

Multiresidue Pesticide Determinations with a Simple Photoconductivity HPLC Detector

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A simple postcolumn photoconductivity detector (PCD) was constructed and shown to be applicable to several classes of pesticides, especially a broad range of herbicides. In some cases, solvent mixture and/or photolysis coil material affected detector response. Measurement of ionic photoproducts by ion chromatography demonstrated the source of the detector response. This detector was easily constructed, and estimated detection limits for several pesticides were similar to those of a commercial PCD. Application of the simple PCD to multiresidue pesticide in soils and feeds was demonstrated.

Determination of pesticides by high-performance liquid chromatography (HPLC) has lagged behind gas chromatography (GC) largely because the lack of sensitive and selective detectors. A photoconductivity detector (PCD) that uses postcolumn photolysis of analytes followed by conductometric detection of ionic products has been shown to have the selectivity and sensitivity necessary for pesticide residue analyses (Popovich et al., 1979; Walters, 1983; Zahnow, 1985). Pesticides containing halogen, nitroso, and sulfonamide groups have shown the best sensitivity.

Most of the aforementioned studies have been performed with a commercial PCD (Popovich et al., 1979). This study employs a commercial ion chromatograph (IC) with a laboratory-constructed postcolumn photoreactor (Miles and Moye, 1988). This photoreactor has been used for several types of postcolumn derivatives (Krull, 1986) and recently has become commercially available (Beam Boost, ICT Corp., Scotch Plains, NJ). Increased use and availability of LC conductivity detectors make construction of this PCD simple. The unique selectivity of this detector makes it an attractive tool for the pesticide residue chemist. Some applicable pesticides, detection limits, ion product determinations, and multiresidue analyses are demonstrated.

EXPERIMENTAL SECTION

The liquid chromatograph (LC) was composed of metal-free parts: a Dionex gradient pump module (GPM), a Dionex eluant degas module (EDM II), a Dionex 2000-psi injector (20 and 50 μ L), a Dionex conductivity detector module (CDM II), and a PE Nelson Analytical integrator. For separations a Dionex Ion Pac NS-1 column (4 \times 150 mm; 5- μ m polymer) or Perkin-Elmer C₁₈ column (4.6 \times 30 mm; 3- μ m silica) was used with acetonitrile/water mobile phases delivered at 0.6 or 1.0 mL/min, respectively. Flow injection analysis (FIA; no column) and separations were performed without cation suppression. For anion chromatography a Dionex Ion Pac AS4A column (4 \times 250 mm) with a NG-1 guard column (4 \times 50 mm) was used with a 1.8 mM sodium carbonate/1.7 mM sodium bicarbonate buffer (2.0 mL/min) and a Dionex AMMS suppressor with 0.025 N H₂SO₄ as regenerant. The photoreactor (placed between the injector/column and conductivity detector) consisted of a 9 \times 180 mm UV lamp (2 W; 254 nm; Model 80-1178-01; BHK, Inc.) inserted inside a cylindrical 5.8 m \times 0.8 mm i.d. \times 1.6 mm o.d. (ca. 2.9 mL) TFE or FEP Teflon coil woven as described by Engelhardt and Neue (1982). Further description of the housing and cool-

Table I. Response of Selected Pesticides to Postcolumn Photoconductivity Detector

pesticide	response, ^a area/ng
methylthio aliphatics	
oxamyl	20
methomyl	25
aldicarb	45
aldicarb sulfone	4
captan	73
methylthio aromatic/triazines	
ametryn	45
fenamiphos	76
metribuzin	19
carbamothioates	
ethylene thiourea	4
thiram	74
halogenated triazine/uracils/aromatics	
atrazine	30
bromacil	37
picloram	33
chloramben	41
phosphorothioates	
diazinon	43
famphur	60
fenthion	68
EPN	45
phosphorodithioates	
malathion	73
bensulide	66
ethion	63
carbophenothion	64
dimethoate	71
dioxathion	59

^a Response = [(peak area with lamp on) - (peak area with lamp off)] $\times 10^{-4}$ / amount in nanograms. Analyzed by FIA and 1:1 water/acetonitrile and TFE photolysis coil. Values are average of duplicates with a relative standard deviation of <10%.

ing apparatus is described elsewhere (Miles and Moye, 1988). Caution: Protect eyes from harmful UV irradiation.

Water was obtained from a Milli-Q (Millipore) water system. All mobile phases were degassed with helium purging. Selected pesticides were dissolved in acetonitrile (1 mg/mL). Soil (Wahiawa silty clay; Tropeptic Eustrux, clayey, kaolinic, isohyperthermic) was fortified with selected pesticides and extracted with acetonitrile by shaking at room temperature. After centrifugation the extract was filtered, evaporated at dryness, and reconstituted in water. Alfalfa feed extracted by the modified Storherr method (Carson, 1981) followed by Florisil cleanup (AOAC, 1984) was fortified with selected pesticides, dried, and reconstituted in acetonitrile.

Table II. Comparison of PCD Response Ratios of Selected Pesticides Using Different Solvents and Different Photolysis Coil Material

pesticide	1:1 CH ₃ CN/H ₂ O TFE/FEP	1:1 CH ₃ OH/H ₂ O TFE/FEP	TFE CH ₃ CN/CH ₃ OH	FEP CH ₃ CN/CH ₃ OH
alachlor	1.02	1.05	1.67	1.76
aldicarb	1.35	1.08	1.57	1.21
aldicarb sulfone		1.43	0.78	
ametryn	0.52	0.71	0.86	1.13
atrazine	1.32	0.78	1.29	0.75
captan	0.76	0.92	0.83	1.00
diuron	0.74	0.88	0.69	0.82
ETU	1.29	0.80	0.58	0.37
fenamiphos	0.83	0.93	0.75	0.83
malathion	0.27	0.93	0.29	1.02
maloxon	0.96	0.92	16.3	15.6
metobromuron	0.89	0.91	1.13	1.14
metribuzin	2.50	0.17	8.13	0.59

Table III. Identification and Yields of Ionic Photoproducts of Selected Compounds

pesticide	ionic photoproduct	% yield ^a
aldicarb	sulfate	30
ametryn	sulfate	27
atrazine	chloride	28
bromacil	bromide	83
chloramben	chloride	59
diazinon	sulfate	25
dimethoate	sulfate	14
fenamiphos	sulfate	15
fluoroaniline	fluoride	45
iodotyrosine	iodide	107
malathion	sulfate	30
metobromuron	bromide	118
metribuzin	nitrate	31
monuron	chloride	47
propanil	chloride	52
swep	chloride	44
thiram	sulfate	99

^a Yield is based on only one precursor per molecule.

RESULTS AND DISCUSSION

Flow injection analysis (FIA) was used to screen several types of pesticides, and the difference between the response per nanogram of pesticide with the UV lamp on and lamp off was used for comparison. Methylthio, halogen, and phosphorothioate functional groups in pesticides produced a sensitive response with the simple photoconductivity detector (PCD) (see Table I). Phosphorothioates and carbamothioates with a thiono sulfur gave a better response than their oxygenated analogues. Other investigators have found that nitrosamines and sulfonamides (Popovich et al., 1979), sulfonylureas (Zahnow, 1985), and permethrins (Walters, 1983) also yield a sensitive response. Other pesticides did not give a sensitive response probably because they are not photolyzed by 254-nm UV light or have no ionic photoproducts.

Addition of organic modifier (acetonitrile or methanol) to the mobile phase increased PCD sensitivity in most cases, and these solvent mixtures were tested because of their widespread use in reversed-phase HPLC. The type of organic solvent affected response of some pesticides but no obvious trends were observed with the compounds tested (Table II). The eluant affected the production of detectable products in other HPLC postcolumn photolysis detectors (Miles and Moye, 1987, 1988). This simple PCD did not have severe problems with acetonitrile as solvent, although sloping base lines were observed during some gradient runs. Some problems with acetonitrile were reported with the commercial PCD (Walters, 1983) and were probably the result of ion-exchange resins used postcolumn.

Table IV. Estimated Detection Limits (EDL) for Selected Compounds Using Reversed-Phase Separation^a

compd	EDL	
	ng	pg/s ^b
aldicarb	1.5	31
atrazine	7.3	143
barban	10.0	292
bromacil	9.4	140
butachlor	6.7	129
butylate	2.5	53
captan	15.0	103
dimethoate	0.9	11
diuron	3.1	68
fenamiphos	4.8	48
iodotyrosine	3.8	32
ioxynil	9.4	138
linuron	5.4	49
L-thyroxine	0.6	10
malathion	5.0	30
metobromuron	4.2	54
monuron	1.5	27
oryzalin	11.5	385
oxyfluorfen	11.3	154
pronamide	13.1	342
propanil	2.0	30
swep	4.9	52
thiobencarb	3.2	74
thiram	3.4	36

^a NS-1 column using 1:1 water/acetonitrile at 0.6 mL/min or HS-3 C₁₈ using gradient described in Figure 4. EDL was based on S/N = 3.
^b pg/s = picograms/second; determined by dividing picograms injected by the peak width (in seconds) at half-height.

Use of FEP (fluorinated ethylene-propylene) Teflon in place of TFE (tetrafluoroethylene) also had various effects, depending upon the pesticide (Table II). Both Teflon coils produced an increased conductivity background when the UV lamp was on (1 μ S lamp off vs ca. 2–6 μ S lamp on). This effect was caused by photolytic release of fluoride ions from the Teflon, which we measured by IC and has been reported previously (Bately, 1984). Irradiation of Teflon also produces protons (Bately, 1984) but the pH effluent of both coils (with UV lamp on) was neutral to slightly basic (ca. pH 7–8). Other investigators have shown that there is no significant difference in detector response for diuron and atrazine between equivalent-sized Teflon FEP and quartz coils used in the commercial PCD (Ciccioli et al., 1981).

Acetone acts as a photosensitizer, giving increased response for several pesticides in water as observed with another photolytic detector (Miles and Moye, 1987). Significant increases were observed in this study with ametryn, ETU, and malathion upon addition of acetone (0.005%) to the mobile phase. This approach has limited use because of the large increase in background conductivity (20 μ S) with 0.005% acetone. Also, addition

Table V. Herbicides Selected for Study

herbicide class	examples	response, ^a area/ng
N-arylcarbamates	sweep	68
	barban	52
	chlorpropham	45
arylcarboxylic acids	dicamba	21
	chlorfenac	27
arylalkanoic acids	2,4-D	15
	2,4,5-T	35
	fenoprop	38
N-aryl-N',N'-dimethylureas	diuron	67
	monuron	45
	linuron	53
	metobromuron	47
anilides	propanil	65
	monalide	27
chloracetamides	alachlor	47
	butachlor	41
	metolachlor	45
	propachlor	44
halogenated phenols	bromoxynil	50
	ioxynil	37
phenol ethers	oxyfluorfen	11
	nitrofen	<1
	bifenox	15
6-chlorotriazines	atrazine	30
	simazine	21
	cyanazine	38
6-(methylthio)triazines	ametryn	45
	terbutryn	47
	prometryn	41
S-alkyl carbamothioates	butylate	35
	molinate	31
	thiobencarb	52
2,4-dinitro-6-alkylphenols	pebulate	16
	dinoseb	3.2
	DNOC	4.1
2,6-dinitroanilines	dinocap	10
	trifluralin	6.9
	oryzalin	1.2
	benfluralin	1.1
others	profluralin	4.6
	asulam	49
	sulfallate	72

^a Response values determined as described in Table I. Values are average of duplicates where the relative standard deviation is <10% except for DNOC (16%) and benfluralin (10.3%).

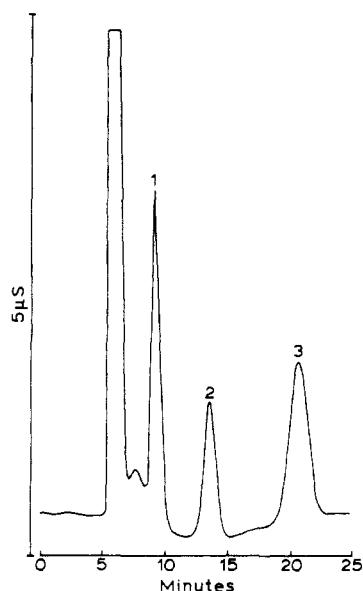


Figure 1. Soil extract containing 10 ppm (500 ng each) of (1) bromacil, (2) atrazine, and (3) ametryn. Conditions are NS-1 column and 1:1 acetonitrile/water at 0.6 mL/min.

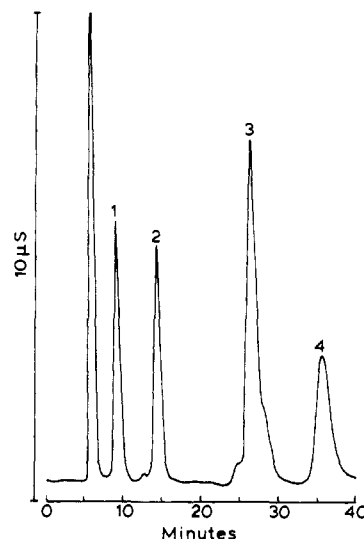


Figure 2. Alfalfa extract fortified with 10 ppm (500 ng each) of (1) aldicarb, (2) diuron, (3) captan, and (4) thiram. Conditions identical with those of Figure 1.

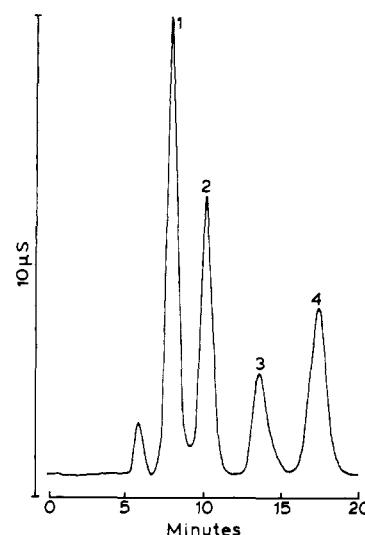


Figure 3. Alfalfa extract fortified with 10 ppm (500 ng each) of (1) dimethoate, (2) monuron, (3) atrazine, and (4) fenamiphos. Conditions identical with those of Figure 1.

of acetonitrile to this mixture produced bubbles, which adversely affected detection.

Collection of photolytic products and analysis by IC showed expected ions (Table III). Halogenated aromatics or triazines produced the corresponding halides, and ion yields of monohalo aromatics increased as C-X bond strength decreased (I > Br > Cl > F). Phosphorothioates and carbamothioates produced sulfate, and higher yields were observed from pesticides with thiono sulfur, presumably due to the greater ease of photooxidation. Interestingly, metribuzin produced nitrate by oxidation of the azo amine whereas anilines tested did not form nitrate. Also, the lack of nitrate or nitrite production from photolyzed nitro aromatics suggests that these pesticides preferentially decompose to other ionic products.

Application of the PCD to analysis of several types of pesticide residues in soil and alfalfa was successful (Figures 1-3). Chromatograms had only minor, early eluting interferences. Separations were limited to 50% organic modifier, as the photolysis coils developed leaks above this concentration (Miles and Moye, 1988). Estimated detection limits (EDLs) for selected pesticides (Table IV) were in the low-nanogram range, which is similar to those

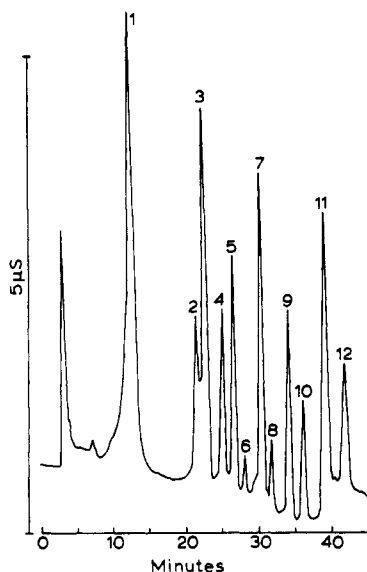


Figure 4. Alfalfa extract fortified with 10 ppm (200 ng each) of (1) ioxynil (30 ppm), (2) atrazine (20 ppm), (3) diuron (20 ppm), (4) propanil, (5) sweep, (6) pronamide (50 ppm), (7) barban (20 ppm), (8) oryzalin (50 ppm), (9) thiobencarb, (10) butylate, (11) butachlor (20 ppm), and (12) oxyfluorfen (30 ppm). Conditions are P&E C_{18} column and 1.0 mL/min of 5% CH_3CN in water for 2 min, then linear gradient to 1:1 CH_3CN /water in 30 min, and then hold for 10 min.

described for the commercial PCD (Popovich et al., 1979; Walters, 1983).

Weaving the Teflon coils decreases longitudinal band broadening associated with long reaction coils. Band spreading in this coil ($\sigma^2 = 52.5 \pm 1.7 \text{ s}^2$ for 2.9-mL volume) was comparable to that observed for other knitted photoreaction coils ($\sigma^2 = 35\text{--}41 \text{ s}^2$ for 1.7-mL volume) (Selavka et al., 1987). Changes in mobile phase composition and flow did not significantly affect this simple PCD as was described by Walters (1983) using the commercial PCD. Stable base lines were achieved in about 30 min.

Observation of the types of pesticides applicable to this detector suggested that it may be useful for a broad range of herbicides. Table V lists several classes and examples of herbicides selected for analysis with this PCD. All the herbicides tested gave a sensitive response with the exception of most of the phenol ethers and the dinitro derivatives.

A multicomponent separation of 12 herbicides in fortified alfalfa extract is possible by gradient elution on a reversed-phase HPLC column (Figure 4). Acidic herbicides can be retained by LC with ion suppression on reversed-phase and anion exchange. Since both usually

require addition of other anions, background conductivity increases and sensitivity decreases. Perhaps ion pairing with a weakly conducting ion such as tetrabutylammonium hydroxide and postphotolysis ion suppression may alleviate this problem.

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