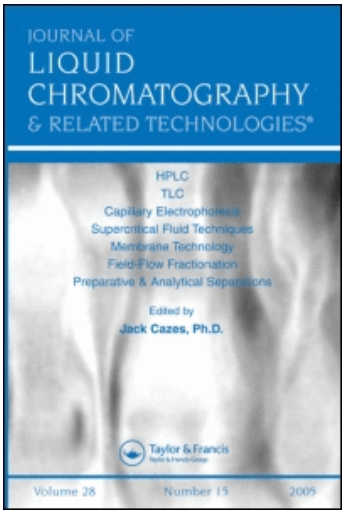

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ANALYSIS OF A NEW HERBICIDE (PYRIBENZOXIM) RESIDUES IN SOIL USING DIRECT-EXTRACT-INJECTION HPLC WITH COLUMN SWITCHING

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ABSTRACT

A simple and efficient analysis method of the herbicide residues in soil has been developed and applied to residual analysis of a new herbicide, pyribenzoxim. Extraction and separation were performed in sequential mode by on-line column switching. On-line analysis shows better specificity than off-line analysis does. The analyte was well separated without interference and baseline distortion.

Recovery yields for standard spiking were 97.9 ± 1 (S.D.) and 92.1 ± 4 (S.D.) % at the concentration of 0.04 and 0.1 ppm in soil, respectively (n=3). The correlation coefficient was greater than 0.999 over the range between 0.1 and 10/mL. The on-line solid phase extraction (SPE) analysis is described, as compared to off-line SPE analysis.

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INTRODUCTION

Although the analysis of herbicide residues in soil is one of the most important things in the agrochemical field, the selective extraction of herbicides from complex matrix, and following sample clean-up, is a critical and time consuming step.[1-3] These are the essential steps in the residual analysis. Efficient and accurate analysis methods have been designed to speed up the residual analysis.[4-6] A typical extraction method is a liquid-liquid extraction using partition between solvents of different polarities. Following this procedure is the sample clean-up with chromatography, using silica gel or florisil.[7, 8]

The clean-up step of herbicides from extracts is usually inefficient and it is hard to get enough recovery for further analysis. We have improved this method by combination of on-line extraction, sample clean-up, and separation. In this study, we established a new on-line column switching method by sequential configuration of the switching valve before introducing samples into the analytical column without pre-treatment of the soil for residual analysis of the new herbicide, pyribenzoxim.

EXPERIMENTAL

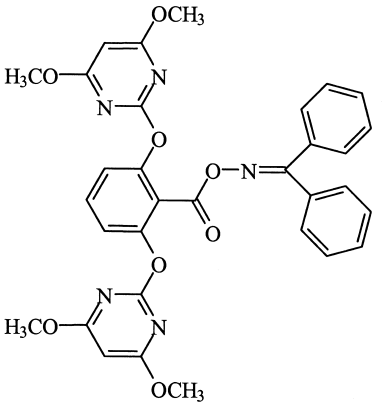
Chemicals

The new herbicide, pyribenzoxim, was synthesized and developed by the Agrochemical Research Center in LG Chemical Research Park. The structure is shown in Fig. 1. All solvents used in this study were HPLC grade and purchased from J. T. Baker (Phillipsburg, NJ, USA). Distilled and deionized water was used in this study (Milli-Q Water Purification System, Millipore, MA, USA).

Apparatus

Chromatography was carried out on Waters HPLC systems which consist of two 510 HPLC pumps, a gradient controller, Rainin AI-1A autosampler coupled switching valve (Rainin, CA, USA), and Waters 486 tunable wavelength detector (Waters, MA, USA).

A TCM column oven (Waters, Milford, MA, USA) was used to regulate the temperature of the column. Data integration was performed on a model 746 integrator (Waters, Milford, MA, USA). The HPLC columns used were a Microsorb C_{18} (4.6 mm I.D. × 250 mm L., 5 μm, Rainin, CA, USA) for the analytical column, a Asahipak GF-1G 7B (7.6 mm I.D. × 50 mm L., Shodex, Japan) for the



2,6-bis[(4,6)-dimethoxypyrimidine-2-yl) oxy]benzoic acid, benzhydrylidine amino ester (pyribenzoxim)

Figure 1. The structure of pyribenzoxim.

clean-up column of the on-line analysis, and Speri-5 C_{18} (4.6 mm I.D. × 30 mm L., 5 μm, Brownlee, USA) for the trap column.

A Sep-pak plus cartridge (Silica, Waters, Milford, MA, USA) was used as a clean-up column for off-line analysis.

Preparation of Standard Solutions

A stock solution of pyribenzoxim was prepared at 1.002 mg/mL in acetonitrile. Additional standard solutions were prepared by dilution, with acetonitrile ranging from 0.1 to 10 μg/mL.

Sample Preparation

Soil, 50.0 g, was weighed into 200 mL bottles equipped with teflon-lined cap. Recovery samples were prepared by spiking the appropriate standard solution to obtain the concentration range of 0.04, 0.1, and 0.6 μg/g, respectively. Each sample was suspended in 100 mL of acetone and shaken for 2 hours.

Extracted samples were filtered using a glass filter (G-3), placed on a 500 mL separating funnel, and introduced to 100 mL of saturated NaCl solution and

50 mL of methylene chloride. The separating funnel was shaken at approximately 300 excursions/min for 30 min. Then, the methylene chloride layer was carefully collected, and this partition procedure was repeated twice. The extracts were evaporated to dryness under vacuum, on a water bath set at 35°C.

Sample Purification

For On-Line Analysis

The dried residues were dissolved in 1 mL of 60% acetonitrile aqueous solution, and the sample solution was filtered by a membrane syringe filter. 50 μL of the resulting solution was injected into the HPLC and then sample clean-up and the analysis were performed by an automatic procedure.

For Off-Line Analysis

The dried residues were purified using silica SPE cartridges that were pre-equilibrated by eluting 10 mL of n-hexane. The residues were dissolved in 2 mL of 10% ether in n-hexane. Then, the sample solution was loaded into the silica SPE cartridge by slowly passing the extract through a membrane syringe filter attached to a 10 mL of disposable syringe to remove suspended solids. The cartridge was rinsed with 10 mL of 10% ether in n-hexane. Then, the cartridge was eluted with 40 mL of 20% ether in n-hexane and this fraction was collected and evaporated to complete dryness under vacuum at 35°C.

The final dried residues were dissolved in 1 mL of 60% acetonitrile aqueous solution and the resulting solution was filtered by a membrane syringe filter. Then, 50 μL of the sample solution was introduced into the HPLC.

Chromatographic Procedure

For On-Line Analysis

As shown in Fig. 2, the on-line system consisted of two independently controlled HPLC pumps. The extracts were injected into the HPLC system directly, and eluted into the clean-up column (0-10 min, the position of switching valve: counterclockwise). A part of the sample matrix was washed out. Pyribenzoxim was transferred to the trap-column using a switching valve ("heart-cut," 10-14.8 min, the position of switching valve: clockwise). Then, the fraction of heart-cut was back-flushed to the analytical column using a switching valve (14.8-end run, the position of switching valve: counterclockwise).

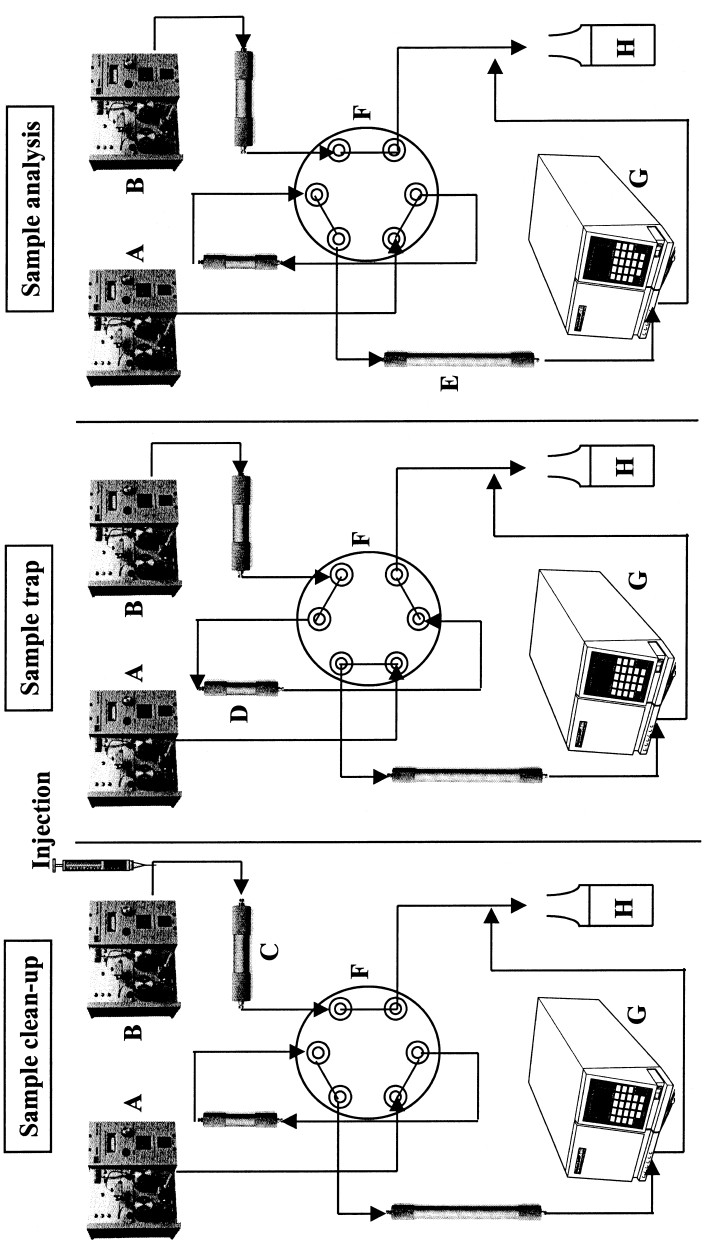


Figure 2. Schematic diagram of the on-line SPE analysis. A: Binary pump A, B: Binary pump B, C: Clean-up column, D: Trap column, E: Analytical column, F: Switching valve, G: Detector, H: Waste.

In this system, the clean-up column was eluted with a mixture of 10% tetrahydrofuran, 30% acetonitrile, and 60% H_2O at the flow rate of 1.2 mL/min, and the analytical column was eluted with 55% acetonitrile in water at the flow rate of 1.3 mL/min. The temperatures of the clean-up column and analytical column were controlled at a constant 40°C. Pyribenzoxim was detected with a UV detector at 247 nm.

For Off-Line Analysis

In off-line analysis, pretreated samples were injected into an analytical column and separated from other sample matrices. The analytical column was eluted with 57% acetonitrile in water at a flow rate of 1.3 mL/min. In this case, the column temperature was 55°C and the detection wavelength was 247 nm.

Calculation

The correlation coefficient, slope, and intercept of the calibration curve were obtained by the least square fit of the weights, vs. the peak area count of pyribenzoxim standard solutions. The weight of pyribenzoxim residue in soil samples was calculated from the regression line. The resulting weight of pyribenzoxim residue was converted to part per million (ppm) unit.

RESULTS AND DISCUSSION

For On-Line Analysis

A filtered extract was injected directly into the HPLC. Then, the desired fraction was collected, so-called "heart-cut," and transferred to the analytical column using a switching valve. The flow diagram of on-line analysis is present in Fig. 3. As shown in this figure, major components of soil matrices were removed to produce a well-separated chromatogram, in which there were no interferences. The typical chromatogram of pyribenzoxim in soil is present in Fig. 4.

Recovery yields were 97.9 ± 1 (S.D.) and 92.1 ± 4 (S.D.)% for the spiking concentration of 0.04 and 0.1 ppm in soil, respectively (n=3). Linearity was determined, ranging over 0.1-10 μg/mL, and measured on separate days before sample analysis. The correlation coefficients were always greater than 0.999. The limit of detection was 2 ppb. The results of residual analysis of pribenzoxim in soil are illustrated in Table 1. The half-life was 6-8 days for field soil and 23 days for laboratory soil.

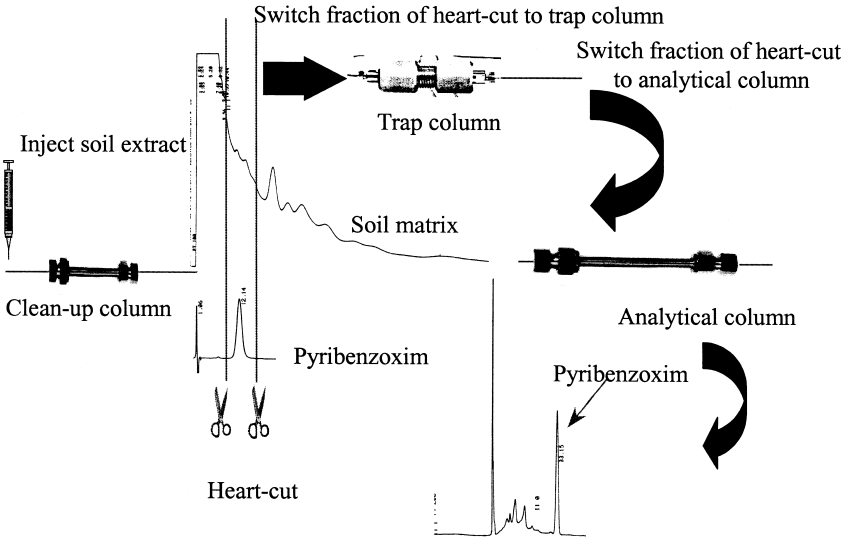


Figure 3. The flow diagram of on-line SPE analysis.

For Off-Line Analysis

Recovery yields were 97.4 ± 2.4 (S.D.) and 92.2 ± 1.2 (S.D.) % in soil for a spiking concentration of 0.1 and 0.6 ppm, respectively. The correlation coefficient and limit of detection were approximately the same as that of on-line analysis. The results of the pyribenzoxim residue are shown in Table 2.

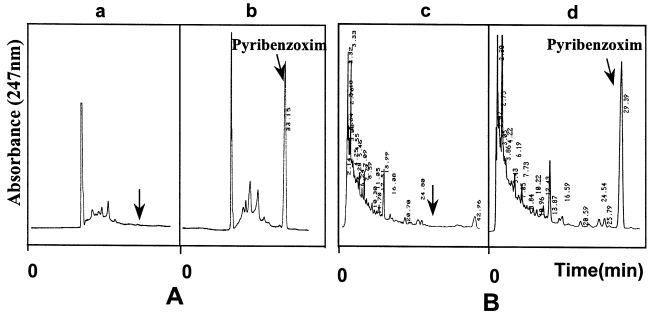


Figure 4. The comparison of on-line and off-line SPE methods by chromatograms. A: On-line SPE analysis; a: Blank, b: Spiking 0.1ppm. B: Off-line SPE analysis; c: Blank, d: Spiking 0.1ppm.

Table 1. The Results of Residual Analysis of Pyribenzoxim Using On-Line SPE Method in Soil

Soil	Treatment quantity of pyribenzoxim	Days after treatment	Residues of pyribenzoxim (ppm)				Half-life (days)
			Rep.1	Rep.2	Rep.3	Average (±SD*)	
Field soil	Blank	—	<0.002	<0.002	<0.002	<0.002	
	0.04 μg/g	0	0.047	0.053	0.044	0.048 (±0.005)	Residues (ppm) $= 0.048 \times e^{-0.0837t}$ r^2=0.984 $t_{1/2}$=8 days
		1	0.030	0.034	0.029	0.031 (±0.003)	
		7	0.021	0.021	0.021	0.021 (±0.000)	
		16	0.011	0.011	0.012	0.011 (±0.001)	
		30	0.003	0.003	0.003	0.003 (±0.000)	
		60	<0.002	<0.002	<0.002	<0.002	
	0.1 μg/g	0	0.113	0.111	0.108	0.110 (±0.003)	Residues (ppm) $= 0.110 \times e^{-0.1134t}$ r^2=0.969 $t_{1/2}$=6 days
		1	0.097	0.080	0.099	0.092 (±0.010)	
		7	0.050	0.047	0.056	0.051 (±0.005)	
		16	0.010	0.011	0.010	0.010 (±0.001)	
		30	0.005	0.004	0.004	0.004 (±0.001)	
		60	<0.002	<0.002	<0.002	<0.002	
Lab. soil	Blank	—	<0.002	<0.002	<0.002	<0.002	
	0.1 μg/g	0	0.094	0.098	0.099	0.097 (±0.003)	Residues (ppm) $= 0.110 \times e^{-0.1134t}$ r^2=0.969
		1	0.090	0.091	0.086	0.089 (±0.003)	
		3	0.080	0.081	0.084	0.082 (±0.002)	
		7	0.077	0.077	0.075	0.077 (±0.001)	
		14	0.077	0.078	0.075	0.077 (±0.002)	
		30	0.026	0.026	0.022	0.025 (±0.002)	
		60	0.018	0.016	0.017	0.017 (±0.001)	

*SD : Standard deviation

Table 2. The Results of Residual Analysis of Pyribenzoxim Using Off-Line SPE Method in Soil

Soil	Treatment quantity of pyribenzoxim	Days after treatment	Residues of pyribenzoxim (ppm)				Half-life (days)
			Rep.1	Rep.2	Rep.3	Average (±SD*)	
	Blank	—	<0.002	<0.002	<0.002	<0.002	
		0	0.394	0.398	0.396	0.396 (±0.002)	Residues (ppm)
Field		5	0.232	0.225	0.230	0.229 (±0.004)	$= 0.369 \times e^{-0.09316t}$
soil	0.4 μg/g	10	0.185	0.190	0.187	0.187 (±0.003)	$r^2 = 0.939$
		15	0.155	0.151	0.152	0.153 (±0.002)	$t_{1/2} = 7$ days
		20	0.043	0.048	0.051	0.047 (±0.004)	
	Blank	—	<0.002	<0.002	<0.002	<0.002	
		0	3.922	3.768	3.842	3.844 (±0.077)	Residues (ppm)
Lab.		7	3.654	3.338	3.475	3.489 (±0.158)	$= 3.844 \times e^{-0.0304t}$
soil		14	2.695	2.627	2.654	2.659 (±0.034)	$r^2 = 0.983$
	0.4 μg/g	21	2.045	2.092	2.074	2.070 (±0.024)	$t_{1/2} = 23$ days

*SD : Standard deviation

CONCLUSION

The quantitative analytical methods of residual herbicide and pyribenzoxim, using on-line SPE and off-line SPE in soil were compared. New analytical methods (on-line SPE analysis) shows several advantages over off-line SPE methods for determination of pyribenzoxim residue. The on-line SPE analysis of determination of pyribenzoxim residue using a column-switching technique, allowed fully automated rapid processing of soil samples. The determination of pyribenzoxim residues, including sample clean-up, could be accomplished within 40 min.

The results of recovery, precision, and sensitivity using on-line SPE analysis were generally accepted in residual analysis. The on-line SPE analysis method provides a fast, solvent-saving, and fully automatic analysis procedure for herbicide residues.

REFERENCES

1. Marek, Le.J.; Koskinen, W.C. J. Agric. Food Chem. **1996**, *44*, 3878-3881.
2. Shackelford, D.D.; Duebelbeis, D.O.; Snell, B.E. J. Agric. Food Chem. **1996**, *44*, 3570-3575.
3. Murakami, M.; Takesada, H.; Tenma, H.; Moriaka, H. J. Pesticide Sci.**1997**, *22*, 222-225.
4. Menezes, M.L.; Felix, G. J. Liq. Chrom. & Rel. Technol. **1996**, *19* (19), 3221-3228.
5. Leira, E.; Botana, A.; Cela, R. J. Chromatogr. A **1996**, *724*, 67-78.
6. Bagli, M.; Rao, M.L.; Sobanski, T.; Laux, G. J. Liq. Chrom. & Rel. Technol. **1997**, *20* (2), 283-296.
7. Gennaro, M.C.; Giacosa, D.; Baglietto, C. J. Liq. Chrom. & Rel. Technol. **1996**, *19* (6), 911-924.
8. Aston, L.S.; Seiber, J.N. J. Agric. Food Chem. **1996**, *44*, 2728-2735.

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