

Fast Measurement of Acidic Pesticides in Water

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Key Words: GC-TOFMS, Environmental, Deconvolution, Surface Water

1. Introduction

An existing GC/MS method for the determination of pesticides out of the Phenoxy alkane carbonic acid group should be accelerated without losing accuracy, sensitivity, or selectivity.

2. Experimental Conditions

Target Compounds

4-Cl-phenoxyacetic acid	Dicamba
MCPP	MCPA
2,4-DP	2,4-D
2,4,5-TP	MCPB
Bentazon	

Internal Standard: 4-bromobenzoic acid

All compounds measured as their methyl esters.

Realization

The original GC method, which usually takes 30 minutes for completion (see Figure 1), was translated into fast GC conditions using a column that was shorter and had a smaller inner diameter.

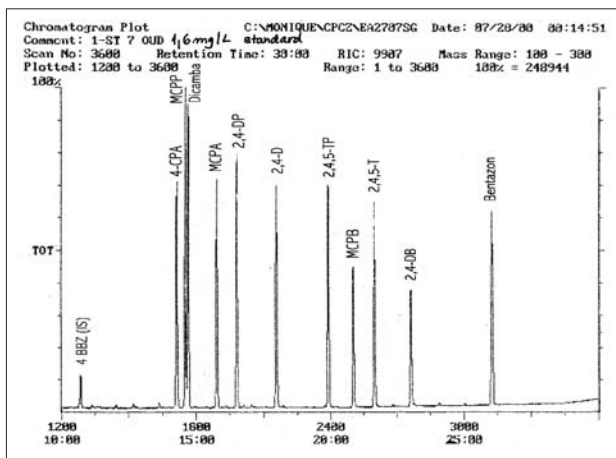


Figure 1. Standard chromatogram of original method.

GC-Parameters

Column:

J&W™ DB-5 MS; 20 m x 0.18 mm x 0.8 μm

Injector Temperature: 180°C

Split Rate: 10:1

Heating Program:

70°C initial temperature, hold for 0.3 minute, with 60°/minute to 270°C, hold for 1 minute

Flow Rate:

1.2 mL/minute Helium constant flow

MS-Parameters

Mass Range: 50 to 300 amu

Scan Rate: 30 spectra/second

Ion Source: 165°C

Total Run Time: 230 seconds

3. Results

In Figure 2, the obtained total ion chromatogram for a standard mixture using fast measurement is shown.

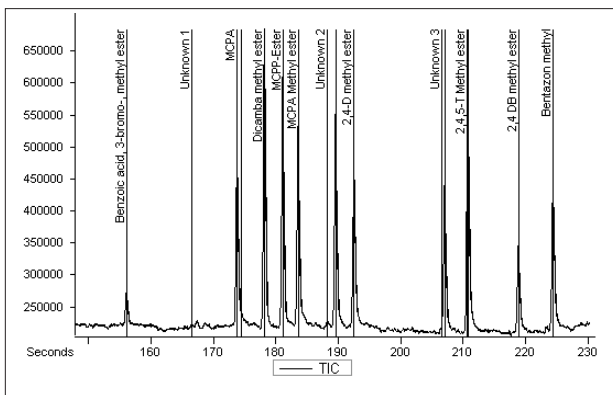


Figure 2. Total Ion Chromatogram (AIC) of the accelerated method.

Some substances in the chromatogram were coeluting. The Pegasus deconvolution software can mathematically separate the spectra of the overlapping compounds and thus supply background subtracted spectra as shown in Figure 3.

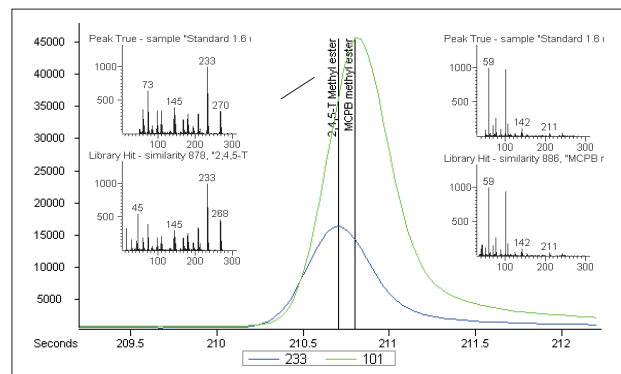


Figure 3. Coeluting substances and their deconvoluted spectra.

Real World Samples

For further evaluation, some water extracts obtained from surface water samples were measured and then compared to the originally obtained data. By means of the data processing software of the Pegasus, the chromatogram was automatically searched for peaks. By this, not only the target analytes were found, but also other components present in the sample could be detected. As all mass traces are being considered, it is possible to find signals even below the baseline, and to identify those according to the deconvoluted (mathematically derived) background subtracted mass spectra. In Figure 4, the TIC of a surface water extract is shown.

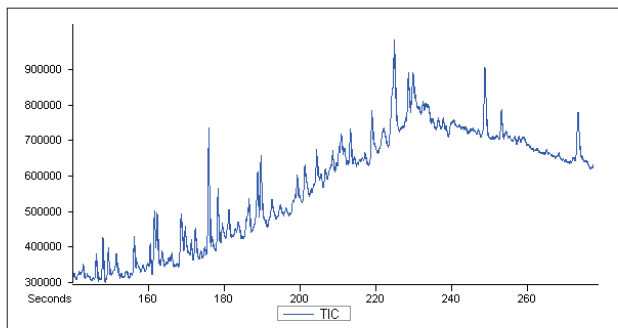


Figure 4. Total ion chromatogram of an extract from a polluted surface water sample.

By automatic peak finding, 165 compounds were found using a S/N threshold of 20. A time window showing the characteristic mass traces of the present components around the elution of MCP is shown in Figure 5.

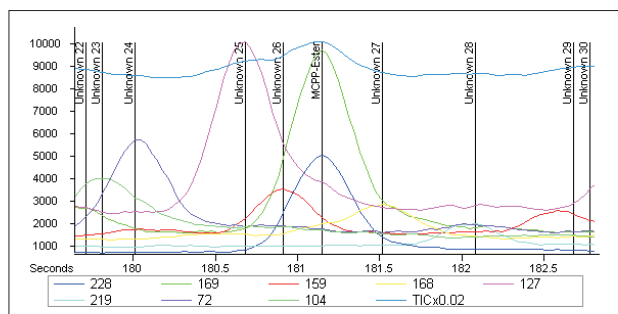


Figure 5. Characteristic mass traces of MCP (0.17 µg/L) and coeluting compounds in this polluted surface water.

A comparison between the data obtained by the original method and the Pegasus method is shown in Table 1.

Table 1. Analysis of a surface water sample using both methods.

Analyte	Original Method	Pegasus Method
MCP	0.17	0.17
Dicamba	0.24	0.25
MCPA	0.02	"not found" (mass 214 was present but spectrum did not match at all. When integrating the result would be 0.01)
2.4 DP	0.44	0.44
2.4-D	0.18	0.16
MCPB	0.21	0.20
2.4 DB	0.12	0.11
Bentazon	0.27	0.26

Figure 6 shows the detection of MCP in a less polluted surface water, also together with the characteristic mass traces of surrounding substances. At the present concentration level of an equivalent of 30 ng/L (30 p.p.t.) in the water, the full mass spectrum is still clearly identified as MCP (see Figure 7).

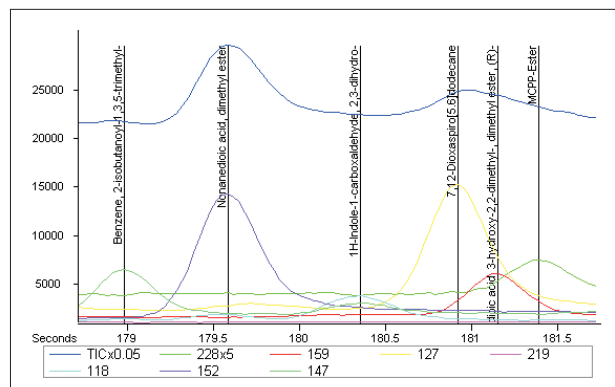


Figure 6. Characteristic mass traces of MCP (0.03 µg/L) and coeluting compounds in a less polluted surface water.

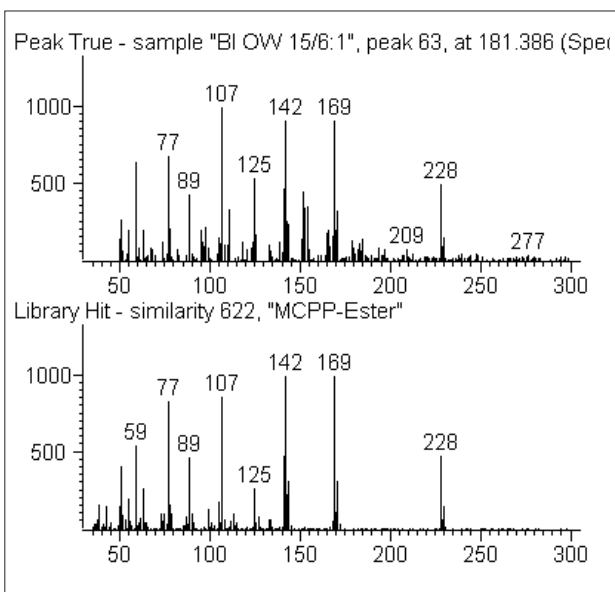


Figure 7. Measured spectrum and the corresponding reference spectrum of MCP methyl ester at a water concentration of 30 ng/L.

Ruggedness of the System

To show the stability and the ruggedness of the system, a series of spiked drinking water and surface water extracts have been analyzed and compared. As can be seen in Table 2, the obtained results are very consistent despite the differences in matrix content in the samples. The discrepancy between theoretical and obtained results reflects the recoveries of the applied extraction method.

Table 2. Results of a measurement of seven spiked sample extracts with the Pegasus (concentrations given in ng/mL).

Name	ow add	ow add	dw add	dw add	dw add	ow add	dw add	Average	Dev.	Theory
	1	2	1	2	3	3	4			
4-Bromobenzoic acid (IS)	178%	149%	154%	141%	137%	132%	113%	144%	20%	
4CP	0.19	0.21	0.2	0.2	0.2	0.23	0.22	0.21	0.01	0.266
Dicamba	0.22	0.23	0.22	0.23	0.22	0.23	0.24	0.23	0.01	0.279
MCPPP	0.23	0.25	0.21	0.21	0.2	0.24	0.23	0.22	0.02	0.264
MCPA	0.2	0.21	0.2	0.19	0.19	0.22	0.21	0.20	0.01	0.258
2.4DP	0.21	0.22	0.19	0.19	0.19	0.23	0.2	0.20	0.02	0.257
2.4-D	0.21	0.21	0.2	0.2	0.19	0.24	0.22	0.21	0.02	0.272
2.4.5	0.2	0.22	0.21	0.2	0.2	0.23	0.2	0.21	0.01	0.247
2.4.5-T	0.21	0.24	0.22	0.21	0.22	0.23	0.23	0.22	0.01	0.313
MCPB	0.22	0.25	0.24	0.23	0.24	0.25	0.26	0.24	0.01	0.295
2.4 DB	0.17	0.18	0.18	0.17	0.17	0.2	0.18	0.18	0.01	0.253
Bentazon	0.25	0.27	0.23	0.22	0.22	0.25	0.23	0.24	0.02	0.271

dw: drinking water ow: surface water

4. Conclusion and Outlook

As demonstrated in this application, the Pegasus is ideal for performing fast, sensitive determination of environmentally-relevant compounds such as acidic pesticides. The data processing software detects and identifies the target compounds by comparison of complete spectra (even when the components are buried in the baseline) as well as performing a search for unknown substances after separating overlapping spectra. A proper library identification can also be achieved using derived (background subtracted) spectra. Further acceleration and increase in sensitivity could easily be accomplished by means of higher scan rates, larger injection volume, etc. The maximum scan rate of the system, 500 full mass spectra per second, would allow even further acceleration of such a method.

5. Acknowledgements

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