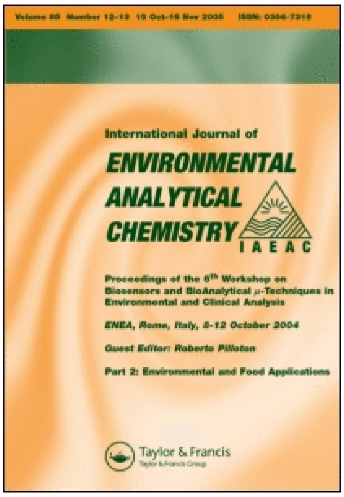

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Optimisation of the Sulphur Phosphorus Emission Detector and Comparison with the Electrolytic Conductivity Detector to some Sulphur-containing Insecticides and Herbicides

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Optimisation of the Sulphur Phosphorus Emission Detector and Comparison with the Electrolytic Conductivity Detector to some Sulphur-containing Insecticides and Herbicides†

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The flame parameters of the sulphur phosphorus emission detector (SPED) were examined for maximum response to a thiocarbamate, a phosphate and a phosphorothioate, under a given set of gas chromatographic conditions. An oxygen flame was preferred for the sulphur compound, with an oxygen/hydrogen ratio of 0.2–0.25 and a low hydrogen flow of 100–150 ml/min, whereas for the phosphorus compounds an air flame gave the best response with an oxygen/hydrogen ratio of 0.1–0.15 and a higher hydrogen flow of 200 ml/min. The response of the SPED was similar to that of other flame photometric detectors in that it gave a linear response in the phosphorus mode, a squared relationship in the sulphur mode for sulphur compounds and a quadratic response for compounds that contained

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both phosphorus and sulphur. With the latter, the amount of cross-channel interference in the sulphur mode from phosphorus was greatly reduced when an air flame was employed.

A comparative study of the response of 31 sulphur-containing compounds with the SPED and Coulson electrolytic conductivity detector (CCD) indicated the latter to be more sensitive by a factor of three; however, it was not specific. Of all the compounds studied, which included triazines, thiocarbamates, phosphorothioates and phosphorodithioates, Supracide and its metabolite were the only compounds which gave anomalous responses. The thiodiazolinyl sulphur atom did not appear to give S_2 on combustion, whereas it could be detected by the CCD in the pyrolytic mode.

The flame photometric, the thermionic[1] and the microcoulometric[2] detectors show some specificity to phosphorus and sulphur. The first two detectors employ a flame to excite the molecules to be detected. In the thermionic detector, compounds are burnt in an oxidising flame which contains an alkali halide and changes in the conductivity of the flame are measured. Sulphur compounds give a negative response. The flame photometric detector, on the other hand, employs a reducing flame and monitors the chemiluminescence of HPO and S_2 species produced on combustion. This detector is less sensitive than the thermionic detector to phosphorus by a factor of 10 or more, but is much more sensitive to sulphur by a factor of at least 10^3.

The feasibility of detecting phosphorus and sulphur by the use of a hydrogen-rich flame was demonstrated in 1962 by Dräger and Dräger.[3] Later, the development of very sensitive photomultiplier tubes led to the production of the first commercial flame photometric detector in 1966 by Tracor. The performance of this detector has been reported by Brody and Chaney[4] and others.[5,6] In 1970, the Bendix Corporation introduced the sulphur phosphorus emission detector (SPED). This detector employs the same basic principles as the Tracor, differing only in the means of transmitting light from the flame to the photomultiplier tubes. It is also easily adaptable to different GC instruments. This paper describes the optimisation of the SPED for sulphur and phosphorus compounds and compares the response of some sulphur compounds to those obtained with the Coulson electrolytic conductivity detector (CCD). The latter can detect sulphur but not phosphorus.

EXPERIMENTAL

Compounds

The samples of herbicides, organophosphorus and carbamate insecticides were of analytical grade. All the synthesised products had a purity of >98%, by micro-elemental and GC analysis.

Apparatus

The SPED was modified by making an entry port in the base and it was mounted on a Pye gas chromatograph model 104. The jet height was set at 6.5 mm. A solvent venting system similar to that of Watts[7] was installed, but with stainless steel connectors. A glass column, 3′ × 1/4″ o.d., containing 100/120 mesh Gas Chrom Q coated with 3% OV–17, was employed after being conditioned as previously described.[8] The same photomultiplier tube and fibre optic were used on both sulphur and phosphorus modes to ensure a true comparison. The photomultiplier was cooled with water, which resulted in a lower noise level, particularly in the S mode.

Method

Three replicate injections of 100 ng Ro-neet, 10 ng each of diethyl phenyl phosphate (DEPP) and diethyl phenyl phosphorothioate (DEPPT) were used for optimising the gas flow conditions. The hydrogen flow to the detector was set first, and then the air or oxygen flow was varied in order to obtain the required oxygen/hydrogen (O/H) ratio. The response study involved five replicates. The column flow of nitrogen was maintained at 40 ml/min; the retention time being kept in the range 3–6 min by variation of the column temperature. All flow meters were calibrated by bubble flow meters, because of the large errors in the readings. The response was measured by an Infotronic digital integrator model CRS 208.

RESULTS AND DISCUSSION

In all detectors which employ a flame, the gas flow rates are critical factors in optimising detector performance. Mizany[9] showed that large changes occurred in the signal/noise (S/N) value when the O/H ratio was varied for the flame photometric detector. For diethyl sulphide, the maximum response was obtained with O/H ratio of 0.4–0.5. In order to examine the effects of gas flow on the response of the SPED, three compounds were chosen to represent the different classes of interest to a pesticide analyst. These were the phosphorus compounds DEPP and DEPPT and the thiocarbamate Ro-neet.

The response expressed at the S/N ratio for Ro-neet in the sulphur mode is shown in Figure 1. The curves for the different hydrogen flows when only oxygen was premixed with the carrier gas are seen in Figure 1A. They differ from those obtained when air was used, in that they show a maximum. The maxima are seen to change to lower O/H values as the hydrogen flow increases, and they occur in the range of O/H ratios of 0.37 to 0.10.

The largest S/N value was 43, obtained with an oxygen flame, a hydrogen flow of 100 ml/min, and an O/H ratio of 0.25. When air was premixed with the carrier gas, no S/N maxima were observed, but the curves for different hydrogen flows moved to lower O/H ratios as the hydrogen flow increased.

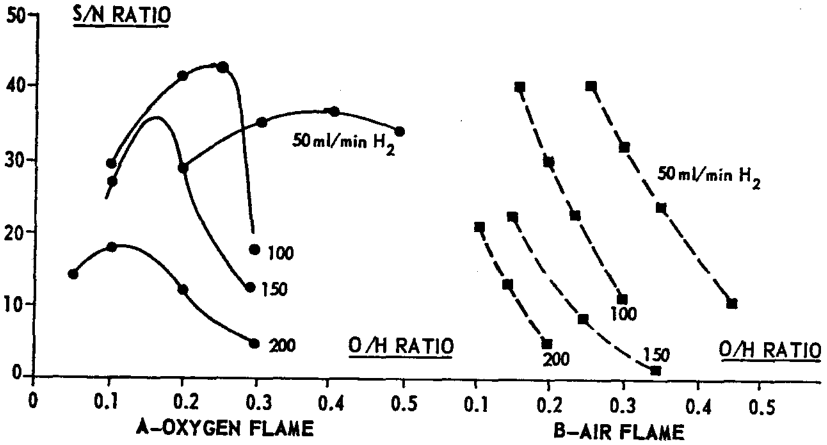


FIGURE 1 Variation of response with the oxygen/hydrogen ratio for Ro-neet in the sulphur mode.

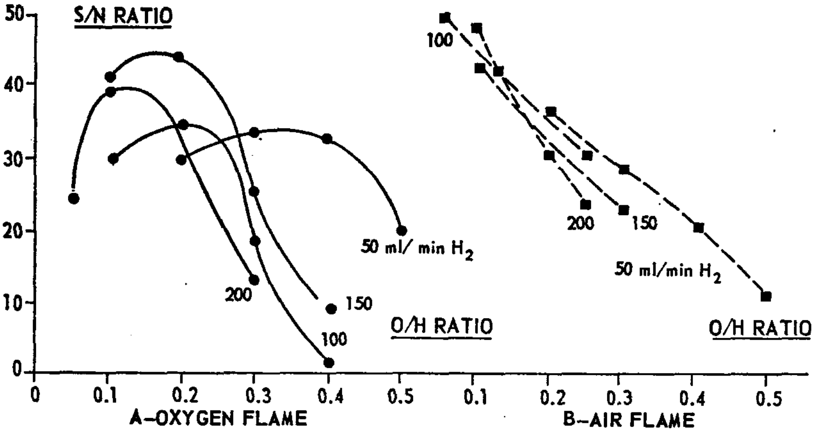


FIGURE 2 Variation of response with the oxygen/hydrogen ratio for DEPPT in the sulphur mode.

An S/N value of 40 was obtained with hydrogen flows of 100 and 50 ml/min and O/H ratios of 0.17 and 0.26, respectively. The peak height was greater when a flame with oxygen was used, but so was the noise.

The experiment was repeated with DEPPT, which contains both phosphorus and sulphur atoms. The response in the sulphur mode is shown in Figure 2, and is similar to that obtained with Ro-neet. The range of O/H values in which the maxima occur is 0.4–0.15 with an oxygen flame. Again the maxima moved to lower O/H values with increasing hydrogen flow. The maximum S/N value of 41 was obtained with an oxygen flame, a hydrogen flow of 150 ml/min, and an O/H ratio of 0.15.

The response of DEPPT in the phosphorus mode is illustrated in Figure 3. The most striking feature is the large difference in response between the flame with air and oxygen. Air gave a maximum S/N value of 148, which is nearly twice that obtained with oxygen. Since the peak heights in air and oxygen do not differ by that much, the difference in the S/N ratios can be attributed to the lower noise level of the flame when it is premixed with air. The maxima of the curves again go to lower O/H values with increasing hydrogen flow. They occur in the O/H range of 0.3–0.1. The greatest response was with a hydrogen flow of 200 ml/min, and an O/H ratio of 0.1.

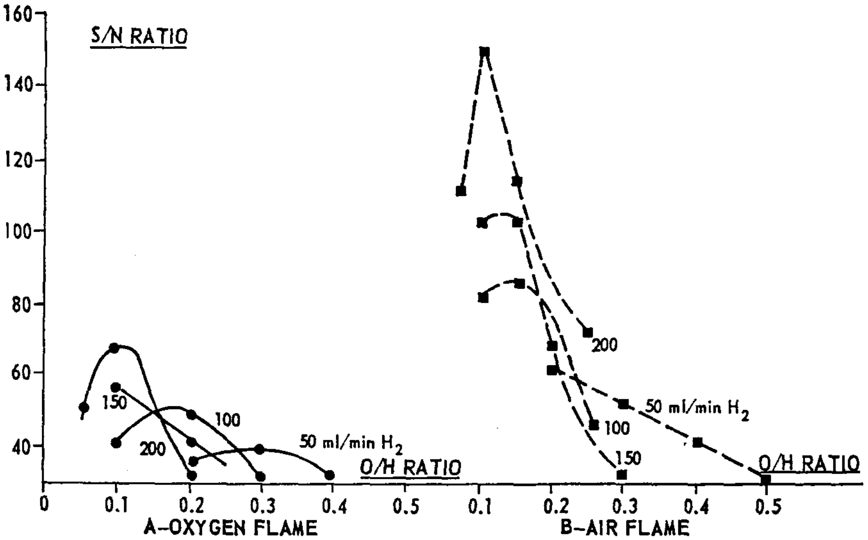


FIGURE 3 Variation of response with the oxygen/hydrogen ratio for DEPPT in the phosphorus mode.

Figure 4 gives the response of DEPP in the phosphorus mode as the flame parameters are varied. The overall response for the same amount of phosphorus is less than that for DEPPT. This reduced response can be partly attributed to the fact that phosphates exhibit broader peaks on OV–17 than do phosphorothioates. The range of O/H values in which the maxima occur, i.e. 0.35–0.1, is similar to that for DEPPT. The maximum response of 78 is obtained with an air flame, a hydrogen flow of 200 ml/min, and an O/H ratio of 0.1.

With the GC conditions used, an oxygen flame appears to be preferable for sulphur compounds. The S/N value is slightly better than with an air flame, and the response will not be as susceptible to small changes in the gas flow, due to operating on a plateau of the S/N versus O/H plot rather than on a slope. Optimum conditions require a hydrogen flow of 100–150 ml/min and an O/H ratio of 0.2–0.25. On the other hand, the best response for phosphorus is obtained using an air flame, at O/H ratio 0.1–0.15 and a hydrogen flow of 200 ml/min. These O/H ratios differ markedly from those reported by Mizany[9] for sulphur compounds, in that they are much lower. Factors such as the height of the jet, and the different heights of the viewing ports above the flame, could possibly account for this variation.

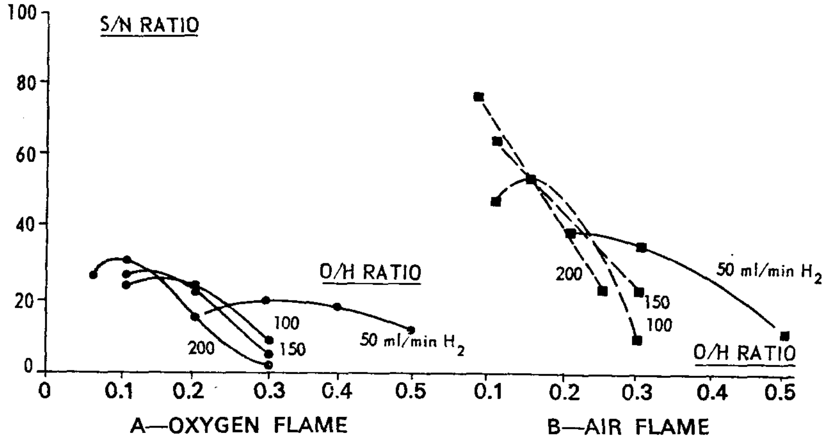


FIGURE 4 Variation of response with the oxygen/hydrogen ratio for DEPP in the phosphorus mode.

In the SPED, it is possible to view the region above the flame at two different levels, since the port normally used for phosphorus is 5 mm above the port for rulphur. Chromatography of 100 ng of Ro-neet gave very little signal when viewed in the upper port with a 394-nm filter in place. Conversely, the response to phosphorus in the lower port using a 526-nm filter was slightly enhanced. The S/N value for an air flame increased only slightly from 78 to 90, whereas for an oxygen flame the value increased from 32 to 74. However, these conditions were found to increase cross-channel interference.

Using the gas flow parameters established for optimum response to phosphorus and sulphur, the linearity of the reponse was examined with the three model compounds. A log/log plot of peak height against the amount injected is shown in Figure 5. The response in the phosphorus channel was obtained with an air flame. Both DEPP and DEPPT show straight lines over three decades of concentration, the slope of the lines being 1.04 and 1.09 respectively, indicating a linear relationship between response and the amount injected. The calculated minimum amounts were 2.3×10^{-13} g phosphorus/sec for the phosphate and 1.6×10^{-13} g phosphorus/sec for the corresponding phosphorothioate at twice noise level and a retention time of 3 min.

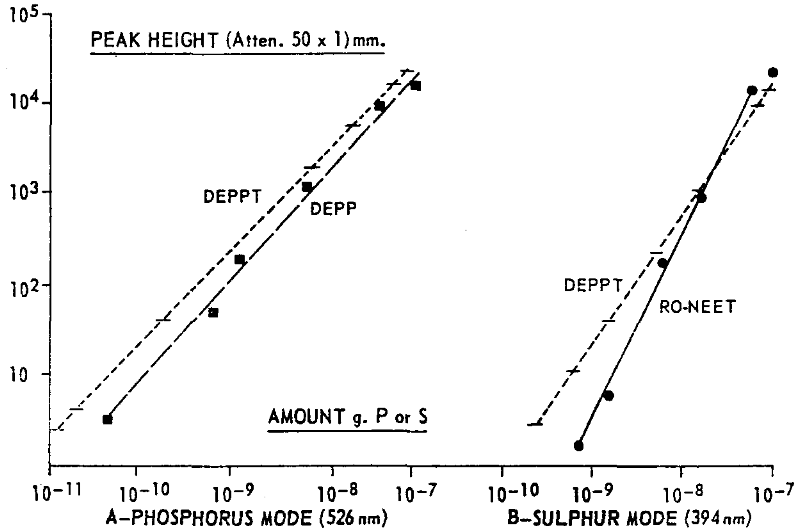


FIGURE 5 Response of DEPP, DEPPT and Ro-neet in the phosphorus and sulphur modes.

It is well known that the response of sulphur compounds varies as the square of the amount injected. This is also seen to be the case for Ro-neet with an oxygen flame, the slope of the line for the response/amount injected plot (Figure 5B) is 2.1. The response for Ro-neet is linear over two decades of concentration. The calculated minimum detectable amount, again at twice the noise level and with a retention time of 3 min, is 5×10^{-11} g sulphur/sec. The response of the DEPPT in the sulphur mode can be drawn as a straight line with a slope of 1.5, but it really a curve, which comprises the sum of the sulphur and phosphorus response resulting from cross-channel interference. It is best expressed as a quadratic relationship between the response and the amount injected. Similar results have been reported by Brody and Chaney,[4] Bowman and Beroza,[6] and Shiller and Campbell.[10]

The phenomenon of cross-channel interference with the SPED was examined using Ro-neet and DEPP; the results are shown in Figure 6. In the phosphorus mode (526 nm) the phosphate gave a straight line with a slope of 1.09, whereas the slope for Ro-neet was 2.03. For small amounts of compound, i.e. $<10^{-9}$ g phosphorus, there will be no interference from sulphur compounds in the phosphorus mode. Some interference may be expected at larger concentration due to the nature of the response shown by sulphur.

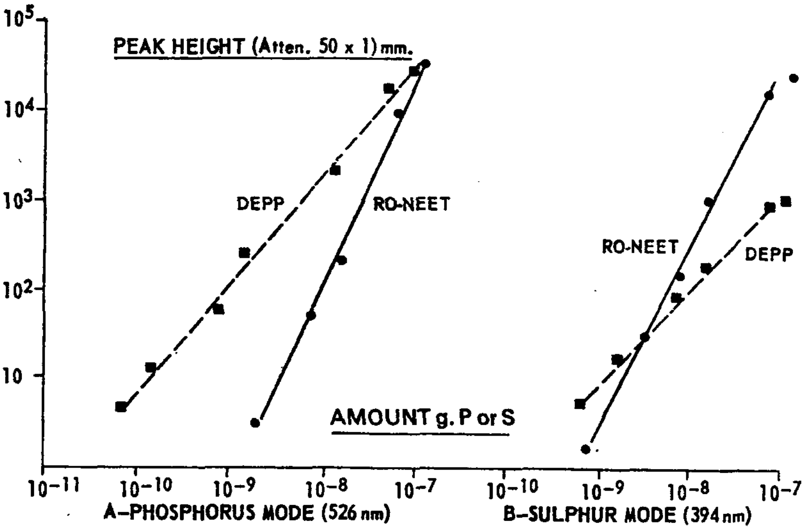


FIGURE 6 Cross-channel interference in the phosphorus and sulphur modes for DEPP and Ro-neet.

In the sulphur mode (394 nm), the phosphate gives a line with a slope of 1.0 which intersects the line for Ro-neet at approx. 10^{-9} g. Thus, with an oxygen flame, the response of a phosphorothioate below 10^{-9} g would tend towards linearity, due to its dependence on phosphorus, whereas for larger amounts, the reponse will approach a square relationship, due to its dependence on sulphur.

The nature of the flame was found to influence the cross-over point. The response in the sulphur mode with an air flame is seen in Figure 7. The effect is to reduce the amount of cross-channel interference from phosphorus. Thus, the contribution of the linear phosphorus term in the quadratic equation for the response will be less and the expression should approach more to that of a square relationship. With an air flame, small amounts of interference from phosphorus will occur in the sulphur channel below 10^{-9} g phosphorus, but as the amount injected gets larger the interference decreases. Therefore, although an oxygen flame results in a better response for sulphur compounds, an air flame is preferred for phosphorothioates because the cross-channel interference is minimised.

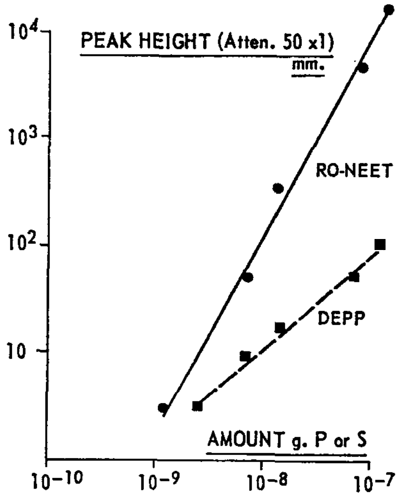
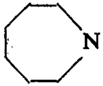
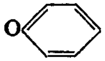
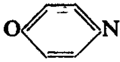


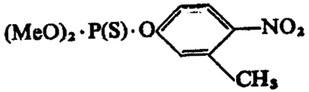
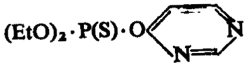
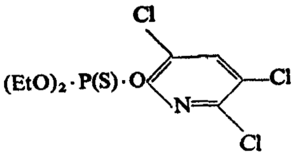
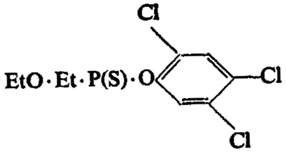
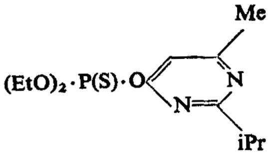
FIGURE 7 Cross-channel interference in the sulphur mode with DEPP and Ro-neet for an air flame.

A study was made of the responses of 31 sulphur-containing compounds obtained with the SPED and compared with those obtained using the CCD in the pyrolytic mode.[11] The compounds included thiocarbamates, triazines, phosphorothioates and phosphorodithioates. The results are given in Table I, expressed as counts/picomole. For the SPED, they are surprisingly constant. The overall average is 15.44 ± 10, or, excluding the unaccountably high values for triethyl phosphorothioate and Zytron, the average is 14.48 ± 5. It is interesting to note that the response for Ro-neet is only 9.58. In the last column are the results for the CCD, these are not corrected for the presence of other hetero atoms. Work with the CCD[11] indicated that sulphur itself

TABLE I

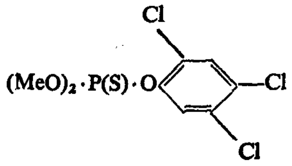
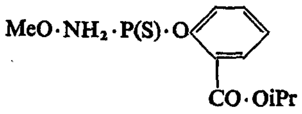
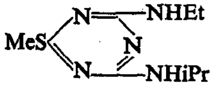
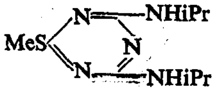
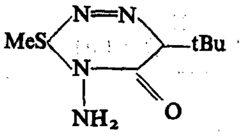
Response of the SPED in the sulphur mode and the CCD in the pyrolytic mode to some pesticides and herbicides containing one sulphur atom

	Compound	Col. temp. (°C)	Rt (min)	Response (counts/picomole)	Precision (%)	CCD response[a,b] (counts/picomole)
Tillam	$Bu \cdot Et \cdot N \cdot C(O) \cdot SPr$	136	3.7	12.26	3.32	24.32
Sutan	$(Pr_2) \cdot N \cdot C(O) \cdot SPr$	136	2.8	14.88	4.30	26.30
Eptam	$(Pr)_2 \cdot N \cdot C(O) \cdot SEt$	136	2.2	18.22	4.48	26.13
Molinate	 $N \cdot C(O) \cdot SEt$	145	4.7	13.04	4.12	21.0
Ro-neet	$Cyclohexyl \cdot Et \cdot N \cdot C(O) \cdot SEt$	145	6.25	9.58	7.57	43.88
Diallate	$(iPr)_2 \cdot N \cdot C(O) \cdot SCH_2 \cdot CCl{:}CHCl$	175	3.1	11.76	4.57	119.41
Triallate	$(iPr)_2 \cdot N \cdot C(O) \cdot SCH_2 \cdot CCl{:}CCl_2$	175	4.9	15.20	2.08	150.44
	$(EtO)_3 \cdot P(S)$	110	2.4	25.70	2.64	54.91
	$(EtO)_2 \cdot P(S) \cdot O$ 	175	2.2	14.68	2.30	46.60
Parathion	$(EtO)_2 \cdot P(S) \cdot O$  NO_2	200	3.7	16.02	2.23	49.20

Fenithrothion		200	3.5	17.04	4.06	49.05
Zinophos		175	2.9	18.62	2.97	64.32
Dursban		200	3.4	17.08	4.10	199.20
Trichlornat		200	3.6	19.63	1.19	150.81
Diazinon		175	5.15	10.58	6.65	54.43

Continued

TABLE I—*continued*

Compound		Col. temp. (°C)	Rt (min)	Response (counts/picomole)	Precision (%)	CCD response[a,b] (counts/picomole)
Ronnel		200	2.6	15.46	4.24	168.70
Bay 93820		210	3.3	10.18	4.61	25.33
Ametryne		200	2.8	14.52	2.42	84.01
Prometryne		200	2.6	14.10	4.77	96.34
Sencor		200	3.0	10.92	3.62	74.21
				15.44±10	4.01	

[a] Compiled from ref. 11.

[b] Values are not corrected for the presence of nitrogen or chlorine.

gives an average value of 51.07 counts/picomole. The presence of chlorine has an additive effect and nitrogen has a subtractive effect, depending on its state of oxidation. Comparison of the values for DEPPT with the two detectors indicates the CCD to be three times more sensitive.

In Table II the response of some phosphorodithioates in the sulphur mode are given. The average value per S atom is 15.57 ± 5, which agrees quite well with the value obtained from compounds having only one S atom, as shown in Table I. Mizany[9] reported that the response of sulphur compounds in the flame photometric detector was dependent on the state of oxidation of the S atom. Although no sulphoxides or sulphones were included in this study, apart from Supracide and its oxygen analog, the response obtained appears to be independent of structural effects. Both Supracide and its analog gave a response equivalent to one sulphur atom less than they contain. The sulphur atom in the thiodiazolidyl ring apparently does not give the S_2 species on combustion in a reducing flame; however, it is detected on pyrolysis using the CCD. In agreement with the previous results the sensitivity of the two detectors differs by a factor of three in favour of the CCD. The precision of the determinations was better for the CCD, mean rel. S.D. values of 2.1 and 1.96 being obtained for compounds in Tables I and II, respectively. This would be expected since the response of the CCD is linear, whereas that of the SPED varies as the square of the amount injected.

After the SPED had been in operation for over 6 months, the response was found to have decreased. The calculated detectable amount for diazinon in the phosphorus mode changed from 2.0×10^{-13} to 1.94×10^{-12} g phosphorus/sec. The trouble was located in the fibre optic bundle, which had become brownish in colour. This occurred while operating the detector block at 180°, which is slightly above the temperature suggested by the manufacturer. Apparently the epoxy resin bonding the optical bundle had decomposed at the higher temperature and affected the light-transmitting properties. The manufacturers now provide a new type of fibre optic bundle which is claimed to be more heat-stable. Two thin quartz windows have been installed to isolate the ends of the fibre optics from the hot reactant gases in the chamber.

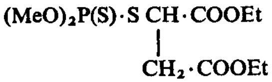
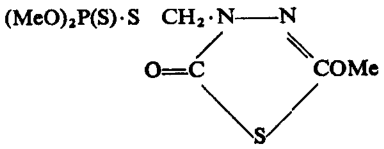
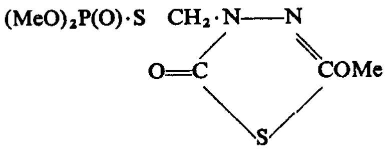
In summary, sulphur compounds exhibit a square relationship between response and the amount injected, whereas for phosphorus it is linear. The use of an oxygen flame is preferred for sulphur with low O/H values, (0.20–0.25), whereas for compounds containing phosphorus alone and phosphorus and sulphur together, an air flame is better, with an O/H ratio of 0.1–0.15. The air flame reduces the amount of cross-channel interference in the sulphur channel found with phosphorothioates.

For the routine analysis of sulphur compounds, the advantages of the ease of operation and the specificity for sulphur shown by the flame photo-

TABLE II

Response of the SPED in the sulphur mode and the CCD in the pyrolytic mode to some pesticides containing two or more sulphur atoms

	Compound	Col. temp. (°C)	Rt (min)	SPED response (counts/picomole)		Precision (%)	CCD response[a] (counts/picomole)
	$(EtO)_2P(S)SEt$	136	2.75	31.18	(15.59)	4.49	45.10
	$(EtO)_2P(S)S$ 	175	5.0	26.42	(13.21)	3.98	56.85
Dyfonate	$(EtO)\cdot Et\cdot P(S)S$ 	175	5.3	28.04	(14.02)	5.23	55.51
Thimet	$(EtO)_2P(S)S\cdot CH_2SEt$	175	3.4	30.1	(10.00)	3.61	49.13
Disyston	$(EtO)_2P(S)S\cdot CH_2SEt$	175	5.7	60.06	(20.00)	4.16	57.50
Ethion	$(EtO)_2P(S)S\cdot CH_2\cdot SP(S)\cdot(EtO)_2$	230	3.4	58.22	(14.55)	2.63	45.35
Dimethoate	$(MeO)_2P(S)S\ CH_2\cdot C(O)\cdot NHCH_3$	200	1.9	39.32	(19.66)	3.02	54.00[b]

Malathion	 $(MeO)_2P(S)\cdot S\,CH(CH_2\cdot COOEt)\cdot COOEt$	220	4.5	33.18	(16.59)	2.77	47.05
Supracide		211	4.85	31.85	(15.92)[c]	3.22	45.00[b]
Supracide oxon		211	4.18	15.63	(15.63)[c]	2.02	—
					15.57±5	3.6	49.8±7

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[a] Compiled from ref. 11.

[b] Corrected for nitrogen.

[c] Corrected for one less sulphur atom.

metric detector are offset by its non-linear response and slightly lower sensitivity as compared to the CCD. However, the CCD is not specific for sulphur; introduction of silver scrubbers as prescribed by the manufacturer[12] has been found to give irreproducible results.[13]

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