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High sensitive MID detection method for toxaphenes by Magnetic Sector GC-HRMS

Authors

Frank Theobald,
Environmental Consulting,
Cologne, Germany

Dirk Krumwiede, Heinz Mehlmann,
Thermo Fisher Scientific,
Bremen, Germany

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Goal

Assess the quantitative performance of the Thermo Scientific DFS Magnetic Sector GC-HRMS for the analysis of toxaphenes in compliance with existing regulations.

Introduction

The analysis of toxaphenes still is challenging, not limited to the almost impossible chromatographic separation of the vast amount of isomers, the injection technique as well as the ionization performance have a great influence over reproducibility, linearity and sensitivity.[1,4] Magnetic Sector technology offers the potential for a sensitive analysis providing the selectivity to overcome limiting interferences with matrix components as well as possible coelutions with other xenobiotica.

Toxaphenes are included in the Annex A of the Stockholm Convention to protect human health and the environment from persistent organic pollutants (POPs).[2] The international community has called for urgent global actions to reduce and eliminate releases of these listed chemicals including toxaphenes.

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Toxaphene is a complex mixture of polychlorinated camphenes (polychlorinated bornanes) that was first introduced in 1945 as broad band insecticide. The vast number and complexity of isomers results from the simple production process from the UV catalysed reaction of chlorine with camphene providing a product with a chlorine content of about 67 to 69%. Until the mid 1980s, it was mass produced and widely used particularly in the cotton-growing industry. Between 1945 and 1974 more than 450,000 mt have been produced and deployed in agriculture[3].

Figure 1. Thermo Scientific DFS Magnetic Sector GC-HRMS.

The lipophilic, persistent and volatile nature of toxaphene has contributed to its global dispersion throughout freshwater and marine environments. Therefore, increased attention has been focused on toxaphene, both in the analytic and toxicologic fields. Toxaphene is believed to present a potential carcinogenic risk to humans.[3]

Analytical method

By Magnetic Sector technology high sensitive toxaphene analyses have been characterized with the background for providing risk management data to comply with the monitoring program of the Stockholm Convention.

The known degradation of toxaphene congeners in a hot split/splitless injector can be significantly reduced by using cold injection techniques.[4] In this application a programmable temperature injector (PTV) was used with additional surge pressure for an accelerated sample vapour transfer to the analytical column. The parameters for the chromatography method are given in Table 1.

Table 1. Gas Chromatography Parameters.

Gas Chromatography Parameters	
Injector type	PTV
Injection mode	Splitless, 2 min, split flow 12 mL/min
Surge pressure	150 kPa, 1 min
Injector program	90 °C
Transfer rate	10 k°C/s
Transfer temperature	290 k°C, 5 min
Cleaning rate	10 °C/s
Cleaning temperature	310 °C, 5 min
Cleaning flow	70 mL/min
Carrier gas	He
Carrier gas flow	1.5 mL/min
Oven program	95 °C, 2 min 15 °C/min to 160 °C 6 °C/min to 280 °C, 1 min

Table 2. Mass Spectrometer Parameters.

Mass Spectrometry Parameters	
Ionization	NCI
Reagent gas	iso-butane, 3.5 x 10^{-4} mbar
Ion source temperature	100 °C
Electron energy	120 eV
Filament current	0.3 mA
Detection mode	MID, 3 windows
Cycle time	0.5 s
Resolution	10,000 at 5% peak height (10% valley definition)

As ionization mode negative chemical ionization with isobutane was applied. NCI provides less fragmentation and focuses the ion stream on only few isomers typically as the molecular ions M.- which can be detected at lowest LODs. The resulting compound spectra are shown in Figure 2-6. The reagent gas pressure in the ion source is of highest importance for a consistent spectral quality and high response. The optimization of the reagent pressure resulted in a minimum required ion source pressure at 2 x 10^{-4} mbar.

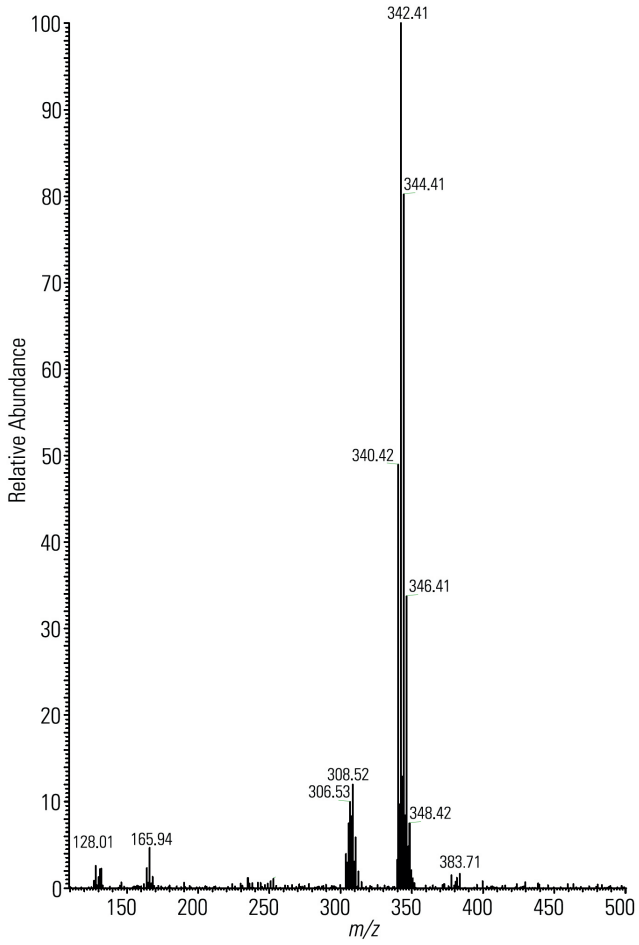

Figure 2. P32 Mass spectrum in NCI Mode (M 340, hepta Cl).

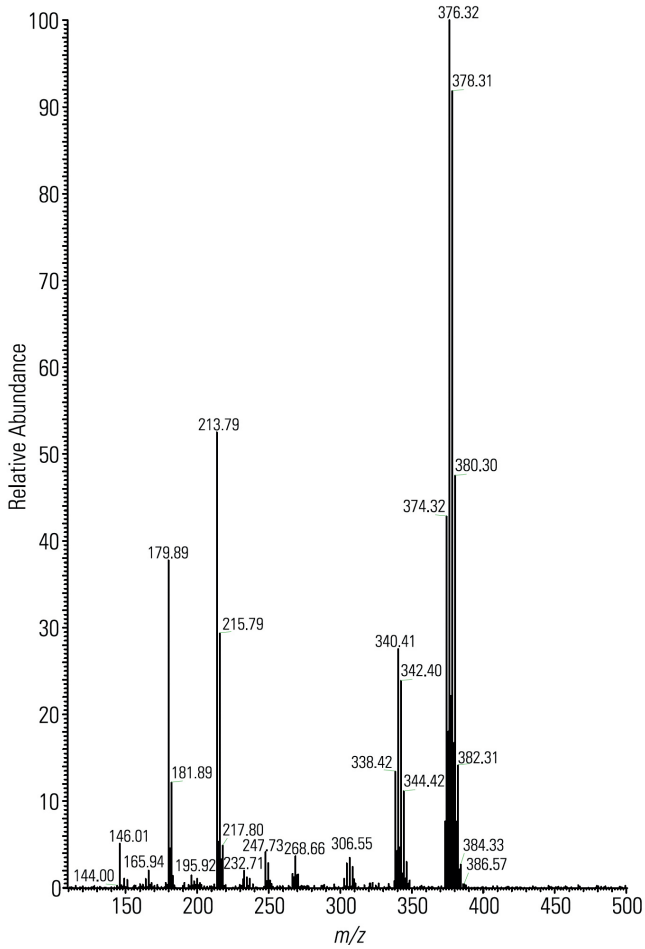

Figure 3. P26 Mass spectrum in NCI Mode (M 374, octa Cl).

The toxaphene congeners used in this study have been, in the nomenclature given by Parlar, P32 (hepta Cl), P26 (octa Cl), P50 , P62 (both nona Cl) and P69 (deca Cl). The components P26, P50 and 62 have been analyzed as the stable lead congeners while Parlar 32 and 69 are subject to natural degradation in a sample indicating a fresh contamination.[4,5] The congeners P26, P50, and P62 also are focused on in the monitoring program of the Stocholm convention[3] of which P62 is known to be thermolabile in gas chromatography.[4] The standards measured and a sample extract has been prepared in i-octane, 2.5 µL have been injected for each run by a Thermo Scientific TriPlus autosampler. The quantitation of the toxaphene congeners has been done by the internal standard method (ISTD) using PCB 169 as ISTD in MID window #3.

Experimental conditions

Thermo Scientific™ DFS™ Magnetic Sector GC-HRMS coupled with a Thermo Scientific TRACE GC Ultra* and a Thermo Scientific TriPlus Autosampler was used for this analysis. The chromatographic separation was achieved on a 30 m x 0.25 mm x 0.1 µm Thermo Scientific TRACE -5MS column.

Results

Negative chemical ionization is the ionization method of choice for providing high selectivity in real life sample as well as high response values leading even to sub fg LODs.

The investigation on the spectral composition showed the structural dependence of the fragmentation pathways, see Figure 2-6. For all congeners in this study an intense molecular ion response was achieved by NCI. The twomost intense ions have been identified for setup of the multiple ion detection method (MID) used for quantitation and isotope ratio confirmation, see Table 3.

As qualifier besides of the accurate mass, the retention time and isotope ratio of the monitored masses can be checked.

*The analysis can be readily undertaken on the latest Thermo Scientific™ TRACE™ 1310 Gas Chromatograph.

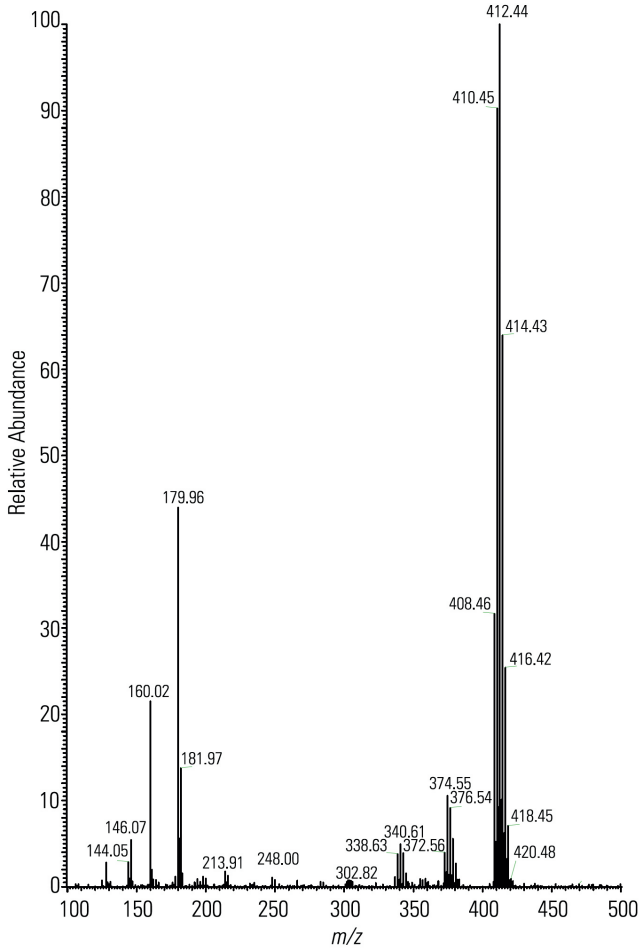

Figure 4. P50 Mass spectrum in NCI Mode (M 408, nona CI).

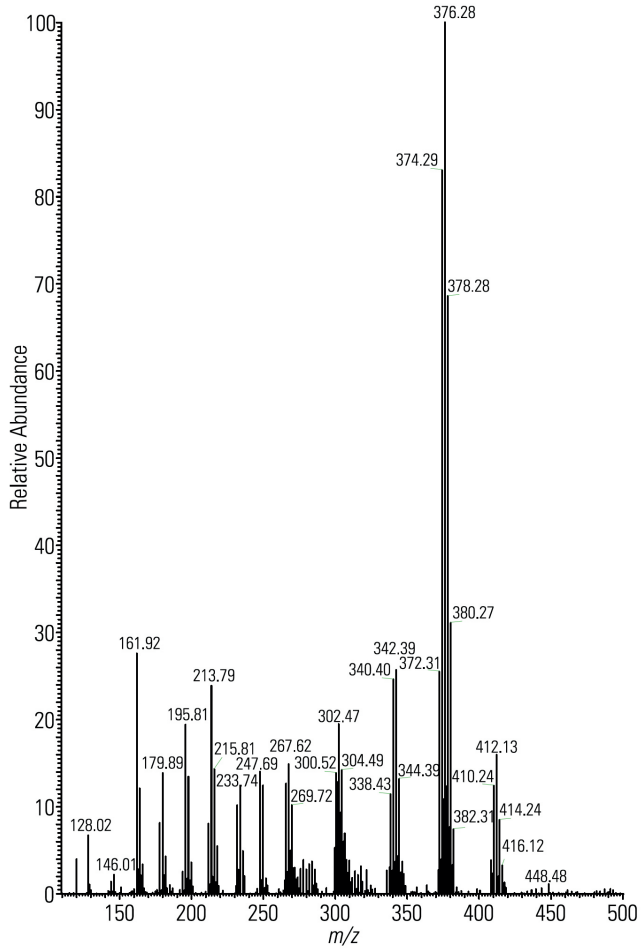

Figure 5. P62 Mass spectrum in NCI Mode (M 372, nona CI).

Table 3. Multiple Ion Detection parameters with the exact masses used for the quantification of P26, P50 and P62.

Window #1, start at 8:00 min (for P26)		
Mass [Da]	**Function**	**Time [ms]**
368.9766	lock mass	10
376.8578	native	210
378.8549	native	210
380.9766	cali mass	10
Window #3. start at 18:00 min (for P62)		
Mass [Da]	**Function**	**Time [ms]**
392.9766	lock mass	10
410.8189	native	210
412.8159	native	210
430.9734	cali mass	10
Window #3. start at 18:00 min (for P62)		
Mass [Da]	**Function**	**Time [ms]**
359.8420	internal standard	12
361.8391	internal standard	12
368.9766	lock mass	10
374.8422	native	210
376.8392	native	210
380.9766	cali mass	10

For MID detection, the chromatographic separation has been optimized in order to achieve a fast separation within 30 min with good peak separation of the congeners P26, P50 and P62 used in the Stockholm convention monitoring program. In MID quantification, a strong response could be achieved with high individual S/N ratios. LOQs have been estimated from a S/N value of 36 for 2.5 fg P50 to range down into the sub fg range. Linear quantitative calibrations have been achieved over 6 orders of magnitude for the stable P26 and P50, and with 5 orders of magnitude for the thermolabile P62. The analysis of a sample with a technical congener distribution showed excellent selectivity at a resolution of 10,000 with a reliable peak integration.

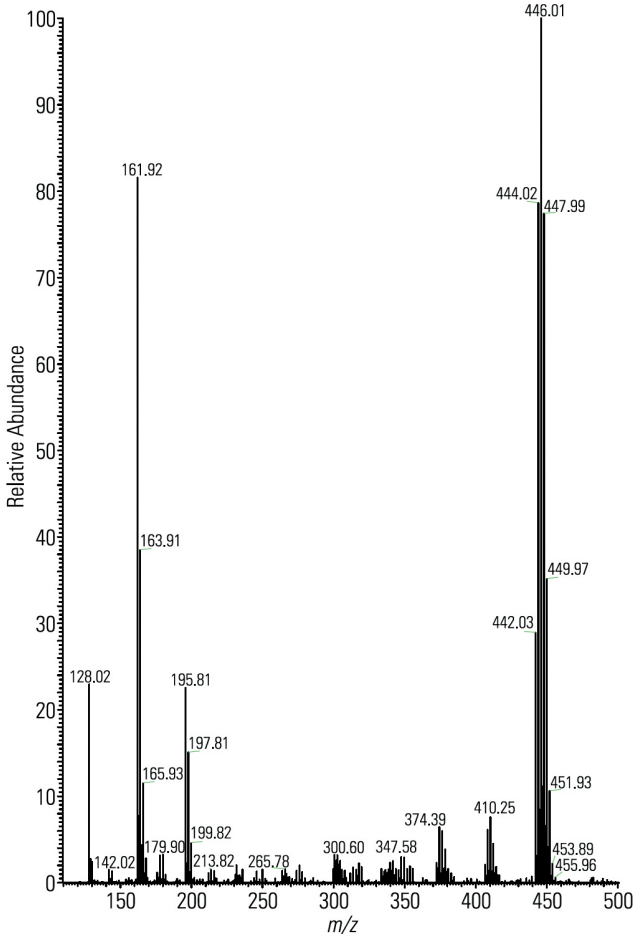

Figure 6. P69 Mass spectrum in NCI Mode (M 442, deca Cl).

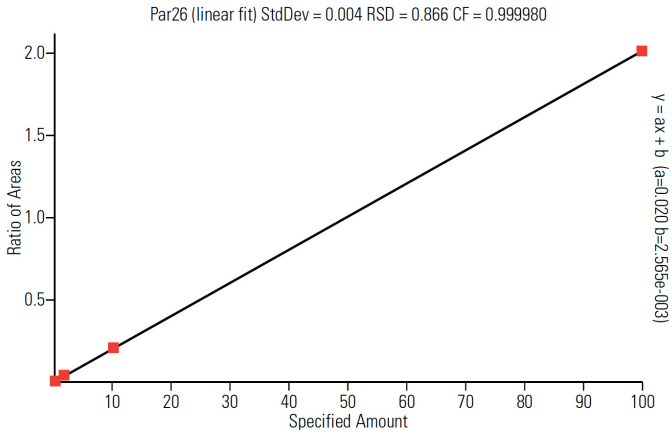

Figure 7. Linear response calibration for P50 in the range of 2.5 fg to 100 pg and P62 in the range of 10 fg to 50 pg.

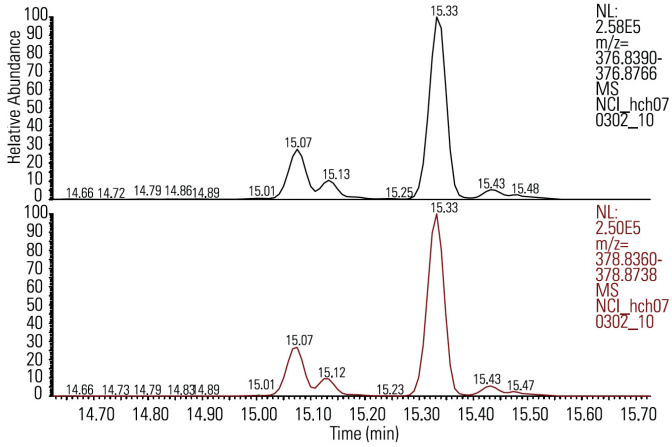

Figure 8. High resolution MID mass chromatograms of a sample analysis, P26 content determined as 4.3 pg/µL at 15.07 min.

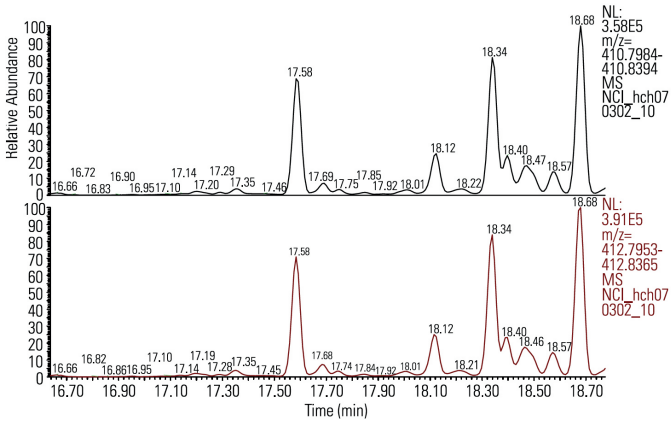

Figure 9. High resolution MID mass chromatograms of a sample analysis, P50 content determined as 1.4 pg/µL at 17.58 min.

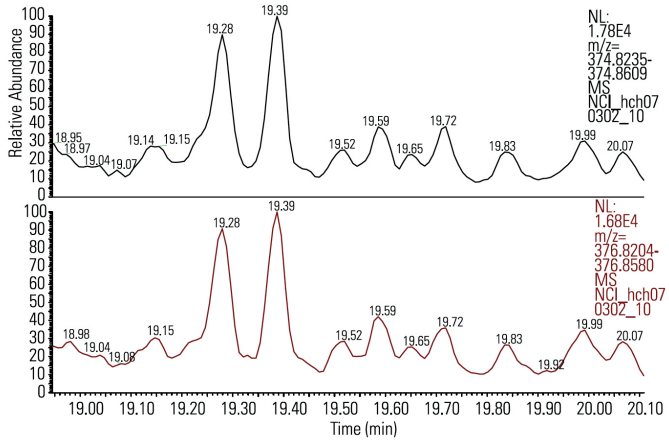

Figure 10. High resolution MID mass chromatograms of a sample analysis, P62 content determined as 2.9 pg/µL at 19.28 min.

Conclusions

The demonstrated data of the toxaphenes congeners P26, P50 and P62 excellently show the new capabilities of modern high resolution mass spectrometry for trace analysis and the highly sensitive monitoring of toxaphenes.

The chromatography conditions using PTV cold injection technique have successfully been applied to avoid thermal degradation even of the labile P62 congener. Negative chemical ionization with DFS Magnetic Sector GC-HRMS has been shown to provide consistent ionization with high response on molecular ions of highest response and specificity. The quantitative calibrations show excellent linearity down to the low fg range with estimated LOQs in the sub fg range.

References

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