Application Note 7

Monitor Pesticides in Water Samples Using a Deactivated Reversed Phase HPLC Column

Because HPLC offers significant advantages compared to GC for many nonvolatile, thermally labile, and polar materials, this technique is becoming a preferred analytical method for monitoring many pesticides and their metabolites. A SUPELCOSIL LC-ABZ column was used to separate a mixture of organochlorine and organophosphorous insecticides, triazines, phenylurea derivatives, carbamates, and other products in water samples. The SUPELCOSIL LC-ABZ column, which has a unique deactivated stationary phase, provided excellent resolution and peak symmetry. Using this technique, samples of lake water, taken at varying depths, were found to contain traces of triazine herbicides — simazine, atrazine, and terbutylazine.

Key Words:
Herbicides • HPLC • Pesticides

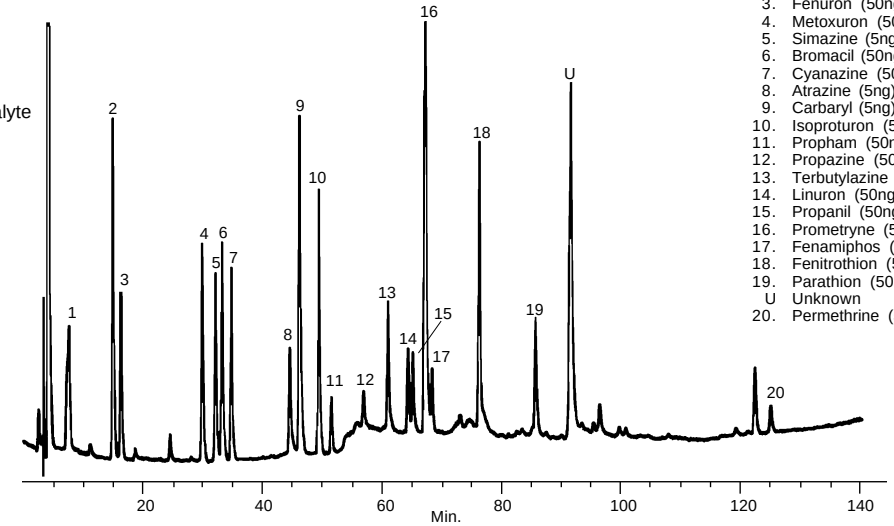
United States Environmental Protection Agency (US EPA) methods for monitoring pesticides in water specify predominantly gas chromatography (GC) methods. Currently, there are only a few US EPA methods for high performance liquid chromatography (HPLC) analyses of pesticides, including Method 632 for urea and carbamate compounds, Method 629 for cyanazine, and the proposed Method 8318 for carbonyl. However, HPLC could be a useful method for a much broader range of pesticides, as demonstrated by investigators in Switzerland, using a SUPELCOSIL™ LC-ABZ column.

With the trend toward biodegradable, more thermally labile, pesticides, HPLC is becoming a preferred analytical method for monitoring many insecticides and their metabolites, as well as herbicides, and plant growth regulators. HPLC offers significant advantages compared to GC for many nonvolatile, thermally labile, and polar materials. HPLC analysis minimizes the adsorptive loss encountered in GC analysis due to inlet and reactive column effects. Large volume injections of aqueous samples are possible using HPLC (e.g., sample screening, analysis of soluble but non-extractable compounds using on-column trace enrichment techniques). HPLC also allows the use of additional sensitive and selective detectors (UV/VIS variable wavelength, diode array, fluorescence, electrochemical, and others). The non-destructive nature of LC analysis allows the collection of the separated pesticides, and the use of post-column reactions to enhance sensitivity with LC detectors.

The SUPELCOSIL LC-ABZ column is ideal for HPLC quantitation of pesticides and herbicides in water samples. This column features a unique surface deactivation process that provides well-resolved, symmetrical peaks, suitable for quantitative monitoring of these compounds.

Figure A. Pesticides and Herbicides Resolved on a SUPELCOSIL LC-ABZ Column

Column:	**SUPELCOSIL LC-ABZ, 25cm x 4.6mm ID, 5µm particles**
Mobile Phase:	10% to 90% acetonitrile in water at 0.5%/min
Col. Temp.:	40°C
Flow Rate:	1mL/min
Det.:	225nm UV
Inj.:	50µL water, spiked with analyte quantities shown on figure



1. Caffeine (100ng)
2. Metamitron (50ng)
3. Fenuron (50ng)
4. Metoxuron (50ng)
5. Simazine (5ng)
6. Bromacil (50ng)
7. Cyanazine (50ng)
8. Atrazine (5ng)
9. Carbaryl (5ng)
10. Isoproturon (50ng)
11. Propham (50ng)
12. Propazine (50ng)
13. Terbutylazine (5ng)
14. Linuron (50ng)
15. Propanil (50ng)
16. Prometryne (50ng)
17. Fenamiphos (50ng)
18. Fenitrothion (50ng)
19. Parathion (50ng)
U Unknown
20. Permethrine (50ng)

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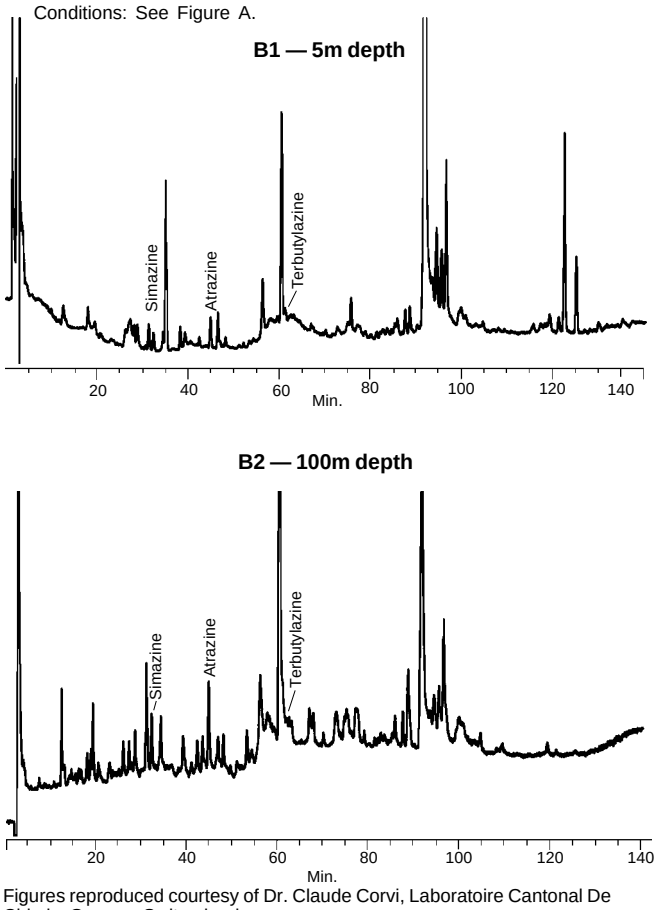
Investigators in Geneva, Switzerland have characterized the ability of the LC-ABZ column to separate mixtures of organochlorine and organophosphorous insecticides, triazines, phenylurea derivatives, carbamates, and related compounds in water samples. A mixture of twenty such compounds in water was separated with sharp, symmetrical peaks (Figure A). Of particular interest is the excellent recovery of carbaryl (peak 9), which is difficult to detect using GC because it thermally decomposes. The 70% recovery of metamitron (peak 2) using the HPLC method was far better than under GC conditions, where it thermally decomposes, producing two small, inconsistent peaks. Samples of water from Lake Geneva, taken at varying depths, were found to contain traces of triazine herbicides — simazine, atrazine, and terbutylazine — as well as unidentified impurities (Figure B).

Figure B. Herbicides Detected in Water Samples from Lake Geneva



Figures reproduced courtesy of Dr. Claude Corvi, Laboratoire Cantonal De Chimie, Geneva, Switzerland.

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The choice of UV wavelength (225nm) in this separation was the best compromise for the twenty compounds. For example, carbaryl is not detected at 245nm, but is well detected at 218 or 225nm, and cyanazine and metoxuron maxima occur at approximately 220nm and 240nm, respectively.

Although EPA methods that specify HPLC do not exist for all pesticides and herbicides used throughout the US, this technique could be a useful, versatile method for various classes of compounds. We recommend the SUPELCOSIL LC-ABZ column for pesticides analysis because of its surface deactivation and superior performance over a wide range of analyte functionalities.

Ordering Information:

SUPELCOSIL LC-ABZ HPLC Columns
5µm particles, 100Å pores

5cm x 4.6mm ID	**59141**
15cm x 4.6mm ID	**59140-U**
25cm x 4.6mm ID	**59142**

Guard Column

2cm x 4.6mm ID	**59545-U**

Guard Column Kit

2cm x 4.6mm ID	**59544-U**

Iso-Disc™ N-253 Syringe-Tip Filters, pk. of 50

25mm diameter, nylon, 0.2µm pores	**59321**

Triazine Pesticides Standard
100µg/mL each component in methanol

Ametryn	Propazine	
Atrazine	Simazine	
Prometryn	Terbutryn	
Prometon		
	1mL	**48392**

Neat Triazine Pesticides Kit
100mg each pesticide, individually packaged

Ametryn	Propazine	
Atrazine	Simazine	
Prometryn	Terbutryn	
Prometon		
	1mL	**49092**

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Acknowledgment

We are grateful to Dr. Claude Corvi and Dr. Sophal Khim-Heang of Laboratoire Cantonal De Chimie, Geneva, Switzerland for their work on the use of HPLC for environmental analyses.