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Short Communication

Use of low-purity solvents and reagents for analysis of residues of synthetic pyrethroid pesticides by gas chromatography with electron-capture detection

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ABSTRACT

As most of the impurities commonly encountered in solvents and reagents elute from a gas chromatographic column at retention times much smaller then those of synthetic pyrethroids, inexpensive laboratory-grade solvents and reagents can be acceptable for the determination of residues of these pesticides. However, before analysis of the samples, it is desirable to check the suitability of such solvents and reagents by running reagent blanks.

INTRODUCTION

The use of solvents and reagents of exceptionally high purity is considered mandatory when performing pesticide residue analysis so that no undue interferences or spurious results are obtained [1–3]. This is especially true when gas chromatography with electron-capture detection (GC–ECD) is employed for final determinations as a number of contaminants such as polychlorinated biphenyls (PCBs) and phthalate esters have high electron-capturing capabilities and can therefore produce GC peaks that may match the retention characteristics of pesticide residues being determined [4,5]. Elaborate purification procedures and stringent quality control measures have therefore been recommended for the solvents and reagents [1–3,6]. However, most of the prescribed purification procedures are laborious, time consuming and result in losses of volatile solvents of up to 25% [6].

In recent years, synthetic pyrethroid pesticides have become widely used as efficient pest control agents [7]. As several compounds belonging to this group possess moieties with electron-capturing capabilities, GC–ECD has been widely employed for the determination of residues of these compounds [8]. However, such synthetic pyrethroids elute late under the GC conditions commonly followed for the deter-

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mination of other organochlorine pesticides and environmental pollutants. Consequently, shorter GC columns, elevated oven temperatures and/or enhanced carrier gas flow-rates have to be used to complete their analysis in a reasonable length of time.

During studies of the determination of residues of compounds belonging to this group, we observed that most of the impurities commonly encountered in solvents and reagents elute from GC columns at retention times similar to those of organochlorine compounds such as BHC, DDT, dieldrin and PCBs and are therefore not likely to interfere in the analysis of synthetic pyrethroids which are retained by commonly used GC stationary phases for relatively much longer times. This study was therefore undertaken to investigate the possibility of using laboratory grades of common solvents and reagents, wich are cheap but have low purity in as comparing to with analytical-reagent or purer grade chemicals, for the determination of residues of halogenated synthetic pyrethroid pesticides, without subjecting them to any purification procedures.

EXPERIMENTAL

Gas chromatograph

A Becker Model 417 gas chromatograph (Packard) equipped with a ^{63}Ni electron-capture detector and a 1 m × 2 mm I.D. glass column packed with 1.5% SP-2250 + 1.95% SP-2401 on 100–120-mesh Supelcoport (Supelco, Bellefonte, PA, U.S.A.) was used. The injection port temperature was 260°C, the column oven temperature 240°C and the detector temperature 250°C. The carrier gas was nitrogen at a flow-rate of 80 ml/min.

Reference standards

Permethrin [3-phenoxybenzyl (1*R,S*)-*cis, trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate], cypermethrin [(*R,S*)-α-cyano-3-phenoxybenzyl (1*R,S*)-*cis,trans*-3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropanecarboxylate], fenvalerate [cyano(3-phenoxyphenyl)methyl 4-chloro-α-(1-methylethyl)benzeneacetate] and deltamethrin ({1*R*-[1α(*S*),3α]}-cyano(3-phenoxyphenyl)methyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate) having purities of 100, 94.5, 99.4 and 99.5%, respectively, were obtained from the U.S. Environmental Protection Agency (Research Triangle Park, NC, U.S.A.).

Reagents

Acetone, acetonitrile, anhydrous sodium sulphate, light petroleum (b.p. 67–70°C) and sodium chloride were used. Laboratory-grade solvents and reagents of three different brands for each chemical were used as received without subjecting them to any purification procedure. Each substance was checked by using it in amount and manner in which it is likely to be employed in the determination of residues, of synthetic pyrethroids. Other solvents and reagents used during the evaluation of a particular chemical were of nano-grade (GC grade) and had been pre-checked to ensure that they did not produce any spurious peaks during analysis. The procedures for checking various chemicals were as follows.

Light petroleum. Two 100-ml portions of light petroleum were partitioned with 600 ml of 5% aqueous sodium chloride, pooled, dried over anhydrous sodium sulphate and concentrated to about 5 ml with a rotary vacuum evaporator.

Acetone. A 200-ml volume of acetone diluted with 600 ml of 5% aqueous sodium chloride was partitioned with two 100-ml portions of light petroleum, pooled, dried and concentrated as described above.

Acetonitrile. A 200-ml volume of acetonitrile diluted with 600 ml of 5% aqueous sodium chloride was partitioned twice with 100-ml portions of light petroleum, then processed as above.

Sodium chloride. A 600-ml volume of 5% aqueous sodium chloride was partitioned with two 100-ml portions of light petroleum, then processed as described above.

Sodium sulphate. A 200-ml volume of light petroleum was passed through anhydrous sodium sulphate packed to a height of 5 cm in a glass column (I.D. 2 cm) and concentrated as described above.

GC determination

The volume of each concentrated light petroleum extract obtained from purity checks for various solvents and reagents was adjusted to 5 ml and a 5-μl aliquot was injected onto the GC column. The suitabilities of different chemicals were evaluated by comparing the retention times of the peaks thus obtained with those of synthetic pyrethroids run under identical GC operating conditions (Fig. 1).

RESULTS AND DISCUSSION

The chromatograms of batches of solvents and reagents found to contain maximum contaminants are shown in Fig. 1. In almost all instances some early-eluting peaks were observed. However, no extraneous peaks were encountered at the retention times of the synthetic pyrethroids during the purity evaluation of any of the chemicals.

Assuming that the purity checking procedure for a chemical represented the processing of a 50-g sample for residue analysis, eah aliquot injected corresponded to 50 mg of sample. In the pesticide residue analysis program of the U.S. Food and Drug Administration (FDA), aliquots of extracts equivalent to 25 mg of sample are recommended to be injected during regular residue determinations [9]. Hence the amounts of solvents and reagents evaluated for purity in this study were twice those recommended by the FDA. The pesticide retained by the GC column for the longest time in this study was deltamethrin, with a retention time of about 12 min. The gas chromatograms were therefore examined for interferences up to 25 min, *i.e.*, double the retention time of deltamethrin.

It has been reported that solvents and reagents occasionally contain impurities that cannot be detected by running reagent blanks but may degrade pesticide residues during analysis [1,2]. Therefore, one batch of each chemical being evaluated for purity was checked by carrying 2 μg of different synthetic pyrethroids, which is equivalent to a concentration of 0.04 μg/g for a sample size of 50 g, through a procedure extending the AOAC multi-residue method to the determination of these pesticides [10]. The analysis was carried out in duplicate and the amounts of permethrin, cypermethrin, fenvalerate and deltamethrin recovered were 93.3 $\pm$ 0.1, 98.8 $\pm$ 0.8, 102.4 $\pm$ 1.2 and 100.1 $\pm$ 1.6% (n = 2), respectively, thereby indicating that no losses of residues of these compounds occurred during their determination.

The use of comparatively low-purity solvents can also adversely affect the

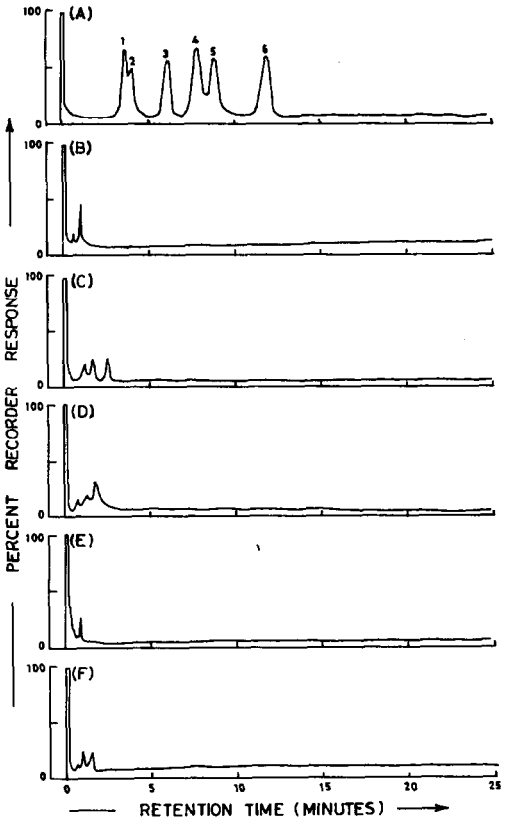

Fig. 1. Gas chromatograms of batches of solvents and reagents found to contain maximum contaminants. (A) Mixture of standards; (B) light petroleum; (C) acetone; (D) acetonitrile; (E) sodium chloride; (F) sodium sulphate. Peaks: 1 = *cis*-permethrin; 2 = *trans*-permethrin; 3 = cypermethrin; 4 = *cis*-fenvalerate; 5 = *trans*-fenvalerate; 6 = deltamethrin.

separating power of the GC column or response of the detector. However, no deterioration in performance was observed when the resolution and sensitivities of permethrim, cypermenthim, fenvalerate and deltamethim, before and after the injection of 50 aliquots (each equivalent to a 50-mg sample size) of the extracts obtained by using laboratory-grade solvents and reagents were compared.

Hence inexpensive laboratory-grade solvents and reagents, which may not be suitable for the analysis of organochlorine insecticides or PCBs, can be acceptable for synthetic pyrethroids if reagent blanks performed with them reveal the absence of spurious peaks at or close to the retention times of the compounds of interest.

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REFERENCES

1 Food and Drug Administration, *Pesticide Analytical Manual*, Vol. I, U.S. Department of Health, Education and Welfare, Washington, DC, 1977, Ch. 1, Section 120.
2 J. Sherma, *Manual of Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples*, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1979, p. 53.
3 W. Horwitz (Editor), *Official Methods of Analysis of the Association of Official Analytical Chemists*, Association of Official Analytical Chemists, Washington, DC, 1980, Section 29.001.
4 J. H. Ruzicka, in C. A. Edwards (Editor), *Environmental Pollution by Pesticides*, Plenum Press, London, 1973, p. 11.
5 H. Roseboom, in J. F. Lawrence (Editor), *Food Constituents and Food Residues: Their Chromatographic Determination*, Marcel Dekker, New York, 1984, p. 489.
6 W. W. Thornburg, *Residue Rev.*, 14 (1966) 1.
7 G. Zweig and J. Sherma, in G. Zweig and J. Sherma (Editors), *Analytical Methods for Pesticide Residues and Plant Growth Regulators, Vol. XIII, Synthetic Pyrethroids and Other Pesticides*, Academic Press, Orlando, 1984, p. 3.
8 E. Papadopoulou-Mourkidou, *Residue Rev.* 89 (1983) 179.
9 B. McMahon and J. A. Burke, *J. Assoc. Off Anal. Chem.*, 61 (1978) 640.
10 H. E. Braun and J. Stanek, *J. Assoc. Off. Anal. Chem.*, 65 (1982) 685.