Determination of Selected Herbicides and Phenols in Water and Soils by Solid-Phase Extraction and High-Performance Liquid Chromatography

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Abstract

A high-performance liquid chromatography procedure or the determination of the herbicides simazine, propazine, bromacil, metoxuron, and hexazinone is elaborated. Stationary phases RP_8 and RP_{18} and mixtures of methanol–water (2:1 and 1:1, v/v) as a mobile phase are applied for this purpose. The conditions for solid-phase extraction are established, allowing the separation of phenols and herbicides in their mixtures and the extraction of phenols (from river and coke plant water) and herbicides (from the soil samples).

Introduction

The problem of considerable contamination of the environment with phenol, its derivatives, and pesticides still requires the development of quick and simple methods for the separation and determination of these compounds. Most often, high-performance liquid chromatograhy (HPLC) is applied for this purpose. Analysis of phenols by HPLC has been carried out using C_{18} stationary phases and gradient elution with the following eluants: methanol and water (1), phosphate buffer with acetonitrile (2), or acetic acid with acetonitrile and water (3). These methods allow the determination of phenol in the presence of other aromatic compounds and chlorophenols in their mixtures. Chlorophenols were separated with a gradient system of 0.005M KH_2PO_4–methanol from 20 to 60% (v/v) on a Hypersil column (4). Phenols were also determined in the presence of aromatic amines (5,6). Hydroxy-*s*-triazines were analyzed in a mixture of acetonitrile and water using isocratic elution (acetonitrile –KH_2PO_4, 3:17, v/v) (7) and gradient elution (up to 70% of acetonitrile for 32 min) (8). Simultaneously, bromacil, simazine, and atrazine were determined in drinking water by Froehlich and Meier (9) on an octadecyl siloxane (ODS) column in a 40% solution of acetonitrile in water. Bromacil was also analyzed on octadecyl columns (10) using acetate buffer (pH 5.8) as a mobile phase, were as hexazinone was determined in samples of ground water with an acetonitrile and water (5:5, v/v) mobile phase (11). In the literature, there are papers dealing with the analysis of phenols and certain herbicides separately, but there is a lack of information on allowing the separation and determination phenols and herbicides in the presence of each other. In a previous paper (12), the authors developed HPLC chromatographic methods allowing the separation of phenol and its methyl and chloro derivatives on C_8 and C_{18} stationary phases, and in another paper (13), stationary phases containing diol, amino, and cyano groups were used to separate phenol and its methyl and chloro derivatives. In this work, chromatographic methods were developed to analyze herbicides in the presence of phenols.

Experimental

Reagents and apparatus

Standard water solutions of phenol; 2-, 3-, and 4-methylphenol; 2,3- and 3,4-dimethylphenol; 2,4-, 2,5-, 2,6-, and 3,4-dichlorophenol; 2,4,5-trichlorophenol; pentachlorophenol (analytically pure, POCh, Gliwice, Poland); 2-chloro-4, 6-bis(ethylamino)-1,3,5-triazine (simazine); 2-chloro-4, 6-bis-(isopropylamino)-1,3,5-triazine (propazine); 3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione

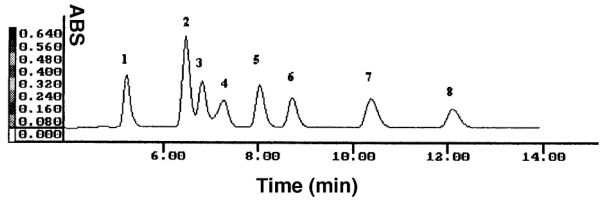

Figure 1. Chromatogram of a mixture of methyl- and chloro- derivatives of phenol on the RP_8 column after preconcentration octadecylsilane bed. The mobile phase was methanol–water (2:1, v/v). Peaks: 1, phenol; 2, 3-, and 4-methylphenol; 3, 2-methylphenol; 4, 2,6-dichlorophenol; 5, 3,4-dichlorophenol; 6, 2,3-dimethylphenol; 7, 2,5-dichlorophenol; 8, 2,4-dichlorophenol.

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Table I. Retention Parameters of the Separation of Herbicides

Column	Eluent (v/v)	Flow rate (mL/min)	Retention time (min)				
			Metoxuron	Bromacil	Simazine	Hexazinone	Propazine
RP18 (7 µm)	methanol–water 3:1	1.0	3.02	3.30	3.48	3.94	4.53
	methanol–water 1:1	1.0	6.96	8.45	9.52	12.99	23.80
	methanol–water 2:1	0.8	4.64	5.36	5.23	6.35	9.10
	methanol–water 2:1	1.0	3.79	4.32	4.48	5.60	7.24
RP18 (4 µm)	methanol–water 2:1	1.0	3.84	4.80	4.65	5.57	7.56
RP8 (7 µm)	methanol–water 2:1	0.8	4.88	5.49	5.44	6.45	9.34
	methanol–water 2:1	1.0	3.92	4.43	4.99	5.20	7.74
	methanol–water 1:1	1.0	7.09	8.67	10.96	11.07	24.08

Table II. Recovery Test on Synthetic Contaminated Water According to Cycle 1

	4 × 2 µg/mL added			4 × 5 µg/mL added			4 × 10 µg/mL added			4 × 20 µg/mL added		
	Found (µg/mL)	SD*	Recovery (%)	Found (µg/mL)	SD*	Recovery (%)	Found (µg/mL)	SD*	Recovery (%)	Found (µg/mL)	SD*	Recovery (%)
10 µg/mL herbicides added to all samples												
3-methylphenol	1.97	0.12	98.5	4.56	0.16	91.2	9.43	0.24	94.3	19.2	0.09	96.0
4-methylphenol	1.89	0.23	94.5	4.42	0.32	88.4	9.25	0.14	92.5	18.8	0.12	94.0
3,4-dimethylphenol	2.02	0.04	101.0	5.03	0.08	100.6	9.90	0.07	99.0	19.7	0.04	98.5
2,5-dichlorophenol	2.02	0.06	101.0	5.12	0.12	102.4	10.10	0.09	101.0	20.9	0.08	104.5
Mean recovery (%)			98.8			95.7			96.7			98.3
20 µg/mL herbicides added to all samples												
3-methylphenol	1.95	0.13	97.5	4.53	0.26	90.6	9.25	0.12	92.5	18.90	0.32	94.5
4-methylphenol	1.85	0.15	92.5	4.43	0.18	88.6	9.05	0.18	90.5	18.70	0.36	93.5
3,4-dimethylphenol	1.92	0.09	96.0	4.98	0.02	99.6	9.60	0.10	96.0	19.30	0.22	96.5
2,5-dichlorophenol	1.98	0.04	99.0	5.04	0.04	100.8	9.90	0.08	99.0	20.30	0.19	101.5
Mean recovery (%)			96.3			94.9			94.5			96.5
20 µg/mL phenols added to all samples												
Simazine				4.84	0.12	96.8	9.83	0.16	98.3	19.88	0.14	99.4
Propazine				4.88	0.09	97.5	9.88	0.12	98.8	20.16	0.15	100.8
Metoxuron				4.99	0.02	99.9	10.12	0.08	101.2	20.46	0.24	102.3
Bromacil				5.09	0.08	101.8	10.32	0.22	103.2	20.90	0.22	104.5
Mean recovery (%)				99.0				100.4				101.8
40 µg/mL phenols added to all samples												
Simazine				4.73	0.21	94.6	9.64	0.21	96.4	19.78	0.09	98.9
Propazine				4.79	0.18	95.8	9.79	0.19	97.9	19.68	0.13	98.4
Metoxuron				5.01	0.01	100.2	10.14	0.09	101.4	20.21	0.07	101.8
Bromacil				5.10	0.06	102.0	10.27	0.09	102.7	20.72	0.08	103.6
Mean recovery (%)				98.2				99.6				100.7

* SD, standard deviation (n = 5).
† Herbicides: simazine, propazine, metoxuron, bromacil.
‡ Phenols: 3-methylphenol, 4-methylphenol, 3,4-dimethylphenol, 2,5-dichlorophenol.

(hexazinone); 5-bromo-3-sec-butyl 6-methyluracil (bromacil), and 3-(3-chloro-4-methoxyphenyl)-1,1-dimethylurea (metoxuron) (> 99.3%, Promochem, Warsaw, Poland) were all 0.1 mg/mL.

HPLC

A Merck (Darmstadt, Germany) Hitachi L 4500 A chromatograph with a diode-array detector (DAD) was used. Measurements were taken at ambient temperature. The values were collected from the computer integrator with 0.01-min accuracy for retention time and 0.0001 of absorbance scale. The following columns were used: LiChroSorb and Supersphere RP_8 (7 µm) and RP_{18} (4 and 7 µm) produced by E. Merck (Darmstadt, Germany). Columns were 250 × 4 mm; injections were 20 µL.

The mixtures of methanol–water (1:1 and 2:1, v/v) at a flow speed of 0.8 and 1.0 mL/min were applied as a mobile phase. All solvents were produced by E. Merck.

SPE

A J.T. Baker set (Phillipsburg, NJ) was used for the preliminary treatment of samples. The analyzed compounds were extracted using the Bakerbond SPE octadecylalkylsilane (500 mg packing), phenyl (500 mg packing), octyl (500 mg packing), and sulfonic (500 mg packing) columns. Reservoirs were used.

Bakerbond SPE columns

Preconcentration of phenols

The octadecylalkylsilane, phenyl, or octadecylalkylsilane POLAR PLUS beds were activated by passing methanol, acetonitrile, and water (in 5 mL portions) successively through them twice.

Preconcentration of herbicides

The sulfonic columns were activated with a mixture of acetic acid–water (1:99, v/v), and octadecylalkylsilane columns were conditioned successively with methanol and water passing through the mentioned bed solvents twice (in 3 mL portions). The analyzed compounds were extracted using solvents produced by J.T. Baker.

Procedure

Sorption of phenols on a sorbent bed

Water samples. Water (100 mL) containing 2–200 µg of phenols was acidified to pH ~2 (1M HNO_3). Then, 0.2 g/mL of solid NaCl was added to the solution, and samples were introduced onto the

Table III. Recovery Test on Synthetic Contaminated Water According to Cycle 2

	4 × 2 µg/mL added			4 × 5 µg/mL added			4 × 10 µg/mL added			4 × 20 µg/mL added		
	Found (µg/mL)	SD*	Recovery (%)	Found (µg/mL)	SD*	Recovery (%)	Found (µg/mL)	SD*	Recovery (%)	Found (µg/mL)	SD*	Recovery (%)
10 µg/mL herbicides added to all samples												
Phenol	1.97	0.04	98.3	4.93	0.06	98.6	9.76	0.14	97.6	19.48	0.22	97.4
2-Methylphenol	1.95	0.06	97.4	4.86	0.12	97.2	9.68	0.24	96.8	19.28	0.26	96.4
2,3-Dimethylphenol	2.04	0.02	102.1	5.09	0.08	101.8	10.08	0.12	100.8	20.08	0.14	100.4
2,4-Dichlorophenol	2.03	0.03	101.4	5.06	0.06	101.2	10.06	0.09	100.6	20.04	0.08	100.2
Mean recovery (%)			99.8			99.7			99.0			98.6
20 µg/mL herbicides added to all samples												
Phenol	1.97	0.04	98.4	4.91	0.02	98.2	9.72	0.22	97.2	19.56	0.28	97.8
2-Methylphenol	1.95	0.04	97.3	4.86	0.05	97.2	9.66	0.28	96.6	19.30	0.35	96.5
2,3-Dimethylphenol	2.03	0.03	101.5	5.04	0.04	100.8	9.98	0.10	99.8	19.88	0.11	99.4
2,4-Dichlorophenol	2.01	0.02	100.4	5.00	0.01	100.0	9.92	0.08	99.2	19.72	0.14	98.6
Mean recovery (%)				99.4			99.1		98.2			98.1
20 µg/mL phenols added to all samples												
Simazine				4.67	0.24	93.4	9.55	0.18	95.5	19.74	0.18	98.7
Propazine				4.66	0.26	93.2	9.54	0.14	95.1	19.60	0.22	98.0
Metoxuron				4.94	0.12	98.7	10.02	0.04	100.2	20.36	0.21	101.8
Bromacil				4.96	0.08	99.1	10.07	0.08	100.7	20.48	0.26	102.4
Mean recovery (%)				96.1					97.8			100.2
40 µg/mL phenols added to all samples												
Simazine				4.68	0.24	93.8	9.59	0.16	95.9	19.68	0.16	98.4
Propazine				4.67	0.24	93.4	9.54	0.08	95.4	19.58	0.24	97.9
Metoxuron				4.92	0.15	98.4	9.97	0.04	99.7	20.08	0.09	100.4
Bromacil				4.95	0.04	98.9	10.0	0.02	100.0	20.36	0.18	101.8
Mean recovery (%)				96.1			97.8			99.6		

* SD, standard deviation (n = 5).
† Herbicides: simazine, propazine, metoxuron, bromacil.
‡ Phenols: phenol, 2-methylphenol, 2,3-dimethylphenol, 2,4-dichlorophenol.

preliminary prepared columns (octadecylsilane, phenyl bed). The pressure was kept at 85–90 kPa. Phenols adsorbed on a column bed were rinsed with 10 mL of 0.01M HNO_3. After drying the column for 2 min (diminished pressure), bed phenols were eluted with two portions of acetonitrile or methanol (2.5 mL each) and diluted to 10 mL.

Soil samples. To 100 g of soil, 2 mL of standard solutions of phenols (0.2 mg/mL) were added, and the sample was extracted with chloroform (2 × 25 mL) and filtered. After evaporating the solvent, the residue was dissolved in 25 mL of water. The obtained solution was introduced onto a conditioned octadecylsilane bed, and herbicides were adsorbed according to the procedure in the previous paragraph.

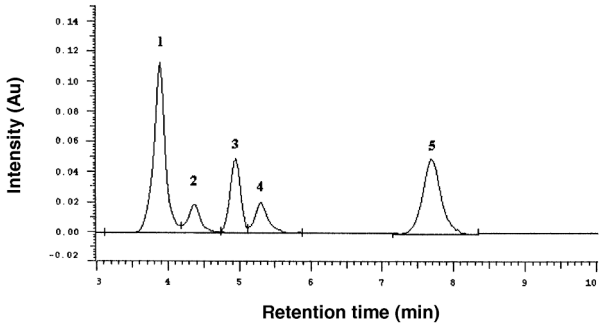

Figure 2. Chromatogram of a mixture of herbicides on the RP_8 column using methanol–water (2:1, v/v) after preconcetration octadecylsilane bed. Peaks: 1, metoxuron; 2, bromacil; 3, simazine; 4, hexazinone; 5, propazine.

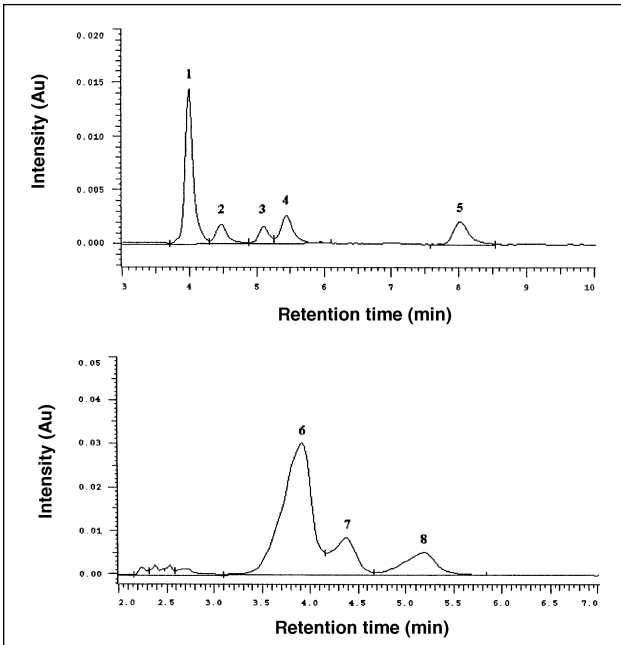

Figure 3. Chromatogram (A) of a mixture of herbicides separated from phenols on the octadecylsilane bed SPE: RP_8 column, methanol–water (2:1, v/v) mobile phase. Peaks: 1, metoxuron. t_R = 4.00 min; 2, bromacil, t_R = 4.48 min; 3, simazine, t_R = 5.09 min; 4, hexazinone, t_R = 5.44 min; 5, propazine, t_R = 8.02 min. Chromatogram (B) of a mixture of phenols separated from herbicides on the octadecylsilane bed SPE: RP_8 column, methanol–water mobile phase (2:1, v/v). Peaks: 6, 3- and 4-methylphenol, t_R = 3.92 min; 7, 3,4-dimethylphenol, t_R = 4.37 min; 8, 2,5-dichlorophenol, t_R = 5.17 min.

Sorption of herbicides on a sorbent bed

Water samples. Samples (50 mL) of water containing 20–200 µg of investigated herbicides were introduced onto an activated column (octadecylsilane or sulfonic bed of Bakerbond SPE) bed. The applied pressure was approximately 85–90 kPa. Herbicides adsorbed on an octadecylsilane bed were rinsed with 5 mL of water, and then the bed was dried under diminished pressure for 3 min. Next, the herbicides were eluted with methanol (2 × 3 mL) and diluted to 10 mL. Herbicides sorbed on a sulfonic bed were rinsed successively with 3 mL of the mixture of acetic acid–water (1:99, v/v), 2 mL of acetonitrile, 3 mL of water, and 2 mL of 0.1M K_2HPO_4. After drying the column bed for 20 s under diminished pressure, adsorbed herbicides were eluted with three portions (2 mL each) of the mixture of acetonitrile–0.1M K_2HPO_4 (1:1,v/v) and filled with the same solution to 10 mL.

Soil samples: octadecylsilane column. To 100 g of soil, 2 mL of the mixture of herbicides simazine, propazine, bromacil, and metoxuron (0.2 mg/mL) was added, and the sample was extracted

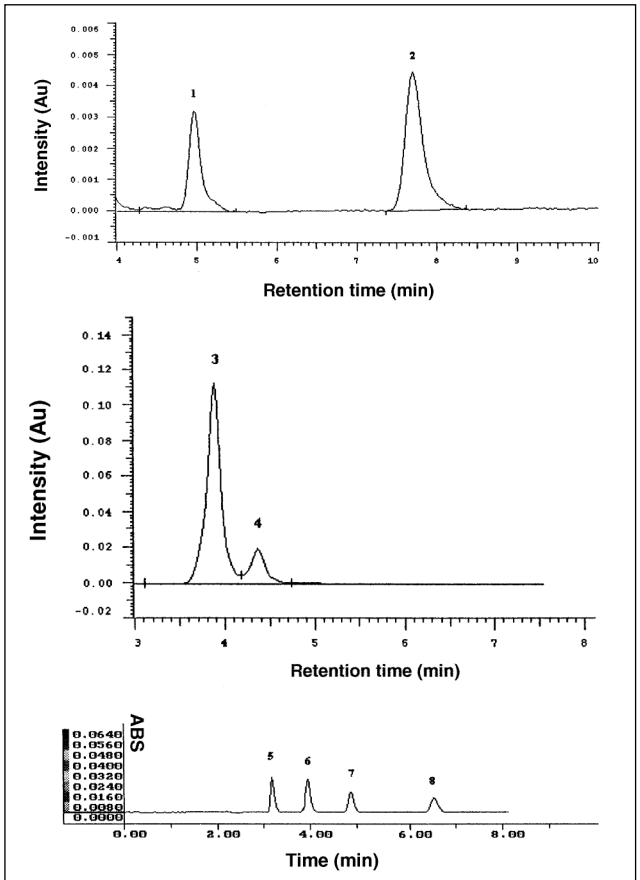

Figure 4. Chromatogram (A) of a mixture of herbicides on the RP_8 using methanol–water (2:1, v/v). The solution was obtained after elution from sulfonic bed SPE with the mixture of acetonitrile–0.1M K_2HPO_4 (1:1, v/v). Peaks: 1, simazine, t_R = 4.96 min; 2, propazine, t_R = 7.73 min. Chromatogram (B) of a mixture of herbicides on the RP_8 using methanol–water (2:1, v/v) of the filtrate from a sulfonic bed and after elution from octadecylsilane bed SPE. Peaks: 3, metoxuron, t_R = 3.89 min; 4, bromacil, t_R = 4.37 min. Chromatogram (C) of a mixture of phenols separated from herbicides on the sulfonic and octadecylsilane bed SPE of the RP_8 sing methanol–water (2:1, v/v). Peaks: 5, phenol, t_R = 3.16 min; 6, 2-methylphenol, t_R = 3.91 min; 7, 2,3-dimethylphenol, t_R = 4.84 min; 8, 2,4-dichlorophenol, t_R = 6.65 min.

with chloroform (2 × 25 mL) and filtered. After evaporating the solvent, the residue was dissolved in 25 mL of water. The obtained solution was introduced onto a conditioned octadecylsilane bed, and herbicides were adsorbed according to the procedure in the previous paragraph.

Soil samples: sulfonic column. To 100 g of soil, 2 mL of standard solutions of simazine, propazine, bromacil, and metoxuron (0.2 mg/mL) was added, and the sample was mixed thoroughly. Next, 200 mL of the mixture of acetonitrile–water (9:1, v/v) was added, the extraction was carried out for 5 min, and then the precipitate was filtered. The sample was then introduced to a conditioned sulfonic bed and followed the procedure above.

Separation of phenols from herbicides by SPE

Cycle 1. Samples of water containing phenols and herbicides were introduced to the conditioned octadecylsilane bed. Herbicides were adsorbed on the column bed, while phenols remained in the filtrate.

Adsorbed herbicides were eluted from the bed with methanol, and then chromatographic analysis was carried out.

The filtrate containing phenols was acidified to pH 2, solid NaCl was added, and then the mixture was once again introduced to the octadecylsilane bed.

Adsorbed phenols were eluted with acetonitrile and analyzed chromatographically.

Cycle 2. Samples of water containing phenols and herbicides were introduced to a sulfonic bed, where herbicides of a triazine group were adsorbed while other herbicides and phenols moved to the filtrate.

Adsorbed herbicides were eluted by the mixture of acetonitrile–0.1M K_2HPO_4 (1:1, v/v), and chromatographic analysis was carried out.

The filtrate (phenols–metoxuron–bromacil) was introduced to the conditioned octadecylsilane bed. Herbicides adsorbed on this bed, whereas phenols ran through the column.

Adsorbed herbicides were eluted from the bed with methanol, and then chromatographic analysis was carried out.

Filtrate containing phenols was acidified to pH 2, solid NaCl was added, and then it was introduced onto the octadecylsilane bed.

Phenols adsorbed on a bed were eluted with acetonitrile, and the chromatographic analysis was carried out.

Extraction of phenols and herbicides with environmental samples

The analysis of environmental samples was preceded with sample preparation according to cycle 1 or 2.

Table IV. Recovery Test on Synthetic Contaminated Soil According to Cycle 1

	4 × 2 µg/mL added			4 × 5 µg/mL added			4 × 10 µg/mL added			4 × 20 µg/mL added		
	Found (µg/mL)	SD*	Recovery (%)	Found (µg/mL)	SD*	Recovery (%)	Found (µg/mL)	SD*	Recovery (%)	Found (µg/mL)	SD*	Recovery (%)
5 µg herbicides added to all samples												
3-Methylphenol	1.86	0.11	93.0	5.00	0.04	100.0	10.04	0.06	100.4	20.02	0.02	100.1
4-Methylphenol	1.98	0.04	99.0	4.93	0.09	98.6	10.07	0.08	100.7	20.09	0.10	100.5
3,4-Dimethylphenol	2.11	0.07	105.5	5.02	0.02	100.4	10.02	0.04	100.2	20.01	0.02	100.1
2,5-Dichlorophenol	2.09	0.10	104.5	5.13	0.16	102.6	10.02	0.02	100.2	20.04	0.04	100.2
Mean recovery (%)			100.0			100.4			100.4			100.2
20 µg herbicides added to all samples												
3-Methylphenol	2.08	0.10	104.0	4.99	0.06	99.8	10.05	0.06	100.5	20.02	0.01	100.1
4-Methylphenol	2.21	0.05	110.5	5.11	0.11	102.2	10.05	0.05	100.5	20.02	0.02	100.1
3,4-Dimethylphenol	2.14	0.02	107.0	5.18	0.12	103.6	10.09	0.10	100.9	20.08	0.09	100.4
2,5-Dichlorophenol	2.18	0.12	109.0	5.08	0.08	101.6	10.08	0.06	100.8	20.08	0.04	100.4
Mean recovery (%)			107.6			101.8			100.7			100.3
20 µg phenols added to all samples												
Simazine				5.08	0.09	101.6	10.08	0.08	100.8	20.10	0.12	100.5
Propazine				5.12	0.10	102.4	10.06	0.05	100.6	20.12	0.12	100.6
Metoxuron				4.98	0.08	99.6	10.04	0.04	100.4	20.04	0.04	100.2
Bromacil				5.02	0.02	100.4	10.02	0.02	100.2	20.06	0.08	100.3
Mean recovery (%)				101.0				100.5				100.4
50 µg phenols added to all samples												
Simazine				5.06	0.12	101.2	10.09	0.12	100.9	20.09	0.10	100.5
Propazine				5.09	0.12	101.8	10.08	0.09	100.8	20.08	0.09	100.4
Metoxuron				5.00	0.02	100.0	10.03	0.02	100.3	20.04	0.08	100.2
Bromacil				5.03	0.04	100.6	10.03	0.04	100.3	20.04	0.06	100.2
Mean recovery (%)				100.9				100.6				100.3

* SD, standard deviation (n = 5).
† Herbicides: simazine, propazine, metoxuron, bromacil.
‡ Phenols: 3-methylphenol, 4-methylphenol, 3,4-dimethylphenol, 2,5-dichlorophenol.

Results and Discussion

Investigations concerning the chromatographic analysis of herbicides with respect to their analysis in mixture with phenolic compounds were carried out. Investigations on the separation of herbicides were carried out by reversed-phase HPLC. The established retention parameters for herbicides are given in Table I.

In the worked out chromatographic systems, satisfactory differences in the retention times were obtained. It was found that it was possible to separate the mixture of herbicides and analyze particular compounds on each tested stationary phase, applying the suitable mobile phase.

In a previous paper (12), the authors presented results of the separation of the group of phenol derivatives on RP_8 and RP_{18} columns in the methanol–water system with rations. The chromatographic analysis was performed in an RP_8 column with methanol–water (2:1, v/v) as a mobile phase. This system was found to be best for herbicides and phenols.

Comparing the results of the determination of herbicides and phenols by the HPLC method, it can be found that there are systems in which it is impossible to analyze herbicides in the presence of phenols due to similar retention times (e.g., 3-methylphenol and metoxuron, simazine and 2,6-dichlorophenol, or 2,3-dimethylphenol and bromacil).

To carry out the analysis of the mixture of herbicides and phenols, SPE preceeding HPLC determination was applied.

Conditions of SPE on phenyl, octadecylsilane, and octadecylsilane POLAR PLUS were established. The best results for absorption and preconcentration of the phenols were obtained on an octadecylsilane POLAR PLUS bed using acetonitrile as an eluant. The elution efficiency for phenols was 98–99%. The results are described in a previous paper (14), and the representative chromatogram is shown in Figure 1.

According to Sherma (15), herbicides from a triazine group can

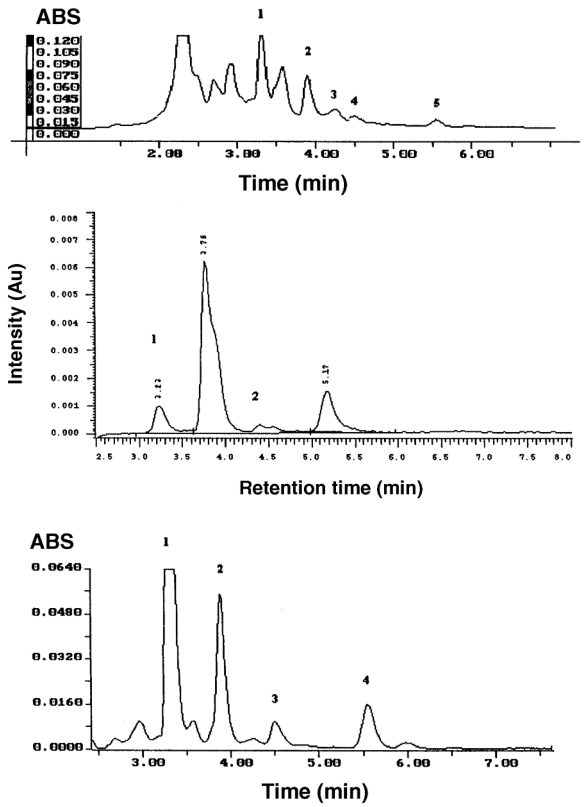

Figure 5. Chromatogram (A) of water sample from the river Rawa before preconcentration using the RP_8 column and methanol–water (2:1, v/v) eluant. Peaks: 1, phenol; 2, metoxuron and methylphenols; 3, bromacil; 4, 2,3-dimethylphenol; 5, 2,4-dichlorophenol. Chromatogram (B) of water sample from the river Rawa after separation and preconcentration on sulfonic and octadecylsilane bed. Peaks: 1, metoxuron; 2, bromacil. Chromatogram (C) of water sample from the river Rawa after preconcentration on octadecylsilane bed. Peaks: 1, phenol; 2, methylphenols; 3, 2,3-dimethylphenol; 4, 2,4-dichlorophenol.

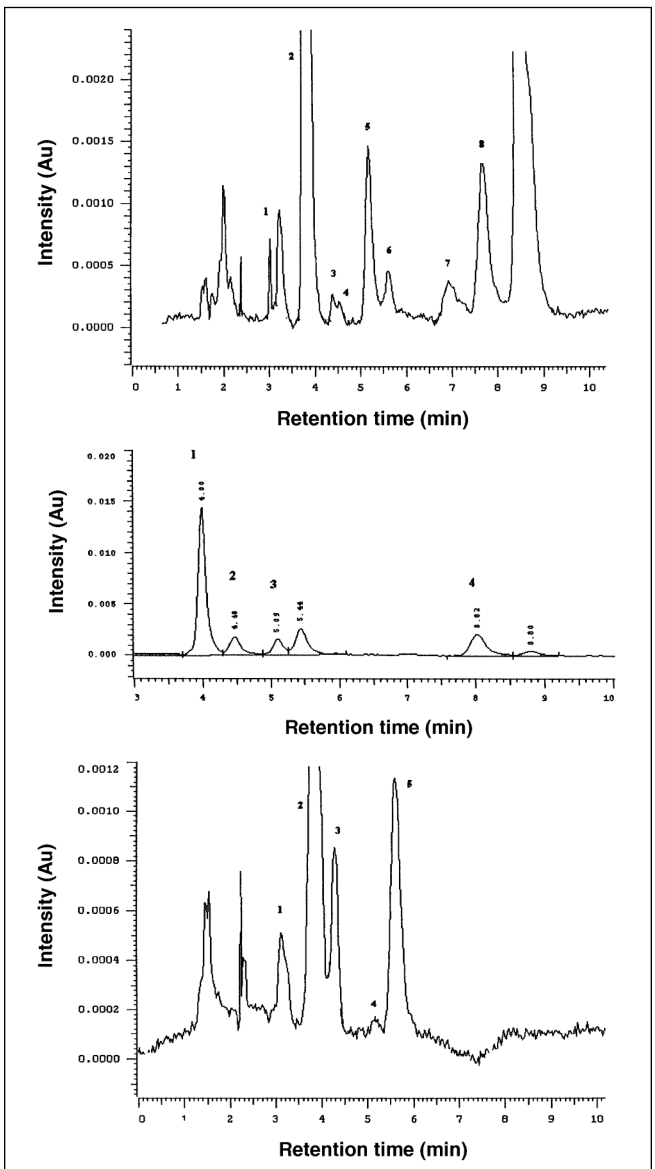

Figure 6. Chromatogram (A) of the extract of soil sample on the RP_8 column and methanol–water (2:1, v/v) eluent. Peaks: 1, phenol; 2, metoxuron and methylphenols; 3, 3,4-dimethylphenol; 4, 2,3-dimethylphenol; 5, simazine; 6, 2,5-dichlorophenol; 7, 2,4-dichlorophenol; 8, propazine. Chromatogram (B) of herbicides in the soil sample after separation of phenols on octadecylsilane bed. Peaks: 1, metoxuron; 2, bromacil; 3, propazine; 4, simazine. Chromatogram (C) of phenols in soil sample after separation of herbicides on the octadecylsilane bed. Peaks: 1, phenol; 2, methylphenols; 3, 3,4-dimethylphenol; 4, 2,5-dichlorophenol; 5, 2,4-dichlorophenol.

be adsorbed on an octadecylsilane bed. Our investigations, however, revealed that on this bed, all tested herbicides are adsorbed. A representative chromatogram of the mixture of herbicides obtained on an RP_8 column using methanol–water (2:1, v/v) as an eluant and a flow rate of 1 mL/min is shown in Figure 2. The retention times (t_R) are as follows: metoxuron, t_R= 3.89 min; bromacil, t_R = 4.27 min; simazine, t_R = 4.96 min; hexazinone, t_R = 5.29 min; and propazine, t_R = 7.68 min.

According to the literature (16), herbicides from a triazine group can be adsorbed on a sulfonic bed. In this way, in the work presented here, herbicides of a triazine group (simazine, propazine, and hexazinone) were separated from those of urea (metoxuron) and uracil (bromacil) groups.

The usability of the method for the determination of a mixture of herbicides and phenols in water and soil samples were examined in the test on synthetic contaminated water and soil according to cycles 1 and 2.

In Figure 3, the examples of chromatograms obtained for the mixture of herbicides and phenols after separation on an octadecylsilane bed according to cycle 1 are shown. The results of the recovery test are given in Table II. In Figure 4, the examples of chromatograms obtained for the mixture of herbicides and phenols after separation on a sulfonic and octadecylsilane bed according to cycle 2 are shown. The results of the recovery test are given in Table III. Mean recoveries were 94.5–98.8% for phenols (3-methylphenol, 4-methylphenol, 3,4-dimethylphenol, 2,5-dichlorophenol) in cycle 1 and 98.1–99.8% for phenols (phenol, 2-methylphenol, 2,3-dimethylphenol, 2,4-dichlorophenol) in cycle 2. Mean recoveries for herbicides (simazine, propazine, metoxuron, bromacil) were 98.2–101.8% in cycle 1 and 96.1–100.2% in cycle 2.

Soil samples with herbicides and phenols added were also examined. In cycle 1, mean recoveries were 100–107.6% for phenols (3-methylphenol, 4-methylphenol, 3,4-dimethylphenol, 2,5-dichlorophenol) and 100.3–101% for herbicides (simazine, propazine, metoxuron, bromacil). In cycle 2, mean recoveries were 93–99% for phenols and 95–102% for herbicides. The representative results of analyses obtained in cycle 1 are shown in Table IV. Standard deviation (for n = 5), mean value, and recoveries are shown in the tables. They demonstrate that the developed methods provide good repetition in the range of concentrations examined. The methods described here were applied to the analysis of environmental samples. River and coke plant water, as well as soil samples, were examined. Water samples for the phenols and soil samples for the herbicides and phenols were determined. Cycle 2 was applied for the preparation of river water samples. The volume of sample amounted to 250 mL. The obtained results are presented in Table V, and chromatograms obtained during the analysis of water from the Rawa river (Poland) are presented in Figure 5.

Water samples collected from the process of cooling gas and the quenching of coke were also analyzed. Samples (1.0 mL) of industrial water were extracted to the solid phase for the separation of the interfering matrix according to the procedure in the Sorption of phenols on a sorbent bed section. It was found that extraction to solid phase allows the simultaneous preconcentration of the analyzed compound and its separation from the matrix.

The soil samples were analyzed for herbicides after the isolation of phenols according to cycle 1. The chromatogram of the extract of the soil sample according to cycle 1 is shown in Figure 6. The figures show the advisability of application of the elaborated method.

The quantitative analysis of investigated herbicides was carried out in the range of 10 to 1×10^4 ng. The following parameters of the equation $y = Ac + B$ have been obtained: for metoxuron, $y = 1.726 \times 10^{-3}c + 0.4 \times 10^{-8}$; for bromacil, $y = 1.800 \times 10^{-3}c + 0.24 \times 10^{-8}$; for simazine, $y = 1.242 \times 10^{-3}c - 0.52 \times 10^{-8}$; for hexazinone, $y = 1.806 \times 10^{-3}c + 0.18 \times 10^{-8}$; and for propazine, $y = 1.291 \times 10^{-3}c - 0.58 \times 10^{-8}$. Detection limits of various herbicides were 0.06–0.3 µg/L for water and 0.24–1.4 µg/kg for soil.

Herbicides and phenols were identified by comparison with retention times and spectra of standards added to water and soil samples.

Conclusion

Based on the analysis of the data from the experiments, such as separation of phenols from herbicides by SPE, recovery of the examined compounds from preconcentration processes, and precision and accuracy of the method, it can be concluded that cycles 1 and 2 proposed for the water and soil analysis can be used in the analysis of environmental samples.

Table V. Results of Phenols and Herbicides Determination on an RP_8 Column*

Sample number	Water samples	Detected	Amounts found, respectively (mg/L)
1	River Klodnica	phenol, methylphenol, hexazinone	13.21, 8.85, 0.38
2	River Rawa	phenol, methylphenol, 2,3-dimethylphenol, 2,4-dichlorophenol, metoxuron, bromacil	8.64, 7.86, 0.18, 0.42, 0.42, 0.22
3	River Bierawka	phenol, methylphenol, 2,3-dimethylphenol, simazine, propazine	0.75, 0.45, 0.18, 0.12, 0.21
4	River Jeziorka	phenol, methylphenol, 2,5-dichlorophenol, simazine, propazine	0.84, 0.66, 0.24, 0.16, 0.24
5	From the process of cooling gas	phenol, methylphenol, 2,3- and 3,4-dimethylphenol, 2,4-,2,5-, 2,6-dichlorophenol	1.56, 0.92, 0.74, 0.76, 1.25, 1.16, 0.98 (g/L)
6	From the process of the quenching of coke	phenol, methylphenol, 2,3- and 3, 4-dimethylphenol, and 2,4-, 2,5-, and 2,6-dichlorophenol	1.12, 0.88, 0.65, 0.63, 1.02, 0.96, 0.87 (g/L)

* Eluent was methanol–water (2:1).

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Manuscript accepted March 24, 2000.