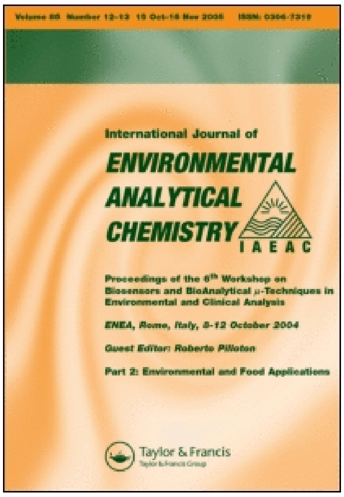

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L. A. Pranoto-soetardhi[a]; M. A. H. Rijk[a]; N. De Kruijf[a]; R. H. De Vos[a]
[a] TNO-CIVO Food Analysis Institute, ZEIST, The Netherlands

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Automatic Headspace Sampling for Determination of Ethylene Dibromide Residues in Cereals†

L. A. PRANOTO-SOETARDHI, M. A. H. RIJK, N. DE KRUIJF and R. H. DE VOS‡

TNO-CIVO Food Analysis Institute, P.O. Box 360, 3700 AJ ZEIST, The Netherlands

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The possibility was investigated to apply a commercially available automatic headspace sampler in trace analysis of ethylene dibromide (EDB, 1,2-dibromoethane), in cereals.

Samples of rice and wheat flour were thermostatted in closed vials at 70°C for 30 min. The top gas was then automatically introduced into a gas chromatograph equipped with an electron capture detector. Quantitation was performed using external standards (untreated samples spiked with solutions of EDB in *N,N′*-dimethylacetamide).

The relative standard deviation of the method was 3.4% for rice and 4.5% for wheat flour, at a residue level of 0.008 mg/kg. The detection limit was 0.001 mg/kg (the official EC residue tolerance is 0.01 mg/kg).

Preliminary experiments with other fumigants were carried out as well.

The headspace technique in question has the following advantages over other methods for determining EDB residues in cereals: 1. No sample pre-treatment like extraction, steam distillation, purge and trap etc.; 2. Automated sample handling; 3. "Clean" chromatograms.

KEY WORDS: Residues, ethylene dibromide, cereals, automatic sampling, headspace GLC.

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‡Author to whom all correspondence should be addressed.

INTRODUCTION

Ethylene dibromide (EDB, 1,2-dibromoethane) is used as a fumigant against insect pests in stored food commodities like grains. Because of its high toxicity, residue tolerances are low. The official EC tolerance is 0.01 mg/kg.

These low EDB levels are usually determined by electron-capture gas chromatography, being the most sensitive procedure.

Various methods have been described for isolating EDB from the matrix, such as steam distillation,[1] purge and trap,[2] solvent extraction,[3,4] hexane codistillation,[5] headspace sampling.[6] Headspace sampling has the advantage that sample pretreatment is less elaborate than with the other principles mentioned.

Moreover, equipment for automatic headspace analysis has become commercially available. This prompted us to investigate the possibilities of such equipment for automated EDB residue analysis in cereals.

EXPERIMENTAL PROCEDURE

Apparatus and reagents

Gas–liquid chromatograph Perkin Elmer Sigma 2000. Equipped with 3 m × 2 mm (i.d.) stainless steel column packed with 20% Carbowax 20 M and 5% OV 101 on 80–100 mesh Chromosorb W(AW) and a constant current Ni63 electron capture detector.

Operating conditions: carrier gas: nitrogen, 20 ml/min; oven 140°C; detector 300°C.

Headspace autosampler Perkin Elmer HS-100.[7] Thermostatting, pressurization and injection at 70°C.

Chemicals Ethylene dibromide (No. 800952, Merck, Darmstadt, F.R.G.) dissolved in *N,N'*-dimethylacetamide (Merck No. 803235) to give a working stock solution of 20 microgram/ml.

Preparation of samples

The method was tested with wheat flour and whole rice as sample materials. Batches having no detectable EDB residues (less than

0.001 mg/kg) were selected. These batches (500 g) were fortified with a known amount of EDB (ca. 0.005 mg) dissolved in 0.25 ml *N*,*N*′-dimethylacetamide, followed by rotation in closed jars for 4 hours to effect even distribution of the analyte. Subsamples were taken for analysis as described below.

Analytical procedure

The general procedure was as follows: 8 g wheat flour or 10 g rice were weighed into a 23 ml HS-100 sample vial; the vial was capped with a crimp seal containing a PTFE lined septum; the vial was then placed in the HS-100 sample rack. Each sample was equilibrated for 30 min at 70°C in the thermostatting chamber of the sampler. Subsequently the septum was pierced with the sampling needle of the instrument, introducing carrier gas and pressurising the headspace to column head pressure. At the end of the pressurisation period (0.5 min) the gas in the headspace of the vial was allowed to expand into the sampling needle, transferring volatiles onto the GLC column. Sample injection was stopped after a selected transfer period of 0.08 min. The GLC conditions are described under "Apparatus and reagents".

Calibration samples were prepared by adding known amounts of EDB in *N*,*N*′-dimethylacetamide to vials containing blank rice or wheat flour. (Fortification levels 0–0.05 mg/kg). A calibration curve was made by plotting peak heights of EDB measured in chromatograms of calibration samples against concentrations.

RESULTS AND DISCUSSION

Typical chromatograms of EDB in rice and wheat flour are presented in Figures 1 and 2, while Figure 3 depicts a calibration curve. As shown in the figures no interfering peaks occurred in the region of the EDB peak.

In order to determine the precision of the method and the recovery percentages, 10 subsamples of the fortified batches of rice and wheat flour were analysed. The results obtained are presented in Table I. The mean recoveries found (79% for rice and 82% for wheat flour) are satisfactory as they are overall figures for the analytical

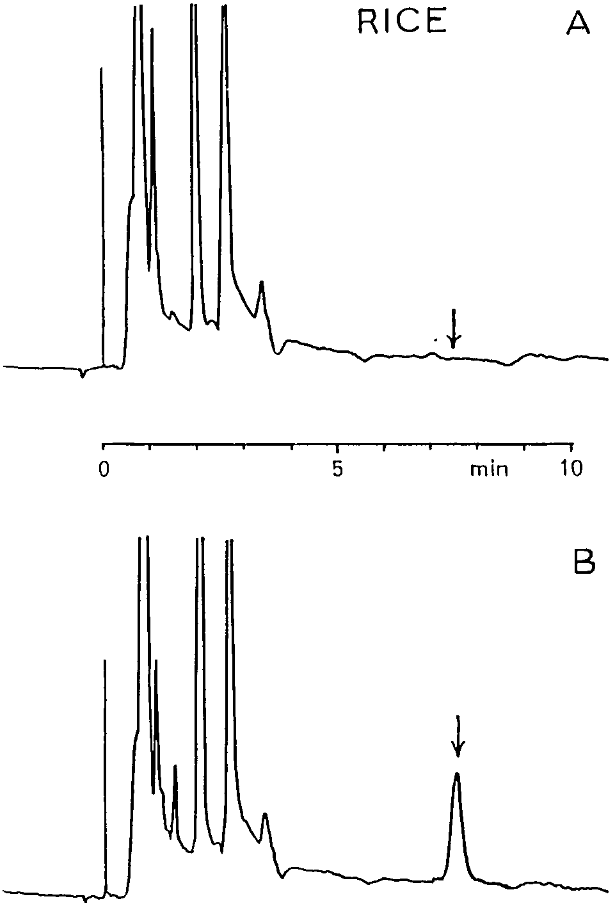

FIGURE 1 Chromatogram of untreated rice (A) and rice containing 8 μg EDB/kg (B).

method plus the fortification procedure. In the latter, theoretically, losses of a rather volatile compound like EDB may occur. The repeatability reported in Table I is defined as 2.83 times the standard deviation of the determination.[8]

From the chromatograms obtained a detection limit of 0.001 mg EDB/kg sample (corresponding to a peak height of 5 mm) could be derived.

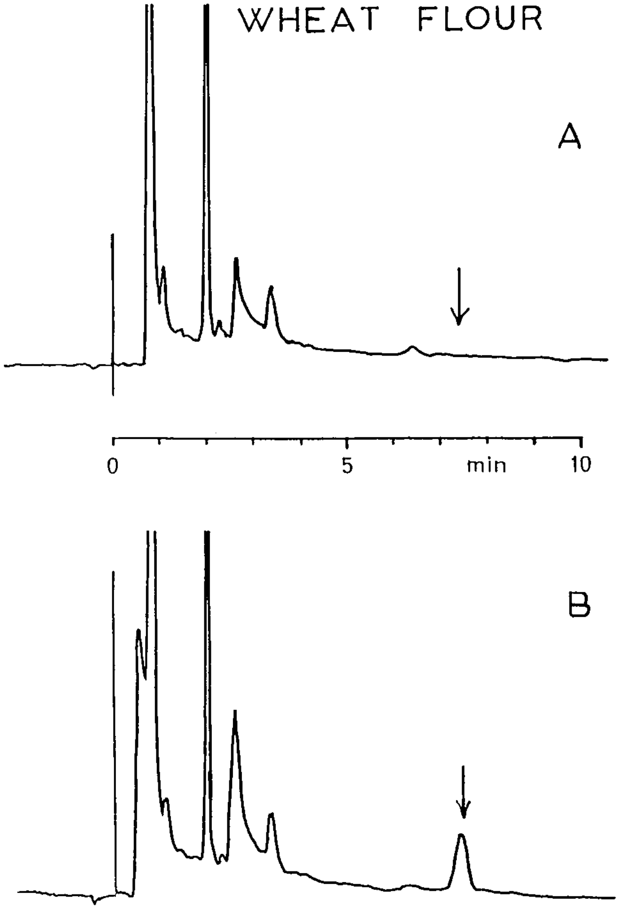

FIGURE 2 Chromatogram of untreated wheat flour (A) and wheat flour containing 8 μg EDB/kg (B).

Theoretically, headspace concentrations in the vials are independent of sample size. In order to check this in practice various amounts of the fortified batches of rice and wheat flour were analysed as described before. The results are given in Table II. The analytical result had not been significantly influenced by sample weights ranging from 4–10 g. For wheat flour the situation was somewhat different. The figures of Table II indicate that a smaller sample in the

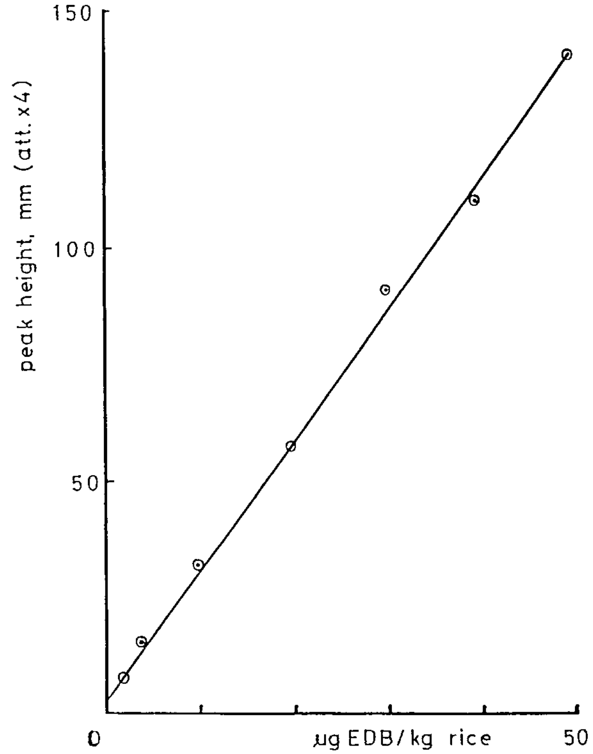

FIGURE 3 Calibration graph.

TABLE I

Precision of the method and recovery percentages

Matrix[a]	EDB concentration, μg/kg ($n=10$) Mean	S.D.	r	C.V. (%)	Mean recovery (%)[b]
Rice	7.83	0.27	0.76	3.4	79
Wheat flour	8.10	0.37	1.0	4.6	82

S.D. = standard deviation; r = repeatability; C.V. = coefficient of variation.

[a] 500 g batches fortified with EDB, homogenised by rotating for 4 h in a closed jar.

[b] Including any losses during "fumigation".

TABLE II

Relationship between sample size and EDB concentration measured

Sample size (g)	EDB concentration[a] (μg/kg) measured in	
	rice	wheat flour
4	7.4	10.0
5	8.1	9.6
6	—	9.5
7	8.2	8.5
8	8.4	8.1
10	7.8	—

[a] Mean of duplicates.
— Not measured.

vial gave higher EDB results. Most probably 8 g is too large a sample for optimum yields of EDB in the headspace. A sample weight of approximately 5 g seems more appropriate in this case.

Headspace gas chromatography is a suitable method for determining volatile halocarbons other than EDB as well. Entz and Hollifield[6] applied this technique for determining a number of volatile chlorinated hydrocarbons in foods, while an automatic headspace gas chromatographic method for determining traces of tetrachloroethylene in animal feeds has been described by Kolb.[9] A preliminary investigation into the performance of our method in this area was carried out as follows: to 8 g of wheat flour in a headspace sampler vial 1 microlitre of a *N*,*N*′-dimethylacetamide solution was added containing nanogram amounts of carbon tetrachloride, trichloroethylene, chloroform, tetrachloroethylene and ethylene dibromide. The fortified sample and the corresponding unspiked material were analysed with the usual procedure, except that a temperature program was applied in the GLC run (see Figure 4).

EDB appears as a shoulder on the broad peak caused by temperature programming, but can still be measured and is well separated from the other halocarbons. The chromatogram of unspiked wheat flour shows peaks with retention times of carbon tetrachloride and chloroform. It can certainly not be excluded that

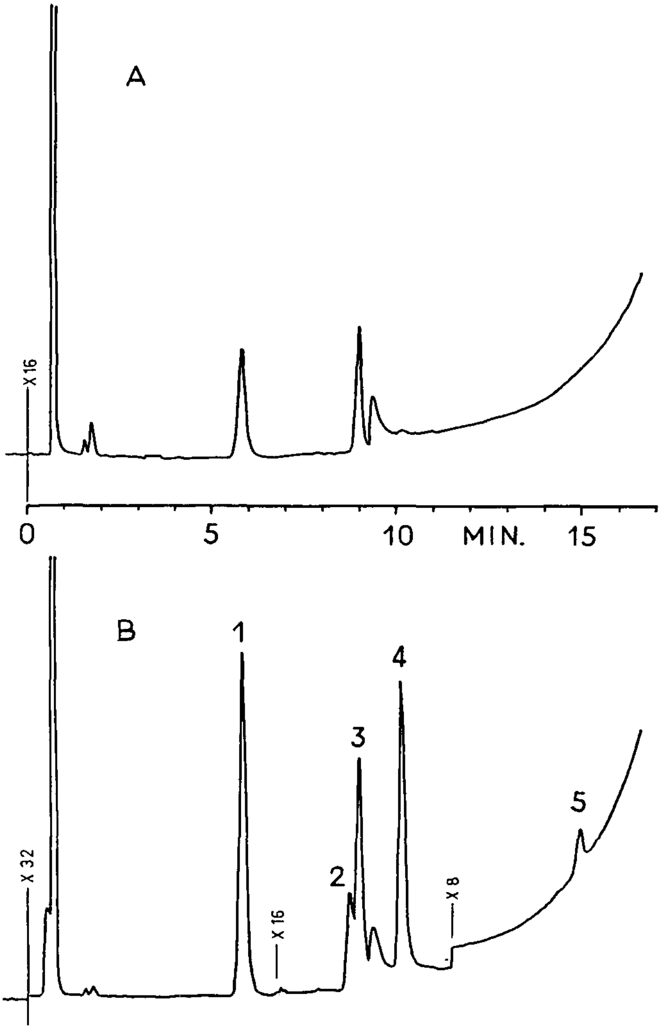

FIGURE 4 Chromatogram (A): untreated wheat flour. Chromatogram (B): wheat flour fortified with: (1) Carbon tetrachloride (5.3 μg/kg); (2) Trichloroethylene (6.5 μg/kg); (3) Chloroform (3.8 μg/kg); (4) Tetrachloroethylene (8.0 μg/kg); (5) Ethylene dibromide (4.9 μg/kg) Oven temperature 70°C isothermal for 5 min, then programmed at 10°C/min up to 190°C and held for 5 min. See text for other instrumental conditions.

these compounds are actually present in the sample, for instance due to contamination by the laboratory atmosphere. This can be avoided by loading the sample vials in an uncontaminated area. Headspace gas chromatography itself can be performed in the laboratory, because the vials are closed. The results demonstrate that automatic headspace gas chromatography has a great potential for multidetection of fumigants and solvent residues in cereals. Further research is necessary however to develop optimum conditions for this purpose.

A disadvantage of the method is that each matrix requires its own calibration curve. This is no major problem however because of the rapid and automated operation of the system. It may be solved by using the so-called multiple headspace extraction technique.[9] Further research in this respect is also necessary.

CONCLUSION

The described automated headspace gas chromatographic method for determining EDB residues in cereals is very fast and straightforward. Extraction and clean-up are not necessary. Sample handling is restricted to putting the sample in a vial, even exact weighing is not required. The method has adequate sensitivity and repeatability and is therefore suitable for use in routine regulatory control, production monitoring etc.

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