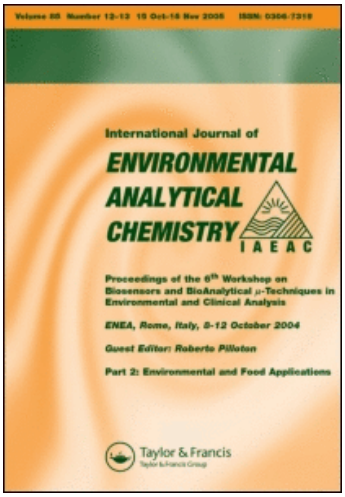

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Some Response Characteristics of the Electrolytic Conductivity Detector in the Pyrolytic Mode to Chlorine; Nitrogen and Sulphur Compounds

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Some Response Characteristics of the Electrolytic Conductivity Detector in the Pyrolytic Mode to Chlorine, Nitrogen and Sulphur Compounds†

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KEY WORDS: detector response, electrolytic conductivity, pyrolytic mode, insecticides, herbicides.

Under pyrolytic conditions at 850°C the electrolytic conductivity (CCD) response of 32 sulphur-containing compounds was examined. For organophosphorus compounds, with the sulphur in a —P=S or —S—P=S configuration, the CCD response is directly proportional to the amount of sulphur present. The effect of other hetero atoms on the sulphur response was also studied. The response contribution of nitrogen depends upon its oxidation state and/or structural configuration within the molecule. In the oxidized form, $-NO_2$ in parathion for example, no contribution is observed whereas the thiocarbamate nitrogen reduces the S response. The additive effect of chlorine was found to be proportional to the number of chlorine atoms present. Variable chlorine responses were obtained from nine organochlorine insecticides, with indications that for these compounds the Cl response is structure-dependent. Due to a high variation in precision, quantitative organochlorine residue analyses using the CCD in the pyrolytic mode is not recommended.

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‡Chemistry and Biology Research Institute Contribution No. 734.

The Coulson electrolytic conductivity detector (CCD) can be made to give a selective response to compounds which contain nitrogen, halogen or sulphur.[1-5] Selectivity is achieved by using different reactant gases (O_2 of H_2), catalytic conditions and chemical abstractors (scrubbers).[6] Nitrogen- and halogen-containing compounds are determined under reductive conditions using hydrogen as the gaseous reactant. Catalytic reduction at 850°C using nickel wire converts organonitrogen to ammonia which is selectively detected after passage through a basic scrubber to remove acid products. In the absence of the catalyst no ammonia is formed, therefore with an empty pyrolysis tube selective response to halides is obtained. Sulphur and also halogen can be determined in the oxidative mode using oxygen as the combustion gas. Selectivity[6] but not reproducibility[7] can be achieved by the use of silver wire as absorbent to remove halides.

In a recent study[7] on the determination of sulphur in the oxidative and pyrolytic modes at 850°C, pyrolytic responses due to nitrogen-containing compounds were observed, as well as the expected halogen responses. Also, the selective CCD detection of amines and N-nitrosoamines has been accomplished by the thermal degradation of these compounds, at 400–600°C, to ammonia.[5] In this temperature range other types of organonitrogen compounds produce little or no ammonia. As little had been published on the use of the CCD in the pyrolytic mode, this study was undertaken to assess its applicability to the determination of pesticidal compounds containing nitrogen, sulphur, chlorine or various combinations of all three elements.

EXPERIMENTAL

Compounds

Samples of insecticides, herbicides, carbamates and phosphorothioates were all of analytical grade. All synthesised products, described elsewhere,[7] had a purity of >99% by micro-analytical and GC analysis.

Apparatus

A Microtek MT 220 fitted with a Coulson electrolytic conductivity detector model C321 was used with a pyrolyser temperature of 850°C and column and sweep flow rates of 60 ml/min helium, respectively. A Pye 104 equipped with a Bendix flame photometric sulphur phosphorus emission detector was employed with a column flow rate of 40 ml/min nitrogen and detector flows of 85, 5 and 60 ml/min for hydrogen, oxygen and air, respectively. A

3 ft × 6 mm o.d. glass column containing 100/120 mesh Gas Chrom Q coated with 3% OV-17 and conditioned as previously described[7] was used with both detectors.

Method

Five replicate injections were carried out for each compound. The peak areas were measured by an Infotronics model CRS 208 digital integrator and expressed in counts.

RESULTS AND DISCUSSION

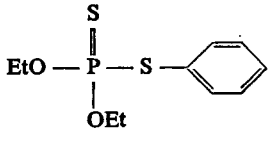
Although it was shown (Table I) that the peak area is independent of retention time and peak shape, all present work was performed by altering column temperature to produce retention times in the range 3–6 min. This assured

TABLE I

Effect of retention time (Rt) on area for diethyl S-phenyl phosphorodithioate[a]

Temperature (°C)	Rt (min)	Amount injected (ng)	Area	Area/ng[b]
150	7.96	48.76	18751	384
170	3.4	48.20	18133	376
185	2.01	49.8	19111	383

[a]



[b] Mean 381.0 and S.D. 4.4, which gives a precision of 1.1% for similar injections at different temperatures.

that each compound had a similar residence time within the gas chromatographic system and would also overcome any initial variation (in 0–2 min region) in baseline due to solvent peaks or vent valve manipulations.

TABLE II

CCD response to compounds containing sulphur

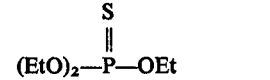
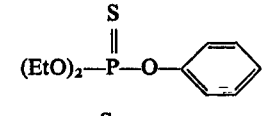
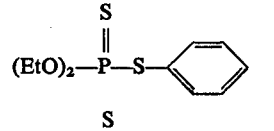
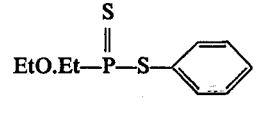
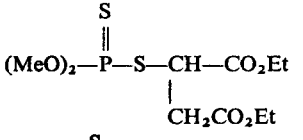
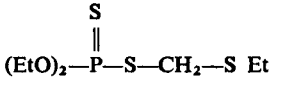
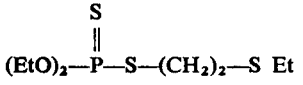
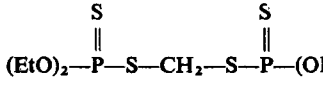
Compound	Structure	Col. temp. (°C)	Rt (min)	Response[a] (counts/ picomole)	Precision (%)
Triethyl phosphorothioate		75	7.35	54.9	2.17
Diethyl phenyl phosphorothioate		150	3.17	46.6	0.2
Diethyl S-ethyl phosphorodithioate		120	3.17	90.2	1.1
Diethyl S-phenyl phosphorodithioate		160	5.08	113.7	0.8
Dyfonate		160	5.87	111.0	1.8

TABLE II—*Continued*

Malathion		185	4.97	94.1	3.1
Thimet		160	3.9	147.4	2.0
Disyston		160	5.8	172.5	2.8
Ethion		225	3.2	181.4	1.1

[a] Response = peak area/mole ≃ (counts/mole).10^{12} = counts/picomole.

TABLE III

CCD response to compounds containing one sulphur and one nitrogen

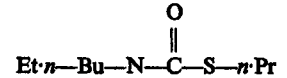
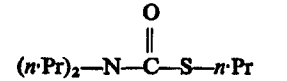
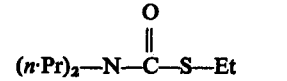
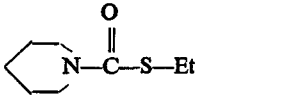
Compound	Structure	Col. temp. (°C)	Rt (min)	Response (counts/ picomole)	Precision (%)
Tillam		120	4.67	24.32	1.2
Sutan		120	3.32	26.29	1.7
Eptam		120	2.6	26.13	1.4
Molinate		135	4.6	21.0	1.3

TABLE III—*Continued*

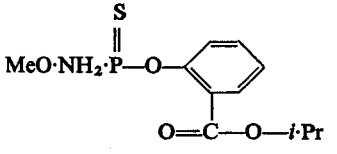
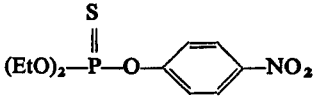
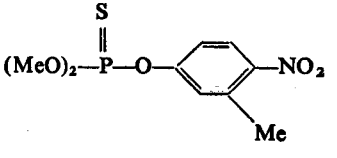
BAY 93820		185	3.87	25.3	4.3
Ro-neet		135	6.31	43.88	0.8
Parathion		185	5.06	49.2	1.1
Accothion		185	4.96	49.0	1.7

TABLE IV

CCD response to some miscellaneous nitrogen- and sulphur-containing pesticides

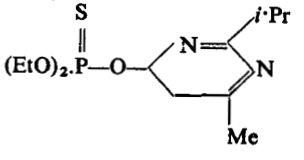
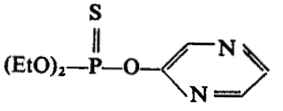
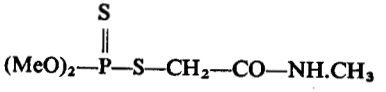
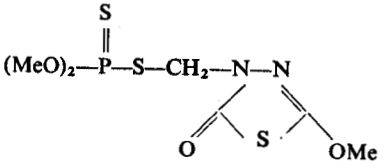
Compound	Structure	Col. temp. (°C)	Rt (min)	Response (counts/ picomole) Obs.	Response (counts/ picomole) Calc.	Precision (%)
Diazinon		160	5.7	54.4	51	0.5
Zinophos		160	3.07	64.3	51	0.7
Dimethoate		185	2.9	82.7	75	1.8
Supracide		200	5.88	90.92	75	5.1

TABLE IV—*Continued*

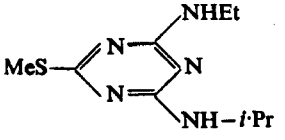
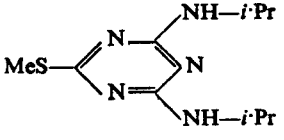
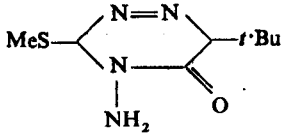
Temik	$MeS.C.Me_2.CH = N—O—\overset{\overset{O}{\|}}{C}.NHMe$	50	3.82	15.64	—	4.0
Temik sulphone	$MeSO_2C.Me_2.CH = N—O—\overset{\overset{O}{\|}}{C}.NHMe$	100	4.09	31.1	25	2.5
Ametryne		185	4.55	84.0	75	1.8
Prometryne		185	4.3	96.3	75	0.5
Sencor		185	4.1	74.2	50	3.9

TABLE V

CCD response to some pesticides containing chlorine and sulphur

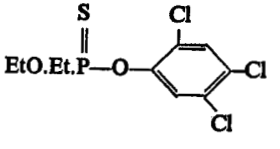
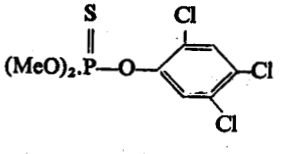
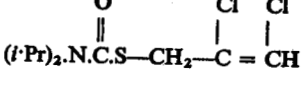
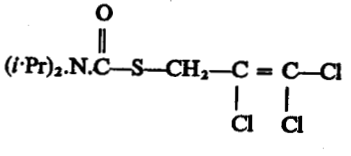
Compound	Structure	Col. temp. (°C)	Rt (min)	Response (counts/ picomole) Obs.	Response (counts/ picomole) Calc.	Precision (%)
Trichloronat		185	4.4	158.8	165	2.1
Ronnel		185	3.74	168.9	165	1.0
Diallate		160	3.72	119.4	102	1.8
Triallate		160	6.08	150.4	140	1.9

TABLE V—*Continued*

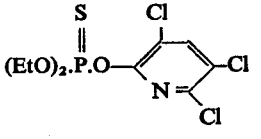
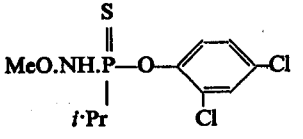
Dursban		185	4.65	199.2	165	0.9
Zytron		185	3.9	155.8	127	4.8

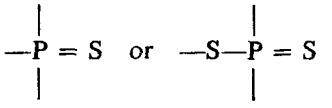
TABLE VI

CCD response to some organochlorine pesticides at 185°C

Compound	No. of Cl		Rt (min)	Response (counts)		Precision (%)
	Actual	Obs.[a]		/picomole	/picomole Ce	
1. α-BHC	6	12	1.5	808.15	134.7	3.7
2. γ-BHC	6	3	2.07	207.7	34.6	7.0
3. Aldrin	6	6	3.15	434.7	72.4	6.0
4. Endrin	6	6	9.8	387.75	63.5	8.1
5. Dieldrin	6	6	7.7	411.87	63.5	10.0
6. Heptachlor	7	4	2.55	261.45	39.04	8.2
7. Heptachlor epoxide	7	4	4.9	260.70	37.24	7.2
8. Oxychlordane	8	5	4.45	384.04	40.47	8.8
9. p,p′-DDE	4	4	8.35	245.93	61.48	23.6

[a] Based on 65 counts/picomole Cl obtained from compounds 3, 4, 5 and 9.

Nine organophosphorus compounds were studied initially. These compounds contained from one to four sulphur atoms which were either in the



molecular configuration. These results showed that the CCD response is directly proportional to the amount of sulphur present in the molecule. The precision (rel. S.D.) of the replicate injection ranged from a low of 0.2% for diethyl phenyl phosphorothioate to a high of 3.1% for malathion. An average value of 51.07 (counts/picomole) was obtained for those compounds which contained only one sulphur. This increased to 102.2 for two sulphur, 159.9 for three and 181.4 for ethion, the only four-sulphur-containing compound studied. From the first eight compounds listed in Table II an average of 51.4 counts/picomole *S* was obtained.

The effect of nitrogen on the sulphur response is shown in Table III. In this series, each compound contains one nitrogen and one sulphur atom. Five of these compounds gave a result in the region of half the expected sulphur response of 51.4 and three gave results close to this figure. Examination of the various structures reveals that in parathion and accothion the nitrogen is already in the oxidized form, $—NO_2$, and consequently not detected, whereas in BAY 93820 and the thiocarbamates (except Ro-neet) the nitrogen is most likely converted to ammonia or amines which then interact with the acidic sulphur moiety. By difference, the effect of nitrogen was found to contribute a negative response in the region of 25 counts/picomole.

Table IV shows results obtained from a number of insecticides in which both the number of sulphur and nitrogen atoms in the molecule vary. Using the above values obtained for sulphur and nitrogen a theoretical picomole response was calculated for each compound and compared with the observed result. In some instances reasonable correlation was obtained, e.g. dimethoate, supracide, diazinon, zinophos, ametryne and prometryne. Temik, temik sulphone and sencor appear to be anomalous but this may only be a matter of interpretation. Temik sulphone, which has the sulphur atom in the oxidized form, $—SO_2—$, gives an observed value of 31.1, roughly half the expected sulphur figure. If a negative contribution is made by only one nitrogen atom, namely the —NHMe— grouping, a theoretical response of 26 would then be expected. Since the second nitrogen atom is in the form —HC=N— it seems likely that this is pyrolysed to HCN which would add to the expected response. Similarly, only one nitrogen atom in temik would detract from the expected response. Since the sulphur atom in temik is not attached to phos-

phorus but to a methyl group, the observed response is most probably a summation of the HCN and methyl mercaptan contributions.

As a final extension to this study, six pesticides which contained sulphur and chlorine were investigated (Table V). From trichloronat and ronnel, each containing one sulphur and three chlorines, an additive chlorine contribution of approx. 40 counts/picomole was obtained. When this figure was applied to the remaining four compounds containing sulphur, nitrogen and chlorine atoms, reasonable correlation was obtained.

To verify the additive effect of chlorine by direct measurement rather than by difference, nine organochlorine insecticides were studied (Table VI) and various values were obtained depending upon the structure of the compound. An average of 65 counts/picomole Cl was observed with the dimethanonapthalenes (aldrin, etc.) and 38 counts/picomole Cl with the methanoindenes (heptachlor, etc.). This latter figure is very close to that of 40 obtained from the chlorine-containing herbicides. No explanation can be given at present for the large response variation between γ- and α-BHC, or for the variation of the organochlorines in general. The figure for p,p'-DDE can be discarded since a large difference in response was obtained between identical injections (rel. S.D. 23.6%), due primarily to a tailing peak which was typical of the other DDT-type homologues.

A similar study to that already described was accomplished using the Bendix flame photometric detector (FPD) in the sulphur mode.[8] The results indicated the CCD in the pyrolytic mode to be more sensitive than the FPD to sulphur-containing compounds. Also, the precision between repeated injections obtained with the CCD was slightly better than the FPD with reference to thiocarbamate, triazine and organophosphorus compounds. However, due to a high variation in precision the quantitative analysis of organochlorine pesticide residues using the CCD in the pyrolytic mode is not recommended.

Acknowledgment

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