Analysis of Toxaphene by Tandem Mass Spectrometry

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Introduction

Toxaphene is a complex mixture mainly consisting of polychlorinated bornanes (CHBs, 76%), bornenes (18%) and bornadienes (2%) and other chlorinated and non-chlorinated hydrocarbons with an average elemental composition of $C_{10}H_{10}Cl_8$ [1]. This organochlorine pesticide was widely used in insect control on cotton, vegetables, grain and soya bean crops, and in the control of the external insects on livestock [2]. In the early 1980s, the use of toxaphene was restricted in the USA, Canada and some European countries because of its toxicity, environmental persistence and bioaccumulating capabilities [3].
The analysis of toxaphene is difficult due to the complexity of the mixture (more than 670 compounds). The components elute over a wide range of GC retention times and are not completely resolved even by high resolution GC. Additionally, interference from many other organochlorine compounds can cause problems in chromatographic separations. Moreover, the composition and pattern of toxaphene in environmental samples is different from those of commercial toxaphene mixtures due to the extensive environmental and metabolic transformations and atmospheric transport of certain congeners, [4] which further complicates toxaphene quantification. Capillary gas chromatography coupled with electron-capture detection (ECD) and electron-capture negative ion mass spectrometry (ECNI-MS) in selected ion monitoring mode are the two most commonly used techniques for the analysis of toxaphene in biological and environmental samples and they are recognized as being a sensitive and specific methods but are susceptible to various interferences [5]. However, the ionization of CHB congeners is affected by ECNI conditions giving a range of responses that can lead to false negative results [6]. High resolution mass spectrometry (HRGC/HRMS) has been also applied to the characterization of toxaphene mixture [7] and in environmental samples [8].
In the present work Tandem mass spectrometry (HRGC/EI-MS/MS) [9], on multi-reaction monitoring (MRM) mode, have been also applied for the characterization of polychlorobornanes in technical toxaphene. The ionization conditions, collision energy and collision gas pressure (Xe) have been optimised. Precursor and Product-Q ion experiments were carried out in order to determine the EI fragmentation pathways of the polychlorobornanes and to choose the specific

parent/products ion transitions for the MRM experiments. A comparative study of the use of these techniques for the analysis of toxaphene is discussed.

Materials and Methods

Chemicals

Toxaphene was purchased from Chem-Service (West Chester, PA, USA), a standard solution USL 421, a mixture of four CHB congeners: Parlar No 26, 32, 50 and 62 was obtained from Promochem (Wesel, Germany) and Toxaphen 22 components Mix 2, from Dr.Ehrenstorfer (Augsburg, Germany).

High resolution gas chromatography-Tandem mass spectrometry

HRGC/EI-MS/MS analyses were performed on an AutoSpec-Q hybrid (E_1BE_2qQ) mass spectrometer (VG Instruments, Manchester, UK) with an OPUS 2.0 data system interface and DEC VAX 3100 M38 Workstation for data processing coupled with a Hewlett-Packard (Palo Alto, CA, USA) model 5890 Series II gas chromatograph. A DB-5 (J&W Scientific, Folsom, CA, USA) fused-silica capillary column (60m x 0.25 mm I.D., 0.25 μm film thickness) was used with helium as the carried gas at a linear velocity of 30 cm/s. The temperature programme was from 90°C (held for 3 min) to 200°C (held for 1 min) at 20°C/min, and then from 200°C to 300°C (held for 5 min) at 2.5°C/min, using the split-less injection mode during 1 min.
For the EI-MS/MS mode, the instrument was calibrated with perfluorokerosene (PFK) by the selected dissociation of PFK precursor ions and the monitoring of product-Q ions on a quadrupole analyzer.The product-Q ions spectra were obtained by selecting the precursor ion by MS1 with a resolution of *ca.* 1,000. The precursor ion collided with xenon ($3.16x10^{-6}$ mbars) in the collision cell (rf-only quadrupole collision cell, q) and Q was scanned at 2 s/scan over the m/z range between 50 and 450. For precursor ions spectra, the product-Q was selected in the MS2 with a unit resolution and the magnetic field was scanned at 2 s/decade. Multi-reaction monitoring mode were used selecting the Parent/Product-Q ions specific of each homologue group, previously determined in the fragmentation studies.

Results and Discussion

Initial experiments were conducted to optimize the EI parameters using the standard solution USL 421, which containing the chlorobornanes Parlar No. 26, 32, 50 and 62. The optimized parameter were: source temperature 160°C, electron energy 35 eV and trap current 500 μA. The EI+ mass spectra obtained in this conditions allowed to increase the abundance of the fragment ions at higher mass. In all cases, no molecular ions were observed and the $[M\text{-}CHCl_2]^+$, $[M\text{-}Cl\text{-}3HCl]^+$, fragment ions were the most abundant ions for Parlar No. 26 and 32, respectively, and $[M\text{-}Cl\text{-}2HCl]^+$ was the most abundant ion for Parlar No. 50 and 62.
EI-MS/MS experiments were carried out in order to optimize the conditions for the recording of the precursor and product-Q ions for each homologue group using a toxaphene standard. Initially, experiments were conducted to optimize the collision energy and collision gas pressure in the collision-induced dissociation cell by maximizing the formation of the product ions from the precursor ions of each homologue group.The optimal conditions for collision energy and collision gas pressure were obtained at 35 eV and $3.16x10^{-6}$ mbars. HRGC/MS/MS experiments were used to determine the precursor/product-Q ions specific of each homologue group.The

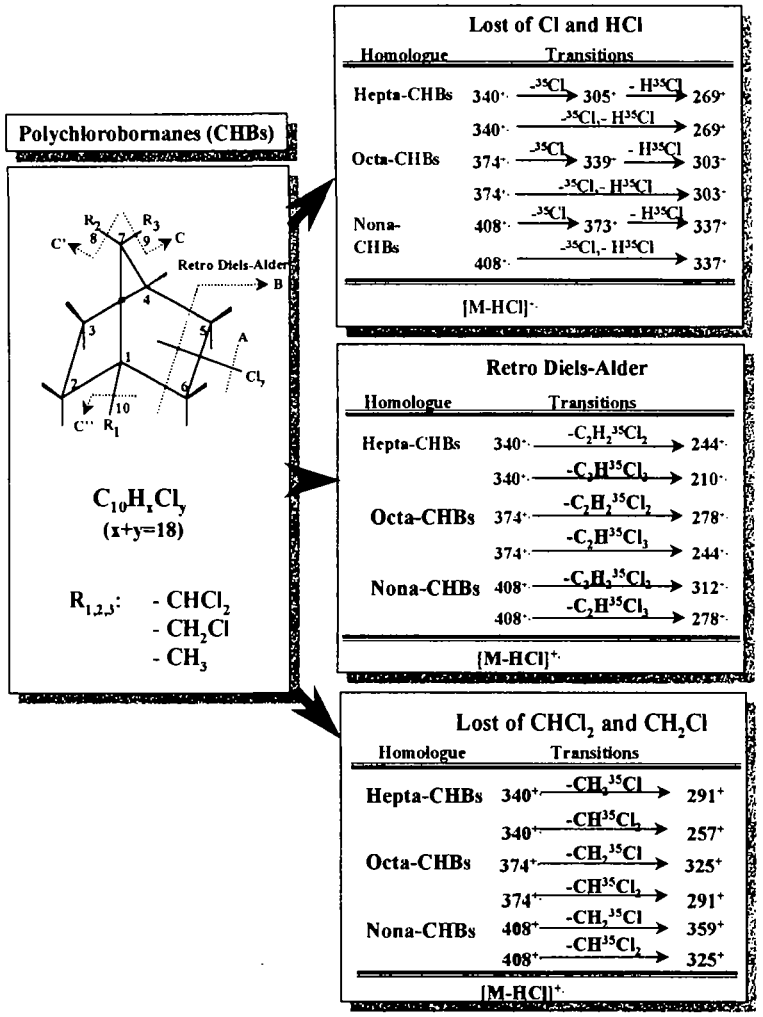

Figure 1 Selected MRM-Q transitions of each CHB homologue for the mainly pathway fragmentations of polychlorobornanes.

precursor ions spectra of individual chlorobornanes showed three mainly pathway of fragmentation: lost of Cl and HCl, retro Diels-Alder and lost of $CHCl_2$ and CH_2Cl (figure 1). As an example, the profile of MRM-Q transitions obtained for the Hepta-CHBs are given in figure 3. As can be seen, the mainly fragmentation pathways of the precursor ions to give the selected fragment ions were by retro Diels-Alder and succesive loss of HCl.

As can be seen the selected transitions for each homologue group showed a high selectivity and sensibility for the lost of $CHCl_2$ and CH_2Cl and for retro Diels-Alder fragmentation, while for the lost of Cl and HCl the specificity of this transition was very low.

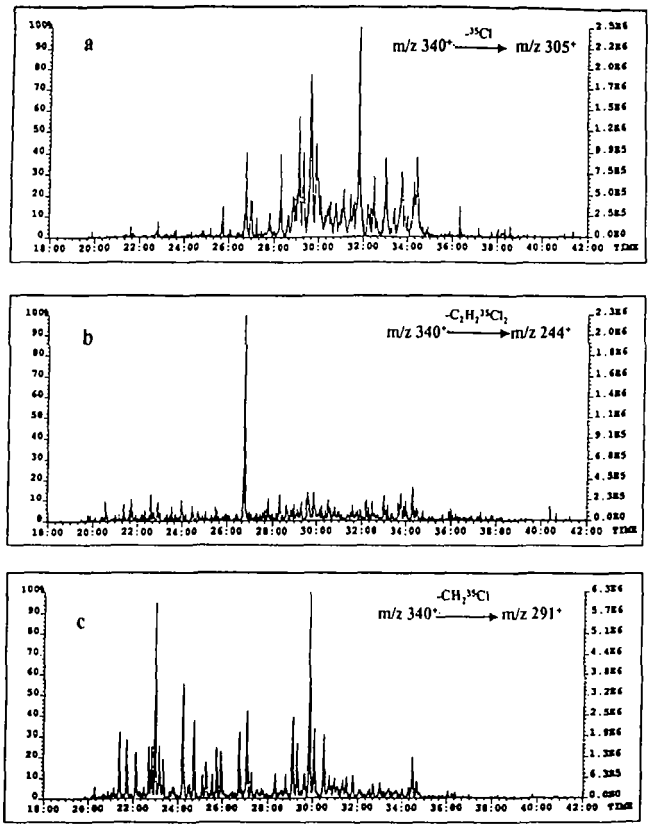

Figure 2 MRM-Q traces for heptachlorobornanes of toxaphene mixture. Pathway fragmentations of : (a) lost of Cl, (b) Retro Diels-Alder and (c) lost of $CHCl_2$.

References

1. M.A. Saleh. *J. Agric. Food Chem.*, **31** 748-751 (1983).
2. T. Cairns, E.G. Siegmund,J.E. Foberg. *Biomed. Mass Spectrom.*, **8**, 568-574 (1981).
3. World Health Organization, *Environ. Health Criteria.*, **45**, (1984). Geneva; E.C. Voldner and A. Li, *Workshop on the analytical and environmental chemistry of Toxaphene*, (February 4-6, 1993, Burlington, Ontario, Canada).
4. J.W. Gooch and F.Matsumura. *Arch. Environ. Contam. Toxicol.*, **16**, 349 (1987).
5. B. Lau, D. Weber and P. Andrews. *Chemosphere*, **32**, 1021-1041 (1996).
6. B. Lau, D. Weber and P. Andrews. *Rapid Commun. Mass Spectrom.*, **8**, 849-853 (1994).
7. F.J.Santos, M.T. Galceran, J.Caixach , J.Rivera and X.Huguet ; *Rapid Commun. Mass Spectrom.* **11**, 341-348 (1997).
8. P.Andrews, W.H. Newsome, M.Boyle and P.Collins ; *Chemosphere*, **28**, 1865 (1993).
9. H.R. Buser, M. Oehme, W.Vetter and Bernd Luckas; *Fresenius J Anal Chem* ,**347**, 502-512 (1993).