Fast Determination of Organophosphorous Pesticides in a Complex Food Matrix

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Key Words: GC-TOFMS

1. 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 equally important as reliability and sensitivity of the applied methods.

Standard routine GCMS methods usually require between 30 and 60 minutes measurement time in addition to requiring a complicated sample preparation procedure.

This application note describes the combination of a sophisticated injection system like the ATAS OPTIC 2 (allowing for simplification of the necessary sample preparation by means of large volume injection), and the Pegasus II Time-of-Flight GCMS 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 and detectivity.

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	

2. Experimental Conditions

A standard GC method requiring a 30 minute runtime was translated into fast GC conditions using a column which was shorter and had a narrower inner diameter. The applied conditions were as follows.

Large Volume Injection-Parameters

Injection Volume: 10 µL
Vent Time: 30 seconds
Initial Temp: 40°C
Ramp Rate: 16°/minute
Final Temp: 270°C
Split Open Time: 100 seconds
Purge Pressure: 8 PSI
Vent Flow: 50 mL/minute
Transfer Pressure: 17.1 PSI
Transfer Time: 85 seconds
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 initial temperature, hold for 1.8 minutes, with 70°/minute to 150°C, then 25°/minute to 300°C, hold for 1.5 minutes

Flow Rate:
1.0 mL/minute Helium constant flow

MS-Parameters

Mass Range: 50 to 500 amu
Scan Rate: 20 spectra/second
Ion Source: 165°C
Total Run Time: 11 minutes

3. Results

In figure 1 the ion chromatogram (background corrected) for a standard mixture is shown.

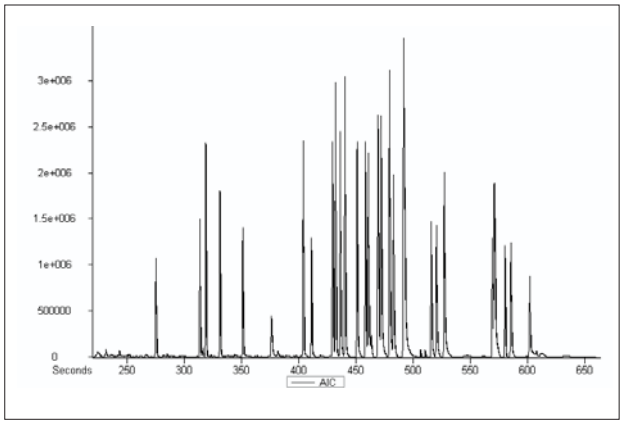

Figure 1. Analytical Ion Chromatogram (AIC) of a standard mixture.

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

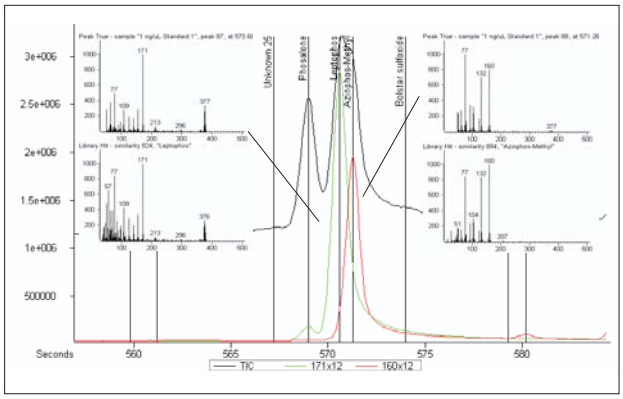

Figure 2. Coeluting substances and their deconvoluted spectra.

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Orange Juice Extracts

For further evaluation, some orange juice extracts 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 Oasis HLB 6cc (Waters). After washing of the cartridge, the compounds were eluted using 10 mL methanol/MTBE (10/90) and the extracts then dried with Na_2SO_4. Instead of further reducing the extract volume, the extracts were directly analyzed using large volume injection.

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) mass spectra.

In Figure 3, the TIC of an orange juice extract is shown.

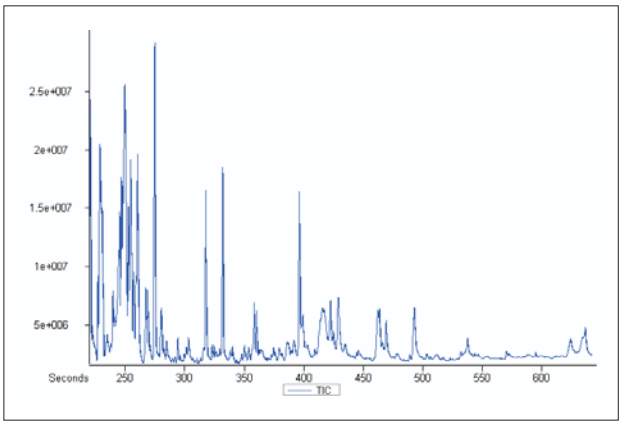

Figure 3. Total ion chromatogram of an orange juice extract spiked to a level of 1 µg/L.

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.

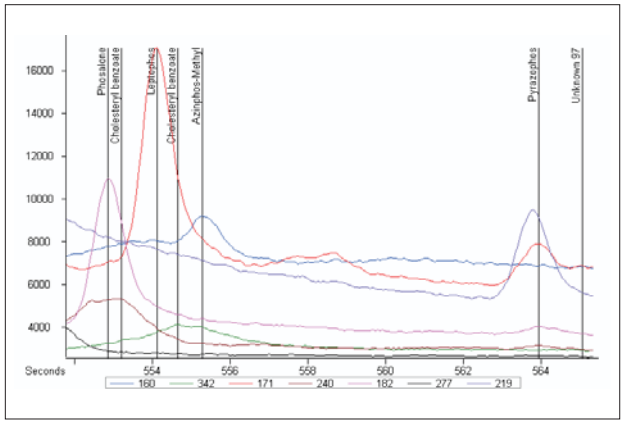

Figure 4. Characteristic mass traces of Phosalone, Leptophos, Azinphos-methyl and Pyrazophos besides coeluting compounds in the spiked orange juice extract

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

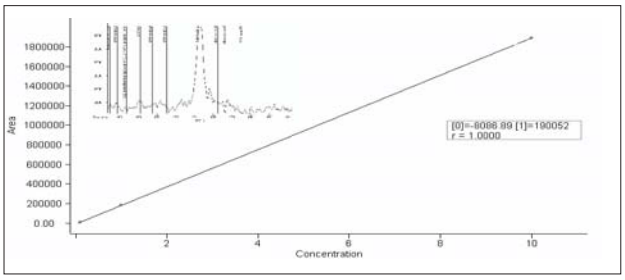

Figure 5. Calibration plot of Iodofenphos between 0.1 and 10 µg/L together with the mass chromatogram for m/z 377 of the 0.1 µg/L extract.

4. Conclusion

As demonstrated in this application, the Pegasus, in combination with a large volume injection system (such as the OPTIC 2) is ideal for performing fast, sensitive determination of pesticides in complex food matrices. 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.

5. Acknowledgements

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