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Note

Optimization and response of the Pye flame photometric detector to some insecticides in the phosphorus and sulphur modes*

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Since Melpar produced the first commercial flame photometric detector (FPD) in 1966, there has been little change in the original design, although various companies now make these detectors. Minor modifications, such as the introduction of fibre optics, did not alter the parameters that affect the sensitivity and selectivity, as reported by Brody and Chaney[1].

The Pye FPD, which was introduced in 1974, is an exception to the above statement since it employs concentric glass and metal tubes for the jet as opposed to the single metal jet of the Melpar design. Air flows in the centre tube and the column effluent plus hydrogen is in the outer tube. This permits the use of very small hydrogen flow, resulting in a small flame that does not flame out with solvent and eliminates the need of a mask[2].

With the different jet design it becomes necessary to establish the optimum gas flows in order to obtain the best response. Mizany[3] has established that the gas flow-rates for the Melpar design, reported by Brody and Chaney[1] for phosphorus compounds did not correspond to those required for optimum sulphur response. He also indicated that the oxygen to hydrogen ratio and total gas flow were important parameters for optimizing the sulphur response, which was structure dependent. Another study by Greenhalgh and Cochrane[4] showed that the hydrogen flow was also important, the maximum oxygen to hydrogen ratio varied with different hydrogen flows.

The sulphur response is less than the square of the number of sulphur atoms in the molecule and values for the exponential proportionality factor have been reported between 1.5 and 2.0[3–5]. Eckhardt *et al.*[6] demonstrated that this factor is also critically dependant on gas flows. They reported optimum conditions for maximising this factor (*i.e.* as close to 2 as possible) in terms of the oxygen to hydrogen ratio, hydrogen flow and total jet flow for SO_2, H_2S and CH_3SH.

In this note the optimum gas flow-rates for the Pye detector are established in both the phosphorus and sulphur modes, and the sensitivity to some organophosphorus insecticides and sulphur herbicides is determined.

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EXPERIMENTAL

A Pye GCV gas chromatograph equipped with a Pye FPD and containing a 1 m × 4 mm I.D. glass column packed with 100–120 mesh Gas-Chrom Q coated with 3% OV-17 was used. The carrier gas (nitrogen) flow-rate was 50 ml/min; all other gas flow-rates were measured by bubble flow meter for accuracy. In each experiment, the hydrogen flow was adjusted first and the oxidant flow varied. S-Ethyl cyclohexylethyl thiocarbamate (Ro-Neet) and diethyl phenyl phosphorothioate (DEPPT) were used as standards for the sulphur and phosphorus mode, respectively.

RESULTS

The response, expressed as signal to noise ratio, of DEPPT in the phosphorus mode (526 nm) is shown plotted against the oxygen to hydrogen ratio for various hydrogen flows in Fig. 1 for carrier gas flows of 30, 60 and 100 ml/min. First, it is seen that the maximum value of the signal to noise ratio is approximately the same for the three widely differing column flows. Next, at any one column flow, the oxygen to hydrogen maximum moves to a lower value with increasing hydrogen flow. At a carrier gas flow of 60 ml/min, the maximum response occurred with a hydrogen flow of 30 ml/min and oxygen to hydrogen ratio of 0.13. Plotting the peak height response against the amount injected gave a line with a slope 0.98, which was linear over at

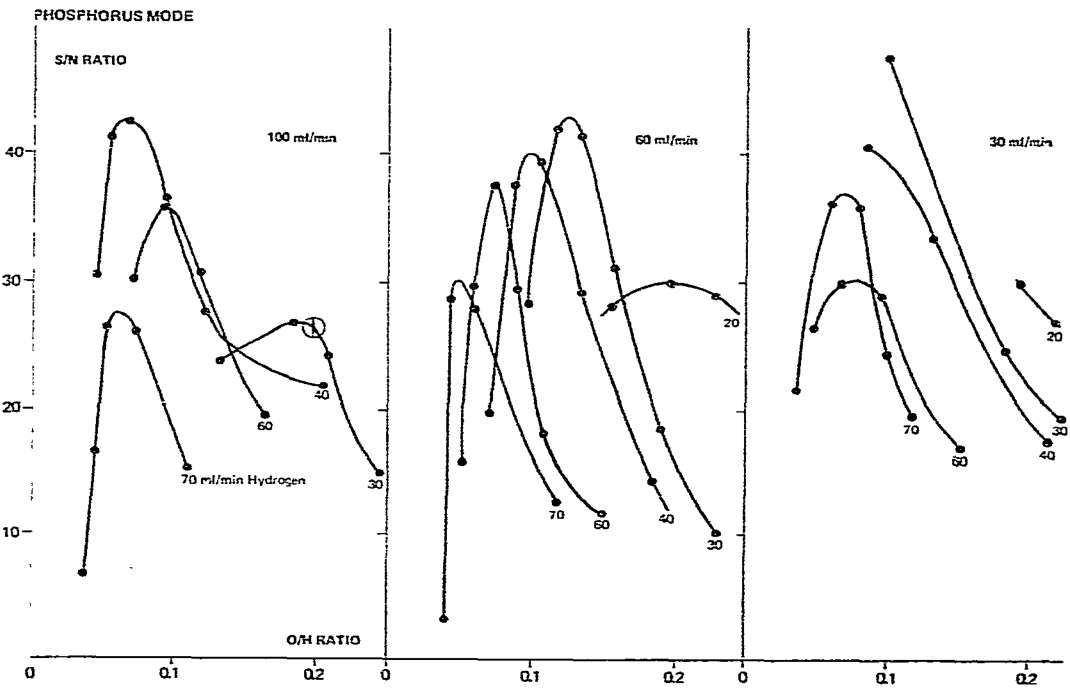

Fig. 1. Variation of the signal to noise (S/N) ratio with oxygen to hydrogen (O/H) ratio at different hydrogen and carrier gas flow-rates for diethyl phenyl phosphorothioate in the P mode.

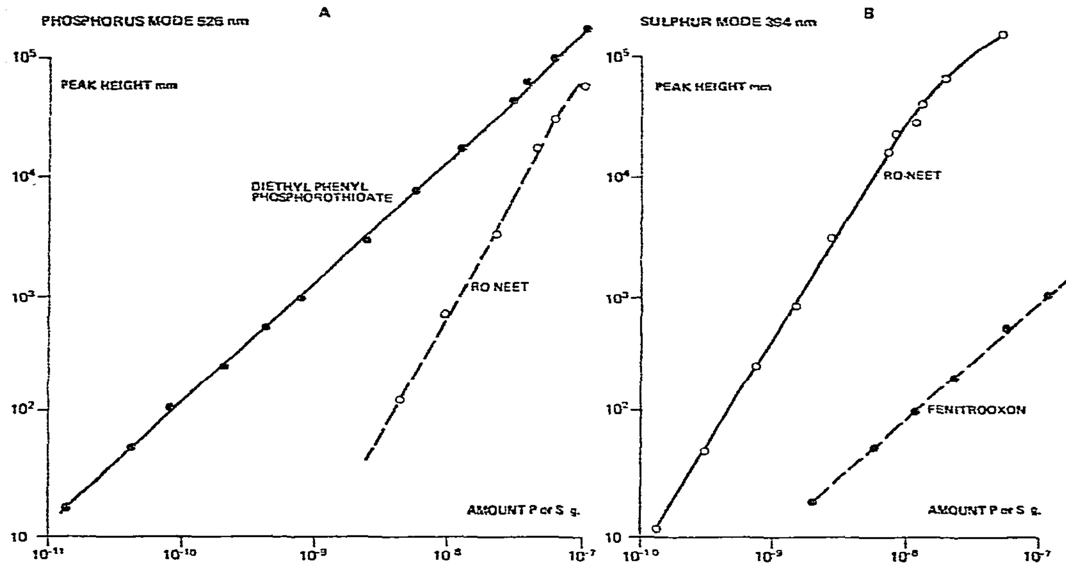

Fig. 2. Variation of response with concentration for Ro-Neet and DEPPT in the phosphorus and sulphur mode. (A) Diethyl phenyl phosphorothioate and Ro-Neet in the P mode; (B) Ro-Neet and fenitrooxon in the S mode.

least 4 orders of concentration (Fig. 2A). Fenitrothion and diazinon gave a response with slopes of 1.01 and 1.02, respectively, over the same linear range. The selectivity (phosphorus to sulphur) decreases with increasing concentration.

Retaining the column flow at 60 ml/min, the experiment was repeated in the sulphur mode (394 nm) using Ro-Neet. The optimum response occurred at an oxygen to hydrogen value of 0.16 and a hydrogen flow 30 ml/min. (Fig. 3). A log–log plot of the peak height response *versus* amount gave a straight line with a slope 1.74, which was linear over two orders of concentration (Fig. 2B). With the Melpar design, the work of Eckhardt *et al.* showed that optimum gas flow conditions gave exponential factors in the range 1.81–1.97 for SO_2, H_2S and CH_3SH. The selectivity (sulphur to phosphorus) increases with increasing concentration.

The optimum oxygen to hydrogen ratio and the hydrogen flow contrast with those obtained by Burgett and Green[7] for the Melpar design in both the conventional and new gas flow configuration. In the latter configuration, an oxygen to hydrogen ratio of 0.15 with a hydrogen flow of 200 ml/min was found to be optimum for methyl parathion in the phosphorus mode. For the sulphur mode, an oxygen to hydrogen ratio of 0.4 and a hydrogen flow of 50 ml/min gave the best response.

The sensitivity, expressed as the minimum detectable amount (MDA) at twice the noise level, of some insecticides is given in Table I. In the phosphorus mode, values for the phosphorothioates range from $1.21–2.72 \cdot 10^{-13}$ g P per sec, the only phosphate examined gave a high value of $6.7 \cdot 10^{-13}$ g P per sec. It is interesting to observe the four-fold increase in sensitivity of fenitrothion over fenitrooxon. In the sulphur mode, the minimum detectable amounts ranged from $1.49–5.62 \cdot 10^{-12}$ g S per sec.

Gas chromatograms of diazinon and chlorpyrifos (Dursban) in the phosphorus

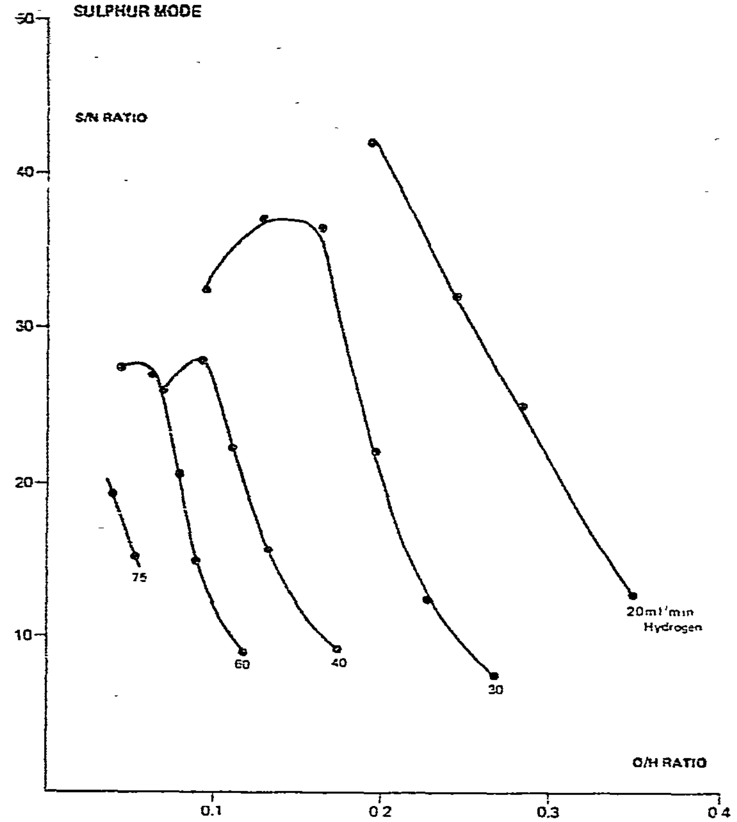

Fig. 3. Variation of the signal to noise (S/N) ratio with oxygen to hydrogen (O/H) ratio at different hydrogen flow-rates for Ro-Neet in the S mode.

TABLE I

DETECTION LIMITS OF SOME ORGANOPHOSPHORUS AND SULPHUR COMPOUNDS WITH THE PYE FPD

Column: 1 m × 4 mm 3% OV-17 on 100–120 mesh Gas-Chrom Q; retention times: 3–4 min.

Mode	*Compound*	*Minimum detectable amounts*		
		Compound (g/sec)	*P (g/sec)*	*S (g/sec)*
Phosphorus	Diazinon	$2.67 \cdot 10^{-12}$	$2.72 \cdot 10^{-13}$	
	Chlorpyrifos	$1.98 \cdot 10^{-12}$	$1.57 \cdot 10^{-13}$	
	Fenitrothion	$1.46 \cdot 10^{-12}$	$1.64 \cdot 10^{-13}$	
	Fenitrooxon	$5.65 \cdot 10^{-12}$	$6.71 \cdot 10^{-13}$	
	DEPPT	$0.96 \cdot 10^{-12}$	$1.21 \cdot 10^{-13}$	
Sulphur	Ro-Neet	$1.60 \cdot 10^{-11}$		$2.38 \cdot 10^{-12}$
	DEPPT	$1.05 \cdot 10^{-11}$		$1.49 \cdot 10^{-12}$
	Mesurol	$3.96 \cdot 10^{-11}$		$5.62 \cdot 10^{-12}$

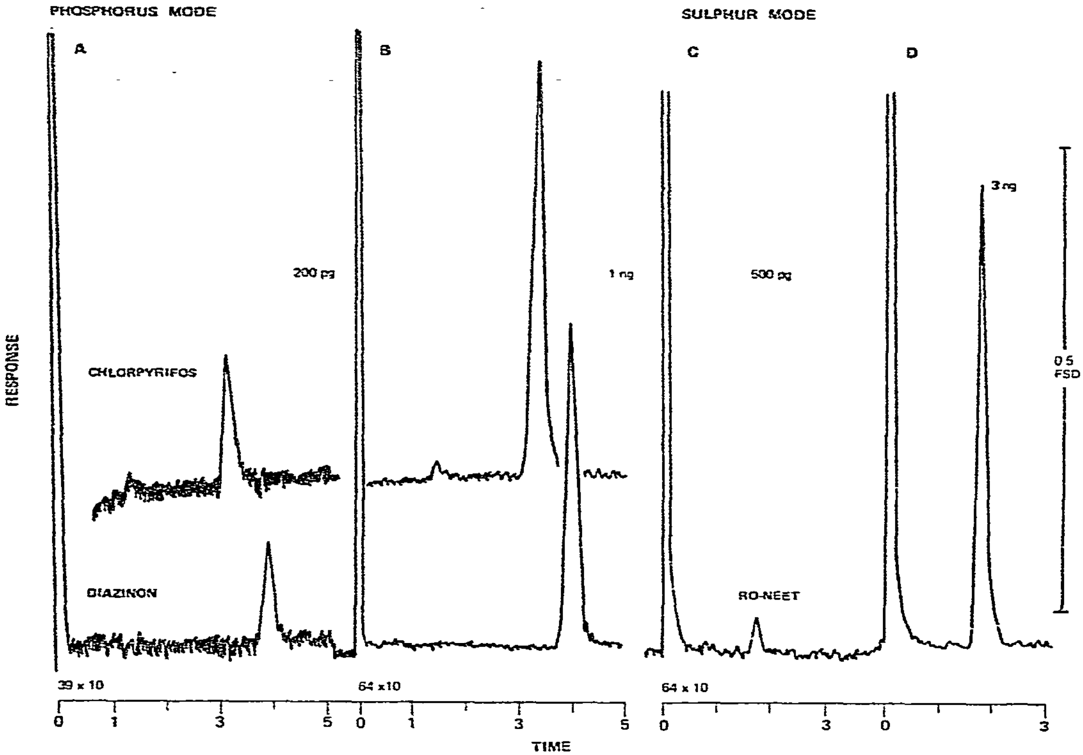

Fig. 4. Gas chromatograms of diazinon, chlorpyrifos and Ro-Neet standards at different concentrations. (A) P mode, diazinon (200 pg) and chlorpyrifos (200 pg), attenuation 32 × 10; (B) P mode, diazinon (1 ng) and chlorpyrifol (1 ng), attenuation 64 × 10; (C) S mode, No-Neet (500 pg); (D) S mode, Ro-Neet (3 ng).

mode and Ro-Neet in sulphur mode are shown in Fig. 4. Examples of gas chromatograms of extracts of field treated crops are shown in Fig. 5. Apples were treated with mixtures of ethephon (2-chloroethyl phosphonic acid) and fenoprop to facilitate mechanical harvesting. The apples were blended with methanol and the crude filtrate treated with diazomethane and the ethephon residues determined. Fig. 5A shows a second standard of the dimethyl ethephon and Fig. 5B the methylated extract containing 0.86 ppm. Blueberries were experimentally treated with Mesurol (4-methythio-3,5-xylyl methylcarbamate) as a bird repellant. Gas chromatograms of 5 ng of Mesurol standard and a cleaned up acetone extract of the fruit containing 0.04 ppm of Mesurol as determined in the sulphur mode are shown in Figs. 5C and D, respectively. The gas chromatogram of the blueberry extract shows a negative peak, following Mesurol. This is thought to result from the elution of hydrocarbons in the presence of sulphur or phosphorus contaminants, which reduces the emission[2].

Summarizing, the optimum conditions for the Pye FPD are a hydrogen flow of 30 ml/min and an oxygen to hydrogen ratio of 0.16 for sulphur and 0.13 for phosphorus, with a column flow of 60 ml/min. The fact that the optimum gas flow-rates are very similar in both the phosphorus and sulphur modes can be attributed to the jet design of the Pye FPD. These flow-rates differ appreciably from those for the Melpar

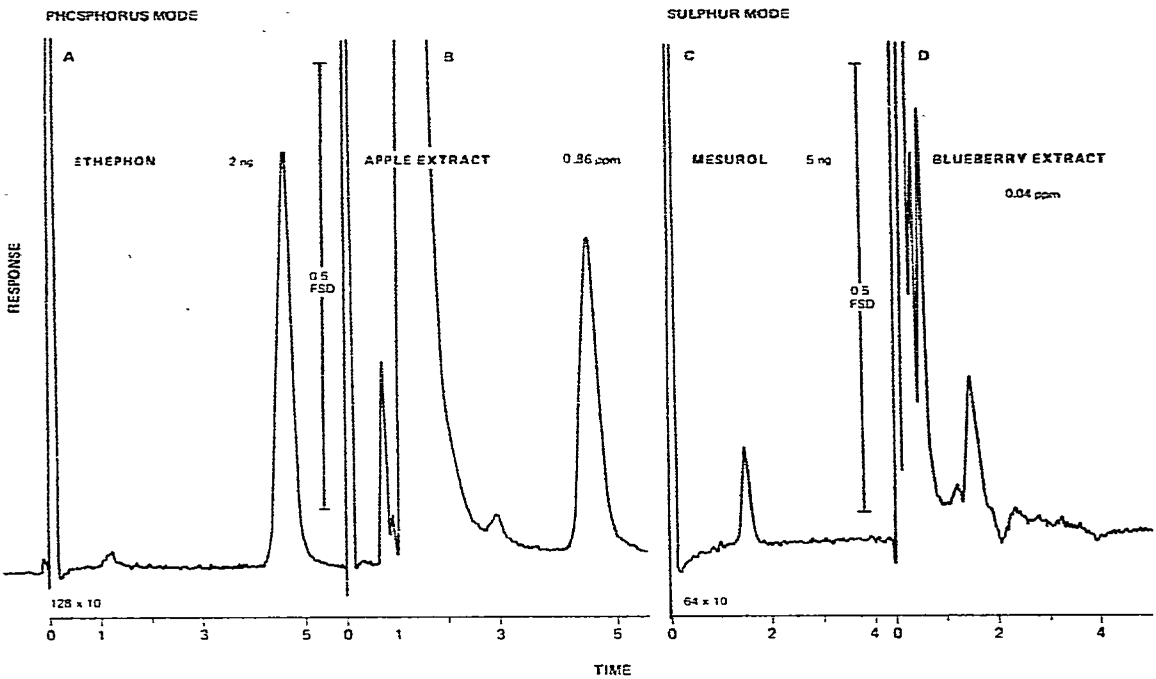

Fig. 5. Gas chromatograms of extracts of ethephon field treated apples and Mesurol field treated blueberries. (A) P mode, dimethyl ethephon (2 ng); (B) P mode, methanol extract of apple, partitioned and treated with diazomethane, showing 0.86 ppm; (C) S mode, Mesurol (5 ng); (D) S mode, acetone extract of blueberries, partitioned, cleaned-up, on silica gel showing 0.04 ppm.

design at the same column flow as quoted by Burgett and Green[7]. The MDA for organophosphorus insecticides ranged from $1.2–5.4 \cdot 10^{-13}$ g P per sec and for sulphur compounds $1.7–5 \cdot 10^{12}$ g S per sec. These values are equal or better than those reported by Natusch and Thorpe[8] for a Melpar design FPD.

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