SPECIAL GUEST EDITOR SECTION

Determination of Pesticides in Water Samples from the Wieprz-Krzna Canal in the Łęczyńsko-Włodawskie Lake District of Southeastern Poland by Thin-Layer Chromatography with Diode Array Scanning and High-Performance Column Liquid Chromatography with Diode Array Detection

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High-performance thin-layer chromatography with diode array scanning (TLC-DAD) and high-performance column liquid chromatography with a diode array detector (HPLC-DAD) were used to screen water samples for pesticides. Atrazine, clofentezine, chlorfenvinphos, hexaflumuron, terbuthylazine, lenacyl, neburon, bitertanol, and metamitron were enriched from canal water samples by solid-phase extraction (SPE) on octadecyl silane (C18)/styrene-divinylbenzene-1, C18, C18 Polar Plus, and cyanopropyl (CN) cartridges. Recovery rates were high for all extraction materials except CN, for which values for all pesticides were lower. SPE was used for both preconcentration and fractionation of the analytes. Analytes were eluted by means of methanol and dichloromethane. Methanol eluates were analyzed by HPLC-DAD and dichloromethane eluates by TLC-DAD. The method was validated for precision, repeatability, and accuracy. Calibration graphs were linear between 0.1 and 50.0 μg/mL for all pesticides, and correlation coefficient (r) values were between 0.9994 and 1.000 as determined by HPLC-DAD. Calibration graphs were linear between 0.1 and 1.5 μg/spot for all pesticides, and r values were between 0.9899 and 0.9987 as determined by TLC-DAD. The limit of detection was between 0.04 and 0.23 μg/spot for TLC-DAD and 0.02 and 0.45 μg/mL for HPLC-DAD.

Pesticides occur frequently in the form of multicomponent mixtures (contamination of rivers, dumping of toxic waste, storage) that are difficult to analyze in a single analytical process. Real samples containing pesticides have very different compositions—river waters, for example, carry solutes from vast territories. Analysis of complex mixtures of pesticides can be simplified by preliminary fractionation into simpler mixtures by micropreparative chromatography. Thin-layer chromatography (TLC) is especially suitable for this process because it makes use of simple equipment that can be applied even under field conditions. The main problem of the separation of complex mixtures is to find a system of appropriate selectivity for a single analytical process. For preparative separations, normal-phase systems are preferable because of the wide range of different selectivity of a variety of mobile phases with polar adsorbents. Based on preliminary experiments, it is possible to fractionate mixtures of pesticides into several simpler ones (1, 2).

Analysis of environmental samples requires a good extraction method for sample preparation. Solid-phase extraction (SPE) can be used in water analysis, owing to the fact that it provides a high concentration ratio. It also enables satisfactory cleanup of contaminated samples. Large amounts of water can be extracted with barely any effort and recovered compounds can be eluted with small quantities of organic solvent. Eluates are ready for further analysis chosen according to the nature of analyzed compounds and the chromatographic system applied. If analyzed substances represent different classes, SPE may be used not only to preconcentrate but also to partially fractionate complex mixtures, enabling analysis of each fraction with a smaller amount of interferences. SPE is one of the techniques available to an analyst to bridge the gap that exists between the sample collection and analysis steps. If the concentration of the pesticides in original samples is very low, a preconcentration method should be applied.

The objective of analysis is, as a rule, separation and identification of the composition of pesticide mixtures and their quantitative analysis. TLC combined with modern scanning densitometry provides the possibility of quantitative analysis. The method offers a simple and economical

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Table 1. Method validation parameters for the quantitation of clofentezine, neburon, chlorfenvinphos, and lenacyl by the proposed SPE-HPTLC-DAD method

Parameter	Clofentezine	Neburon	Chlorfenvinphos	Lenacyl
Instrumental precision (CV, %, *n* = 5)	0.84	0.76	0.88	0.98
Repeatability of standards (CV, %, *n* = 5)	1.01	1.19	0.98	1.26
Repeatability of sample (CV, %, *n* = 5)	0.23	0.18	0.45	0.14
Optimal λ, nm	278.25	249.42	246.95	273.31
Limit of detection, μg/spot	0.23	0.06	0.16	0.04
Limit of quantitation, μg/spot	0.70	0.18	0.493	0.12
Specificity	Specific	Specific	Specific	Specific
Linearity (correlation coefficient, r)	0.9899	0.9979	0.9921	0.9987
Range, μg/spot	0.1–1.5	0.2–1.0	0.5–1.0	0.2–1.0

alternative to other chromatographic techniques, especially column high-performance liquid chromatography (HPLC).

Application of a modern fiber optic TLC scanner with a diode array detector (DAD) has several advantages (3–7), e.g., the scanner can measure TLC plates simultaneously at different wavelengths without destroying the plate surface and permits parallel recording of chromatograms and in situ UV spectra in the range of 191–1033 nm; therefore, it is possible to obtain doubly credible correct identification of the compounds on a chromatogram. The TLC-DAD scanner permits analysis of each compound at its optimum wavelength, thus offering optimum sensitivity for detection of each component. The TLC-DAD scanner permits measurement of a 3-dimensional chromatogram, A = f (λ, t), with absorbance as a function of wavelength and time. The TLC-DAD scanner can compare parallel UV spectra of an unknown compound and a standard from a library of spectra. Software is available that allows the user access to all common parameters used in HPLC-DAD: peak purity, resolution, identification via spectral library match, etc. The TLC-DAD scanner is especially useful for correct identification of components of difficult, complicated mixtures, such as in plant extract and toxicological analysis.

At present, only a limited number of papers describe fiber optic scanning in TLC. An analytical procedure using HPTLC in combination with fiber optic scanning densitometry for identification of drugs in biological samples was described (7). In other work, fiber optic scanning densitometry was used for identification and quantitative analysis of fenitrothion in fresh apple juice (8). Application of SPE and TLC with DAD for the qualitative and quantitative analysis of dyes in beverages was also published (9). The purpose of the present work was to demonstrate an application of TLC-DAD and HPLC-DAD for identification and quantitative analysis of pesticides in water samples from the Łęczyñsko-Włodawskie Lake District in southeastern Poland, a region where intensive agricultural activity takes place and farmers use large quantities of pesticides.

Experimental

Pesticide Standards

The standards of the investigated pesticides were obtained from the Institute of Organic Industry (IPO, Warsaw, Poland). All standards were dissolved in methanol.

Solvents and Mobile Phase Solution

Acetonitrile, dichloromethane, methanol, *n*-heptane, and tetrahydrofuran were pro chromatographic grade from E. Merck (Darmstadt, Germany); ethyl acetate was pro analysis grade from Polish Reagents (P.O. Ch., Gliwice, Poland). Bidistilled water was used.

Apparatus

(**a**) *Spotting device*.—AS 30 applicator (Desaga, Heidelberg, Germany).

(**b**) *Syringe*.—100 μL (Hamilton, Bonaduz, Switzerland).

(**c**) *TLC chamber for chromatogram development*.— TLC plates were developed to a distance of 9 cm in horizontal, Teflon DS chambers (Chromdes, Lublin, Poland).

(**d**) *Adsorbent*.—10 × 20 cm glass-backed precoated silica gel 60 F_{254} TLC plates (E. Merck, No. 1.05729).

(**e**) *TLC scanner*.—TLC-DAD scanner (J&M, Aalen, Germany).

(**f**) *SPE*.—A Baker SPE 12G system with pump (No. N022.AN18) and C18/SDB-1 [C18 500 mg on top + styrene divinylbenzene copolymer (SDB) 200 mg on bottom/6 mL], C18 (2000 mg/6 mL), C18 Polar Plus (3000 mg/6 mL), and CN (1000 mg/6 mL) Bakerbond SPE cartridges (J.T. Baker, Deventer, Holland) were used.

(**g**) *HPLC system.*—Agilent Technologies Inc. (Wilmington, DE) 1200 Series with DAD.

Procedures

(**a**) *Preparation of water samples*.—Samples were collected in 1 L glass bottles, sampling at 20–50 cm below the surface of water. Just after collection, water samples were passed through 0.45 μm membrane filters (Millipore,

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Table 2. Method validation parameters for the quantitation of pesticides by the proposed SPE-HPLC-DAD method

	HPLC																					
	202 nm				212 nm				222 nm				240 nm				254 nm					
Pesticide	LOD, µg/mL	LOQ, µg/mL	Range, µg/mL	r	LOD, µg/mL	LOQ, µg/mL	Range, µg/mL	r	LOD, µg/mL	LOQ, µg/mL	Range, µg/mL	r	LOD, µg/mL	LOQ, µg/mL	Range, µg/mL	r	LOD, µg/mL	LOQ, µg/mL	Range, µg/mL	r
Atrazine	0.17	0.52	0.3–50	0.9999	0.14	0.43	0.15–50	1.0000	0.13	0.39	0.1–50	1.0000	0.15	0.46	0.3–50	1.0000	0.21	0.63	1.2–50	1.000
Clofentezine	0.34	1.02	0.5–15	0.9996	0.36	1.08	0.5–15	0.9996	0.34	1.04	0.5–15	0.9996	0.35	1.07	0.5–15	0.9996	0.36	1.09	0.5–15	0.9996
Chlorfenvinphos	0.03	0.08	0.15–33	1.0000	0.02	0.07	0.2–33	1.0000	0.02	0.06	0.6–33	1.0000	0.02	0.07	0.6–33	1.0000	0.04	0.11	0.6–33	1.0000
Hexaflumuron	0.09	0.28	0.15–50	1.0000	0.09	0.28	0.15–3.6	0.9988	0.10	0.29	0.3–50	1.0000	0.11	0.32	0.6–50	1.0000	0.09	0.28	0.3–50	1.0000
Terbuthylazine	0.03	0.09	0.6–50	1.0000	0.04	0.13	0.1–50	1.0000	0.02	0.06	0.1–50	1.0000	0.03	0.08	0.3–50	1.0000	0.05	0.14	1.2–50	1.0000
Lenacyl	0.06	0.17	0.3–50	1.0000	0.05	0.15	0.3–50	1.0000	0.06	0.19	0.3–50	1.0000	0.08	0.24	1.2–50	1.0000	0.07	0.22	0.6–50	1.0000
Neburon	0.08	0.24	0.15–50	1.0000	0.07	0.22	0.1–50	1.0000	0.10	0.30	0.3–50	1.0000	0.08	0.24	0.3–50	1.0000	0.08	0.24	0.15–50	1.0000
Bitertanol	0.06	0.19	0.3–50	1.0000	0.07	0.23	0.3–50	1.0000	0.22	0.65	1.8–50	1.0000	0.08	0.25	1.2–50	1.0000	0.06	0.18	0.6–50	1.0000
Metamitron	0.24	0.74	0.1–50	0.9998	0.26	0.77	0.3–50	0.9999	0.25	0.75	0.3–50	0.9999	0.28	0.86	1.2–50	0.9999	0.45	1.37	2.4–50	0.9999

Bedford, MA). They were brought to the laboratory the same day of sampling and were stored at 4°C in the dark until SPE, which was performed within 7 days or less after sampling. Dates of acquisition were April, May, June, July, and August of 2007.

(**b**) *SPE*.—For SPE assays, each cartridge was conditioned with 3 × 2 mL dichloromethane, 3 × 2 mL methanol, and 3 × 2 mL water. After being loaded with the water samples (1 L, flow rate 10 mL/min, pressure 75 mm Hg), the SPE column was washed with methanol–H_2O (5 + 95, v/v), followed by vacuum drying for 1 min, and then eluted with 5 mL methanol, followed by vacuum drying for 10 min, and then eluted with 5 mL dichloromethane. Next, dichloromethane eluates were evaporated to dryness, redissolved in 1 mL dichloromethane, and analyzed by TLC-DAD.

(**c**) *TLC*.—The plates were developed for a distance of 9 cm in a horizontal, Teflon Dzido-Soczewiński (DS) chamber. The plates were developed with ethyl acetate–*n*-heptane (20 + 80, v/v), (30 + 70, v/v), (40 + 60, v/v), or (70 + 30, v/v) as mobile phases. Next, the plates were scanned in the wavelength (λ) range of 200 to 600 nm with average optical resolution better than 2.0 nm (5). Fifty identical optical fibers transport light of different wavelengths from a deuterium lamp to the TLC plate and then to the DAD. The TLC plate is placed horizontally on a mechanical stage that can be moved by 2 motors from Micropack (Stuttgart, Germany). The linear slide system works at constant speed during the reflection measurements (5).

(**d**) *HPLC*.—After SPE, methanol eluates were analyzed at 22 ± 1°C using an Agilent Technologies 1200 Series chromatograph equipped with a quaternary gradient pump with degasser set at a flow rate of 1 mL/min, and a DAD. Methanol eluates were injected with a Rheodyne 20 µL injector. The HPLC apparatus was equipped with a ZORBAX Eclipse XDB-C18, 150 × 4.6 mm column, particle size (d_p) = 5 µm (Agilent Technologies). The gradient applied was: start 30% B; 30 min linear to 76% B; 35 min 100% B; 35–45 min isocratic 100% B (A = H_2O; B = acetonitrile).

(**e**) *Calibration procedure (TLC)*.—The calibration procedure was performed based on the peak areas of standards of pesticides prepared as methanol solutions at 9 concentration levels (0.1–1.5 µg/spot) with triplicate automated application as 1 cm bands on the silica gel TLC plates. The plates were developed with ethyl acetate–*n*-heptane (20 + 80 or 30 + 70, v/v) mobile phase.

(**f**) *Calibration procedure (HPLC)*.—The calibration procedure was performed based on the peak areas of standards of pesticides prepared as methanol solutions at 9 concentration levels (0.1–50 µg/mL) with triplicate injection onto the Eclipse XDB-C18 column.

(**g**) *Validation of the TLC and HPLC methods*.—The method was validated for precision, repeatability, and accuracy (Table 1). Instrumental precision was checked by

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Table 3. Average recovery (%) on 4 different cartridges by the proposed SPE-HPLC-DAD method

Pesticide	Octadecyl (C18)	C18 Polar Plus	Cyanopropyl (CN)	C18/SDB-1
Atrazine	95.6	96.9	7.2	81.3
Bitertanol	104.1	103.3	105.0	80.6
Chlorfenvinphos	99.4	97.0	86.6	89.0
Hexaflumuron	80.0	81.0	63.0	65.4
Clofentezine	117.0	134.2	59.0	18.9
Flufenoxuron	43.4	55.8	54.3	15.4
Lenacyl	74.1	86.4	5.4	72.0
Metamitron	98.0	90.5	1.3	0
Neburon	91.6	89.2	59.4	76.7
Terbuthylazine	104.1	108.1	45.0	101.8

repeated scanning of all pesticides (400 µg/L) 5 times and was expressed as coefficient of variation (CV). The repeatability of the method was confirmed by analyzing a 400 µg/L of standard solution of all pesticides after application on the TLC plate [number of determinations (n) = 5] and was expressed as CV. Limit of detection (LOD) and limit of quantitation (LOQ) were also calculated according to the respective formulas:

$$\text{LOD} = 3.3\ (\text{SD/S}) \text{ and } \text{LOQ} = 10\ (\text{SD/S})$$

where SD = standard deviation of the response and S = slope of the calibration graph. The HPLC method was also validated (Table 2). Accuracy of the method was tested by performing recovery studies at 3 different levels. The average recoveries were calculated (Table 3).

Results and Discussion

When analytes are present at low concentrations in complex samples, e.g., environmental samples, extraction and concentration procedures must precede the chromatographic step of the analysis. TLC can be used as a pilot technique for estimation of the SPE elution profiles of pesticides (10). If the analyzed substances represent different classes, it is also possible to use SPE not only to preconcentrate, but also to partially fractionate the complex mixtures. Large volumes of water can be extracted with little effort and columns can be eluted with small quantities of organic solvent. Eluates are ready for further analysis, properly chosen according to the nature of analyzed compounds and a chromatographic system applied. Fractionation of complex mixtures of analytes by SPE combined with HPLC-DAD and TLC-DAD for determination of pesticides in water is described.

Analytes were eluted by means of methanol and then dichloromethane. Methanol eluates were analyzed by HPLC-DAD (Figure 1). Analytes were identified on the basis of their retention times and by comparison between the UV spectrum of the reference compound in the library and the UV spectrum of the detected peak in the sample (Figure 2). A match equal to or higher than 990 was fixed to confirm identification between both spectra for all of the pesticides determined (Figure 3).

Dichloromethane eluates were analyzed by TLC-DAD (Figure 4). The identities of the bands of analytes in the water sample chromatograms were confirmed by overlaying their UV absorption spectra with those of the standards of these compounds (Figure 5). A peak-purity index of 1 indicated that the compared spectra were identical. A least-squares fit value of the spectrum from a fortified sample of water and a spectrum from clofentezine standard are shown in Figure 6.

The main purpose of the research was to find a combination of sorbents for the SPE method that would permit the determination of many classes of pesticides.

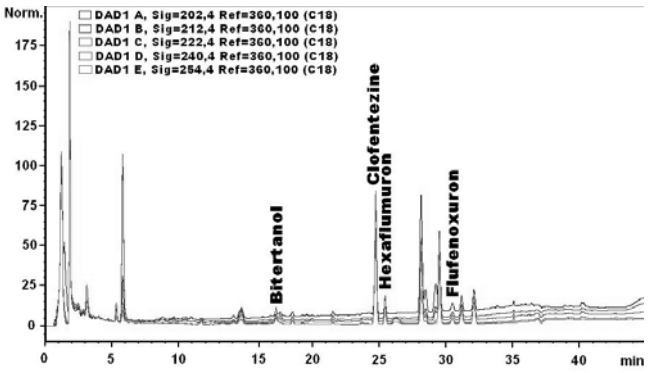

Figure 1. Column liquid chromatogram of water sample obtained from the Wieprz-Krzna Canal (July 2007) showing 4 detected and quantified pesticides.

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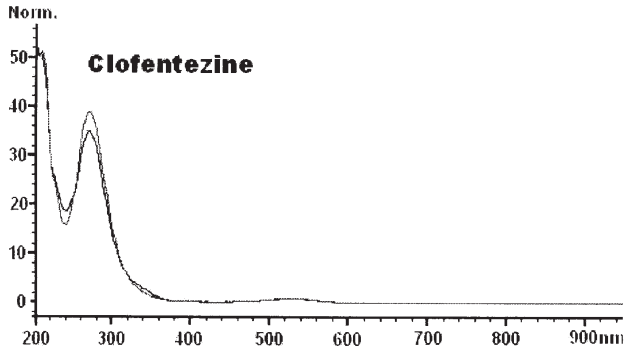

Figure 2. Comparison of UV spectrum of clofentezine found in surface water with UV spectrum of pesticide's standard from the library.

Pesticides were determined on 4 types of SPE sorbents: C18, C18 Polar Plus, CN, and the combination of them C18/SDB-1. Pesticides from water were extracted, concentrated, and fractionated by use of 2 different organic solvents, and the extraction efficiency was checked by recovery experiments (Table 3). Recovery rates were between 74 and 117% for both C18 and C18 Polar Plus extraction materials except for flufenoxuron (43 and 55% on C18 and C18 Polar Plus sorbents, respectively). The lowest recoveries were obtained on cartridges with cyanopropyl, especially for metamitron, lenacyl, and atrazine (1, 5, and 7%, respectively).

The recoveries obtained with connected sorbents, C18 and SDB-1 (C18/SDB-1), after HPLC and TLC are presented in Table 4. Extraction with C18/SDB-1 cartridges led to a very satisfactory sum of recoveries, between 76 and 107%, with a CV of ±0.8–3.8%. For flufenoxuron, the sum of recoveries was lower. The SDB-1 material is highly linked polystyrene-divinylbenzene-ethylvinylbenzene and is strongly recommended for extraction of very polar analytes such as organophosphorous pesticides.

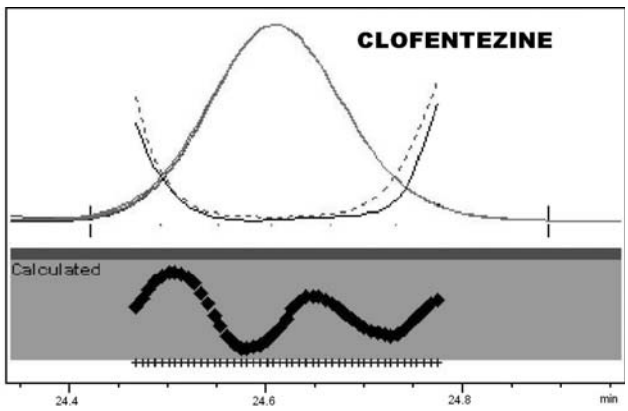

Figure 3. Purity of the peak of clofentezine from the Wieprz-Krzna Canal (July 2007).

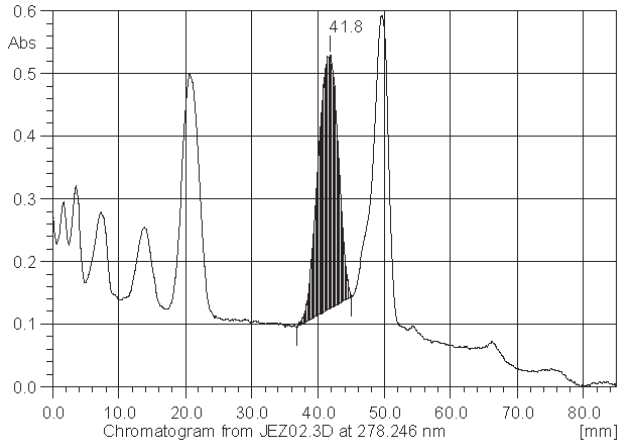

Figure 4. Chromatogram obtained for a fortified water sample after SPE and TLC-DAD at the optimal wavelength for clofentezine (278.246 nm).

The efficiency of the SPE procedure was evaluated using real water samples from Wieprz-Krzna Canal in the Łęczyńsko-Włodawskie Lake District (southeastern Poland). Results are presented in Table 5.

Conclusions

HPLC-DAD or/and TLC-DAD methods, after SPE with 4 different cartridges, are proposed. The methods enable monitoring of popular pesticides of different classes—ureas, triazines, amides, and others—that are widely used in the

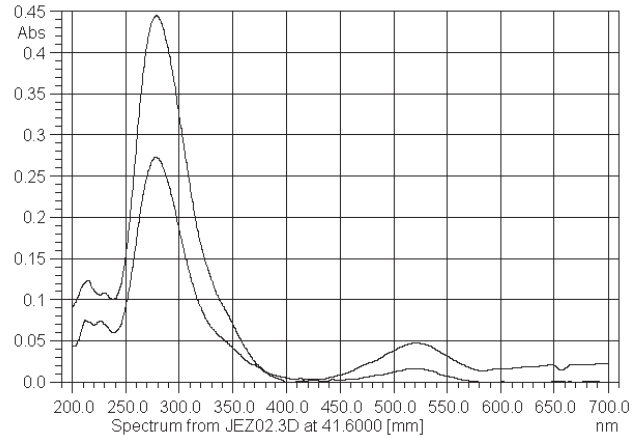

Figure 5. Comparison of the UV spectrum of clofentezine standard with the in situ spectrum of a fortified water sample after SPE and TLC-DAD [purity index (Pearson's r) *P* = 0.9959].

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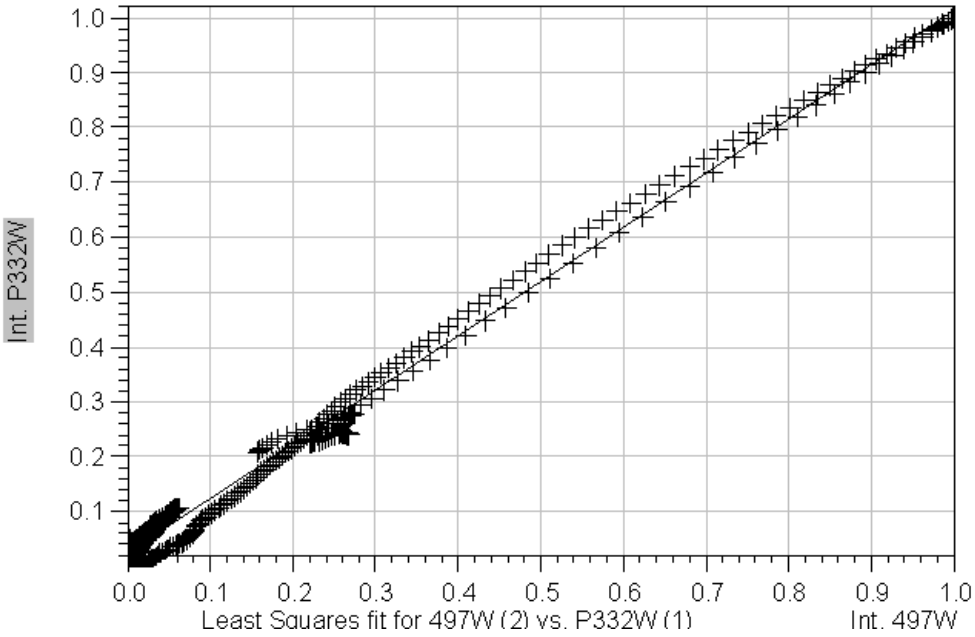

Figure 6. Least-squares fit value (obtained by cross-correlation) of a spectrum from a fortified sample of water and a spectrum of clofentezine standard.

Table 4. Recovery study of pesticides by the proposed SPE-HPLC-DAD and HPTLC-DAD methods

		Average recovery, %, C18/SDB		
Pesticide	C[a], μg/L	HPLC	TLC	HPLC+TLC
Phenylurea herbicides				
Neburon	400	λ = 240 nm, 79	λ = 249.4 nm, 6	85
Flufenoxuron	400	λ = 254 nm, 19	λ = 268.4 nm, 36	55
Organophosphate insecticides				
Chlorfenvinphos	400	λ = 244 nm, 89	λ = 246.9 nm, 6	95
Lenacyl	400	λ = 254 nm, 72	λ = 273.3 nm, 4	76
Pesticides representing other classes				
Clofentezine	400	λ = 300 nm, 5	λ = 278.3 nm, 102	107

[a] C = Concentration.

Łęczyńsko-Włodawskie Lake District in Poland and other locations worldwide.

Chlorfenvinphos, hexaflumuron, and clofentezine were detected with the highest frequency in water samples. Clofentezine was detected in the highest amounts, in the range of 1.39–5.57 μg/L, with the exception of one sample (45.1 μg/L). Clofentezine was also detected in methylene chloride eluates of samples determined by SPE and TLC-DAD in amounts below the level of quantitation and above the level of detection.

The TLC-DAD scanner enables analysis of each compound at its optimum wavelength, thus resulting in optimum sensitivity for detection of each component. The TLC-DAD scanner enables a comparison of the UV spectrum of a compound with that of a standard in the library of spectra.

Software is available that gives the user access to all the common instrument functions used in HPLC-DAD, for example, peak purity, resolution, and identification via spectral library match.

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Table 5. Analysis of pesticides by the proposed SPE-HPLC-DAD method

			Concentration, μg/L				
Sorbent (SPE)	Date of aquisition	Pesticide	λ = 202 nm	λ = 212 nm	λ = 222 nm	λ = 240 nm	λ = 254 nm
C18 Polar Plus	May 2007	Atrazine		0.90	0.77		
		Chlorfenvinphos	1.55	1.56	1.59		
	July 2007	Clofentezine	1.39	1.44	1.41		1.45
		Hexaflumuron	3.01	3.07	3.06	3.26	2.95
		Terbuthylazine		0.69	0.79		
C18	May 2007	Atrazine		1.18	1.27		
		Chlorfenvinphos	2.35	2.32	2.29		
		Metamitron	0.71	0.76			
	July 2007	Bitertanol	2.32	2.22			2.40
		Clofentezine	34.13	32.39	33.70	45.10	43.18
		Hexaflumuron	5.57	5.55	5.54	5.57	5.55
		Flufenoxuron	3.16	3.25	5.30	4.32	4.06
CN	July 2007	Clofentezine	0.60				
		Hexaflumuron	1.39	1.45	1.43		1.44
	August 2007	Chlorfenvinphos	1.94	1.66			
C18/SDB	August 2007	Lenacyl	1.77	1.34	1.47		
		Neburon	1.21				

References

(1) Tuzimski, T., & Soczewinski, E. (2004) *Chromatographia* **59**, 121–128

(2) Tuzimski, T. (2005) *J. Liq. Chromatogr. Relat. Technol.* **28**, 463–476

(3) Spangenberg, B., & Klein, K.F. (2001) in *Planar Chromatography, New Milestones in TLC*, Sz. Nyiredy (Ed.), Research Institute for Medicinal Plants, Budakalász, Hungary, pp 15–21

(4) Spangenberg, B., & Klein, K.-F. (2000) *J. Chromatogr. A* **898**, 265–269

(5) Spangenberg, B., Lorenz, K., & Nasterlack, S. (2003) *J. Planar Chromatogr.-Mod. TLC* **16**, 331–337

(6) Spangenberg, B., Seigel, A., Kempf, J., & Weinmann, W. (2005) in *Planar Chromatography, Milestones in Instrumental TLC*, Sz. Nyiredy (Ed.), Research Institute for Medicinal Plants, Budakalász, Hungary, pp 3–16

(7) Ahrens, B., Blankenhorn, D., & Spangenberg, B. (2002) *J. Chromatogr. B* **772**, 11–18

(8) Tuzimski, T. (2005) *J. Planar Chromatogr.-Mod. TLC* **18**, 419–422

(9) Tuzimski, T. (2008) *J. Planar Chromatogr.-Mod. TLC* **21**, 89–96

(10) Tuzimski, T., & Soczewiński, E. (2002) *Retention and Selectivity of Liquid-Solid Chromatographic Systems for the Analysis of Pesticides* (Retention database of approximately 100 pesticides) in *Problems of Science, Teaching and Therapy,* Medical University of Lublin, Poland, No. 12, 219 pp (limited number available on request by e-mail: tomasz.tuzimski@am.lublin.pl)

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