Identification and Quantitation of Herbicides and Pesticides in Water by LC and Diode Array Detector

LC

Varian Application Note
Number 9

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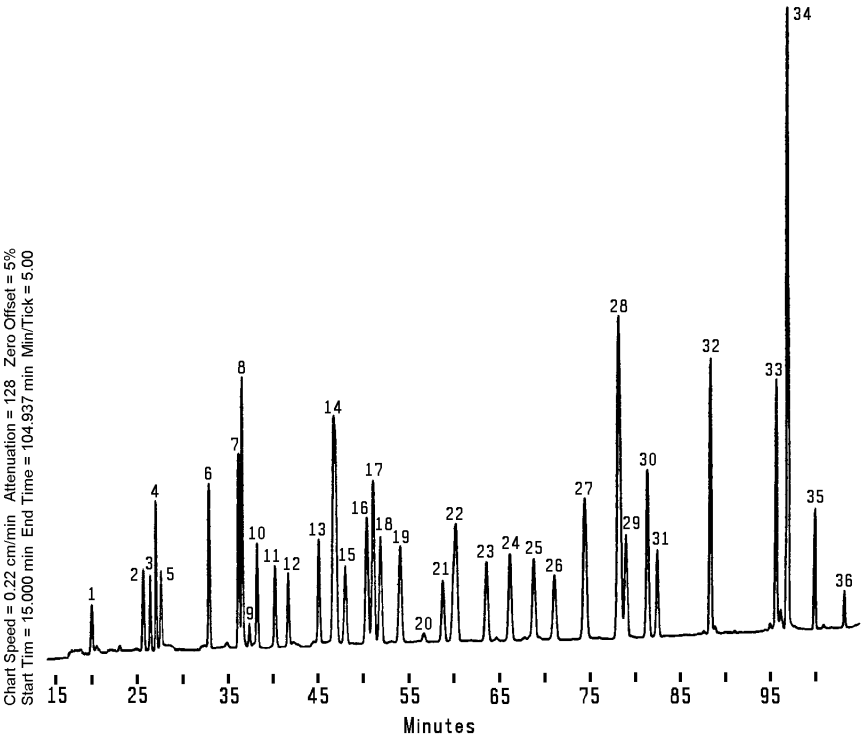
Introduction

In 1992 a new regulation will be effective in France and some other European countries for the determination of herbicides in water. The guidelines in DIN (Deutsche Industrie Norm) 38-407, Teil 12, cover 17 common herbicides. The following method was developed not only for the separation and detection of those 17 herbicides but also 19 additional herbicides and pesticides of possible interest. All 36 compounds are listed on the chromatogram in Figure 1.

The methodology consists of:

- Sample preparation by Solid Phase Extraction using Empore Disk technology
- Separation by HPLC
- Peak identification by Spectral Library Search using a Diode Array Detector



1. Atrazine, deisopropyl
2. Metamitron
3. Dichlorprop
4. Atrazine, 2-hydroxy
5. Atrazine, desethyl
6. Crimidine
7. Metoxuron
8. Hexazinone
9. Bromacil
10. Simazine
11. Cyanazine
12. Atraton
13. Methabenzthiazuron
14. Chlortoluron
15. Atrazine
16. Monolinuron
17. Isoproturon
18. Diuron
19. Metobromuron
20. Metazachlor
21. Sebutylazine
22. Propazine
23. Terbutylazine
24. Linuron
25. Chlorbromuron
26. Anilazine
27. Chlorpropham
28. Metolachlor
29. Barban
30. Dipropetryne
31. Neburon
32. Diazinon
33. Tetradifon
34. Bioallethrin
35. Trifluralin
36. Fenpropathrin

Figure 1. Separation of a mixture of herbicide and pesticide standards in water (5 mg/L). Detection: 239 nm.

Procedure

I. Sample Preparation

1. Condition C_{18} Empore disk with dichloromethane/ ethyl acetate (50:50), followed by methanol and organic-free water.
2. Apply 1L of water sample.
3. Elute with ethylacetate, followed by dichloromethane and finally ethylacetate/dichloromethane (50:50).
4. Combine eluates and evaporate to dryness.
5. Reconstitute with 0.5 mL methanol.

II. HPLC Conditions:

Column: Varian TSK ODS 80TM, 5 µm, 25 cm x 4.6 mm

Column temperature: 40^{O} C

Mobile Phase:

A: Ammonium acetate/2% acetonitrile/2% methanol

B: Acetonitrile/2% ammonium acetate/2% methanol

Gradient from 100% A to 80% B

Detection:

Varian Polychrom® 9065 Diode Array Detector at 239 nm or reprocess at three different selective wavelengths for maximum response:

220 nm (Compounds 5,10,11,15,20,21,23,28)
244 nm (Compounds 7,8,14,16,17,18,19,24)
230 nm (Compound 13)

III. Peak Identification

Peak identities were confirmed with an automated PolyView™ library search routine. The search parameters include retention time windows and Purity Parameter (PuP) range with final ranking based upon "Similarity/Dissimilarity" fit.

Results

Figure 1 shows the chromatogram of the separation of 36 herbicides and pesticides, each of which is identified by the Library Search routine. Figure 2 shows the identification of Atrazine by matching the PuP, "Similarity" and "Dissimilarity" values with those of the standard. While the run time is 105 minutes for all 36 compounds, it can be shortened to 80 minutes or less if only the 17 DIN compounds are of interest. Recoveries of the DIN-required compounds are shown in Table 1.

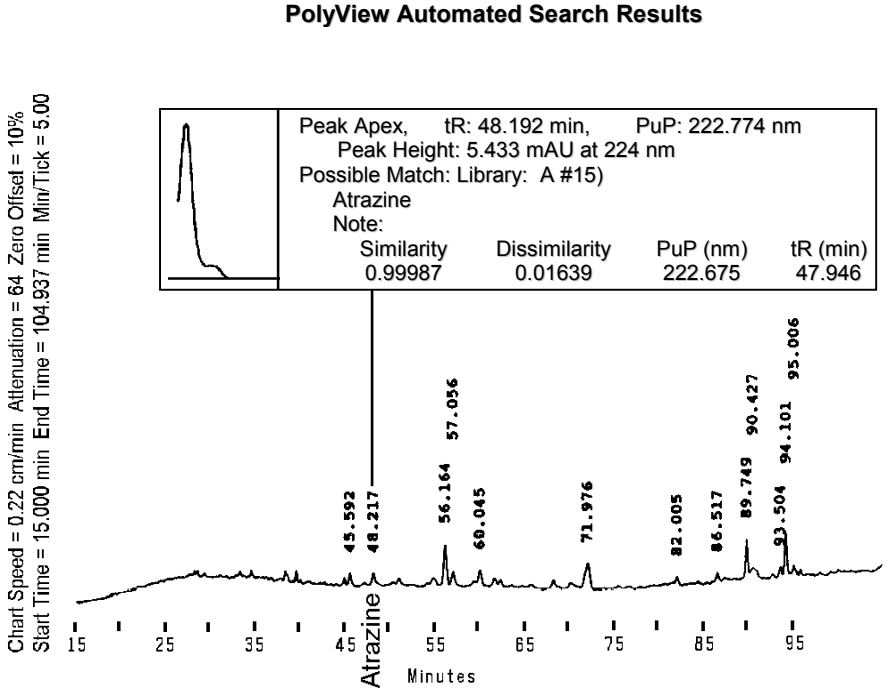


Figure 2. Chromatogram of Local Water (1L extracted with Empore disk). Detection: 239 nm.

Table 1. % Recoveries (from Empore disk) for the 17 DIN Compounds 0.5 µg/L each (N=6)

Metoxuron	72
Hexazinone	68
Simazine	73
Cyanazine	78
Methabenzthiazuron	81
Chlortoluron	76
Atrazine	79
Monolinuron	67
Isoproturon	75
Diuron	73
Metobromuron	78
Metazachlor	93
Sebutylazine	75
Terbutylazine	78
Linuron	78
Metolachlor	83

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These data represent typical results.
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