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PRELIMINARY EVALUATION OF HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH PHOTOCONDUCTIVITY DETECTION FOR THE DETERMINATION OF SELECTED PESTICIDES AS POTENTIAL FOOD CONTAMINANTS

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SUMMARY

The applicability of the Tracor Model 965 photoconductivity detector to the determination of a variety of pesticide chemicals, particularly polar and/or thermally labile compounds which are troublesome in gas chromatographic analysis, has been investigated. The effects of various operating parameters (*e.g.*, mobile phase composition, flow-rate and irradiation wavelength) on signal-to-noise output for selected compounds have been evaluated. A comparison of photoconductivity responses with those obtained from a UV detector connected in tandem was made for selected reference standards and food sample extracts. The photoconductivity detector was found to be suitable for the determination of pesticide residues at sub-parts-per-million levels. The linearity and reproducibility of response are adequate for practical quantitative applications.

INTRODUCTION

Owing to the variety of sensitive and selective detectors developed and refined for use with gas–liquid chromatography (GLC), this technique has been the predominant analytical tool for pesticide residue analysis over the past 20–25 years. However, many compounds of current interest are not well suited for GLC analysis owing to factors such as thermal degradation, involatility or undesirable adsorptive effects. High-performance liquid chromatography (HPLC) provides a suitable alternative for the analysis of many such compounds, but its usefulness for the determination of residues at the parts-per-million level or less in foods has been limited by the lack of detectors with adequate sensitivity and/or selectivity.

Hoodless *et al.*[1] investigated the usefulness of reversed-phase liquid chromatography with UV detection for the determination of a variety of pesticides. They concluded that although most of the compounds studied could be separated and detected, the sensitivities at wavelengths above 210 nm were generally insufficient for desired detection. They also surmised that at lower wavelengths, selectivity would

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probably be a problem owing to UV absorption by non-pesticide components in the samples.

Moye[2] presented an overview of HPLC procedures for the analysis of pesticide residues, which included the use of electrochemical detection and post-column chemical reactions with fluorescence and UV detection as means of increasing sensitivity and selectivity.

Popovich *et al.*[3] reported the development of the Tracor Model 965 photoconductivity detector for HPLC, which was alleged to provide a sensitive response for halogenated and many nitrogen- and sulfur-containing compounds. The operation of the detector is based on the postcolumn formation of ionic species via irradiation of analytes with UV light followed by detection of the ionic products in a conductivity cell.

Büttler and Hörmann[4] utilized this detector for the determination of captan, folpet and captafol residues in fruit and grain samples. They initially investigated GLC with electron-capture detection for this purpose but discarded this approach because of the variable responses caused by adsorption and/or decomposition in the GLC process. They also discarded HPLC with UV detection owing to insufficient sensitivity for captan and captafol.

Locke *et al.*[5] also described a liquid-phase photoionization detector for HPLC in which a microwave-excited continuum xenon source was used to irradiate the HPLC effluent.

The purpose of this investigation was two-fold: (1) to begin testing various operational parameters of the Tracor photoconductivity detector (PCD) as a first step in establishing its suitability as a reliable and useful analytical tool for use in pesticide residue laboratories and (2) to evaluate the applicability of the detector to the determination of a selected variety of pesticides which are potential food contaminants.

The compounds selected for study were chosen to represent several different classes and structural types having functional groups with apparent potential for detection with the PCD instrument. Many of these compounds have also been reported (in most instances through personal experiences and personal communications of experienced pesticide analysts) to be troublesome and not reliably determinable by GLC systems commonly empoyed with "official" pesticide residue methods[6].

A UV detector was connected in tandem to the PCD throughout the investigation. This configuration permitted a concomitant comparison of response between the two detectors to the same column effluent.

MATERIALS AND METHODS

HPLC instrumentation

The instrumental system consisted of a Perkin-Elmer Series 3B reciprocating pump, a Waters U6-K injector, a Perkin-Elmer LC-75 UV detector and a Tracor Model 965 PCD equipped with 254-nm mercury and 214-nm zinc irradiation lamps. The PCD was also equipped with a column effluent flow splitter, permitting adjustment of the rate of flow through the reference compartment (non-irradiated portion) relative to the rate of flow through the analytical compartment (UV-irradiated portion), thereby providing for the balancing of background signals. This splitter was

adjusted so that an even split of the column effluent was maintained through the analytical and reference cells; thus, only half of each analyte eluting from the column was actually irradiated and detected conductometrically.

Both detectors were connected to individual Heath–Zenith Model SR-204 recorders each set at 10 mV output and 0.2 in./min chart speed. In addition, the unattenuated 1-V output of the PCD was connected to a Hewlett-Packard Model 3380 integrator. The UV detector was connected ahead of the PCD, as the latter is molecule-destructive. The detectors were linked with a piece of 0.009- in. I.D. stainless-steel tubing cut as short as possible (about 50 cm) to minimize peak broadening.

Column and mobile phase

Several column–solvent systems were initially evaluated. The system ultimately used to develop the response data presented here consisted of a 25 cm × 4.6 mm I.D. column packed with cyano-bonded, 5-μm spherical silica (Zorbax CN; DuPont, Wilmington, DE, U.S.A.) and methanol–water (55:45) as the mobile phase sparged (deaerated) with helium.

Test solutions

The compounds selected for study were obtained from the laboratory stock of U.S. Food and Drug Administration (FDA) and U.S. Environmental Protection Agency (EPA) standard materials. Those compounds soluble in 2-propanol (Omni-Solv grade; MCB, Cincinnati, OH, U.S.A.) were dissolved in this solvent and diluted serially to appropriate concentrations. Compounds lacking good solubility in 2-propanol were dissolved in 1–2 ml of acetonitrile (UV grade; Burdick and Jackson, Muskegon, MI, U.S.A.) prior to serial dilutions with 2-propanol.

RESULTS AND DISCUSSION

Instrumental operation

The operations manual supplied by Tracor with the PCD presents a chromatogram of captan developed using a normal-phase system of isooctane–methanol–2-propanol (85:10:5) as the mobile phase with a Zorbax CN column. Although Büttler and Hörmann[4] succeeded in separating captan, folpet and captafol using this system, their separation required the use of two 25-cm columns connected in series and a column performance of *ca.* 12,000 theoretical plates (N) for each column. It was decided, as a first step in this investigation, to evaluate reversed-phase chromatography for this separation in pursuit of a more practical system.

Of the several reversed-phase columns tried, including Zorbax C_{18}, C_8 and TMS (trimethylsilyl) columns, only the Zorbax CN column provided a complete separation of captan, folpet and captafol with isocratic mobile phases consisting of either methanol or acetonitrile mixtures with water. Acetonitrile was discarded from further study, however, because an apparent incompatibility was noted when acetonitrile–water mixtures were circulated through the ion-exchange resins which were provided with the detector for the purpose of purifying the mobile phase. This was manifested by an increase in background noise from the PCD and a continuous rise in the UV detector baseline as the solvent was recycled through the resin. This observation was also reported by a fellow worker in another laboratory who found

that acetonitrile–water mixtures became virtually unusable with his PCD after several days of circulation through the resins. Methanol–water mixtures, on the other hand, appeared to produce smoother baselines with continued circulation through the resins. The usefulness of the resins for the purpose of purification depends on the quality of solvents available. The mixture of methanol (OmniSolv; MCB) and water obtained from a Milli-Q system (Millipore, Bedford, MA, U.S.A.) that was used in this investigation did not generally appear to produce significantly smoother baselines as a result of continuous resin circulation.

A chromatogram showing the separation of captan, folpet and captafol on a single, 25-cm Zorbax CN column (N = 7700 for folpet) with methanol–water (55:45) as the mobile phase is shown in Fig. 1. The resolution factors between these peaks are *ca.* 3 with capacity factors (k') of 2.8, 3.6 and 4.5, respectively. The successful application of this relatively simple system to this difficult separation prompted its selection for use in further evaluation of the PCD.

The non-aqueous "normal-phase" system used by Büttler and Hörmann was also evaluated briefly in this investigation. As expected, a separation of captan, folpet and captafol was not achieved using a single, 25-cm CN column with this mobile phase. It was found that the PCD could be operated at a sensitivity setting 10 times that used with the methanol–water mobile phase to obtain equivalent baseline noise. However, the responsiveness (signal-to-noise ratio) of the detector to captan, folpet and captafol in the normal-phase system was found to be *ca.* 5 times less than in the reversed-phase system.

In addition, a pronounced tailing effect was observed in the PCD chromatogram obtained with the normal-phase system, as is shown for folpet in Fig. 2. The explanation for this is not readily clear. However, it has been postulated that a capacitance effect may develop in the conductivity cell; the low dielectric constant and

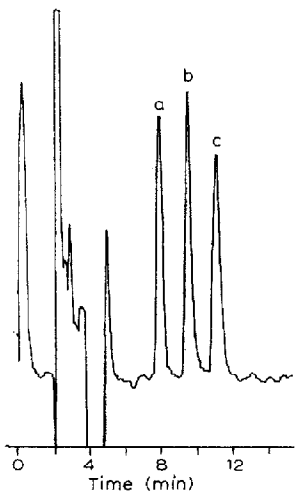


Fig. 1. PCD chromatogram of (a) 6.1 ng of captan, (b) 4.7 ng of folpet and (c) 7.8 ng of captafol in 2-propanol + 0.1% acetonitrile. Column: 25 cm × 4.6 mm I.D. Zorbax CN. Mobile phase: methanol–water (55:45) at 1 ml/min (pH 5.8). Detector conditions: range 10, attenuation × 5, 254-nm mercury irradiation lamp.

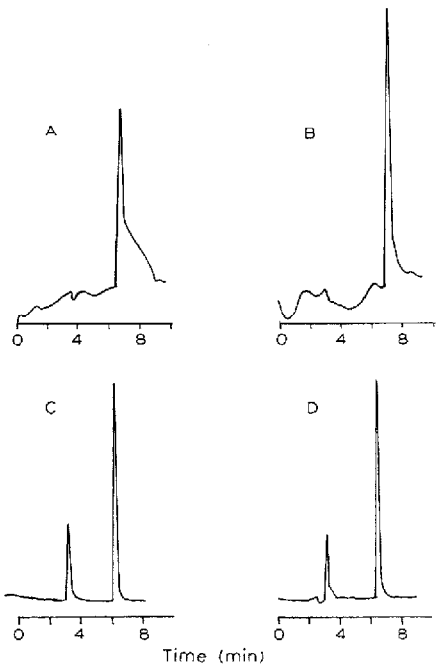


Fig. 2. Effect of addition of water to mobile phase on response of detectors to 50 ng of folpet using normal-phase HPLC system. Column, standard solvent and PCD conditions as in Fig. 1, except range I and attenuation × 5. UV detector conditions: 220 nm and 0.16 a.u.f.s. Mobile phase: isooctane–methanol–2-propanol (85:10:5). Chromatograms: A, PCD response using "dry" mobile phase (no water added); B, PCD response using "wet" mobile phase (0.15% water added); C, UV detector response using "dry" mobile phase; D, UV detector response using "wet" mobile phase.

high resistance of this solvent could restrict ion mobility and capacitance discharge, thus effecting a delayed return to baseline current. To test this theory, some water (0.15%) was added to the normal-phase solvent. After equilibrating the system with this mixture, the PCD tailing effect receded dramatically, as shown in Fig. 2. The folpet peak shape in the UV detector chromatogram obtained concomitantly was the same whether or not the water was added. Thus, it was demonstrated that the tailing peak observed in the PCD was not a manifestation of the chromatographic elution pattern; rather, it appears that this phenomenon occurred within the PCD itself and was attributable to the lack of sufficient mobile phase polarity. It could be surmised that the water content of the particular solvents selected for preparation of this normal-phase mixture is of consequence, especially when using relatively small amounts of the alcohols.

The selection of appropriate solvents for the preparation of test solutions presented some difficulty.The ideal solvent would be the HPLC mobile phase, providing the analytes were adequately soluble in it. That solvent would result in minimal solvent front response and would not contribute significantly to chromatographic band spreading. The solubilities of the compounds selected for study were generally very good in methanol. However, it was observed early on that the stability of at least some of these compounds in either methanol or aqueous methanol solutions

was very poor. Captafol, for example, displayed a significant decomposition peak within 1 h after preparation in these solvents. The captan and folpet responses also diminished relative to freshly prepared solutions after several hours in these solvents. Subsequently, acetonitrile and 2-propanol were evaluated and found to provide solutions of these compounds that remained stable for at least 1 month (these solvents must be fresh and dry). Of these two solvents, 2-propanol was preferred because it produced the smaller response in the PCD. Acetonitrile, however, is generally a better solvent for the compounds selected for study; it was therefore used sparingly to initially dissolve those compounds having insufficient solubility in 2-propanol (*e.g.*, folpet) prior to diluting further with the latter solvent (the concentration of acetonitrile in the final dilution was generally *ca.* 0.1%). As can be seen in the several chromatograms shown here, the solvent front response of both the PCD and the UV detector to these solutions was large. This required the analyte to have a retention volume of at least 5 ml to be resolved adequately from the solvent front.

The use of 2-propanol (or 2-propanol with acetonitrile added) as an analyte solvent required discretion in the selection of the injection volumes used. It was observed that injection volumes greater than about 15 μl resulted in some peak broadening and a subsequent decrease in linearity of peak height responses. Therefore, the injection volumes were limited to 10 μl or less throughout this investigation.

The PCD is necessarily designed such that its internal flow volume is considerably larger than that of UV detectors. Therefore, some decrease in effective chromatographic efficiency would be expected for the PCD. This was evaluated by comparing the theoretical plate counts for captan and folpet eluted through the UV detector *versus* the PCD. For this purpose, the PCD was connected directly to the Zorbax CN column to eliminate any plate count loss due to the UV–PCD connection. The number of theoretical plates determined through the PCD (5600) was 27% less than that through the UV detector under these conditions. Only a minor (*ca.* 5%)

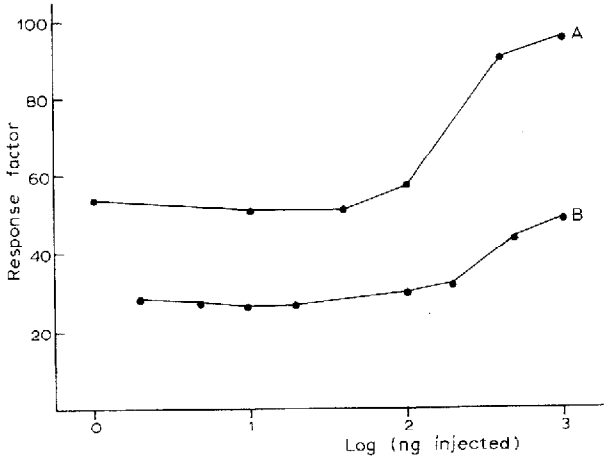


Fig. 3. Dynamic response of PCD to folpet and azinphos methyl over three orders of magnitude (*ca.* 1 to 10^3 ng injected). Response factor = response units/ng injected. Standard solvent, column, mobile phase, flow-rate and irradiation lamp as in Fig. 1. Curves: A, PCD response to folpet; B, PCD response to azinphos methyl.

loss in plate count was determined to be attributable to the UV–PCD connection tubing.

The dynamic response range for folpet and azinphos methyl in the reversed-phase system was determined on both detectors. As expected, the UV detector response was linear over the entire range tested (*ca.* 1 to 10^3 ng). The PCD response to these compounds was found to be linear from about 1 to 100 ng injected but increased sharply above this amount (Fig. 3).

The response of the PCD is a function of the amount of analyte reacted to form ionic products in the reaction coil. Therefore, the mobile phase flow-rate is a very significant factor affecting the PCD response. The UV detector response, on the other hand, is virtually unaffected by the flow-rate. The PCD responses to folpet measured at different flow-rates from 0.5 to 2.0 ml/min were found to decrease in approximately logarithmic proportion to the increase in flow-rate (Fig. 4). This observation is in agreement with the response *versus* flow-rate data presented by Popovich *et al.*[3] for chlorinated benzenes.

The PCD was also observed to be very sensitive to pressure changes. Therefore, the HPLC equipment used must be capable of producing a constant, virtually pulse-free flow. It was noted that at the relatively high sensitivity settings used in this investigation, the PCD baseline could be driven off scale by changing the flow-rate by only 0.1 ml/min. As the flow-rate was decreased, the PCD baseline noise was found to increase approximately in direct proportion. This was probably due, at least in part, to a decrease in pumping stability with decreased flow-rate and back-pressure. Subsequently, the effective response increase obtained as a result of lowering the flow-rate was reduced accordingly when measured as a function of the signal-to-noise ratio. It was concluded that a compromise must be made in selecting a flow-rate that will provide an adequate detector response with a practical chromatographic separation and elution time in accord with the analytical problem at hand. A flow-rate of 1 ml/min was used throughout this investigation.

The reproducibility of response of the PC detector was found to be more variable than that of the UV detector from day to day. This would appear to be expected as the PCD response is dependent on the several variables already discussed (*e.g.*,

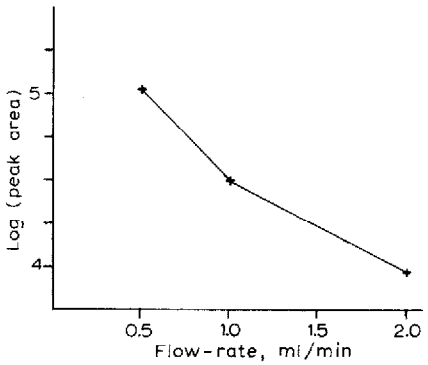


Fig. 4. Effect of mobile phase flow-rate on response (peak areas) of PCD due to difference in photoreaction time. Injection of 9.5 ng of folpet made at each flow-rate. Standard solvent, column, mobile phase and detector conditions as in Fig. 1.

mobile phase flow-rate, analytical:reference cell flow split and intensity of irradiation lamp). However, the reproducibility of response was generally found to be very acceptable (less than 1.5% relative standard deviation) over a period of several hours when monitored with repetitive injections ($n = 14$) of a folpet solution.

Chromatographic response of test compounds

The response and retention data obtained for the compounds tested are shown in Table I. Folpet was selected as a response reference standard for the purpose of testing the day-to-day responsiveness of the detectors and adjusting operational parameters when necessary; thus, a reasonable consistency of peak height response was achieved throughout the study.

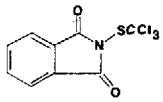
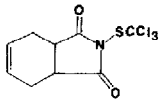
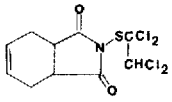
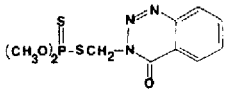
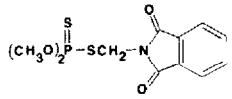
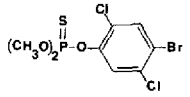
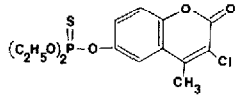
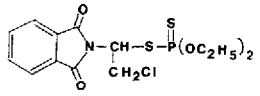
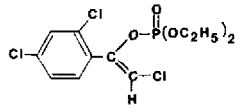
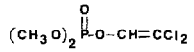
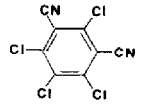
The UV detector wavelength was maintained at 220 nm, which is the approximate wavelength of maximum absorbance for folpet. All of the compounds selected for study were expected to give at least some if not a strong UV response at this wavelength. Therefore, the UV detector was used primarily as a monitor to detect the elution of compounds having relatively unknown and unpredictable responsiveness in the PCD. In addition, the UV detector response remained constant from day to day; it therefore also helped to monitor the stability of the test solutions.

For the purpose of developing relative response data, the sensitivity settings of both detectors were adjusted such that the maximum baseline noise was *ca.* 1% of full-scale deflection (f.s.d.) on the 10-mV recorders. This was achieved on the UV detector at its maximum setting of 0.01 absorbance unit full scale (a.u.f.s.) and remained constant throughout the entire study. At this setting, a peak height response of 50% f.s.d. was produced by about 10 ng of folpet. A baseline noise of *ca.* 1% from the PCD was achieved at a sensitivity setting of range 10 with an attenuation of either × 2 or × 5. As mentioned earlier, the responsiveness of the PCD was variable from day to day; it therefore required occasional attenuation changes to maintain a reasonably consistent signal-to-noise ratio. The amount of folpet producing a 50% f.s.d. response from the PCD at a baseline noise of *ca.* 1% ranged from about 5 to 10 ng during the course of this investigation.

As the signal-to-noise response of folpet was approximately the same on both detectors, it was a convenient compound to use for establishing and maintaining the operating conditions of both detectors simultaneously. It was therefore also selected as a reference compound for determining relative response factors and relative retention times for the other compounds studied. The responsiveness of the detectors was monitored by injecting a folpet solution intermittently throughout the study. For each compound tested, the approximate amount required to produce a peak height of 50% f.s.d. on each detector was determined as a means of comparing the relative responsiveness of the two detectors. In addition, the PCD peak area response of each compound was obtained on the electronic integrator connected to it. This area was divided by the amount injected in nanograms to obtain a response factor in terms of area per nanogram. As the integrator area output could not be attenuated to correct for day-to-day variations in the PCD, the response factor obtained for each compound was divided by the response factor (or average factor) calculated for one or more folpet injections made during the same period of time. These relative area responses are also reported in Table I to provide a better representation of the total PCD response to a particular compound. For example, compounds such as lepto-

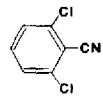
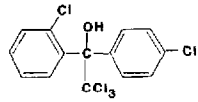
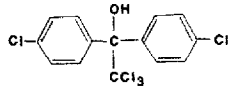
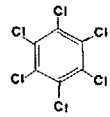
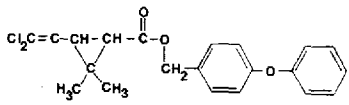
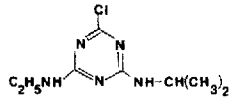
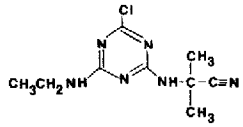
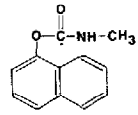
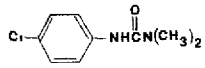
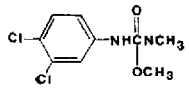
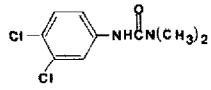
TABLE I

RESPONSE DATA FOR SELECTED PESTICIDES OBTAINED ON UV AND PHOTOCONDUCTIVITY DETECTORS CONNECTED IN TANDEM

Pesticide		*Amount equivalent to 50% f.s.d. (ng)*		*Relative PCD area response*	*Relative retention time*
		UV	*PCD*		
Folpet		10	7.5	1	1
Captan		293	8.3	0.89	0.83
Captafol		492	11	0.65	1.17
Azinphos methyl		17	23	0.32	1.05
Phosmet		10	34	0.21	1.06
Leptophos		102	19	1.54	3.70
Coumaphos		88	2858	0.005	1.64
Dialifor		28	37	0.30	2.13
Chlorfenvinphos		48	5.6	1.20	1.06
Dichlorvos		176	195	0.05	0.59
Chlorothalonil		18	3.3	2.04	1.01

(Continued on p. 236)

TABLE I *(continued)*

Pesticide		*Amount equivalent to 50% f.s.d. (ng)*		*Relative PCD area response*	*Relative retention time*
		UV	*PCD*		
Dichlobenil		45	115	0.04	0.79
o,p'-Dicofol		88	6.6	1.23	1.27
p,p'-Dicofol		152	11	1.68	2.42
Hexachlorobenzene		22	15	0.83	1.87
Permethrins:					
cis-		145	68	0.28	4.35
trans-		154	72	0.42	4.58
Atrazine		6.5	7.6	0.79	0.64
Cyanazine		7.9	8.5	0.85	0.60
Carbaryl		3.2	1829	0.003	0.69
Monuron		47	1.9	1.89	0.61
Linuron		24	3.4	1.38	0.93
Diuron		17	3.8	1.16	0.79

phos and *p,p'*-dicofol appear to be less responsive than folpet in the PCD on the basis of peak height response alone. However, these compounds have long retention times and relatively broad peaks. When measured and compared on the basis of area, they show a considerably larger total response than folpet. The nanograms equivalent to 50% f.s.d. data are useful in estimating the signal-to-noise responses of the compounds in the particular HPLC system used. The relative area responses, on the other hand, provide an indication of the relative degree to which the total amount of each analyte entering the detector is photoionized to electroconductive species. Therefore, it was concluded that relative area response data should be used to compare the PCD responses of the various compounds studied.

As suggested by the data in Table I, the responsiveness of individual compounds in the PCD is unpredictable. Although many of the halogen-, nitrogen- and sulfur-containing pesticides studied responded well, there were several notable exceptions.

The three fungicides folpet, captan and captafol, which are similar in structure (chlorinated phthalimides), were found to be fairly equivalent in PCD response. The PCD offers a significant advantage over the UV detector for captan and captafol, apparently owing to the lesser UV-absorptive conjugation in their structures.

The two non-halogenated thiophosphate insecticides azinphos methyl and phosmet also gave similar responses, apparently attributable to the common dithio group. The azine function of azinphos methyl may also contribute to its response.

Large variations in PCD response were found for the several halogenated organophosphate insecticides tested (*i.e.*, leptophos, coumaphos, dialiflor, chlorfenvinphos and dichlorvos). These variations are apparently associated with the number of electroactive substituents present and their relative positions in the molecule. Coumaphos, having only a single aromatic chlorine and a single thio bond, gave a particularly weak PCD response.

The difference in PCD response between the fungicide chlorothalonil and the structurally similar herbicide dichlobenil was much larger than expected. This is apparently due to the difference in number of reactive species.

The two isomers of the miticide dicofol were very PCD responsive, presumably owing largely to the alkyl-substituted trichloro group. In general, it appears that compounds with alkyl-substituted chlorines are more photo-reactive than those with equal numbers of aromatic-substituted chlorines (especially when only three or less chlorine atoms are present). The relatively strong PCD response to the fungicide hexachlorobenzene suggests that the photoreactivity of chlorinated aromatics increases significantly with increasing chlorine substitution. The presence of the weaker bonded bromine substituent, as seen with leptophos, might be predicted to increase photoreactivity also.

The PCD responses of the synthetic pyrethroid insecticides *cis*- and *trans*-permethrin are presumed to be due largely to the alkyl-substituted dichloro group. The relatively strong and similar PCD responses of the triazine herbicides atrazine and cyanazine are postulated to be attributable mainly to the common azine group, with a smaller contribution from the chlorine substituent.

The PCD response of the carbamate insecticide carbaryl is too small to be of any practical value for its determination with this detector. The urea carbamates monuron, linuron and diuron, on the other hand, responded very well in the PCD.

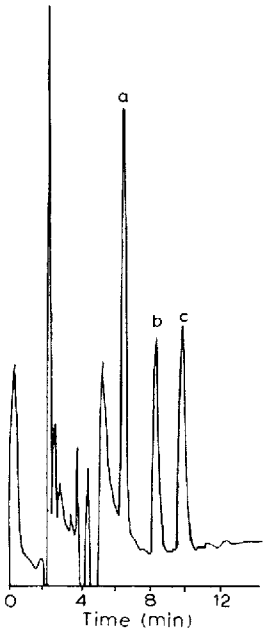


Fig. 5. PCD chromatogram of (a) 1.86 ng of monuron, (b) 1.88 ng of diuron and (c) 1.78 ng of linuron in 2-propanol. All other conditions as in Fig. 1, except attenuation × 2.

The strong responses of the latter compounds appear to be associated with the urea substitution rather than the ring chlorines, especially as the monochlorinated compound monuron gives a considerably stronger response than the dichlorinated compounds linuron and diuron. A PCD chromatogram showing the excellent separation obtained for these three pesticides is presented in Fig. 5.

Selectivity

Three ion-exchange resins are provided with the Tracor PCD. These were described by Popovich *et al.*[3] as a sulfuric acid cation-exchange resin, a quaternary amine anion-exchange resin and a 1:1 mixture of these two resins, respectively. It was stated in their paper and in the manual supplied with the instrument that the choice of different combinations of these resins could be used to control the pH of the mobile phase, thereby achieving further sensitivity and selectivity. Specifically, one resin combination (1 part of the anion exchange resin plus 1 part of the 1:1 mixture) reportedly produced a pH of approximately 8 in the mobile phase circulated through it. This system is designated the "nitrogen mode" of operation. A second resin combination (1 part of the cation-exchange resin plus 1 part of the 1:1 mixture) reportedly produced a mobile phase pH of approximately 6 and is designated the "halogen mode" of operation.

In this investigation, both of these resin combinations were prepared as recommended in the manual. Separate 1-l volumes of the methanol–water (55:45) mobile phase were circulated through the respective resins for at least 48 h. The pH of each mobile phase was then measured on a pH meter. A pH of about 5.5 was determined for the "halogen mode" solvent whereas the "nitrogen mode" solvent pH was about

5.8. Subsequent pH checks made on these solvents after continuous circulation through these resins for 1 week or more showed no change.

An additional test was carried out in which the ion-exchange resin tube supplied with the instrument was filled with fresh amine anion-exchange resin only. A 200-ml volume of Milli-Q purified water (pH≈6) was pumped through the resin and collected for pH measurement (the instrument manual specifies that the first 200 ml of mobile solvent passed through the resin should be discarded). The pH of this 200-ml volume of pre-rinse was about 9. A 500-ml volume of fresh Milli-Q water was then recirculated through the same resin for about 24 h. The pH of the latter solvent was about 6. Thus, it appears that the amine is essentially stripped from the resin in the initial rinse with an aqueous mobile phase and is therefore rendered ineffective for subsequent pH control.

Several of the compounds studied were chromatographed using both the pH 5.5 "halogen mode" mobile phase and the pH 5.8 "nitrogen mode" mobile phase. As expected, no significant differences in the responses were obtained as a result of this slight difference in pH. The response data shown in Table I were all obtained using a pH 5.8 mobile phase.

It would appear that adjustment of mobile phase pH could effect some control over the relative formation of ionic products from different compounds. The use of buffering agents should be effective for this purpose; however, as reported by Popovich *et al.*[3], the background conductivity of the detector could be expected to increase and thus reduce the sensitivity. Further investigation of this aspect of the PCD operation is needed.

To evaluate the potential enhancement of PCD selectivity through the choice of lamps, the 214-nm zinc lamp was substituted for the 254-nm mercury lamp and several compounds were selected for comparative study. The signal-to-noise ratio for folpet was found to be nearly the same using either lamp. As shown in Table II, the responses of chlorothalonil and linuron relative to folpet were found to be much less with the 214-nm lamp. The response for azinphos methyl, on the other hand, did not differ significantly. Therefore, it appears that some further selectivity for some compounds can be achieved through the use of different maximum irradiation wavelengths.

Application to sample extracts

Some limited applications of the PCD–UV tandem detection system were made

TABLE II

EFFECT OF MAXIMUM IRRADIATION WAVELENGTH ON PCD PEAK AREA RESPONSES OF SELECTED COMPOUNDS RELATIVE TO FOLPET

Compound	*Relative response*	
	254-nm mercury lamp	*214-nm zinc lamp*
Chlorothalonil	2.04	0.19
Linuron	1.38	0.21
Azinphos methyl	0.32	0.26

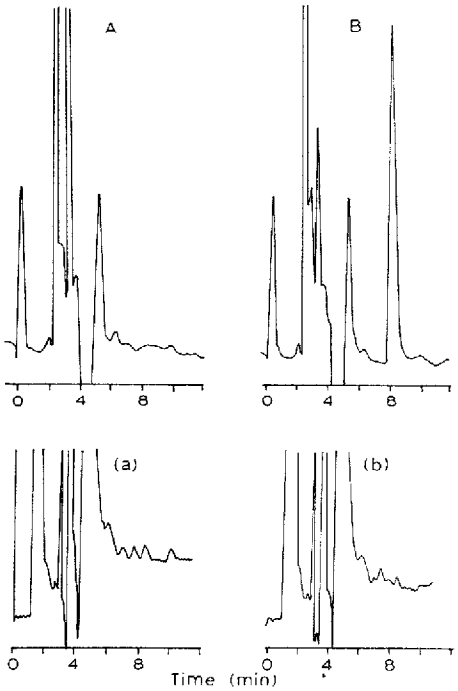


Fig. 6. Chromatograms of corn sample extracts obtained concomitantly on PCD and UV detectors. A and (a), sample extract chromatograms on PCD and UV detector, respectively; B and (b), extract of spiked (2 ppm) sample on PCD and UV detector, respectively. Injection of 10 μl of extract equivalent to 10 mg of sample was made in each instance. Chromatographic and PCD conditions as in Fig. 1, except attenuation × 10. UV detector at 220 nm and 0.01 a.u.f.s.

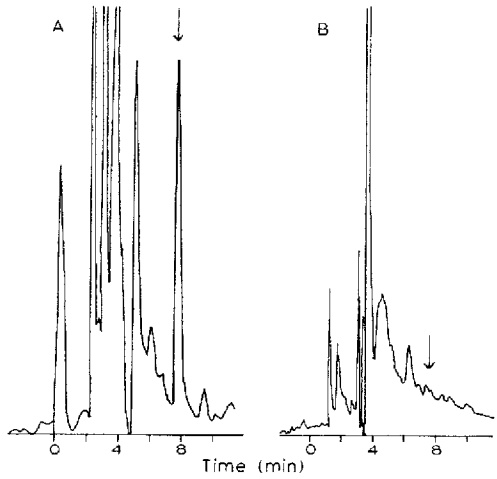


Fig. 7. Chromatograms of extract of fresh strawberry sample containing incurred residue of 0.03 ppm of captan. A, PCD chromatogram; B, UV detector chromatogram obtained concomitantly. Injection of 7 μl of extract equivalent to 486 mg of sample was made. Chromatographic and PCD conditions as in Fig. 1. UV detector conditions as in Fig. 6.

to food sample extracts. An extract of a corn sample, which was prepared by a co-worker using FDA *Pesticide Analytical Manual* methodology[7], was examined for captan after evaporation under nitrogen and dissolution in 2-propanol. UV and PCD chromatograms of the sample extract and of an extract of a spiked (2 ppm) portion of the sample are shown in Fig. 6. Whereas no captan was detected in the sample, the 2 ppm spike was easily determinable on the PCD. The UV detector showed only background responses for the same injections. This sample was found to present problems for GLC analysis owing to severe column deterioration caused by co-extracted corn oil. No detrimental effects on the HPLC system were observed as a result of these injections.

A strawberry sample extract, which was also prepared by a co-worker using another FDA *Pesticide Analytical Manual* method[8], was also examined using the UV–PCD system (after reconstitution in 2-propanol). This sample was found by the PCD to contain 0.03 ppm of an incurred captan residue, which was in agreement with a GLC–electron-capture determination performed previously. As shown in Fig. 7, the UV detector sensitivity was inadequate for this analysis also.

CONCLUSIONS

HPLC with photoconductivity detection was found to be sufficiently sensitive for many of the pesticide chemicals selected for study to permit their determination as food contaminants at sub-ppm levels. The linearity and reproducibility of response are adequate for reliable application to quantitative analysis in the pesticide residue laboratory. Provided that the solvent has adequate polarity, the PCD can be used with either normal-phase or reversed-phase HPLC systems. From the standpoint of sensitivity alone, the PCD appears to be especially advantageous over UV detectors for compounds having photoionizable functional groups but which lack strongly absorbing UV chromophores (*e.g.*, captan and captafol). From the standpoint of selectivity, the PCD appears to be advantageous over UV detection for the determination of photoionizable compounds in the presence of other analytes or of sample co-extractives which lack photoionizable functional groups, but which have medium to strong UV-absorbing chromophores. Further selectivity for individual compounds or classes of compounds is apparently possible with the use of different irradiation wavelengths. Greater selectivity through pH adjustment may be possible but further study of this aspect as a practical operational matter is needed. The PCD is inherently more difficult to operate than are UV detectors; the photoconductivity detection system is more complex and its response is more dependent on the consistency of operating conditions. Therefore, more frequent calibrations of the PCD are required for quantitative analysis.

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