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 µL injection). The applied conditions were as follows:

**Optic Conditions:**
- 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

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](image1)

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](image2)

Varying Injection Volumes

In the following figure a comparison is made between two large volume injections of 10 and 50 µL of a 100 pg analyte of an absolute amount. The concentrations of the standard solutions were 10 ppb and 2 ppb respectively.
A high acquisition rate does not necessarily mean low spectral quality. In fact, 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.

**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.
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.

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