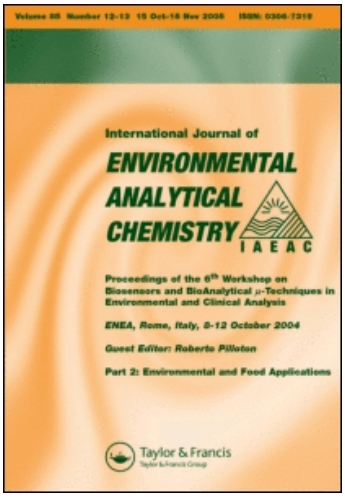

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William J. Trotter[a]
[a] Division of Chemical Technology, Food and Drug Administration, Washington, DC

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Effect of the Solvent on the Response to Organophosphorus Pesticides Determined using Gas Chromatography with Flame Photometric Detection

WILLIAM J. TROTTER

Division of Chemical Technology, Food and Drug Administration, Washington, DC 20204

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The gas chromatographic flame photometric detector (FPD)-phosphorus mode response to organophosphorus (OP) pesticides was studied for the following solvents: acetone, isooctane, acetone-isooctane (1+9), methanol and ethyl acetate. Both single and dual FPDs were used. Some OP pesticides yielded significant differences in FPD response when the various solvents were used. For example, the response to 6.7 ng monocrotophos (azodrin) was 0.37 in isooctane relative to the same amount of monocrotophos in acetone, using a dual flame detector. Because the FPD response to OP pesticides is dependent on the solvent used, OP standard solutions for quantitation of pesticide residues should be prepared in a solvent nearly identical to the solvent in the sample solution.

KEY WORDS: Organophosphorus pesticides, gas chromatography, flame photometric detection.

INTRODUCTION

The flame photometric detector (FPD) in the phosphorus (P) mode is selective for P-containing compounds. The use of a 526 nm band

transmittance filter allows the passage of HPO, which is the emitting species for organophosphorus (OP) compounds.[1] Brody and Chaney[1] reported that FPD gas chromatography (GC) responds to parts per billion (1:1,000,000,000) and is linear over a range of at least four decades of concentration for P-containing compounds. Burgett and Green[2] modified the detector designed by Brody and Chaney by interchanging the hydrogen and air supplies to the burner to prevent solvent flame-out. The configuration for the Tracor FPD burner (Figure 1) uses a (single flame) FPD similar to the Burgett and Green modification in which a mixture of GC effluent and air is conveyed to the flame tip orifice while the hydrogen is introduced from the outer periphery of the flame tip. Figure 2 illustrates the Varian (dual flame) FPD, including the optical train. The optical train of the Tracor FPD is similar;

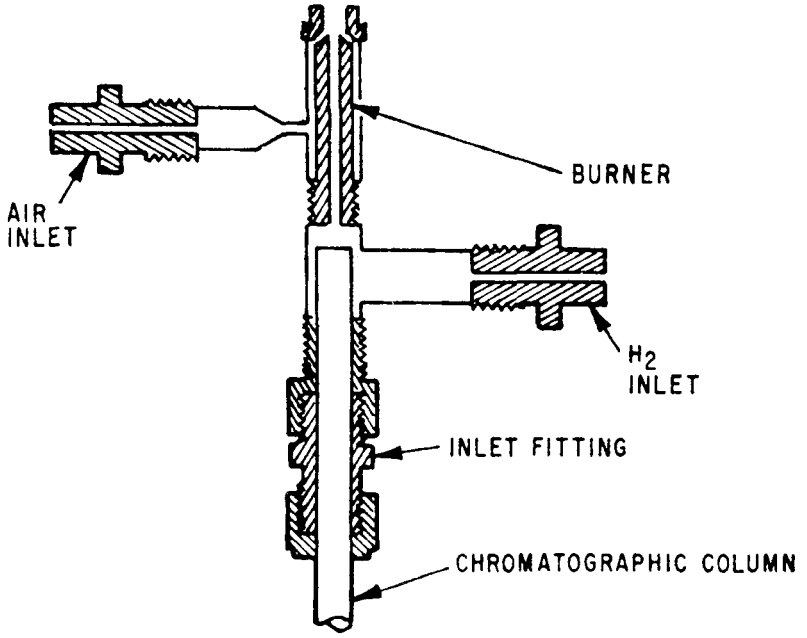

FIGURE 1 Schematic diagram of Tracor (single flame) FPD burner showing air inlet, hydrogen inlet and burner.

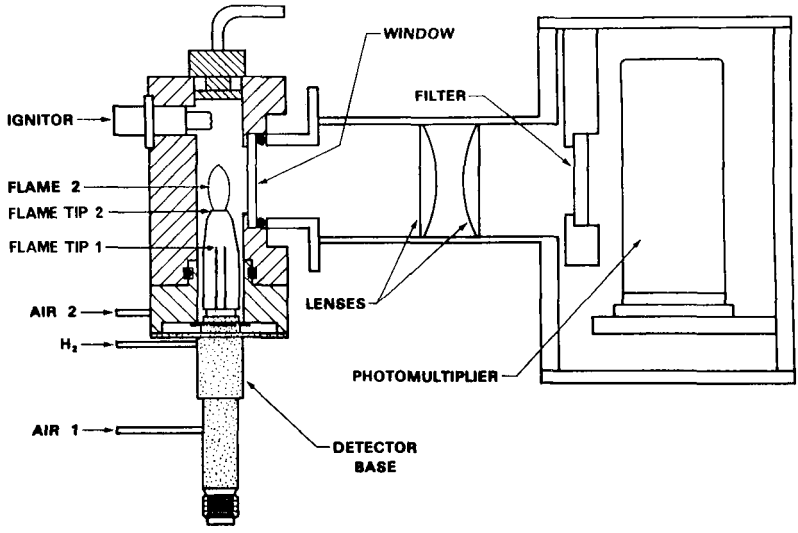

FIGURE 2 Schematic diagram of Varian (dual flame) FPD including the optical train. Flame 1 (not shown) is above flame tip 1.

however, it does not have lenses. In the Varian FPD, air is initially mixed with the GC effluent and hydrogen is introduced from the outer periphery of flame tip 1. A second stream of air (air 2) is introduced from the outer periphery of flame tip 2. Patterson *et al.*[3] and Patterson[4] have reported in depth on the characteristics of the (dual flame) FPD.

The purpose of this study was to determine the optimum solvent for OP pesticide standards for subsequent GC analysis with an FPD in the P mode. This necessitated investigating the effect of the solvent on the GC determination of OP compounds.

EXPERIMENTAL

Gas chromatographs

The Tracor 560 gas chromatograph was equipped with a Tracor (single flame) FPD (Tracor Instruments, Austin, TX 78721). A Varian 8000 autosampler (4.5 μl injected) (Varian Associates, Palo Alto,

CA 94303) and a Spectra Physics 4000 integrating computer (Spectra Physics, Santa Clara, CA 95051) were also used. Temperatures (°C) were: injector 190, column 180 and detector 200. Gas flows (ml/min) were: column nitrogen 30, flame hydrogen 80 and flame air 100. Voltage applied to the photomultiplier tube was 630 V. GC responses were quantitated as peak areas by the Spectra Physics 4000.

The Tracor 565 gas chromatograph was equipped with a Tracor (single flame) FPD. Equipment was similar to and conditions were identical to those used with the above Tracor FPD except for the following: (1) manual injections were performed with 5 μl OP solution plus 2 μl solvent plug flush at the syringe plunger (the same solvent was used for the solvent plug flush as for the OP solution), (2) 600 V was applied to the photomultiplier tube and (3) GC responses were quantitated as peak areas by the Spectra Physics 4000 and as peak heights manually (quantitations by the two techniques were similar).

The Varian 3700 gas chromatograph was equipped with a Varian (dual flame) FPD and a Varian 8000 autosampler (2.0 μl injected). Temperatures (°C) were: injector 190, column 180 and detector 200. Gas flows (ml/min) were: column helium 30, flame hydrogen 140, air 1 (lower flame) 80 and air 2 (upper flame) 190. Voltage applied to the photomultiplier tube as determined by a volt-ohm meter was 660 V. GC responses were manually quantitated as peak heights.

GC Columns

The Varian and Tracor gas chromatographs were each equipped with 5 ft (1.5 m) × 2 mm i.d. glass columns packed with 2% stabilized DEGS with 0.5% phosphoric acid on 80–100 mesh Chromosorb W (AW). Prepared column packing was obtained from Analabs, North Haven, CT 06473. Columns were conditioned for 2 days at 180°C before use.

Solvents

All solvents were distilled-in-glass pesticide analysis quality and were used as received from Burdick & Jackson Laboratories, Inc., Muskegon, MI 49443.

Preparation of OP standard solutions

Reference standards were obtained from the U.S. Environmental Protection Agency, Las Vegas, NV 89114. Each stock solution (ca. 5 mg/25 ml) was prepared by dissolving a single OP standard in 1–2 ml acetone and diluting to volume (25 ml) with isooctane. Acephate stock solutions were prepared in acetone because of poor solubility of acephate in isooctane. For each OP compound, the stock solutions were further diluted with the solvent to be tested. All injections were made with solutions containing a single OP compound.

RESULTS AND DISCUSSION

The ideal solvent for any pesticide would not degrade the pesticide, would have a low vapor pressure so that the concentration of the solution did not change significantly due to evaporation and would not interfere with the analysis for the pesticide. The pesticide chemist usually would choose nonpolar solvents, e.g., isooctane, for standard solutions to minimize possible degradation of the pesticide. However, this laboratory does not use isooctane for OP pesticide standards since we have observed that, in general, FPD responses for OP pesticides in isooctane differ from those in acetone. Acetone is the final solvent used in the Luke *et al.*[5] multiresidue method, which recovers a significant number of OP residues from foods.

Initial experiments using the Tracor FPD indicated that detector responses to OP pesticides were similar whether the solvent was acetone-isooctane (1+9) or acetone. Therefore, it was considered advantageous to use acetone-isooctane (1+9) as the solvent because it is relatively nonvolatile and only slightly polar, properties that can minimize evaporation and possible OP degradation, respectively.

Table I lists the results obtained using the Tracor 560 (single flame) FPD to compare the GC responses to several OP pesticides in acetone-isooctane (1+9) relative to acetone. The relative responses to the OP pesticides in acetone were assigned a value of 1. The relative response to an OP in another solvent was calculated by dividing the OP's peak area in the solvent by the OP's peak area in acetone. The mean coefficient of variation (CV) for three consecutive injections of each solution was 2.8%, with a range of 0.23–7.7%. The

TABLE I

Relative response to OP pesticides with acetone-isooctane (1+9) as solvent relative to acetone as solvent, using the Tracor 560 (single flame) FPD.[a]

Pesticide	Amount injected (ng)	Relative response
Chlorpyrifos	1.3	0.97
Dimethoate	1.9	1.07
Ethyl pirimiphos	1.8	1.00
Malaoxon	4.6	0.97
Malathion	1.8	0.99
Monocrotophos	5.0	1.04
Omethoate	5.2	1.05
Paraoxon	3.7	0.97
Parathion	2.3	0.99
Phenthoate	2.4	0.99

[a]Peak areas were averaged for three consecutive injections of each solution containing a single OP pesticide.

results (Table I) indicate good agreement between the GC responses to the OP pesticides in acetone and in acetone-isooctane (1+9). The OP pesticides studied are diverse in both structure and polarity. Only dimethoate and omethoate yielded differences $\geq 5\%$ in FPD responses between acetone and acetone-isooctane (1+9). The response to six of the ten OP pesticides was greater in acetone than in acetone-isooctane (1+9).

Table II (top) shows the relative FPD responses to the OP pesticides in five solvents using the Tracor 565 (single flame) FPD; the relative responses to each pesticide in acetone were assigned a value of 1 and the relative responses were calculated using area counts. The mean CV for three consecutive injections of each solution was 2.5% with a range of 0.28–13%. The Tracor 560 and the Tracor 565 instruments used in this laboratory have identical FPDs.[6] The relative responses to dimethoate and monocrotophos (azodrin) in acetone-isooctane (1+9) were greater than the responses of these pesticides in acetone (Table II, top); this is similar to the results in Table I. The relative responses to chlorpyrifos (dursban) and parathion in acetone-isooctane (1+9) were less than those in

TABLE II

Relative response to OP pesticides in several solvents (response in acetone = 1), using the Tracor 565 (single flame) and the Varian 3700 (dual flame) FPDs.[a]

Pesticide	Amount injected (ng)	Relative response			
		Isooctane	Methanol	Acetone-isooctane (1+9)	Ethyl acetate
Tracor 565 FPD					
Chlorpyrifos	1.3	0.86	0.65	0.84	1.02
Dimethoate	1.9	0.71	0.94	1.04	1.05
Monocrotophos	5.6	0.12	0.43	1.11	0.68
Parathion	2.7	0.99	0.92	0.98	1.02
Varian 3700 FPD					
Acephate	5.3	0.39	0.99	1.00	1.03
Chlorpyrifos	3.8	1.05	0.89	1.02	0.78
Dimethoate	3.8	1.53	0.89	1.09	1.03
Ethyl pirimiphos	5.8	1.14	0.99	1.07	1.04
Malaoxon	10	1.28	0.88	1.16	1.17
Malathion	7.7	1.05	0.89	1.00	1.09
Monocrotophos	6.7	0.37	0.54	1.25	0.69
Paraoxon	7.2	1.26	0.86	1.12	1.08
Parathion	8.0	1.08	0.94	1.06	1.03
Phenthoate	8.5	1.10	0.88	1.02	1.05

[a]Peak areas and peak heights, respectively, were averaged for three consecutive injections of each solution containing a single OP pesticide, using the Tracor and Varian FPDs.

acetone; this is also similar to the results in Table I. The relative responses to dimethoate, monocrotophos, chlorpyrifos, and parathion in Table II (top) differed somewhat from those in Table I; a significant difference is noted for chlorpyrifos (relative response in acetone-isooctane (1+9) was 0.84 versus 0.97). Table II (top) also shows that the relative responses were <1 for all four OP pesticides in isooctane and methanol and significantly <1 for dimethoate and monocrotophos in isooctane and for chlorpyrifos and monocrotophos in methanol. Ethyl acetate yielded relative responses close to 1 for all OP pesticides except for monocrotophos, for which the relative response was significantly <1. Indeed, the FPD response to

monocrotophos was significantly <1 for isooctane, methanol and ethyl acetate; only in acetone-isooctane (1+9) was the FPD response to monocrotophos somewhat similar to that in acetone. The FPD response to parathion was similar in all five solvents.

Table II (bottom) shows the relative GC responses to the OP pesticides in five solvents, using the Varian 3700 (dual flame) FPD. The mean CV for three consecutive injections of each solution was 4.0%, with a range of 0–16%. Acephate was examined for inclusion in Table II but not for Table I; omethoate was examined for inclusion in Table I but not for Table II. The data in Table II (bottom) show much greater variation than those in Table I among the GC responses to the OP pesticides in acetone-isooctane (1+9) versus acetone. Unlike Table I, Table II (bottom) data show that the response to most of the ten OP pesticides was less in acetone than in acetone-isooctane (1+9). Table II (bottom) shows that the response to seven of the ten OP pesticides was greatest in isooctane, especially the response to dimethoate; however, the response to monocrotophos and acephate was very poor in isooctane. The response to none of the four OP pesticides (Table II, top) was the greatest in isooctane. The response to all OP pesticides in methanol, especially monocrotophos, was less than in acetone. The response to most OP pesticides was greater in ethyl acetate than in acetone; however, the response to monocrotophos was poor in ethyl acetate.

Our results indicate that the more polar OP pesticides yielded the greater diversity of response among the solvents examined. Based upon the results of this work, we recommend that OP standard solutions be prepared in the solvent that is most nearly identical to the solvent in the sample solution.

Acknowledgement

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