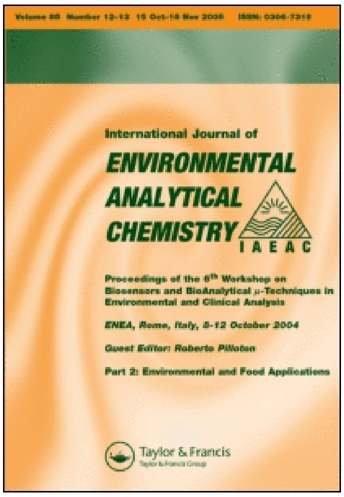

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The Variability of Response of the Gas Chromatographic Flame Photometric Detector to the Phosphorus Content of Organophosphorus Pesticides

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The Variability of Response of the Gas Chromatographic Flame Photometric Detector to the Phosphorus Content of Organophosphorus Pesticides

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Gas chromatographic detector responses to organophosphorus pesticides (OP) relative to their phosphorus (P) content were studied using packed column isothermal gas chromatography (GC) with flame photometric detection (FPD) in the P mode. The FPD responses relative to the amount of P injected (Responses P) were examined for single and dual flame detectors. Responses P were determined to be dependent upon the OP as well as the solvent. For example, Responses P for dimethoate were 0.26 and 0.38 in acetone and isooctane, respectively, relative to Response P for chlorpyrifos (Dursban) using a dual flame FPD. Responses P did not vary proportionately for each OP tested when the gas flows of the dual flame FPD were varied. This indicates that the FPD itself contributes to the variability of responses of the FPD–GC to the P content of the OP.

KEY WORDS: Flame photometric detector, gas chromatography, pesticides.

INTRODUCTION

The flame photometric detector (FPD) in the phosphorus (P) mode is selective for P-containing compounds. HPO is the emitting species for organophosphorus pesticides (OPs) in the FPD. The use of a 526-nm band transmittance filter allows the passage of the green light emitted by HPO to be transmitted to the photomultiplier tube. Brody and Chaney[1] reported that the FPD, when used in packed column gas chromatography (GC), is linear over a range of at least four decades of concentration for P-containing compounds. One might reason that if the OP is efficiently combusted in the FPD, the response of FPD-GC would be dependent only upon the P content of the OP and independent of the chemical structure of the OP. The purpose of this study was to examine the possible dependence of the FPD-GC response relative to the amount of P injected (Response P) upon the structure of the OP.

Both single and dual flame FPDs were used in this study. Figure 1 illustrates the configuration of the Tracor (single flame) FPD. In this detector a mixture of GC effluent and hydrogen is conveyed to the flame tip orifice while air is introduced from the outer periphery of the flame tip. Figure 2 illustrates the Varian (dual flame) FPD, including the optical train. The optical trains of these detectors are similar; however, the Tracor detector does not have lenses. In the

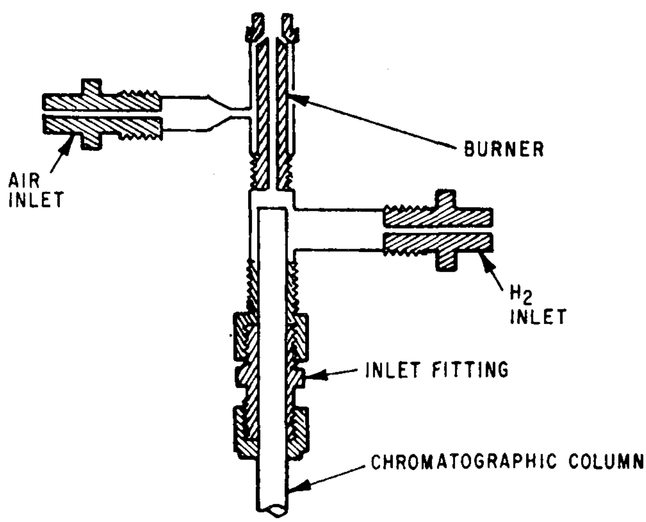

Figure 1 Tracor (single flame) FPD burner showing air inlet, hydrogen inlet, and burner.

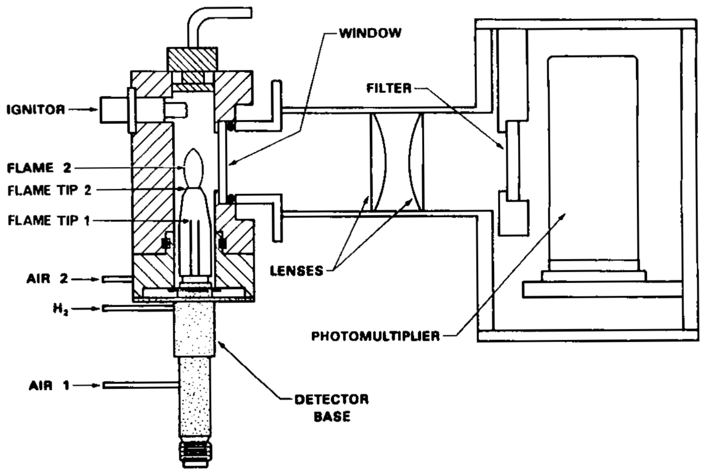

Figure 2 Varian (dual flame) FPD including the optical train. Flame 1 (not shown) is above flame tip 1.

Varian FPD, air (air 1) 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. The characteristics of the (dual flame) FPD have been reported in depth by Patterson *et al.*[2] and Patterson.[3]

MATERIALS AND METHODS

Gas chromatographic systems

Table I The Tracor 560 gas chromatograph was equipped with a Tracor (single flame) FPD (Tracor Instruments, Austin, TX). A Varian 8000 autosampler (4.5 μL injected) (Varian Associates, Palo Alto, CA) and a Spectra Physics 4000 integrating computer (Spectra Physics, Santa Clara, CA) 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 (dc) applied to the detector photomultiplier tube was 630 V. GC responses were quantitated as peak areas by the Spectra Physics 4000.

Table I Relative Responses P[a] to OPs in two solvents using the Tracor 560 (single flame) FPD with DEGS GC column

Pesticide	Amount injected (ng)	Relative Responses P	
		Acetone	Acetone + isooctane (1+9)
Dimethoate	1.9	0.45	0.50
Ethyl pirimiphos	1.8	0.93	0.96
Malaoxon	4.6	0.41	0.41
Malathion	1.8	0.70	0.71
Monocrotophos	5.0	0.25	0.27
Omethoate	5.2	0.13	0.14
Paraoxon	3.7	0.49	0.49
Parathion	2.3	0.92	0.94
Phenthoate	2.4	0.51	0.52
CV (%)[b]		30	30

[a]Relative Responses P were calculated relative to chlorpyrifos.
[b]CV was calculated to include the Relative Response P of 1 for chlorpyrifos.

Table II Relative Responses P[a] to OPs in five solvents using the Tracor 565 (single flame) FPD with DEGS GC column

Pesticide	Amount injected (ng)	Relative Responses P				
		Isooctane	Methanol	Acetone	Acetone + isooctane (1+9)	Ethyl acetate
Dimethoate	1.9	0.45	0.53	0.53	0.66	0.55
Monocrotophos	5.6	0.041	0.13	0.29	0.38	0.19
Parathion	2.7	1.1	0.91	0.93	1.1	0.92
CV (%)[b]		50	40	34	33	37

[a]Relative Responses P were calculated relative to chlorpyrifos.
[b]CV was calculated to include the Relative Response P of 1 for chlorpyrifos.

Table II 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 Tracor 560 FPD system 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 (dc) 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).

Tables III–V 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. For Table III, gas flows (mL/min) were: column helium 30, flame hydrogen 140, air 1 (lower flame) 80, and air 2 (upper flame) 190. Voltage (dc) applied to the photomultiplier tube as determined by a volt–ohm meter was 660 V. For Table III, GC responses were manually quantitated as peak heights. For Tables IV and V, GC responses were quantitated as peak areas by the Spectra Physics 4000; gas flows were varied.

Table III Relative Responses P[a] to OPs in five solvents using the Varian (dual flame) FPD with DEGS GC column

Pesticide	Amount injected (ng)	Relative Responses P				
		Isooctane	Methanol	Acetone	Acetone + isooctane (1 + 9)	Ethyl acetate
Acephate	5.3	0.050	0.15	0.13	0.13	0.18
Dimethoate	3.8	0.38	0.26	0.26	0.27	0.34
Ethyl pirimiphos	5.8	1.1	1.1	1.0	1.1	1.4
Malaoxon	10	0.24	0.19	0.19	0.22	0.29
Malathion	7.7	0.49	0.49	0.49	0.48	0.68
Monocrotophos	6.7	0.035	0.059	0.097	0.12	0.086
Paraoxon	7.2	0.34	0.27	0.28	0.31	0.39
Parathion	8.0	0.52	0.53	0.50	0.52	0.66
Phenthoate	8.5	0.42	0.40	0.40	0.40	0.54
CV (%)[b]		35	35	33	34	40

[a]Relative Responses P were calculated relative to chlorpyrifos.
[b]CV was calculated to include the Relative Response P of 1 for chlorpyrifos.

Table IV Dependence of Relative Responses P[a] on gas flow rates of Varian dual flame FPD with DEGS GC column

Pesticide	Amount injected (ng)	Relative Responses P				
		0/190[b]	0/220	0/270	80/220	80/270
Diazinon	9.6	0.69	0.87	1.1	0.97	0.97
Dimethoate	7.3	0.47	0.49	0.50	0.81	0.78
Malathion	8.1	0.55	0.59	0.58	0.97	0.91
Monocrotophos	6.2	0.021	0.13	0.22	0.51	0.48
Paraoxon	5.9	0.032	0.20	0.34	0.81	0.75
Parathion	5.9	0.96	0.98	1.0	1.0	0.98
CV (%)[c]		40	39	35	18	19

[a]Relative Responses P were calculated relative to chlorpyrifos at each set of flow rates.
[b]Air 1/air 2 flow rates (mL/min). Hydrogen was 140 mL/min for all systems.
[c]CV was calculated to include the Relative Response P of 1 for chlorpyrifos.

Table V Dependence of Relative Responses P[a] on gas flow rates of Varian dual flame FPD with OV-101 GC column

Pesticide	Amount injected (ng)	Relative Responses P		
		80/190[b]	100/170[b]	80/190[c]
Diazinon	9.6	0.94	1.1	1.0
Dimethoate	7.3	0.79	0.78	0.76
Monocrotophos	6.2	0.33	0.27	0.21
Paraoxon	5.9	0.73	0.66	0.62
Parathion	5.9	0.99	0.92	0.98
CV (%)[d]		24	28	29

[a]Relative Responses P were calculated relative to chlorpyrifos at each set of flow rates.
[b]Air 1/air 2 flow rates (mL/min). Hydrogen was 140 mL/min.
[c]Air 1/air 2 flow rates (mL/min). Hydrogen was 160 mL/min.
[d]CV was calculated to include the Relative Response P of 1 for chlorpyrifos.

GC columns

DEGS Columns (*Tables I–IV*) 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 purchased from Analabs, North Haven, CT. Columns were conditioned for 2 days at 180°C before use.

OV-101 Column (*Table V*) The Varian gas chromatograph was equipped with a 5 ft (1.5 m) × 2 mm i.d. glass column packed with 5% OV-101 on 80–100 mesh Chromosorb W (HP). Prepared column packing was purchased from Hewlett-Packard, Avondale, PA. The column was conditioned for 1 day at 225°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.

Preparation of OP standard solutions

Reference standards were obtained from the U.S. Environmental Protection Agency, Pesticides and Industrial Chemical Repository, Research Triangle Park, NC. 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 the poor solubility of acephate in isooctane. For each OP, the stock solutions were further diluted with the solvent to be tested. All injections were made with solutions containing a single OP.

RESULTS AND DISCUSSION

Table I shows the results for the Relative Responses P (relative to chlorpyrifos (Dursban)) to nine OPs in acetone and in (1+9) acetone+isooctane using the Tracor 560 single flame FPD and our experimental conditions. It is not our purpose to document FPD-GC responses which could be routinely reproduced because the exact experimental conditions may be difficult to reproduce. 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 Relative Response P to an OP was calculated by dividing the Responses P to the OP (which is the OP response divided by the ng P injected) divided by the Response P to chlorpyrifos. The Relative Response P to chlorpyrifos is, by definition, equal to 1.

Table I shows considerable variation in the Relative Responses P among the OPs tested. The effect of the solvent was previously discussed by Trotter.[4] The Relative Responses P in various solvents are shown to illustrate that changing the solvent did not yield the same Relative Responses P to the OP. Chlorpyrifos had the greatest Relative Response P (equal to 1) among the OPs in both solvents tested. Parathion and ethyl pirimiphos had Relative Responses P approaching 1. Monocrotophos (azodrin) had the lowest Relative Response P among the tested OPs in both solvents.

Table II shows the Relative Responses P to the OPs in five solvents using the Tracor 565 (single flame) FPD. The Relative Responses P 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 Tracor 565 instruments used in this laboratory have identical FPDs.[5] The Relative Responses P were close to 1 for parathion and lowest for monocrotophos in all five solvents.

Table III shows the Relative Responses P to OPs in five solvents using the Varian 3700 (dual flame) FPD. The Relative Responses P were calculated using peak heights. The mean CV for three consecutive injections of each solution was 4.0% with a range of 0–16%. Ethyl pirimiphos and monocrotophos had the highest and lowest, respectively, Relative Responses P in all five solvents. In general, the variation of the Relative Responses P was greater among the OPs than the variation of the Relative Responses P among the solvents for each OP.

The dependence of the Relative Response P on the OP may result from several causes or combination of causes such as: (1) the amount of OP reaching the FPD may be dependent upon GC column effects or (2) each OP's FPD emission reaching the photomultiplier may be dependent upon structure due to incomplete combustion, quenching, sensitization, etc. Whether the FPD itself contributes to the variation of Relative Responses P among the OPs was investigated.

The gas flows on the dual flame FPD were varied to determine their effect upon the Relative Responses P. It was thought that the same Relative Responses P might be achieved for all OPs using the dual flame FPD if the difference in Relative Responses P was due to FPD causes. In the single flame FPD the decomposition of the combustible GC effluents and the hydrocarbon emissions occur in the same general area as the HPO emission. Quenching of the HPO emission due to hydrocarbon background is a greater problem in the single flame FPD than in the Varian dual flame FPD.[2] In the Varian dual flame FPD, compounds are decomposed in the lower flame.[2] Some HPO emission can occur in the volume between the lower and upper flames. However, the photomultiplier tube views only the HPO emission occurring in the upper flame.

Table IV shows the dependence of the Relative Responses P to OPs on the gas flow rates of the Varian detector with a DEGS column. The Relative Responses P were calculated relative to chlorpyrifos at each set of flow rates. The area count responses to duplicate injections of each OP in acetone solution were averaged.

Table IV shows that the Relative Responses P changed significantly among the OPs when the gas flow rates were varied, indicating that the FPD itself contributes to the variability of response of FPD-GC relative to a given P content of an OP. When air 1 is 0, the Varian FPD acts as a single flame FPD. This is the case for the first three sets of flow rates in Table IV. The last two sets of flow rates in Table IV have a positive flow for air 1 and in that case the Varian instrument acts as a dual flame FPD. Table IV shows that the CVs are greater for the first three sets of flow rates than for the last two sets. Thus, for the examined flow rates, the Relative Responses P are less compound-dependent when the Varian FPD acts as a dual flame FPD than when it acts as a single flame FPD.

Table V shows the dependence of the Relative Responses P to OPs on the gas flow rates of the Varian detector with a 5% OV-101 GC column. The Relative Responses P were calculated relative to chlorpyrifos at each set of flow rates. The area count responses to duplicate injections of each OP in acetone were averaged. Table V shows that the Relative Responses P changed significantly among the OPs when the gas flow rates were varied and that the FPD itself contributes to the variability of response of FPD-GC relative to the P content of an OP. Monocrotophos had the lowest Relative Response P (Table V; see also Tables I–IV).

Our results indicate that the Relative Responses P are variable and depend upon the structure of the OP and its solvent. Variability may be due to incomplete combustion, quenching, sensitization, hydrocarbon emission, and GC column effects. Often in multiresidue analysis, one would like to know the levels at which nondetected contaminants could have been observed. This study indicates, however, that in FPD-GC it is not always possible to predict sensitivities based upon the P content of the OP.

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