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DETERMINATION OF SULPHUR- AND CHLORINE-CONTAINING PESTICIDES WITH AN ELECTROLYTIC CONDUCTIVITY DETECTOR

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SUMMARY

The responses of a number of sulphur-containing compounds, some of which also contained chlorine and nitrogen, were investigated using both the pyrolytic and oxidative modes of operation of the Coulson electrolytic conductivity detector. The effects of variation in furnace temperature and oxygen flow were studied. Half-scale responses for thirty-six sulphur compounds obtained in the pyrolytic mode at 850°, were in the 6–100 ng range which compared favourably with flame photometric detection in the sulphur mode. Also in the pyrolytic mode, a similar range of responses was obtained from a study of thirteen organochlorine insecticides. Responses were found to be linear in the range 2 to 1000 ng of sulphur with as low as 0.5 ng of sulphur and/or chlorine being detected. In the pyrolytic mode nitrogen-containing compounds produced interference. The use of silver scrubbers for chloride removal in the oxidative mode although imparting selectivity also resulted in decreased sulphur response and lack of reproducibility.

INTRODUCTION

There are currently available the flame photometric (FPD), alkali flame (AFD), microcoulometric (MCD) and Coulson electrolytic conductivity (CCD) detectors which are used in gas chromatography (GC) to give a selective response to sulphur-containing compounds. The history, operation and applications of the more popular FPD have been reviewed recently[1]. The molecular emission due to sulphur species is measured at 394 nm by use of an interference filter. Although the FPD response

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depends upon the degree of oxidation of the sulphur atom[2] the differences are not too large and minimum detectable levels in the range 40–200 pg of sulphur have been reported[1,3]. However, the FPD suffers from a slight disadvantage in that the response varies with the square of the concentration[1]. When an AFD is used, DRESSLER AND JANÁK[4] observed that sulphur compounds produced inverted GC peaks with, for example, a level of 1 μg of thiophene producing an approximate half-scale recorder deflection ($1/2$ f.s.d.). The magnitude of this negative response was found proportional to the amount of sulphur present in the organic molecule. AUE et al.[5] recently verified this phenomenon using thioanisole and a number of aliphatic sulphides.

In contrast to these two detectors which employ a flame, the MCD and CCD both utilize a combustion furnace to convert the GC column effluents to species that are either capable of being titrated or can produce a change in the conductivity of "deionized" water, respectively. The MCD can operate in the reductive mode, H_2S being produced and titrated with Ag^+, or the oxidative mode where SO_2 is monitored by titration with iodine[6,7]. MARSH[7] obtained approximately $1/3$ f.s.d. with 64 ng of sulphur using the oxidative pyrolysis mode of the MCD. The CCD, on the other hand, has been used only in the oxidative mode for sulphur since the ionization constant of H_2S in water is low[8,9]. O'DONNELL[3] indicated that the CCD will detect in the region of 1.0 ng of sulphur. As part of a continuing evaluation study of the CCD detector[10,11] the determination of a number of sulphur- and chlorinecontaining compounds and pesticides was investigated using both oxidative and pyrolytic modes of the CCD.

EXPERIMENTAL

Compounds

Samples of insecticides, herbicides and carbamates were all of analytical grade. Phosphorothioates were prepared by reaction of diethyl phosphorothiochloridate with the appropriate alcohols in the presence of base (NaH or pyridine). The products were characterized by NMR and GC. After purification, all had a purity of $> 99\%$ by microanalytical and GC analysis.

GC parameters

A Microtek MT 220 chromatograph fitted with a Coulson electrolytic conductivity detector Model C321 and a 3 ft. × 6 mm O.D. glass column containing 100–120 mesh Gas-Chrom Q coated with 3% OV-17 were used. The column was conditioned at 250° for 1 h with gas flow, then at 340° for 4 h without gas flow and finally at 250° overnight with gas flow. Temperatures: column inlet, 225°; furnace, 400–1060° and column, 120°–225° as indicated. Flow parameters: column, 60 ml/min helium; oxygen, 0–160 ml/min (as indicated for pyrolytic and oxidative modes); and sweep, 60 ml/min helium. Standard pesticide solutions were prepared in redistilled hexane or benzene at an initial concentration of 10 mg/100 ml (100 ng/μl) and serially diluted. In all analyses solvents were vented and injection volumes in the 2–8 μl range were normally used. The peak areas were measured by an Infotronics Model CRS 208 digital integrator and expressed in counts.

RESULTS AND DISCUSSION

Initial experiments were carried out to determine the temperature and oxygen flow parameters required to give maximum response to sulphur- and chlorine-containing compounds. For these studies a standard solution containing three sulphur compounds (diethyl S-phenyl phosphorodithioate, parathion and prometryne) and three organochlorine insecticides (α-BHC, aldrin and heptachlor) was used.

At zero oxygen flow (pyrolytic mode) an increased response for all six standards accompanied an increase in the furnace pyrolytic temperature in the range 400–1060° (Fig. 1). Below 700° a rapid decrease in response was observed for prometryne. For the remaining five standards the responses decreased linearly from 1000° to 550°, then rapidly fell away. To study the effect on response of increasing oxygen flow through the combustion tube, two temperatures were selected from Fig. 1. One in the middle of the linear portion, *i.e.* 850° and one near the upper limit,
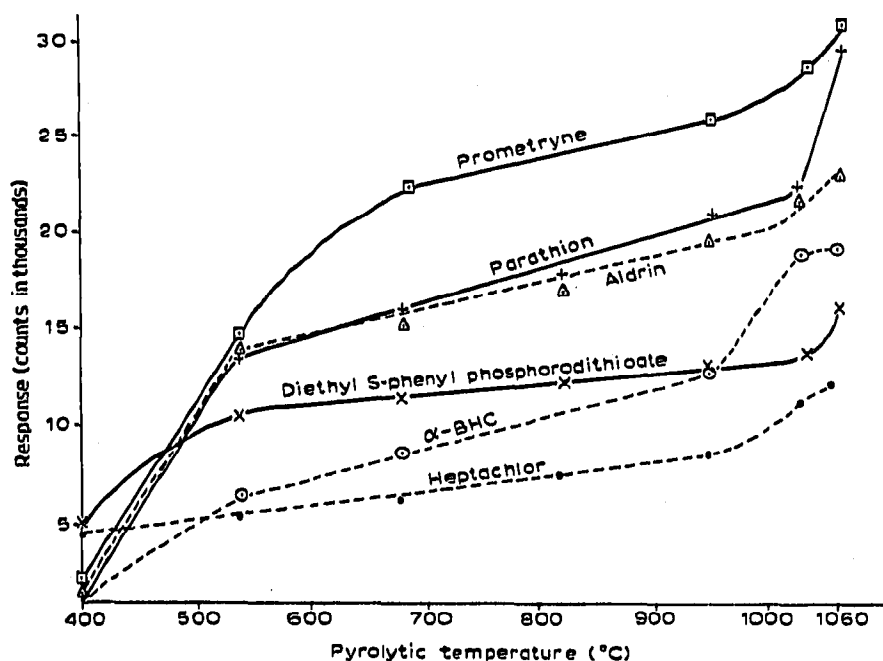

Fig. 1. Effect of furnace temperature on the responses of three sulphur- and three chlorine-containing compounds. Standard solution: α-BHC, 5 ng/μl; diethyl S-phenyl phosphorodithioate, 10 ng/μl; heptachlor, 5 ng/μl; aldrin, 10 ng/μl; prometryne, 20 ng/μl; parathion, 44.8 ng/μl.

namely 1030°. The oxygen was increased from 0 to 160 ml/min. At 1030°, the sulphur response approached that obtained in the pyrolytic mode when 20–30 ml/min oxygen was used. At 850°, oxygen flow-rates in the range 20–40 ml/min were generally required for maximum response (Fig. 2). At both furnace temperatures the response profilse obtained appear dependent upon the structures of the individual compounds, *cf.* prometryne and parathion. No ready explanation of the maxima at 80 ml/min is
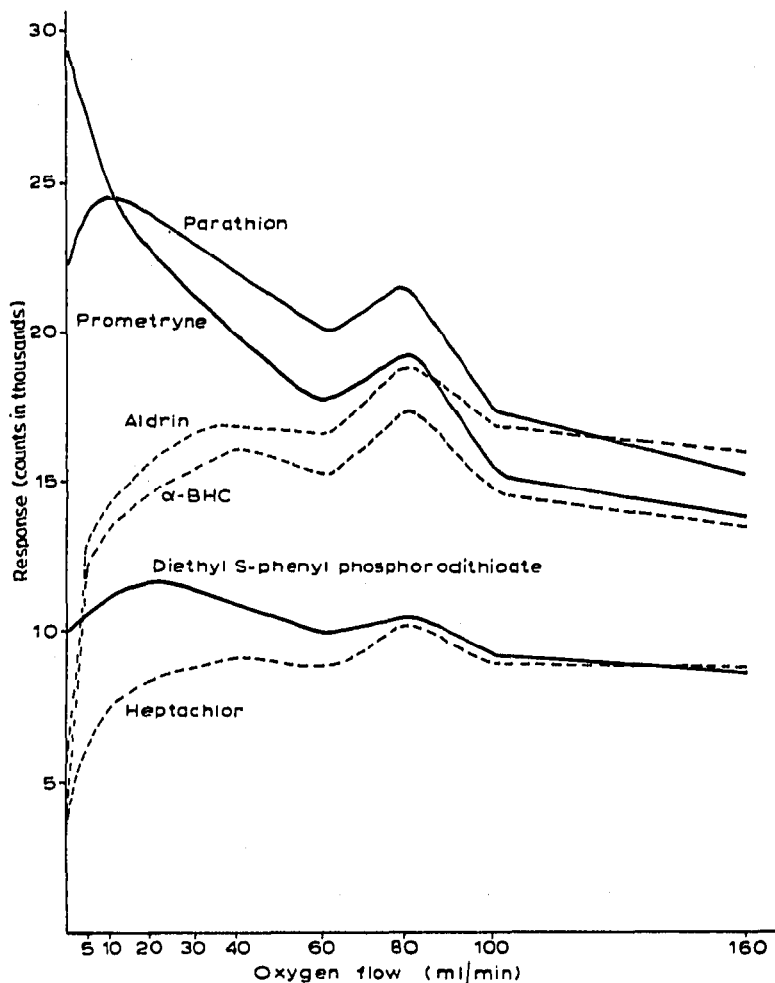
Fig. 2. Variation in CCD response with increase in oxygen flow at a furnace temperature of 850°.

available even though this phenomenon was recorded on three different occasions at 850° and at 1030°. At 1030° the 80 ml/min maxima were much less pronounced for parathion and prometryne and absent in the case of aldrin, α-BHC, diethyl S-phenyl phosphorodithioate and heptachlor.
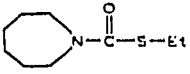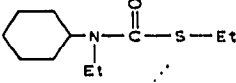
The oxygen flow/response profiles were also found to vary with repeated use of the detector. For example, after a few months of continuous operation, the 850° profiles exhibited slight minima with 5–10 ml/min oxygen. Although a number of reasons can be postulated for this observation, it is most probably due to depletion in the capacity of the ion-exchange resin which normally maintains the water at a pH of 6.7 for sulphur determinations. The increase in response of the organochlorine compounds can be attributed to increased HCl formation due to lack of competition between carbon and chlorine for available hydrogen as is the case under pyrolytic conditions. Therefore, under pyrolytic conditions any elemental chlorine produced will, on dissolution, result in formation of the weaker oxychloro acids. The formation

of HCl under oxidative conditions is due to the fact that the oxidation potential of chlorine is greater than that of oxygen[12].

Tables I–III show the retention time and approximate 1/2 f.s.d. of the thirty-six sulphur-containing compounds investigated. Where possible, parathion was used as reference standard. All these results were obtained using the CCD in the pyrolytic mode at 850°. A temperature of 850° was chosen since at higher temperatures a higher sensitivity was accompanied by the continued breakdown of the quartz pyrolysis tube which manifests itself in shorter tube life together with more frequent contamination of the "deionized" water. As there was good correlation between response in the pyrolytic mode and the best oxidative mode for sulphur-containing compounds (Fig. 2) the results in Tables I–III can also be taken as approximate 1/2 f.s.d. for the oxidative mode.

TABLE I

RELATIVE RETENTION TIME AND DETECTOR RESPONSE OF SOME SULFUR-CONTAINING PESTICIDES AT 150° AND 120°

Compound	Structure	120°		150°	
		½ f.s.d. (ng)	Rt (sec)	½ f.s.d. (ng)	Rt (sec)
Triethyl phosphorothioate	$\overset{S}{\overset{\|}{(EtO)_2-P-OEt}}$	15	62	—	—
Temik sulphone	$Me \cdot SO_2 \cdot C \cdot Me_2 \cdot CH = N \cdot O \cdot \overset{O}{\overset{\|}{C}} \cdot NHMe$	46	104	15	45
Eptam	$(n\text{-}Pr)_2-N-\overset{O}{\overset{\|}{C}}-S-Et$	45	155	15	55
Diethyl S-ethyl phosphorodithioate	$(EtO)_2-\overset{S}{\overset{\|}{P}}-S-Et$	20	184	8	62
Sutan	$(i\text{-}Bu)_2-N-\overset{O}{\overset{\|}{C}}-S-Et$	55	196	18	64
Tillam	$n\text{-}Bu-N-\overset{O}{\overset{\|}{C}}-S-n\text{-}Pr \atop \underset{Et}{\|}$	75	274	25	84
Molinate		130	542	40	155
Diethyl phenyl phosphorothioate		140	755	45	189
Ro-neet		135	792	40	204

Most of the thiocarbamate herbicides (*e.g.* Eptam) had to be chromatographed at 120° or 150°. At 120° a total analysis time of 15 min was required for the nine compounds listed in Table I. Since the amounts required for 1/2 f.s.d. are dependent upon retention time it was observed that a 30° increase in the column temperature resulted in a three-fold increase in sensitivity (Table I). With the OV-17 column, Temik sulphone could be analysed at 120° while the less polar parent compound, Temik, required a column temperature of only 50°. Under these conditions, 50 ng of Temik were required for 1/2 f.s.d. at a retention time of 3.8 min.

TABLE II

RELATIVE RETENTION TIME AND DETECTOR RESPONSE OF SOME SULPHUR-CONTAINING PESTICIDES AT 185°

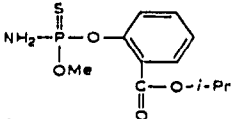| Compound	Structure	$\frac{1}{2}$ f.s.d. (ng)	Rt^a
Diethyl phenyl phosphorothioate	$(EtO)_2-\overset{\overset{S}{\|}}{P}-O-C_6H_5$	15	0.19
Zinophos	$(EtO)_2-\overset{\overset{S}{\|}}{P}-O$—(pyridyl)	23	0.24
Diallate	$(i\text{-Pr})_2-N-\overset{\overset{O}{\|}}{C}-S-CH_2-\overset{\overset{Cl}{\|}}{C}=\overset{\overset{Cl}{\|}}{CH}$	10	0.26
Thimet	$(EtO)_2-\overset{\overset{S}{\|}}{P}-S-CH_2-S-Et$	6	0.29
Diazinon	$(EtO)_2-\overset{\overset{S}{\|}}{P}-O$—(pyrimidinyl, Me, i-Pr)	20	0.40
Triallate	$(i\text{-Pr})_2-N-\overset{\overset{O}{\|}}{C}-S-CH_2-\overset{\overset{Cl}{\|}}{C}=\overset{\overset{Cl}{\|}}{C}-Cl$	6	0.405
Diethyl S-phenyl phosphorodithioate	$(EtO)_2-\overset{\overset{S}{\|}}{P}-S-C_6H_5$	12	0.405
Dyfonate	$EtO-\overset{\overset{\overset{S}{\|}}{P}}{\underset{Et}{}}-S-C_6H_5$	11	0.42
Disyston	$(EtO)_2-\overset{\overset{S}{\|}}{P}-S-(CH_2)_2-S-Et$	9	0.44
Dimethoate	$(MeO)_2-\overset{\overset{S}{\|}}{P}-S-CH_2-CO-NH-CH_3$	60	0.54
Ronnel	$(MeO)_2-\overset{\overset{S}{\|}}{P}-O-C_6H_2Cl_3$	25	0.67
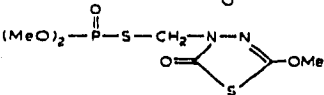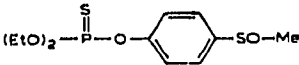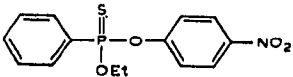
TABLE II *(continued)*

Compound	Structure	$\frac{1}{2}$ *f.s.d.* (ng)	Rp^a
Prometryne	MeS–[triazine, NH-*i*-Pr, NH-*i*-Pr]	40	0.74
Ametryne	MeS–[triazine, NH-Et, NH-*i*-Pr]	30	0.77
Zytron	*i*-Pr–NH–P(=S)(OMe)–O–[2,4-Cl₂-C₆H₃]	27	0.79
Sencor	MeS–[triazinone ring, N=N, *t*-Bu, C=O, NH₂]	55	0.80
Trichloronat	(EtO)₂–P(=S)–O–[3,5,6-Cl₃-pyridine]	24	0.84
Dursban	EtO–P(=S)(Et)–O–[2,4,5-Cl₃-C₆H₂]	20	0.90
Malathion	(MeO)₂–P(=S)–S–CHCO₂Et / CH₂CO₂Et	40	0.98
Accothion	(MeO)₂–P(=S)–O–[4-NO₂-3-CH₃-C₆H₃]	62	0.99
Parathion	(EtO)₂–P(=S)–O–[4-NO₂-C₆H₄]	75	1.00
Supracide	(MeO)₂–P(=S)–S–CH₂–N–N / thiadiazolone ring, O=, OMe	62	2.00
Ethion	(EtO)₂–P(=S)–S–CH₂–S–P(=S)–(OEt)₂	68	3.2

[a] Parathion retention time, 5.0 min.

TABLE III

RELATIVE RETENTION TIME AND DETECTOR RESPONSE AT 225°

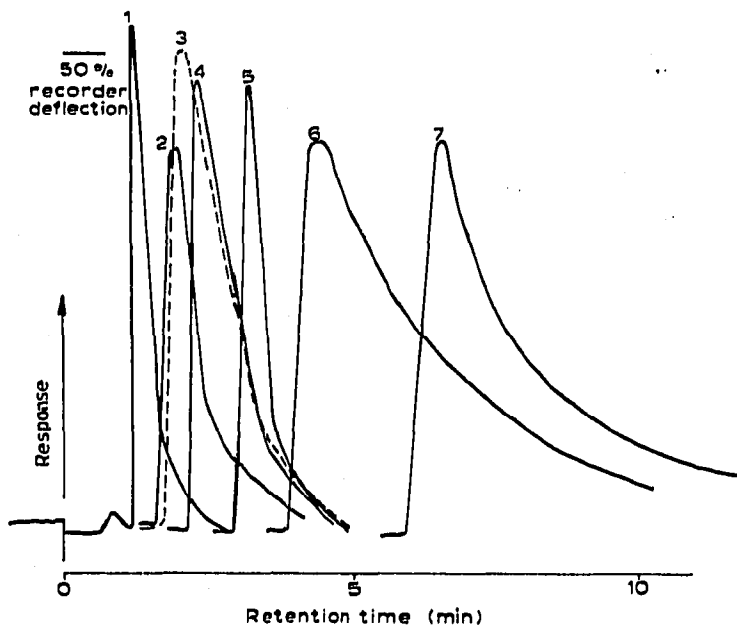| Compound	Structure	$\frac{1}{2}$ f.s.d. (ng)	Rp [a]
Parathion	[b]	63	1.00
BAY 93820	$NH_2-\overset{\overset{S}{\|}}{\underset{\underset{OMe}{\|}}{P}}-O-$ (phenyl) $-\overset{\overset{\|}{O}}{C}-O-i-Pr$	145	1.20
Supracide metabolite	$(MeO)_2-\overset{\overset{O}{\|}}{P}-S-CH_2-N-N$ ... OMe	200	1.65
Supracide	[b]	60	1.85
Ethion	[b]	40	2.5
Dasanit	$(EtO)_2-\overset{\overset{S}{\|}}{P}-O-$ (phenyl) $-SO-Me$	450	3.2
EPN	(phenyl)$-\overset{\overset{S}{\|}}{\underset{\underset{OEt}{\|}}{P}}-O-$ (phenyl) $-NO_2$	550	4.9

[a] Parathion retention time, 1.34 min.
[b] Structures are given in Table II.

Fig. 3. Composite chromatogram of some sulphur-containing pesticides at 225°. 1 = 63 ng of parathion; 2 = 135 ng of BAY 93820; 3 = 200 ng of Supracide metabolite; 4 = 60 ng of Supracide; 5 = 40 ng of ethion; 6 = 400 ng of Dasanit; 7 = 500 ng of EPN.

The other thiocarbamates, $i.e.$ diallate and triallate, together with the bulk of the sulphur compounds were analysed at 185° (Table II). The remaining pesticides, which all exhibited R_p values (retention time relative to parathion) greater than 1.00, were run at 225° (Table III). Dasanit and EPN had unusually high 1/2 f.s.d. values due to the extensive tailing exhibited on the OV-17 column (Fig. 3). From Tables I–III it can be seen that the 1/2 f.s.d. figures obtained in the sulphur pyrolytic mode are in general comparable to those previously obtained in the nitrogen mode[10]. For example, for parathion, which contains one nitrogen atom and one sulphur atom, on OV-17, approximately 100 ng was required for 1/2 f.s.d. in the nitrogen mode (Rt 5.6 min) and 75 ng in the sulphur mode (Rt 5.0 min). Comparable figures for diazinon, which contains two nitrogen atoms and one sulphur atom, are 15 ng and 20 ng, respectively. Also for comparison with the present results ten compounds from Table II were arbitrarily chosen and their 1/2 f.s.d. responses recorded at column temperatures of 175° and 200° employing flame photometric detection (Table IV).

TABLE IV

FLAME PHOTOMETRIC DETECTOR[a] RESPONSE OF TEN SULPHUR-CONTAINING COMPOUNDS

Compound	½ f.s.d. (ng)		
	$175°$	$196°$[b]	$200°$
Zinophos	46	31	—
Diallate	50	38	—
Diazinon	108	62	—
Diethyl S-phenyl phosphorodithioate	42	30	—
Disyston	30	19	—
Dimethoate	—	36	19
Prometryne	—	66	41
Dursban	—	105	64
Malathion	—	61	35
Parathion	—	93	61

[a] Pye 104 gas chromatograph equipped with a Bendix SPED. Flow-rates (ml/min): N_2 (3% OV-17 column), 40; H_2, 85; O_2, 5; air, 60.
[b] At this temperature identical retention times were obtained to those at 185° and CCD detection (Table II).

Since the peak height of a particular compound is dependent on its retention time, a direct comparison of FPD and CCD results could only be accomplished by using identical retention times. This was achieved with an FPD column temperature of 196° and the FPD results in Table IV compared with those in Table II. Therefore, under these conditions the CCD sulphur responses compare very favourably.

While operation of the FPD in the sulphur mode and the CCD in the nitrogen mode are both highly specific, the pyrolytic and oxidative modes of the CCD permit the determination of halogens as well as sulphur. The additive effects of both sulphur and chlorine are observed in the much lower 1/2 f.s.d. values of those compounds which contain both elements, $e.g.$ triallate and trichloronat. Table V shows the results obtained for thirteen organochlorine insecticides. These range from a low 1/2 f.s.d. value of 6 ng for α-BHC to a high value of 70 ng for p,p'-DDT. Very good resolution was achieved with the OV-17 column at 185° (Fig. 4) which resulted in a

TABLE V

RELATIVE RETENTION TIME AND DETECTOR RESPONSE OF SOME ORGANOCHLORINE PESTICIDES AT 185°

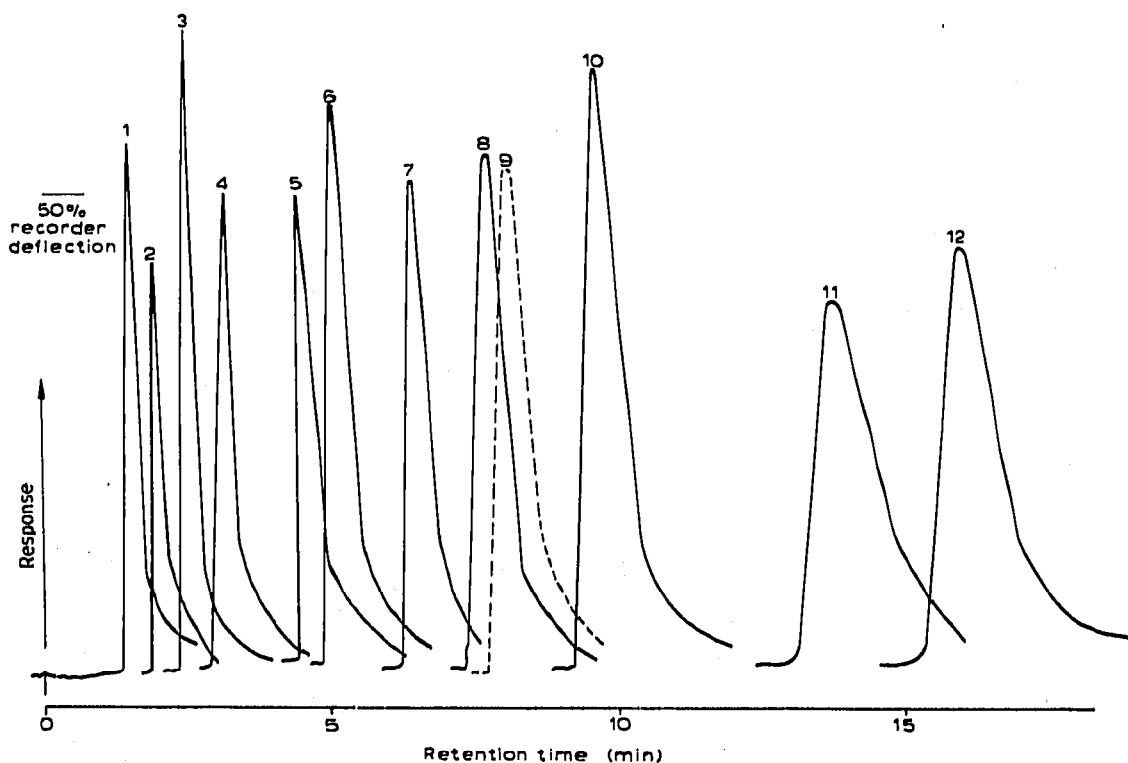| Compound	$\frac{1}{2}$ f.s.d. (ng)	R_a[a]
a-BHC	6	0.48
γ-BHC (Lindane)	18	0.63
β-BHC	25	0.80
Heptachlor	15	0.80
Aldrin	10	1.00
Oxychlordane (1,2-dichlorochlordene epoxide)	15	1.43
Heptachlor epoxide	20	1.55
o,p'-DDE	30	2.08
Dieldrin	20	2.48
p,p'-DDE	40	2.60
Endrin	40	3.13
p,p'-DDD	70	4.21
p,p'-DDT	70	5.28

[a] Aldrin retention time, 3.15 min.

Fig. 4. Composite chromatogram of some organochlorine pesticides at 185°. 1 = 6 ng of a-BHC; 2 = 15 ng of lindane; 3 = 18 ng of heptachlor; 4 = 10 ng of aldrin; 5 = 15 ng oxychlordane; 6 = 20 ng of heptachlor epoxide; 7 = 25 ng of o,p'-DDE; 8 = 20 ng of Dieldrin; 9 = 40 ng of p,p'-DDE; 10 = 45 ng of endrin; 11 = 60 ng of p,p'-DDD; 12 = 65 ng of p,p'-DDT.

total analysis time of less than 20 min. Therefore, in the pyrolytic mode of operation as low as 0.5 ng of sulphur and/or chlorine can be detected.

COULSON made the oxidative mode selective to sulphur by using silver deposited on quartz wool[9] or silver wire[13] as a scrubber for chloride removal. In the present study silver metallic gauze was found to adsorb all effluents obtained in the pyrolytic mode. No response was obtained with parathion even when ten times the 1/2 f.s.d. amount was used. This indicated that a sulphur species other than SO_2 was being monitored in the pyrolytic mode as SO_2 is only partially retained by the silver scrubber.

The use of silver wire (0.01 in. diameter and 4 cm long) strands resulted in very high conductivity of the "deionized" water. This was due to the volatilisation of the silver wire where it extended into the high temperature region of the combustion tube. When the length was shortened to 1.0–1.5 cm the cell conductivity and noise level returned to an acceptable level. Using this scrubber and increasing the oxygen flow, selectivity to sulphur-containing compounds was obtained.but at the expense of sensitivity and reproducibility. Under the best conditions of oxygen flow the response obtained for the three sulphur standards was only one tenth that obtained with optimum oxygen and no silver scrubber. For example, at 80 ml/min oxygen and with a silver wire scrubber the response from each of the three sulphur standards increased with each injection and decreased to its original value overnight. However, removal of the silver scrubber did not give complete return to pyrolytic conditions since small silver deposits on the cooler visible portion of the quartz tube still gave decreased organochlorine responses. Similar results were experienced with silver wool. These results are not unexpected in view of the widespread use of metallic silver adsorbents (wire, electrolytic, gauze, wool, chips, etc.) in organic microelemental analysis for the simultaneous gravimetric determination of sulphur and halogens[14–16].

Using triethyl phosphorothioate at 120° and diethyl S-phenyl phosphorodithioate at 185°, peak height and area responses were found to be linear in the range 2–1000 ng of sulphur. However, interference was obtained from nitrogen-containing compounds in the pyrolytic mode, e.g. 30 ng of prometone giving 1/2 f.s.d. Using atratone and prometone, the effect of increasing oxygen was investigated to determine whether reduction or elimination of this form of interference would occur on conversion of the nitrogen to NO_x. With oxygen flow-rates of 30, 60 and 100 ml/min, the 1/2 f.s.d. values for these two compounds were all in the range 30–35 ng indicating that the use of oxygen does not effect the selectivity of these nitrogen compounds.

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