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Determination of National Survey of Pesticides analytes in groundwater by liquid chromatography with postcolumn reaction detection

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ABSTRACT

Multi-residue methods for pesticides in water were developed using liquid chromatography (LC) with postcolumn reaction detection. Over 100 analytes from the US Environmental Protection Agency's National Survey of Pesticides in Drinking Water Wells were screened for response using postcolumn photolysis followed by fluorescence (PFD), electrochemical (PED) or conductivity (PCD) detection. LC–PED and LC–PFD are suitable for multi-residue pesticide determinations in groundwater. These two detection methods are complementary as PED responds to several sulfur-containing pesticides whereas PFD responds to many nitrogenous pesticides. Approximately half of these analytes could be determined in low nanograms amounts using these two detection systems and multi-residue separations with gradient reversed-phase LC are demonstrated. The LC–PCD system tested was not suitable for sensitive, multi-residue determinations and further examination of this technique is recommended using the commercial PCD instrument.

INTRODUCTION

The US Environmental Protection Agency (EPA) has identified 126 pesticides and degradation products that are potential groundwater contaminants. These compounds have been designated for study because of health effect concerns, high volumes of sales nationally, prior occurrence in groundwater or propensity to leach into groundwater and contaminate drinking water under normal use conditions [1]. The EPA has conducted a National Survey of Pesticides (NPS) in Drinking Water Wells for these analytes to provide nationwide estimates for pesticides and nitrates in drinking water. Results of the survey showed that about 10% of community water system wells have detectable levels of one or more pesticides, although less than 1% have concentrations over the maximum contaminant level (MCL) [1]. A need exists for continued monitoring.

Central to this monitoring effort are the multi-residue methods (MRMs) for groundwater analysis. Although gas chromatography (GC) is the traditional method for pesticides, liquid chromatography (LC) is becoming more widely used. In fact, the polar nature of most of these analytes, which makes them potential groundwater contaminants, also makes LC separation a more viable technique. Of the four MRMs used for the EPA survey, two use LC separation. One employs UV detection at 254 nm (method 4) and the other (method 5) uses postcolumn reaction detection consisting of alkaline hydrolysis followed by fluorogenic labeling with *o*-phthalaldehyde–2-mercaptoethanol (OPA–MERC) [1].

Recently, photolysis has been used as a LC postcolumn reaction for the sensitive determination of pesticides with a variety of detectors. Photolysis–fluorescence detection has been used both with [2–4] and without [3,4] OPA–MERC additions. Photoly-

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sis–electrochemical detection showed sensitive and selective detection of organophosphate insecticides [5] and a wide variety of pharmaceuticals and environmental pollutants [6]. Photolysis–conductivity detection of pesticides has been demonstrated with a commercial unit [7,8] and a laboratory-constructed system [9]. This investigation examined LC separations using postcolumn photolysis with fluorescence (PFD), electrochemical (PED) and conductivity (PCD) detection of 101 of the EPA NPS analytes. Method detection limits were determined for several analytes and mult-residue separations are demonstrated.

EXPERIMENTAL

Reagents and standards

Analytical standards were obtained from the EPA chemical repository (Research Triangle Park, NC, USA) with the following exceptions; tetrachlorvinphos, etridizole, tricyclazole and DCPA diacid (Chem Service, West Chester, PA, USA), deisopropyl atrazine, fenarimol, MGK 264, 4-nitrophenol, methyl paraoxon, terbufos and triadimefon (Crescent Chemical, Hauppauge, NY, USA), aldicarb, aldicarb sulfoxide and aldicarb sulfone (Rhone-Poulenc, Research Trangle Park, NC, USA), disulfoton sulfoxide, disulfoton sulfone, fenamiphos, fenamiphos sulfoxide, fenamiphos sulfone, metribuzin DA, metribuzin DADK and metribuzin DK (Mobay Chemical, Kansas City, MO, USA), 5-hydroxy-dicamba (Sandoz Crop Protection, Des Plaines, IL, USA), carboxin sulfoxide (UniRoyal Chemical, Middlebury, CT, USA), 3,5-dichlorobenzoic acid (Aldrich, Milwaukee, WI, USA), 2,4,5-TP (Dow Chemical,Midland, MI, USA) and pronamide and pronamide metabolite (Rohm and Haas, Spring House, PA, USA). All standards were of $\geqslant$97% purity, except for atraton (88.3%), disulfoton sulfoxide (96.5%), disulfoton sulfone (88.3%), merphos (88.2%), metribuzin DADK (84.8%), methyl paraoxon (96%), swep (95%) and tricyclazole (96%). Stock standard solutions (1 mg/ml) were prepared in acetonitrile except for simazine [0.5 mg/ml in acetonitrile–methanol (1:1)].

Solvents were Fisher (Fairlawn, NJ, USA) OPTIMA grade. All other reagents were of analytical-reagent grade or better. Reagent water was obtained from a Milli-Q water purification system (Millipore, Milford, MA, USA). The *o*-OPA–MERC reagent was prepared as described previously [3]. Borate solution was prepared identically to the OPA–MERC reagent but without *o*-phthalaldehyde or 2-mercaptoethanol added.

Apparatus and procedure

Photolysis conductivity detector. Liquid chromatography and flow-injection analysis (FIA) were performed with a Dionex (Sunnyvale, CA, USA) gradient pump module, a Dionex eluent degas module, a Dionex Model II conductivity detector and a Dionex Model II automated chromatography interface. The interface was connected to an IBM (Southbury, CT, USA) PS2/386 computer. Postcolumn photolysis was achieved in a commercial photoreactor (Beam Boost, ASTEC, Whippany, NJ, USA with a 10 m $\times$ 0.4 mm I.D. PTFE woven reactor coil. Injections (20 μl for LC; 1 μl for FIA) were made with a Perkin-Elmer (Norwalk, CT, USA) Model ISS 100 autoinjector. Reversed-phase columns (Perkin-Elmer, 3 cm $\times$ 0.46 I.D., 3-μm C_{18} with reduced activity) were used.

All analytes were screened by FIA (acetonitrile–water, 1:1) to avoid time-consuming LC separations. Also, FIA eliminates the possibility of a lack of response caused by compounds not eluted from the LC column. The FIA response was calculated as the difference between the average of duplicate peak areas with the lamp on and duplicate measurements with the lamp off divided by the nanomoles of analyte injected. A response ratio was calculated relative to an equimolar amount of bromobenzene (see refs. 3 and 9 for calculations of response ratios). Compounds with a response ratio $\geqslant$ 0.5 (50% of bromobenzene) were analyzed by reversed-phase LC with acetonitrile–water gradients (5 to 90% in 60 min). Two gradients with different slopes were required for input into the DryLab G (LC Resources, Lafayette, CA, USA) computer program designed to optimize multi-component separations by gradient LC [10]. After the optimum gradient had been found, method detection limits (MDLs) were determined on fortified groundwater using the procedure recommended by the EPA [11] and described elsewhere [3]. The recovery of analytes from fortified groundwater was not determined as no sample preparation steps were used except fortifica-

tion of groundwater with analytes. Groundwater was obtained from the Palolo section of the Pearl Harbor–Honolulu basin aquifer.

Photolysis fluorescence detector. LC and FIA were performed with the system described above except using a Gilson (Middleton, WI, USA) Model 121 fluorimeter (λ_{ex} 356 nm; λ_{em} 450 nm), a Hewlett-Packard (Waldbronn, Germany) Model 1046A fluorimeter (λ_{ex} 335 nm; λ_{em} 450 nm) or an Applied Biosystems (Ramsey, NJ, USA) Model 980 fluorimeter (λ_{ex} 235 nm; λ_{em} >418 nm) and a Dionex minipump (Model RP-1). All analytes were screened by FIA (acetonitrile–water, 1:1) with (1) addition of the OPA–MERC reagent (0.2 ml/min), (2) addition of 0.05 *M* borate solution only (0.2 ml/min) and (3) no reagent addition. A response ratio was determined relative to an equimolar amount of methylamine (OPA–MERC addition) or 1-naphthol (borate or no addition). Analytes with a response ratio $\geqslant$0.01 (1% of methylamine) or 0.09 (9% of 1-naphthol) were analyzed by reversed-phase LC with two acetonitrile–water gradients for DryLab G as described above. MDLs were determined as described above.

Photolysis electrochemical detector. LC was performed with the system described above except using a Dionex inert injection valve (20 μl), a Dionex Model II pulsed electrochemical detector (glassy carbon electrode at + 1.0 V *vs.* Ag/AgCl) and a laboratory-constructed photoreactor [3] with a 10 m × 0.6 mm I.D. PTFE reactor coil woven with KOT3 [12]. Because of highly electroactive impurities in many of the pesticide standards, FIA was not reliable. Analytes were screened using a gradient (30 to 90% methanol in 20 min). Acetonitrile could not be used a solvent because photolysis produces compounds that polymerize on the carbon electrode [6]. Analytes with a response ratio $\geqslant$ 0.2 (20% of malathion) were analyzed by a second gradient for DryLab G as described above. MDLs were determined as described above.

RESULTS AND DISCUSSION

Photolysis conductivity detector

Fifty eight of the 103 analytes tested (55%) yielded a response $\geqslant$50% of the response for an equimolar amount of bromobenzene (Table I). Compound types that usually gave a favorable response were phosphorothioates, phosphorodithioates, halogenated aromatics, triazines and uracils and aliphatics, aromatics and triazines with a methylthio group. Photolytic release of halide and sulfate ions acounts for the conductimetric response [9]. MDLs were determined for 33 of these analytes. MDLs were not determined for those compounds which were not retained by the reversed-phase column (*i.e.*, chloramben, dicamba-5OH, etc.) or those compounds which eluted after the gradient was completed (90% acetonitrile; *i.e.*, ametryn, terbutryn). Acidic compounds can be retained by ion suppression but the addition of acid to the mobile phase increases the conductivity background and increases detection limits [9]. Strongly retained compounds can be eluted with >90% acetonitrile, but use of this solvent shortens the lifetime of the Teflon photoreactor coils [3,9].

This photoreaction coil has been tested with an in-line UV detector and shown to add only a minor amount of band spreading to the chromatographic system [13]. Multi-residue separations are possible but changes in the background conductivity during the gradient cause sloping baselines which make peak detection difficult (Fig. 1). However, isocratic analysis using PCD as described here with a small range of analytes is possible [9]. Injection of groundwater caused increased, but consistent, baseline shifts. These problems can be solved in part by a differential cell used on a commercial photoconductivity detector [7], although problems using gradient elution with this detector have been reported [8]. Further study with the commercial PCD instrument is warranted.

Photolysis fluorescence detector

Photolysis of the analytes produced a response with this detector by formation of an aliphatic primary amine which reacts with OPA–MERC, formation of a fluorescent product or a combination of these two responses. To determine the response source, the analytes were screened by FIA with the complete OPA–MERC reagent, with borate only and with no postcolumn reagent addition. With the OPA–MERC reagent, 39 of the 103 analytes tested (38%) yielded a response $\geqslant$1% of the response for an equimolar amount of methylamine (Table I). With borate only added postcolumn, 25 gave a response $\geqslant$9% of 1-naphthol. Most of these re-

TABLE I

METHOD DETECTION LIMIT[a] AND FLOW-INJECTION RESPONSE[b] OF SELECTED PESTICIDES ON THE USEPA NATIONAL PESTICIDES IN GROUNDWATER SURVEY LIST USING LC WITH POSTCOLUMN REACTION DETECTION

Common name	CAS No.	PFD[c]	PFD[d]	PED[e]	PCD[f]
Acifluorfen	62476-59-9	–	–	–	–
Alachlor	15972-60-8	–	–	15	4.3
Aldicarb	116-06-3	0.5	–	0.6	9.6
Aldicarb sulfoxide	1646-87-3	1.3	–	+	+
Aldicarb sulfone	1646-88-4	35	–	–	–
Ametryn	834-12-8	–	–	6.1	+
Atraton	1610-17-9	–	–	ND[j]	–
Atrazine	1912-24-9	–	–	ND	6.5
Atrazine, de-isopropyl	1007-28-9	–	–	–	1.7
Barban	101-27-9	+	+	2.8	5.4
Bentazon	25057-89-0	+	+	+	–
Bromacil	314-40-9	–	–	ND	2.0
Butachlor	23184-66-9	19	–	ND	3.6
Butylate	2008-41-5	5.3	–	+	–
Carbaryl	63-25-2	36	+	+	–
Carbofuran	1563-66-2	5.1	–	9.4	–
Carbofuran-OH	1563-38-8	–	–	0.9	–
Carbofuran-OH,-3KET	11781-16-7	–	–	0.5	–
Carbofuran-3OH	16655-82-6	5.7	–	2.5	–
Carboxin	5234-68-4	–	+	0.9	21
Carboxin sulfoxide[g]	17757-70-9	–	+	0.7	3.1
Chloramben	133-90-4	–	+	+	+
Chloroneb	2675-77-6	–	–	–	–
Chlorobenzilate	510-15-6	–	+	1.6	6.8
Chlorothalonil	1897-45-6	–	–	–	+
Chlorpropham	101-21-3	+	+	1.3	+
Cyanazine	21725-46-2	–	–	ND	16
Cycloate	1134-23-2	11	–	–	–
D-2,4 acid	94-75-7	–	–	10	+
DB-2,4 acid	94-82-6	–	–	+	–
Dalapon	75-99-0	–	–	ND	–
DCPA	1861-32-1	–	–	+	2.1
DCPA diacid metabolite	2136-79-0	–	–	–	–
Diazinon	333-41-5	–	–	+	5.5
Dicamba	1918-00-9	–	–	+	–
Dicamba-5OH	7600-50-2	+	+	+	+
3,5-Dichlorobenzoic acid	51-36-5	–	–	11	–
Dichlorprop	120-36-5	–	–	13	–
Dichlorvos	62-73-7	–	–	ND	–
Dinoseb	88-85-7	–	–	+	–
Diphenamid	957-51-7	0.4	–	0.3	–
Disulfoton	298-04-4	–	–	3.1	2.0
Disulfoton sulfoxide	2497-07-6	–	–	3.0	+
Disulfoton sulfone	2497-06-5	–	–	5.2	+
Diuron	330-54-1	2.0	+	+	6.7
EPTC	759-94-4	6.8	–	–	–
Ethoprop	13194-48-4	–	–	+	+
Etridiazole	2593-15-9		-	+	+
Ethylenethiourea	96-45-7	–	–	+	–
Fenamiphos	22224-92-6	+	–	3.1	3.9
Fenamiphos sulfoxide	31972-43-7	–	–	12	6.5
Fenamiphos sulfone	31972-44-8	–	–	–	6.0
Fenarimol	60168-88-9	9.5	1.5	1.6	7.4
Fluometuron	2164-17-2	32	+	4.0	11

TABLE I *(continued)*

Common name	CAS No.	PFD[c]	PFD[d]	PED[e]	PCD[f]
Fluridone	59756-60-4	–	+	–	–
Hexazinone	51235-04-2	–	–	ND	–
Linuron	330-55-2	9.0	+	28	7.9
Merphos	150-50-5	–	–	ND	40
Methiocarb	2032-65-7	5.0	–	+	15
Methomyl	16752-77-5	2.8	–	1.9	+
Metolachlor	51218-45-2	–	–	3.0	2.5
Metribuzin	21087-64-9	–	–	0.9	–
Metribuzin DA	34045-02-4	–	–	2.0	2.4
Metribuzin DADK	52236-30-3	–	–	5.4	–
Metribuzin DK	56507-37-0	–	–	2.1	–
Mevinphos	7786-34-7	–	–	+	–
MGK 264[h]	70322-82-6	–	–	ND	–
Molinate	2212-67-1	17	–	–	–
1-Naphthol[g]	90-15-3	6.1	0.9	0.7	+
Napropamide	15299-99-7	3.4	0.6	0.7	+
Neburon	555-37-3	11	+	+	1.7
4-Nitrophenol	100-2-7	–	–	+	–
Norflurazon	27314-13-2	+	–	6.8	–
Oxamyl	23135-22-0	2.6	–	24	+
Paraoxon-methyl	950-35-6	–	–	–	–
Pentachlorophenol	87-86-5	–	–	+	+
Pebulate	1114-71-2	4.9	–	–	–
cis-Permethrin	54774-45-7	+	+	ND	+
trans-Permethin	51877-74-8	+	+	ND	+
Picloram	1918-02-1	+	–	+	+
Prometon	1610-18-0	–	–	ND	–
Prometryn	7287-19-6	–	–	6.2	+
Pronamide	23950-58-5	–	–	–	–
Pronamide metabolite[i]	29918-41-0	–	–	10	+
Propachlor	1918-16-7	+	+	1.5	16
Propanil	709-98-8	5.4	0.5	2.9	12
Propazine	139-40-2	–	–	ND	12
Propham	122-42-9	+	+	–	–
Propoxur	114-26-1	1.8	+	6.0	–
Simazine	122-34-9	–	–	ND	–
Simetryn	1014-70-6	–	–	3.6	+
Swep	1918-18-9	+	0.9	3.0	10
T-2,4,5 acid	93-76-5	–	–	11	+
TP-2,4,5 acid	93-72-1	–	–	11	3.8
Tebuthiuron	34014-18-1	57	–	6.7	–
Terbacil	5902-51-2	–	–	–	–
Terbufos	13071-79-9	–	–	ND	19
Terbutryn	886-50-0	–	–	2.8	+
Tetrachlorvinphos	961-11-5	–	–	+	+
Triadimefon	43121-43-3	–	+	1.6	6.9
Tricyclazole	41814-78-2	–	–	ND	–
Trifluralin	1582-09-8	–	–	ND	–
Vernolate	1929-77-7	6.5	–	–	–

[a] MDL in nanograms.
[b] Where + denotes a detector response $\geqslant$ the selected response ratio and – denotes a detector response $\leqslant$ the selected response ratio.
[c] Photolysis–fluorescence detection (with OPA–MERC).
[d] Photolysis–fluorescence detection (with borate only).
[e] Photolysis–electrochemical detection.
[f] Photolysis–conductivity detection.
[g] Not on the USEPA list.
[h] Trade name for N-octylbicyloheptanedicarboximide.
[i] N-(1,1-Dimethylacetonyl)-3,5-dichlorobenzamide.
[j] ND = Not detected.

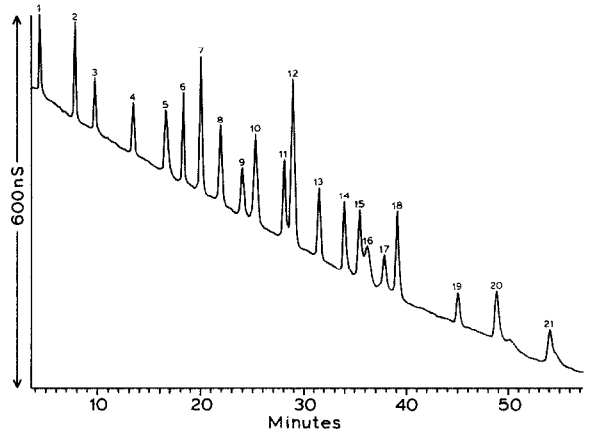

Fig. LC–PCD with gradient elution from 30 to 60% acetonitrile in 60 min. Peaks are 50 ng each of: 1 = desisopropyl atrazine; 2 = carboxin sulfoxide; 3 = metribuzin DA; 4 = bromacil; 5 = fenamiphos sulfoxide; 6 = atrazine; 7 = fenamiphos sulfone; 8 = diuron; 9 = propachlor; 10 = propazine; 11 = methiocarb; 12 = swep; 13 = fenarimol; 14 = fenamiphos; 15 = metolachlor; 16 = alachlor; 17 = barban; 18 = neburon; 19 = DCPA; 20 = disulfoton; 21 = butachlor.

sponses observed with the OPA–MERC reagent flowing were the result of fluorescent products formed during photolysis. The major exceptions were the N-methylcarbamates and carbamoyloximes, carbamothioic acids and some phenylureas

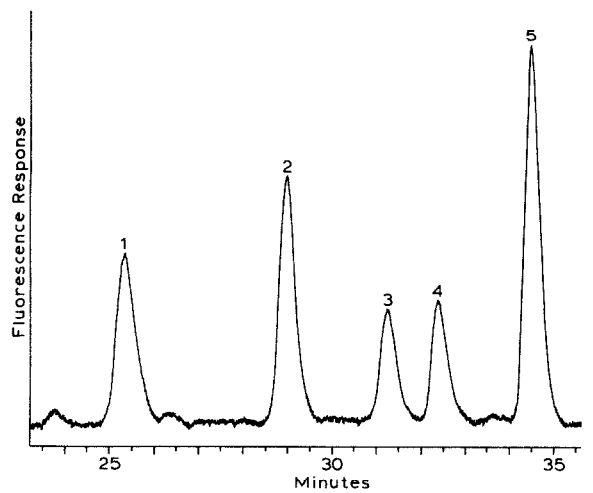

Fig. 2. LC–PFD (borate only) with gradient elution from 5 to 80% acetonitrile in 60 min. Peaks are 10 ng each of: 1 = 1-naphthol; 2 = propanil; 3 = swep; 4 = fenarimol; 5 = napropamide.

which formed primary amines after photolysis [3]. The response from the phenylureas was a mixture of primary amine and fluorescent products as described previously [3].

All compounds that yielded a photolysis–fluorescence response without OPA–MERC gave an enhanced response when borate was added, with the exception of chloramben and carbofuran phenol-3KET. The response for the latter compound was $\leqslant 9\%$ 1-naphthol with the borate reagent. Apparently, most of the fluorescent photodegradation products have higher fluorescence intensity under alkaline conditions. Many of these analytes also responded well with the PED system, suggesting that phenolic moieties are formed during photolysis. Ionization of phenolic groups often results in more conjugation and light absorption at longer wavelengths. The response of many of these analytes was better when no OPA–MERC was present, suggesting that this reagent can interfere with the fluorescent species. Thus, optimum response for some compounds is achieved with the borate reagent addition (Fig. 2).

The MDLs varied significantly with the fluorimeter used. The Gilson and Hewlett-Packard detectors were coupled together and the MDLs were comparable, except for compounds that fluoresced without OPA–MERC addition. Apparently these photodegradtion products fluoresce in the range used by the broad bandpass filter fluorimeter (Gilson) as opposed to the narrow bandpass (excitation and emission grating monochromaters) fluorimeter (Hewlett-Packard). Comparison of the MDLs in this study and similar studies [3,4] indicated that significant improvements could be realized using a different fluorimeters. Using a fluorimeter (ABI) with a deuterium source, excitation grating monochrometer (235 nm) and emission filter (>418 nm), the signal-to-noise ratio improved significantly. Use of the Hewlett-Packard fluorimeter with an excitation wavelength of 235 nm yielded no significant improvement in signal-to-noise ratio. Table I lists data collected with the filter fluorimeter (Gilson) only.

With the exceptions of aldicarb sulfone and carbaryl, the MDLs using the PFD compare favorably with the standard base hydrolysis–OPA–MERC postcolumn reaction detector [1,3,4]. However, the PFD instrument described here also detects several

other analytes on the NPS list, indicating that it is complementary to EPA method 5. Representative chromatograms of multi-residue separations using this detector have been shown [3,4].

Photolysis electrochemical detector

Sixty eight of the 103 analytes (66%) gave a response ⩾ 20% of malathion (Table I). Phenylamides, phenylcarbamates, aliphatic carbamates and carbamoyloximes, methylthiotriazines, phosphorothioates and phosphorodithioates were among the compounds with high sensitivity. Many of the analytes with high sensitivity contained sulfur, although the carbamothioic acids responded poorly as a group. Several analytes, especially phenolic metabolites, gave a good response with the lamp off and the response with the lamp on usually deminished slightly. The species responsible for the electrochemical response are unknown, but photohydrolyses of sulfur-containing compounds to thiols or other oxidizable species and aromatic derivatives to phenols are likely candidates. Other mechanisms for the production of the photolysis–electrochemical response have been discussed [14].

MDLs were determined for 46 analytes using this detector and the sensitivity and selectivity for groundwater analysis was excellent. Several analytes were not detected, probably because of elution after gradient completion. Some acidic analytes were retained on the reversed-phase column at neutral pH, suggesting ion exchange on residual silanol groups. Multi-residue separations are difficult because of the large number of analytes and broad peaks (Figs. 3 and 4). The decreased separation efficiency observed when using methanol compared with acetonitrile is consistent with the higher viscosity of methanol. The broad peaks observed with the methanol–water mobile phase were not significantly affected by the laboratory-constructed photoreactor and the photolysis efficiency was comparable to that of the commercial photolysis unit using a variety of analytes. Band spreading from the laboratory-constructed photoreactor was slightly greater than that from the commercial unit using acetonitrile–water [13]. Negative peaks occurred at the tails of some peaks, suggesting adsorption at the electrode

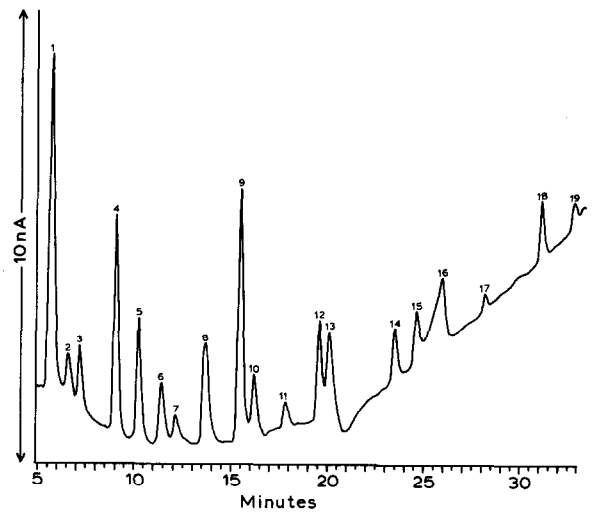

Fig. 3. LC–PED with gradient elution from 30:70 to 77:23 methanol–10 m*M* NaCl in 35.3 min. Peaks are approximately five times the MDL each of: 1 = metribuzin DK and 3,5-DCBA; 2 = carbofuran phenol-3KET; 3 = metribuzin DADK; 4 = metribuzin and 2,4,5-T; 5 = propoxur; 6 = carbofuran phenol; 7 = carboxin; 8 = fenamiphos sulfoxide; 9 = disulfoton sulfoxide; 10 = disulfoton sulfone; 11 = norflurazon; 12 = propanil; 13 = pronamide metabolite; 14 = barban; 15 = prometryn; 16 = alachlor and metolachlor; 17 = fenamiphos; 18 = disulfoton; 19 = chlorobenzilate.

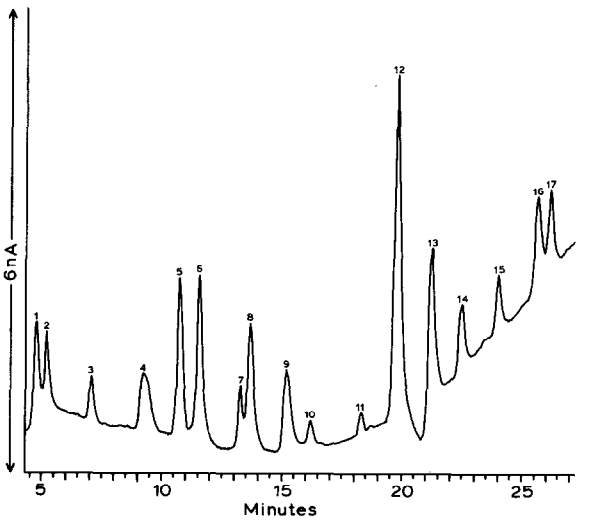

Fig. 4. LC–PED under conditions identical with those in Fig. 3. Peaks are five times the MDL each of: 1 = carbofuran-3OH; 2 = carboxin sulfoxide; 3 = aldicarb; 4 = metribuzin DA; 5 = carbofuran; 6 = tebuthiuron; 7 = fluometuron; 8 = 1-naphthol; 9 = simetryn; 10 = propachlor; 11 = unknown; 12 = diphenamid and linuron; 13 = swep; 14 = chlorpropham; 15 = triadimefon; 16 = fenarimol; 17 = napropamide.

surface. The large negative peak at about 21 min occurred under all conditions and the cause is unknown.

Because of the large number of suitable analytes for each LC system, a gradient that separated all components was not possible. Nevertheless, the DryLab G program was valuable for testing various gradient conditions without additional experiments and eliminated unnecessary time at the front and end of the chromatogram. The DryLab G program also allowed an examination of the effect of column conditions such as length and particle size on these multi-component separations and even allowed the testing of columns types that were not available in our laboratory.

LC–PED and LC–PFD are suitable for multi-residue pesticide determinations in water. These two systems are complementary and approximately half of the analytes tested have MDLs $\leqslant$ 10 ng with these detection methods combined. Low-μg/l detection limits in water samples can be realized by injecting large volumes (*ca.* 500 μl). Although this has been demonstrated with the PFD instrument, similar efforts with the PED instrument have been unsatisfactory. Nevertheless, analyte concentration by solvent extraction, as described in the original NPS methods [1], or by solid-phase extraction [15] can improve detection limits. Coupling these detectors in series (PFD instrument downstream) would decrease the analytical time, but it has not been demonstrated. The LC–PCD system tested was not suitable for sensitive, multi-residue determinations in groundwater, but isocratic analysis of a limited range of analytes is possible.

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