Application Note No. 067

Fast Analysis of Chlorinated Priority Pollutants using Large Volume Injection

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Introduction

The determination of chlorinated compounds such as PCBs, dioxins, etc., has always been of interest in environmental analysis. These compounds are known to be carcinogenic, therefore the detection limits of the applied analytical methods need to be as low as possible. One way of achieving high sensitivity is to use large volume injection.

This application note describes the combination of a sophisticated injection system like the ATAS Optic 2 in large volume injection mode and the Pegasus II time-of-flight 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.

Target Compounds

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

Instrumentation and Conditions

A standard GC method requiring a 50 minute runtime was translated into fast GC conditions using a shorter column with a smaller internal diameter. This resulted in a total run time of 11 minutes (or 13 minutes for a 50 uL injection). The applied conditions were as follows:

Optic Conditons:

Injection volume:	10 µL and 50 µL
Vent time:	Auto
Initial temperature:	40°C
Ramp rate:	16 °C/min
Final temperature:	315 °C
Split open time:	165 sec
Purge pressure:	8 psi
Vent flow:	50 mL/min
Transfer Pressure:	17.1 psi
Transfer time:	90 sec
Initial pressure:	17.1 psi
Final Pressure:	37.6 psi
Solvent Threshold:	40

GC Conditions:

Column:	Restek XTI-5, 20 m x 0.18 mm x 0.2 µm
Oven program:	50 °C (hold 2 mins) (4 min for 50 µL)
	70 °C/min to 150 °C
	31 °C/min to 340 °C (hold 1.5 mins)
Carrier gas:	Helium at 1.0 mL/min

MS Conditions:

Mass range:	50-520 amu
Scan rate:	20 spectra / second

Ion source temperature: 170°C

Performance of the automated method

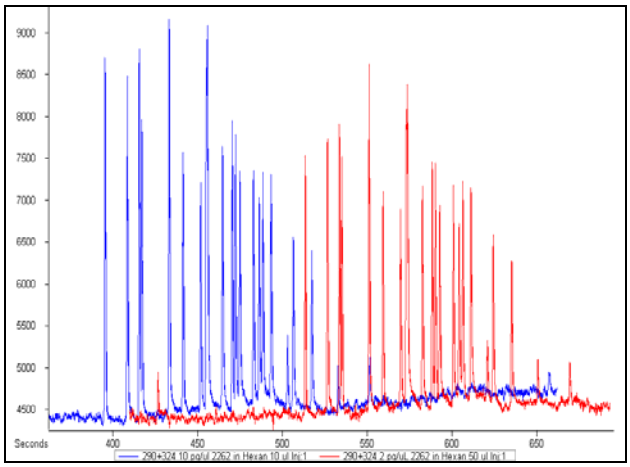

Figure 3: *Characteristic mass traces for Tri- and Tetrachloro-biphenyls, 100 pg of the absolute amount was injected respectively*

A high acquisition rate does not necessarily mean low spectral quality. Infact, the spectral quality is very good as the spectra over a chromatographic peak shows no skewing with the TOF as is observable when using a quadrupole instrument. The resulting spectra are comparable to literature spectra as shown in Figure 4.

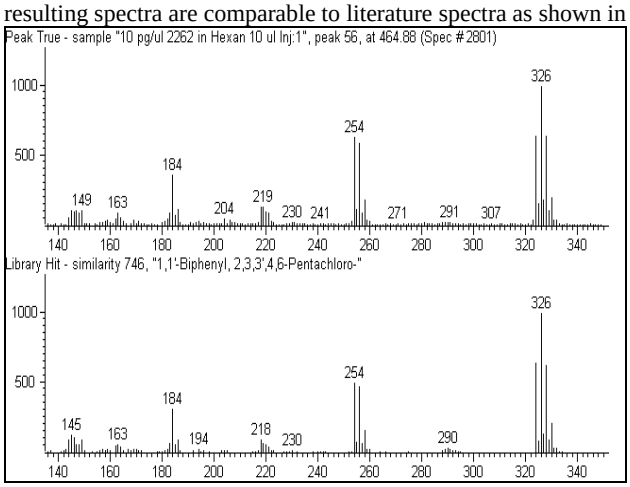

Figure 4: *Enlarged view of a deconvoluted and library spectrum of a Pentachlorobiphenyl*

Real Samples

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

The automatic peak finding and deconvolution software detected more than 280 compounds 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 dibenzofuranes and dibenzop-dioxines were detected. Some characteristic mass traces of hexachloro, heptachloro and octachloro compounds are shown below.

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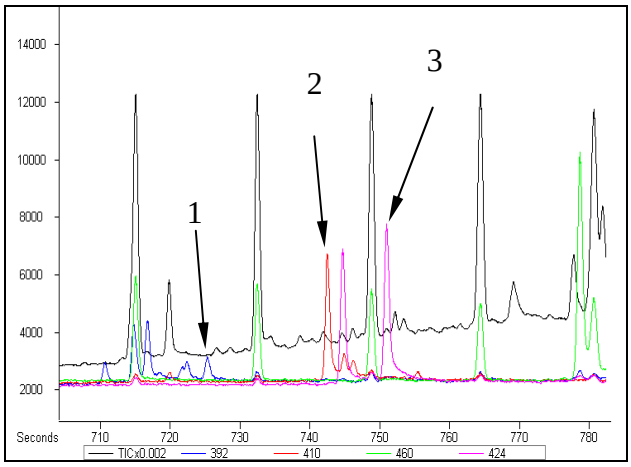

Figure 5: *Characteristic mass traces of (1) hexachloro, (2) heptachloro and (3) octachloro PCBs*

After deconvolution of the mass spectra, a standard library search was performed where the compounds could be identified. Three representative mass spectra and their respective library hits are shown in the Figure 6.

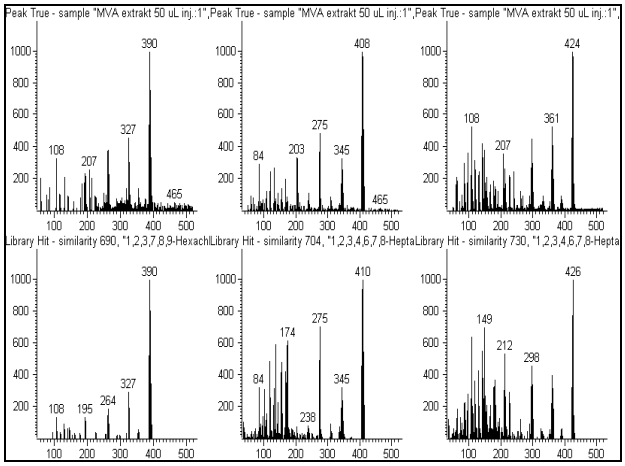

Figure 6: *deconvoluted mass spectra of three Dioxines/Dibenzofuranes*

Conclusion

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 PCBs and dioxins, even from complex matrices. The data processing software does not only allow the detection and identification by comparison of complete spectra of the target compounds, which can even be achieved when the components are buried well below the baseline, but can additionally search for unknown substances after separating overlapping spectra where a proper library identification can be conducted due to a cleaned-up spectra .

By means of higher scan rates, larger injection volume etc., a further acceleration and increase in sensitivity could be easily accomplished.

Acknowledgement

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