bending 150 × 16 mm test tubes fitted with PTFE-lined screw caps.

After releasing the clamp on the Viton tubing, 50 ml of chamber air was drawn through. A syringe was inserted into the tubing and flushed several times with chamber air before sampling (generally 0.5 ml). Each sample was then expelled into a screw-capped bent test tube beyond 10 ml of hexane (Fig. 1b), the PTFE-lined screw cap replaced and the tube shaken to dissolve the EDB. After each sampling, the 50 ml of chamber air was blown back in the chamber. The total time the sample air was in contact with the sample line and syringe was less than 10 sec.

After each fumigation, EDB was desorbed from the Viton and stainless-steel sampling lines by heating at 175°C for 1–2 h, while passing air through the tubing at approximately 40 ml min^{-1}. Tubes were desorbed of EDB by heating at 175°C for 1–2 h. Analysis was generally performed within 1 h of sampling, but if necessary, the EDB could be stored in hexane without any change in concentration for several weeks.

Extraction of EDB from fruit

EDB was extracted from fruit by blending (*ca.* 30 g) with 150 ml acetonitrile for

2 min at high speed in a Sorvall Omni-mixer. The homogenate was filtered and rinsed with two further 15-ml aliquots of acetonitrile and made up to 200 ml. The filtrate was then shaken with 20 ml of hexane in a stoppered 250-ml conical flask. After separation (>2 h) a sample of the hexane layer was taken for injection (typically 0.5–2 μl). For levels of EDB >2 mg kg^{-1} a 1-ml sample of the hexane layer was taken and diluted 1:20 before injection. A clean up of the hexane on Florisil and drying with anhydrous sodium sulphate[19] was not found necessary for levels of EDB as low as 0.2 mg kg^{-1}.

Analytical technique

A Varian 1440 gas chromatograph fitted with a ^{3}H electron-capture detector was used. The column was 1.5 m × 3 mm O.D. stainless steel, packed with 5.5% DC-200 and 11% QF-1 on 80–90 mesh Gas-Chrom Q. Operating temperatures were: column 90°C, injector 175°C and detector 235°C, with nitrogen at 40 ml min^{-1}. Under these conditions, the hexane peak eluted in 19 sec and the EDB peak in 46 sec. Repeat injections were possible every 1.5 min for air samples and every 2.5 min for residue samples. The sensitivity of this technique gave 50% f.s.d. with 0.14 ng of EDB at $2 \cdot 10^{-9}$ A f.s. (recorder 1 mV).

RESULTS AND DISCUSSION

Since EDB was the only component of the chamber air resulting in significant detector response, a column temperature was chosen so that the EDB peak followed

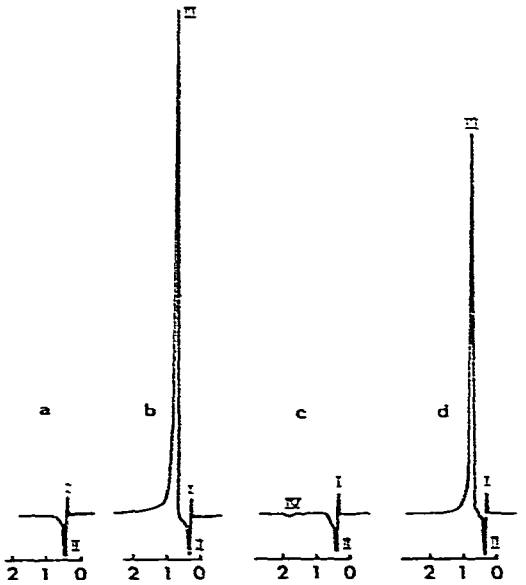

Fig. 2. Gas–liquid chromatograms of EDB dissolved in hexane. (a) Injection of air control dissolved in hexane (0.5 μl); (b) injection of 20 g m^{-3} EDB sample dissolved in hexane peak after 1:20 dilution; (c) injection of whole lemon extract with no EDB present; (d) injection of whole lemon extract from lemon containing 29.4 mg kg^{-1} EDB after 1:20 dilution. Peaks: I = injection artifact; II = hexane; III = EDB; IV = unknown from lemon.

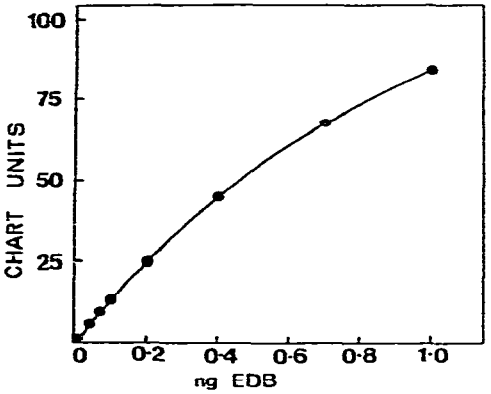

Fig. 3. Typical calibration curve over 0–1 ng for EDB in hexane with the ^3H electron-capture detector. The curve of best fit is ng (hexane) = 0.000 + 0.00541 (cu) + 0.0120 (cu)^2 (r^2 = 0.997), where cu are chart units for $4 \cdot 10^{-9}$ A f.s. (rcorder 1 mV).

as closely after the solvent front as possible (Fig. 2a and b). While temperatures of 120°C gave fastest analysis and best detector response for a given quantity of EDB in standard injections, in this work 90°C gave adequate speed and better separation from the solvent front, particularly with fruit extracts. High-purity hexane, free of aromatic hydrocarbon impurities, was essential to separate adequately the solvent and EDB peaks.

Detector sensitivity was linear only below 0.2 ng EDB. However, an excellent fit up to 2 ng was obtained using a second-order polynomial curve. Since most work was with injections containing 0.1 to 0.8 ng EDB, a polynomial fit from 0–1 ng was most frequently used (Fig. 3).

Using the rapid extraction method reported here, the recovery of EDB from fumigated fruit was 93 ± 4% (Table I). Recovery was slightly better for low levels of

TABLE I

RECOVERY OF ETHYLENE DIBROMIDE FROM LEMONS

Background EDB in lemon fruit	*Added EDB (μg g^{-1} fruit)*	*Amount of EDB found (μg g^{-1})**	*Recovery (%)*
Nil	Nil	0.01	
	1	0.94	95%
	10	9.25	91.5%
Low	Nil	0.62	
(24 h after	1	1.54	92%
fumigation)	10	10.25	98%
High	Nil	21.31	
(0.5 h after	1	22.22	89%
fumigation)	10	30.73	94%
			Average recovery 93 ± 4%

* EDB analyses were done on a whole fruit basis with duplicate analyses.

EDB. Providing hexane of adequate purity was used, the EDB was sufficiently separated from the solvent front and only minor levels of contaminants detected (compare Fig. 2c and d). These recoveries from citrus fruit compared well with the 92 ± 7% obtained by Newsome and Panopio[19] and the 99–100% obtained by Dumas and Bond[3]. However these and other previously published methods, all require lengthy clean up and concentration steps before GC analysis.

The new sampling method reported using bent screw-cap test tubes and a solvent (in which the gas of interest is more soluble than in air) to trap gaseous components, is a technique with potentially wide application. A gas sample of up to 5 ml could be placed beyond the solvent using the size test tubes described and even larger gas samples can be accommodated by dissolving each 5 ml sample before expelling further samples into the tube. This concentration step could be used when very low concentrations of the gaseous components were being analysed.

REFERENCES

1 W. B. Sinclair and D. L. Lindgren, *J. Econ. Entomol.*, 45 (1952) 726.
2 S. T. Seo, J. W. Balock, A. K. Burditt and K. Ohinata, *J. Econ. Entomol.*, 63 (1970) 1093.
3 T. Dumas and E. J. Bond, *J. Agr. Food Chem.*, 23 (1975) 95.
4 G. Swaine, R. J. Corcoran, P. M. Pepper, A. E. Cranny and M. A. Davey, *Pestic. Sci.*, 8 (1977) 497.
5 C. J. Rigney and B. L. Wild, *J. Econ. Entomol.*, 68 (1975) 653.
6 W. B. Sinclair and P. R. Crandall, *J. Econ. Entomol.*, 45 (1952) 80.
7 T. Dumas and R. A. Latimer, *J. Agr. Food Chem.*, 10 (1962) 276.
8 S. G. Heuser, *J. Sci. Food Agr.*, 15 (1964) 114.
9 M. Muthu and S. K. Majunder, *J. Sci. Ind. Res. (India)*, 19B (1960) 273.
10 B. Berck, *J. Agr. Food Chem.*, 22 (1974) 977.
11 W. B. Sinclair and P. R. Crandall, *J. Econ. Entomol.*, 45 (1952) 882.
12 B. Berck, *J. Agr. Food Chem.*, 10 (1962) 158.
13 P. W. West, S. Buddhaden and N. A. Gibson, *Anal. Chem.*, 30 (1958) 1390.
14 W. Fowler, C. H. Duffey and H. C. Miller, *Anal. Chem.*, 51 (1979) 2333.
15 D. L. Lindgren and L. E. Vincent, *J. Econ. Entomol.*, 52 (1959) 1091.
16 B. Berck, *J. Agr. Food Chem.*, 13 (1965) 373.
17 G. Swaine, R. J. Corcoran and M. A. Davey, *Pestic. Sci.*, 7 (1976) 465.
18 L. E. Vincent and D. L. Lindgren, *J. Econ. Entomol.*, 55 (1962) 264.
19 W. H. Newsome and L. G. Panopio, *J. Agr. Food Chem.*, 25 (1977) 998.
20 J. Jagielski, K. A. Scudmore and S. G. Heuser, *Pestic. Sci.*, 9 (1978) 117.
21 T. Dumas and E. J. Bond, *J. Agr. Food Chem.*, 27 (1979) 1206.