

DETERMINATION OF COMPOUNDS OF TECHNICAL TOXAPHEN BY USING GC/ECNI-MSMS IN THE SELECTED REACTION MONITORING MODE

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Introduction

Toxaphene (Camphechlor, Melipax) has been used on a million-ton scale as a pesticide since 1945.¹ It is formed by the photochlorination of camphene which yields ~1000 compounds of technical toxaphene (CTTs).^{1,2,3} Because of its persistence in the environment, the bioaccumulative behavior of selected CTTs along with its toxicity to fish and higher animals, toxaphene was banned in many countries some twenty years ago.⁴ In the environment, the complex technical mixture is significantly changed.⁴ Despite the resulting shifts in the CTT patterns of environmental samples, the control of food and environmental samples for CTT residue is still an important task. Therefore, sensitive and selective detection methods are required. The most widely used method is GC/ECNI-MS in the SIM mode.⁴ Recently, GC/EI-MSMS methods were developed as a potential alternative to GC/ECNI-MS. The introduction of bench top triple quadrupoles enables also the use of GC/ECNI-MSMS. This technique was recently proved to be suitable for the determination of PBBs.⁵ In this study we investigated for the first time the possibilities of a GC/ECNI-MSMS method for the selective and sensitive determination of CTTs.

Materials and Methods

Samples and Chemicals: Toxaphen-Mix 3 (Dr. Ehrenstorfer, Augsburg, Germany) consisted of 1 ng/μL of 2-*endo*-,3-*exo*-,5-*endo*-,6-*exo*-,8,8,10,10-octachlorobornane (B8-1413, P-26), 2-*endo*-,3-*exo*-,5-*endo*-,6-*exo*-,8,9,10,10-octachlorobornane (B8-1414, P-40), 2-*exo*-,3-*endo*-,5-*exo*-,8,9,9,10,10-octachlorobornane (B8-1945, P-41), 2-*exo*-,5,5,8,9,9,10,10-octachlorobornane (B8-2229, P-44), 2,2,5,5,8,9,9,10,10-nonachlorobornane (B9-1025, P-62), and 2-*endo*-,3-*exo*-,5-*endo*-,6-*exo*-,8,8,9,10,10-nonachlorobornane (B9-1679, P-50). To the solution of these six congeners a calibrated solution of 2-*exo*-,3-*endo*-,5-*exo*-,9,9,10,10-heptachlorobornane (B7-1453; c = 6.88 ng/μL) and 2-*endo*-,3-*exo*-,5-*endo*-,6-*exo*-,8,8,9,10-octachlorobornane (B8-1412; c = 4.4 ng/μL) was added and diluted to a final concentration of ~10 pg/μL.

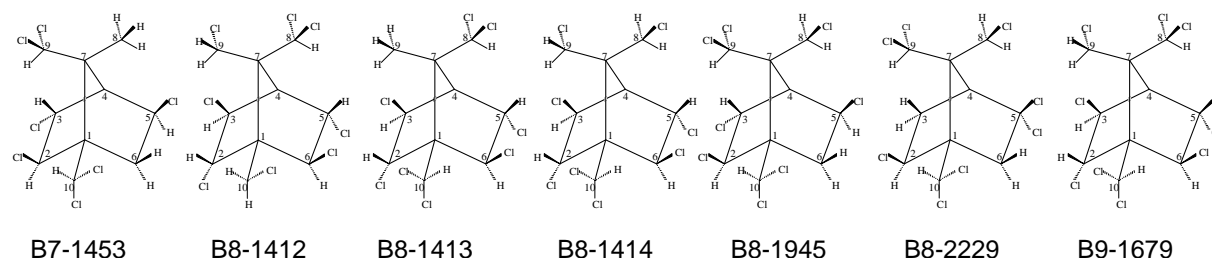


Figure 1: structures of important CTTs studied in this presentation

GC/ECNI-MS. GC/MS measurements were performed with a CP-3800 GC coupled to a 1200 triple-quadrupole MS system (Varian, Darmstadt, Germany). Helium 5.0 was used as carrier gas at a flow rate of 1.0 mL/min. The injector and transfer line temperatures were set at 250 °C and 280 °C, respectively.

The GC analysis were performed with a Factor Four™ VF-5ms column (30 m x 0.25 mm i.d. x 0.25 μm d_f, Varian). The GC oven temperature program started at 60 °C (hold time 3.0 min), which was then raised at 3 °C/min to 110 °C (hold time: 0.33 min) and finally, at 20 °C/min to 270 °C (hold time 24.0 min). The total run

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time was 60 min. Injections were performed in splitless mode (split opened after 2 min). A constant flow rate of 1 mL/min was used throughout the measurements. A solvent delay of 5 min was applied.

The electron energy was set at 70 eV and the filament emission current was set at 150 μ A. The ion source temperature was maintained at 200 °C. Methane 5.0 was used as the reagent gas at approximately 8.5 Torr. GC/ECNI-MS-SIM experiments were carried out by monitoring m/z 340.9, 341.9, 342.9, 343.9 for heptachloro bornanes, m/z 374.9, 375.9, 376.9, 377.9 for octachloro bornanes, and m/z 410.8, 411.8, 412.8, 413.8 for nonachloro bornanes, corresponding with the respective $[M-Cl]^-$ ions of the chlorobornanes determined. The detector was set at 1200 V and the scan rate was two cycles per second, respectively. The SIM peak width was set at 0.5 u.

GC/ECNI-MSMS-SRM experiments were carried out using Argon 4.5 as the collision gas at a pressure of \sim 1.6 mTorr. GC/MS parameters were identical with GC/ECNI-MS-SIM except for the scan rate which was set at 5 cycles per second. In the single reaction monitoring (SRM) mode, the most abundant isotope peak of the $[M-Cl]^-$ were used as precursor ions, respectively, using mass ranges of 3 u. Consequently, m/z 342.9 ± 1.5 was used as precursor ion for heptachlorobornanes, m/z 376.9 ± 1.5 was used for octachlorobornanes and m/z 412.8 ± 1.5 for nonachlorobornanes. The product ions were m/z 36 or m/z 72 at width ranges of 3 u. Thereafter, the mass ranges monitored are not mentioned for reasons of simplicity. The collision voltage was set at 6 V when m/z 36 was measured and was set at 9 V when m/z 72 was measured. The detector voltage was set at 1500 V.

Results and Discussion

The GC/ECNI-MS-SIM methods are usually based on the determination of the $[M-Cl]^-$ fragment ion except for B9-1025 ($[M-HCl-Cl]^-$) which was not included in this study. The SIM chromatogram of the standard mix showed the known elution pattern. Due to the short DB-5 like column, B8-1414 and B8-1945 co-eluted (**Figure 2**).

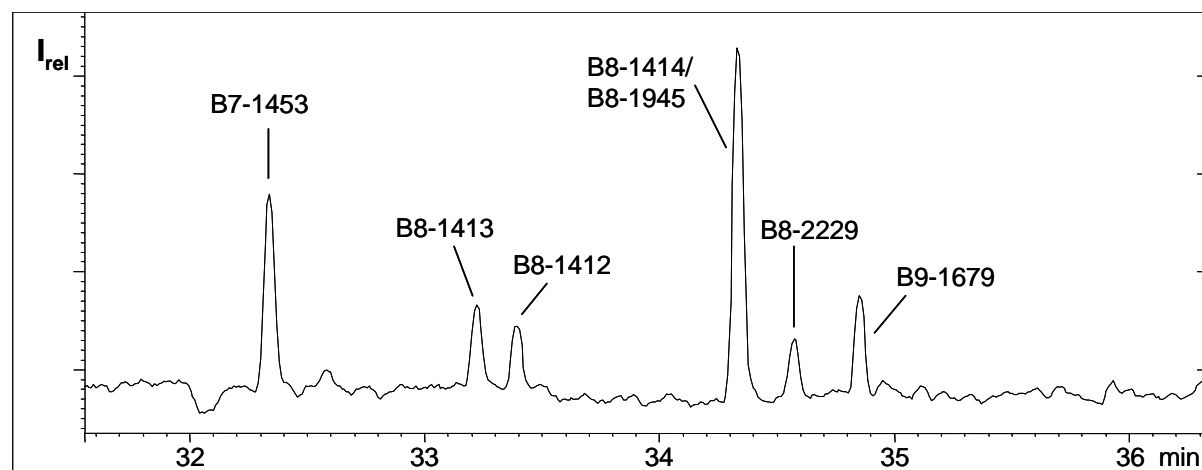


Figure 2: GC/ECNI-MS-SIM chromatogram (TIC) of the CTT standard mixture

GC/ECNI mass spectra are mostly composed of the $[M-Cl]^-$ along with the Cl^- as well as Cl_2^- and/or HCl_2^- fragment ions (**Figure 3**). The former ($[M-Cl]^-$) was considered as a suitable precursor ion whereas the latter ones were thought of being suitable product ions in MSMS. Different collision voltages were tested for both SRMs. The best S/N ratio was obtained with collision voltages of 6 V and 9V for the product ions m/z 36 and m/z 72, respectively. Both SRMs led to the sensitive detection of the target compounds (**Figure 4**). However, m/z 72 was superior to m/z 36 due to the following reasons. First, the Varian 3800/1200 MSMS system showed a background signal for chlorine isotopes which could not be eliminated by the supplier. This unavoidable contaminant in the Varian system limited the screening of the chloride ion in GC/ECNI-MS owing to a high noise level. Moreover, aromatic contaminants such as PCBs give response for the chloride ion but not for Cl_2^- .

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and HCl_2^- .⁶ Therefore, the latter will provide a higher selectivity compared to m/z 36. The SRM chromatograms (Figure 4) of the standard showed a similar pattern compared with GC/ECNI-MS-SIM (Figure 1).

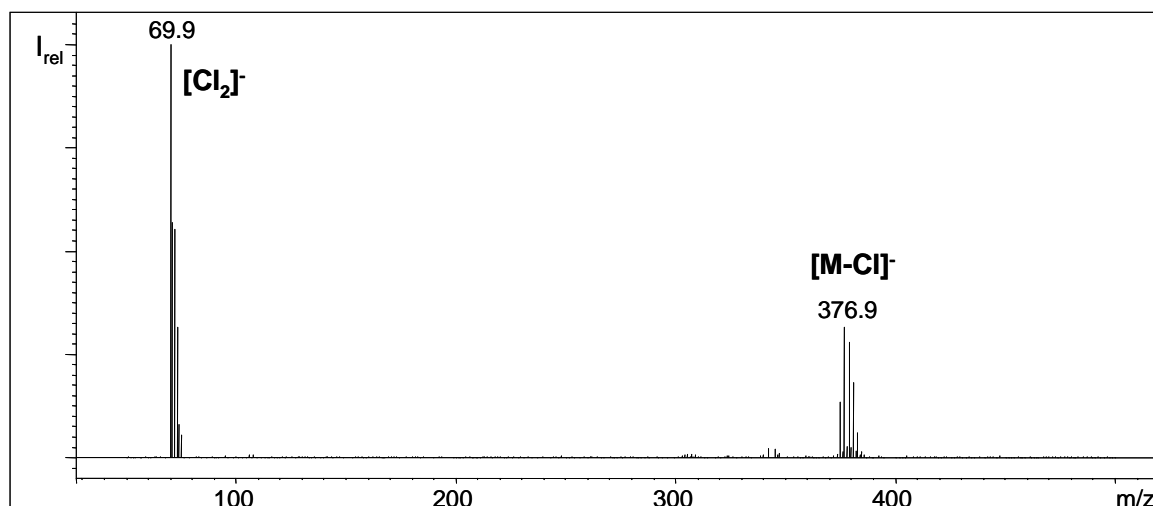


Figure 3: GC/ECNI mass spectrum of B8-1412

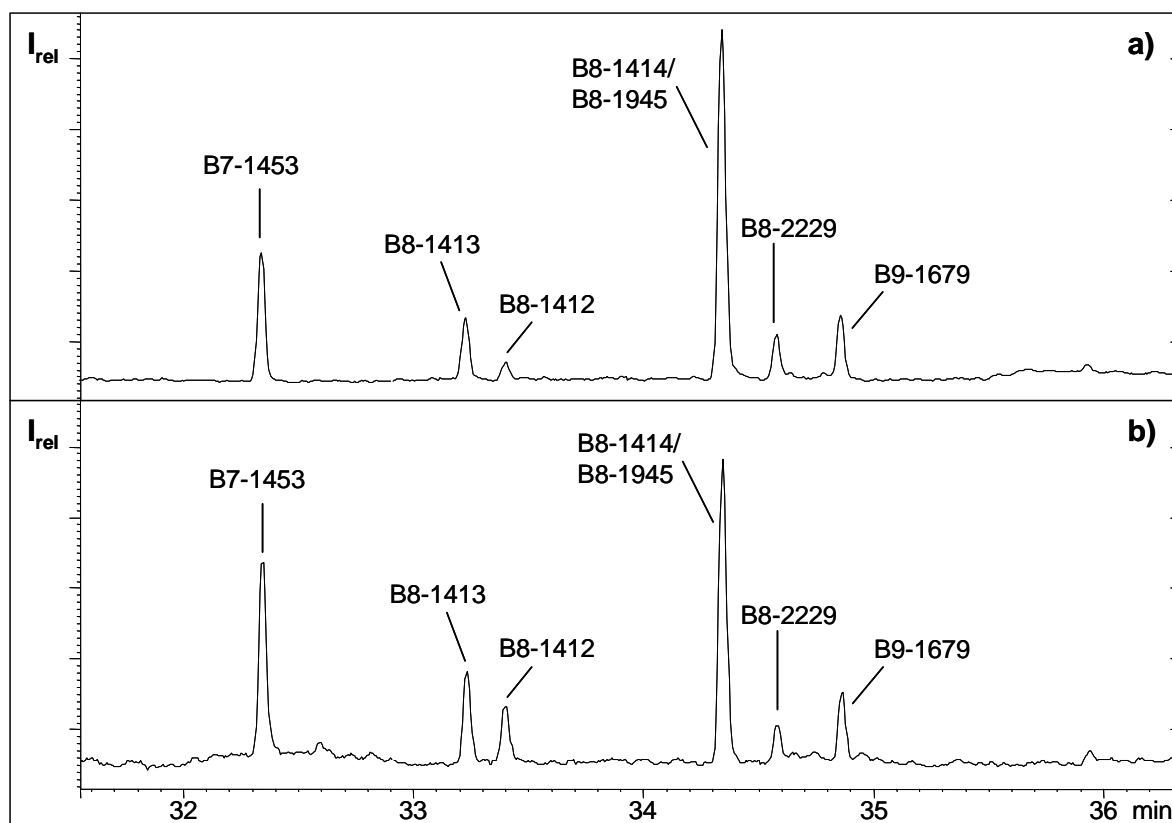


Figure 4: GC/ECNI-MSMS-single reaction chromatograms of the bornane standard solution. (a) SRM $[\text{M}-\text{Cl}]^- \rightarrow m/z$ 72 and (b) SRM $[\text{M}-\text{Cl}]^- \rightarrow m/z$ 36 (see text for details)

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Under the conditions applied, the S/N of GC/ECNI-MSMS-SRM was superior to GC/ECNI-MS-SIM in most cases (exceptions: B8-2229, SRM m/z 376 \rightarrow m/z 36 and B8-1412, SRM m/z 376 \rightarrow m/z 72, **Table 1**). The S/N factor between GC/ECNI-MS-SIM and GC/ECNI-MSMS-SRM ranged from 0.7 to 3.5 (**Table 1**). It appears that higher sensitivity in GC/ECNI-MSMS was particularly obtained for lower chlorinated compounds. However, more CTT congeners need to be analyzed for verification.

Table 1: S/N ratios of the investigated CTTs by GC/ECNI-MS-SIM and GC/ECNI-MSMS-SRM detection

CTT	GC/ECNI-MS		GC/ECNI-MSMS	
	SIM	SRM [M-Cl] ⁻ \rightarrow m/z 36 ⁻	SRM [M-Cl] ⁻ \rightarrow m/z 72 ⁻	
B7-1453	7.4	15.2	24.0	
B8-1413	5.3	8.4	10.0	
B8-1412	3.8	7.0	3.3	
B8-1414/B8-1945	17.9	31.3	33.3	
B8-2229	4.6	3.2	5.6	
B9-1679	4.9	6.4	12.0	

Conclusions

In this study we used for the first time GC/ECNI-MSMS in the selected reaction monitoring mode for the determination of toxaphene. Our initial experiments indicate that GC/ECNI-MSMS-SRM sensitivity may be higher compared to conventional GC/ECNI-MS SIM. However, the method provides a much better selectivity for toxaphene. For instance, it is known that the presence of minute amounts of oxygene will produce artefacts from PCBs that display the same ions as screened by the GC/ECNI-MS-SIM determination of toxaphene.^{7,8} Using GC/ECNI-MSMS-SRM this problem can be overcome by using m/z 72 as the product ion since this fragment ion is not formed for PCBs.⁶ Future research needs to determine the reproducibility of the method. Furthermore, suitable internal standards need to be identified and incorporated in a method dedicated to the quantification of CTTs in food and environmental samples. Although these problems need to be solved, the present results support the idea that GC/ECNI-MSMS-SRM can be an interesting alternative to the GC/ECNI-MS-SIM determination of toxaphene in food and environmental samples.

References

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