Fast Determination of Chlorinated Priority Pollutants Using Large Volume Injection

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Key Words: GC-TOFMS, Environmental, PCBs, Dioxins, Large Volume Injection, Fume Dust

1. Introduction

The determination of chlorinated compounds such as PCBs, Dioxins, etc. has always been of interest in environmental analysis. As those compounds are known to be carcinogenic, the detection limits of the applied analytical methods need to be as low as possible. One way of achieving high sensitivity is the injection of large sample volumes onto the GC column.

This application note describes the combination of a sophisticated injection system, the ATAS OPTIC 2 (allowing 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 monitoring analyses while maintaining the required sensitivity.

For the method development, a PCB standard mixture was taken. This mixture contained 28 congeners from Monochloro- to Decachlorobiphenyl.

A standard GC method requiring a 50-minute run-time was translated into fast GC conditions using a column which was shorter and had a narrower inner diameter.

2. Experimental Conditions

Large Volume Injection-Parameters

Injection Volume:	10 µL and 50 µL
Vent Time:	automatic by OPTIC 2
Initial Temperature:	40°C
Ramp Rate:	16°/minute
Final Temperature:	315°C
Split Open Time:	165 seconds
Purge Pressure:	8 PSI
Vent Flow:	50 mL/minute
Transfer Pressure:	17.1 PSI
Transfer Time:	90 seconds
Initial Pressure:	17.1 PSI
Final Pressure:	37.6 PSI

GC-Parameters

Column:
Restek™ XTI-5™, 20 m x 0.18 mm x 0.2 µm

Oven Program:
50°C initial temperature, hold for 2 minutes
(4 minutes when 50 µL), with 70°/minute to 150°C,
then 31°/minute to 340°C, hold for 1.5 minutes

Flow Rate:
1.0 mL/minute Helium constant flow

MS-Parameters

Mass Range:	50 to 520 amu
Scan Rate:	20 spectra/second
Ion Source:	170°C
Total Run Time:	11 (13) minutes

3. Results

In Figure 1 the obtained selected ion chromatogram of a PCB standard mixture is shown.

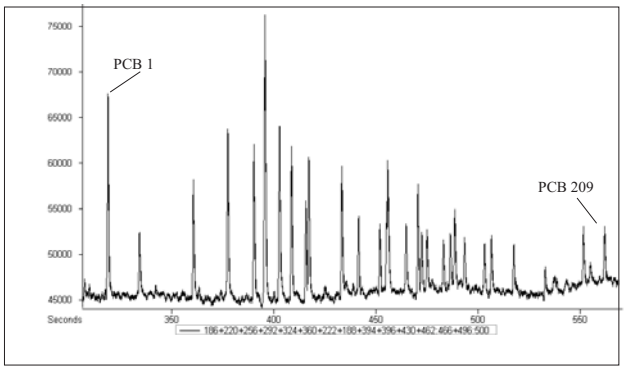

Figure 1. Selected Ion Chromatogram of a PCB standard mixture.

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

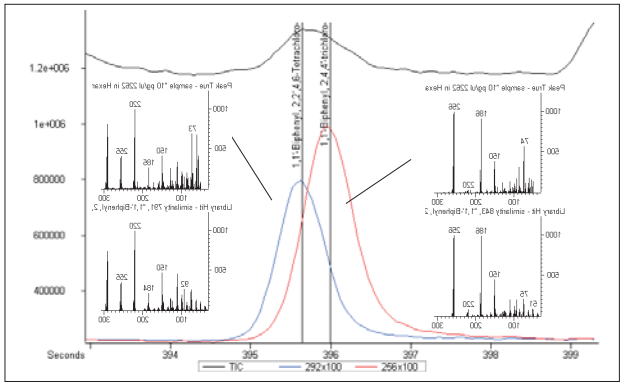

Figure 2. Coeluting PCB #50 and #28 and their deconvoluted spectra.

Varying Injection Volumes

In the following figure a comparison between two large volume injections with 10 and 50 µL injections of a 100 pg absolute analyte amount is shown. The concentrations of the standard solutions were 10 ppb and 2 ppb respectively.

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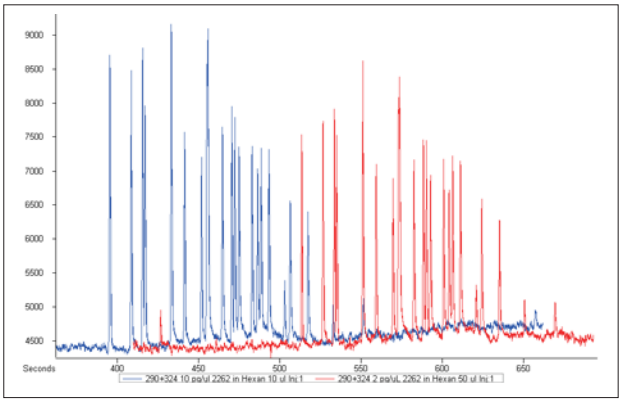

Figure 3. Characteristic mass traces for Tri- and Tetrachlorobiphenyls. 100 pg absolute amounts injected respectively.

High acquisition rate does not mean low spectral quality. In fact, the spectral quality is very good as the spectra over a chromatographic peak show no skewing, which can be observed using quadrupole instruments. The resulting spectra are comparable to literature spectra as shown below.

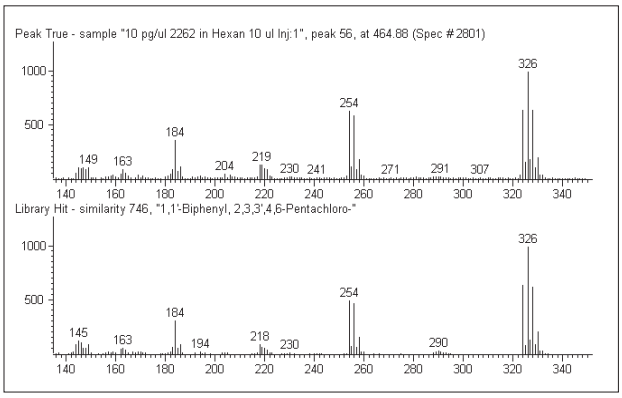

Figure 4. Enlarged view of a deconvoluted and library spectrum of a Pentachlorobiphenyl.

Real World Sample

In order to demonstrate the applicability of the developed method, 50 µL of an extract derived from a municipal waste combustion facility fume dust sample was analyzed.

The Automatic Peak Finding and Deconvolution software detected more than 280 compounds, each with a signal to noise ratio larger than 30.

Besides some PAHs and other combustion products no PCBs were detected in this sample. Instead, a variety of polychlorinated Dibenzofurans and Dibenzop-dioxins were detected. Some characteristic mass traces of hexa-chloro, heptachloro and octachloro compounds are shown below.

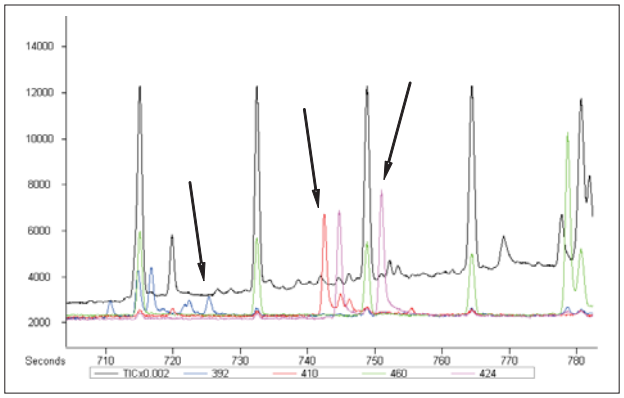

Figure 5. Characteristic mass traces.

After deconvolution of the mass spectra, a standard library search was performed and the compounds could be identified. Three representative mass spectra and their respective library hits are shown in the following figure.

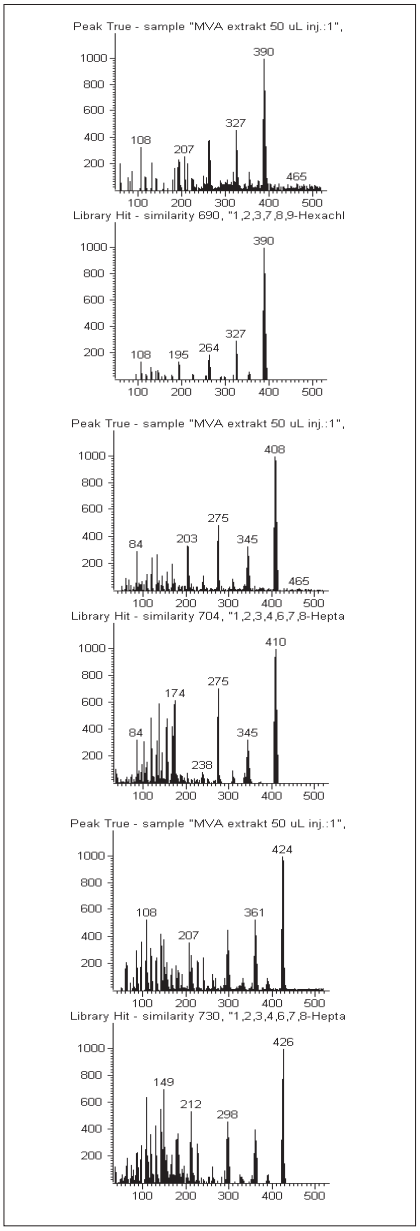

Figure 6. Deconvoluted mass spectra of three Dioxins/Dibenzofurans.

4. Conclusion and Outlook

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 PCBs and dioxins—even out of complex 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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