Application Note No. 064

Fast Analysis of Organophosphorus Pesticides in a Complex Food Matrix

Dr Roman Hirsch, LECO Instrumente GmbH, Moenchengladbach, Germany

Introduction

The analysis of food products for organic problem compounds such as organophosphorous pesticides is an important task in quality control to assure maximum safety for the customers. High throughput capabilities are as important as reliability and sensitivity of the applied methods. Standard routine GC/MS methods usually require between a 30 and 60 minute run time in addition to a more or less complicated sample preparation procedure.

This application note describes the combination of a sophisticated injection system like the ATAS Optic 2 which allows simplification of the necessary sample preparation by means of a large volume injection; and the Pegasus II Time-Of-Flight GC/MS detector enabling the application of fast GC conditions. Together, a powerful analysis system is set up allowing the acceleration of standard food monitoring analyses while maintaining the required quality.

Target Compounds

Azinphos-ethyl	Azinphos-methyl	Bromophos-ethyl
Bromophos-methyl	Chlorfenvinphos	Chlormephos
Chlorpyriphos-ethyl	Chlorpyriphos-methyl	Chlorthiophos
Coumaphos	Cyanophenphos	Dichlorvos
Etrimphos	Fenchlorphos	Fonophos
Heptenophos	Isofenphos	Jodfenphos
Leptophos	Methacrifos	Mevinphos
Monocrotophos	Phosalone	Pirimiphos-ethyl
Pirimiphos-methyl	Profenophos	Prothiophos
Pyrazophos	Quinalphos	Sulprophos
Tetrachlorvinphos	Tolclophos-methyl	

Instrumentation & Conditions

- ATAS Optic 2-200 programmable injector
- LECO Pegasus II Time-Of-Flight MS
- Agilent 6890 GC

A standard GC method requiring a 30 minute run time was translated into fast GC conditions using a column with a shorter length and a smaller internal diameter. The total run time for this method was 11 minutes.

Optic Parameters:

Liner:	Capillary Liner	
Mode:	Large Volume	
Gas flows:	Split:	20 mL/min
	Vent:	50 mL/min
Initial temp:	40 °C	
Vent rate:	30 s	
Ramp rate:	16 °C/s	
Final temp:	270 °C	
Split open time:	100 s	
Purge pressure:	8 psi	
Transfer pressure:	17.1 psi	
Transfer time:	85 s	
Initial pressure:	17.1 psi	
Final pressure:	37.6 psi	

GC Parameters:

Column:	J&W DB-5 MS; 20 m x 0.18 mm x 0.18 µm
Oven program:	50 °C (hold 1.8 min) 70 °C/min to 150 °C, 25 °C/min to 300°C (hold 1.5 min)
Flow rate:	1.0 mL/min.Helium constant flow

MS Parameters:

Mass range:	50-500 amu
Scan rate:	20 spectra/second
Ion source temperature:	165 °C
Total run time:	11 minutes

Results

Figure 1 shows the total ion chromatogram (TIC) (background corrected) of a standard mixture.

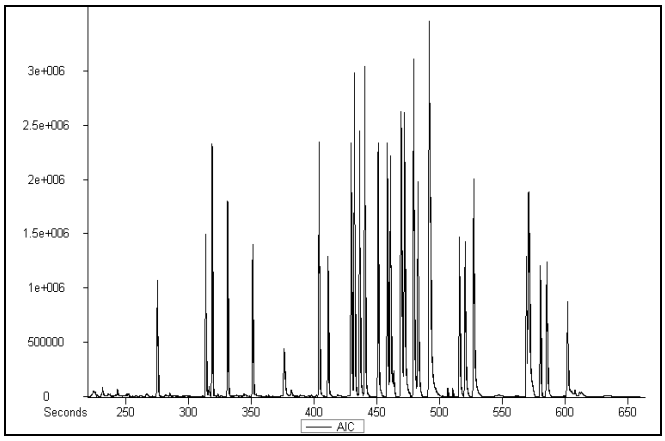


Figure 1: *Analytical Ion Chromatogram (AIC) of a standard mixture*

Some peaks in the chromatogram were coeluting. The Pegasus deconvolution software can mathematically separate the spectra of the overlapping compounds and thus supplies undisturbed spectra as shown in Figure 2.

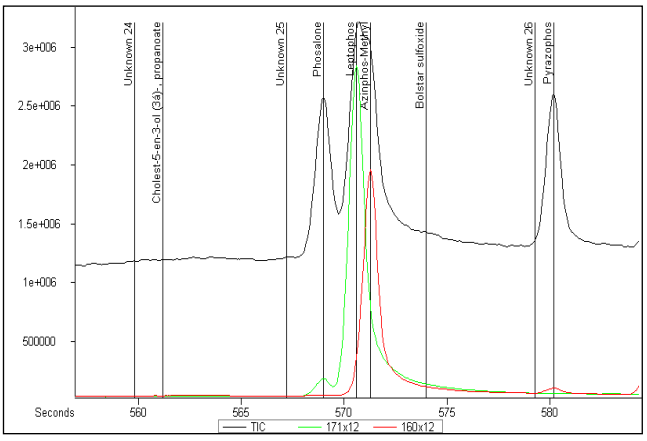
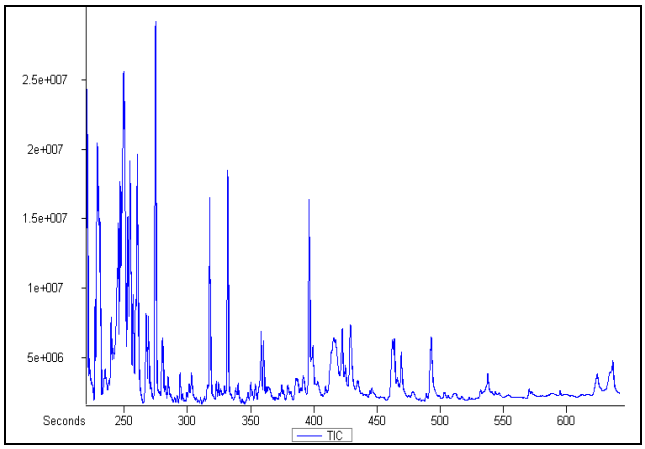


Figure 2*: Coeluting substances and their deconvoluted spectra*

Orange Juice Extracts

For further evaluation of this system, some orange juice extracts stemming from an uncontaminated regular juice brand were spiked with a pesticide standard mixture and measured.

The extraction procedure consisted of a centrifugation followed by a solid phase extraction of 500 mL juice over 200 mg of an Oasis HLB 6cc (Waters) phase. After washing of the cartridge, the compounds were eluted using 10 mL methanol/MTBE (10/90) and the extracts were then dried with Na_2SO_4. Instead of further reducing the extract volume, the extracts were directly analyzed using large volume injection.



Figuur 1

***Figure 3**: Total ion chromatogram of an orange juice extract spiked to a level of 1 µg/L*

By means of the data processing software of the Pegasus the chromatogram was automatically searched for peaks. By this, not only were the target analytes 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 cleaned) mass spectra. In Figure 3, the TIC of an orange juice extract is shown.

Besides the spiked analytes, more than 400 compounds were found by the automatic peak finding algorithm of the Pegasus software using a S/N threshold of 30. A time window showing the characteristic mass traces of some pesticides and other detected compounds is shown in Figure 4.

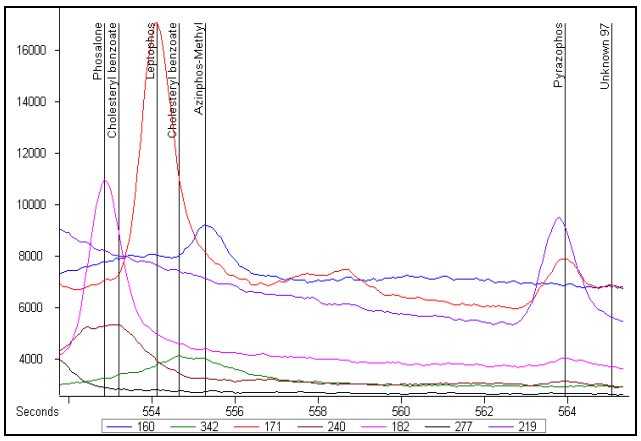


***Figure 4**: Characteristic mass traces of Phosalone, Leptophos, Azinophos-methyl and Pyrazophos besides the co-eluting compounds in the spiked orange juice extract*

In order to demonstrate the linearity behavior within a complex matrix, several spiking levels where measured. An exemplary plot is shown in Figure 5 for Iodophenfos within the concentration range of 0.1 to 10 µg/L.

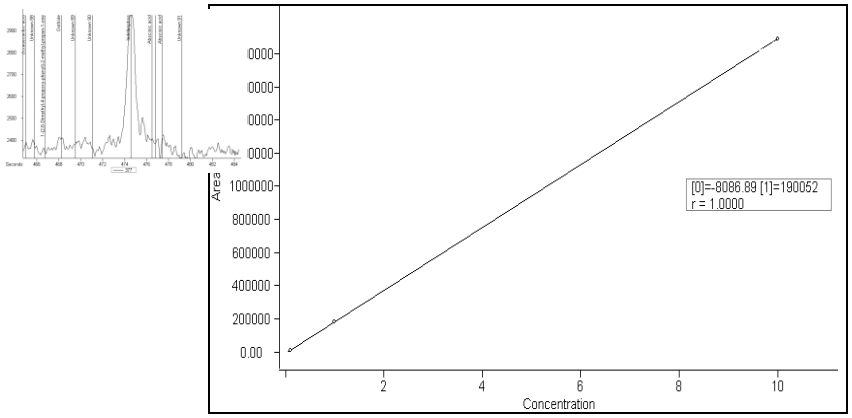


Figure 5: *Calibration plot of Iodofenphos between 0.1 and 10 µg/L together with mass trace 377 of the 0.1 µg/L extract*

Conclusions

The described application shows that the Pegasus II in combination with a large volume injection system like the Optic 2 is very suitable for performing fast, sensitive analysis of pesticides from complex food matrices. The data processing software does not only allow the detection and identification of the target compounds by comparison of complete spectra, even when the components are well buried below the baseline, but can additionally search for unknown substances after separating overlapping spectra and due to cleaned spectra can conduct a proper library identification. By means of higher scanning rates and a larger injection volume a further acceleration and increase in sensitivity could be easily accomplished

Acknowledgements

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