

Gas Chromatography Mass Spectrometry

This session is comprised of ca. 16 contributions dealing with various aspects of mass spectrometric detection of halogenated compounds in different matrices. Method improvements, instrumental modifications and methodological problems are addressed. A large variety of compounds classes is addressed including polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF), biphenyls (PCB), bornanes (toxaphenes), hexabromocyclododecane, polybrominated bipenylethers (PBDE), chlorophenols as well as a large variety of pesticides.

Though gaschromatography (GC) combined with mass spectrometry (MS) has reached a high level of maturity, there are still challenges due to the request of lower detection limits and higher selectivity for the separation of complex compound classes.

Costa et al. (646) demonstrates that comprehensive two-dimensional gas chromatography increases the selectivity so much that the analysis of PCDD/PCDF and PCB can be performed by low resolution MS with comparable results as for high resolution MS (HRMS). Alternatively, a dual GC system with two different stationary phases can minimise systematic errors due to interferences (Tirler et al. 530). Von der Recke et al. (351) remind us that a enantiomer selective separation of chiral or atropisomeric structures can yield valuable information about enantiomer ratios as shown for PBB149.

Krumwiede et al. (82) report that a dual column set-up combining a 30 m and short 6 m capillary connected to the same transfer line, allows to reduce thermal degradation of the PBDE 209 without losing analysis time.

The decrease of PCDD/PCDF and co-planar PCB levels in human serum during the past decades requires lower detection limits to maintain the precision of the quantification as Turner et al. (596) states. They present the state-of-the-art concerning limits of determination on the last generation of high resolution MS and conclude that 18 ml of serum is required to achieve a LOD of 1 pg/g lipid, if also matrix effects are considered. Lowering the LOD demands either more sample or the injection of a larger portion of the sample extract. This is proposed by Tobiishi et al. (591) by using a commercial solvent cut large volume injection (SCLV) system. It allows to transfer 5 µl to very narrow bore capillaries (10 m length, 0.1 mm id.). Retention times were reduced to about half compared to 0.25 mm id. and 30 m length. Precision and detection limits were comparable injecting on both systems 5 µl.

Recently, several proposals were made, that ion trap MS/MS can be a reasonable screening technique with detection limits around 1 pg. Santos et al. (553) could show that ion trap MS/MS give results comparable with HRMS for PCDD/PCDF in food and feed, however, at a much lower price of instrumentation. This investigation was part of the European research project "Dioxins in food and feed - Reference methods and new certified reference materials". Kim et al. (162) discuss the further improvement of this technique by optimising the dampening gas pressure in the ion trap.

Improvements of methods for polybrominated flame retardants are presented by Worrall et al. (70) and Hanari et al. (244). The latter describe a clean-up technique which allows to quantify both PCDD/PCDF and PBDE in the same sample by separating these compound classes completely by a combination of HPLC columns with graphitic carbon and pyrenyl silica. Worrall et al. (70) investigated the performance of triple quadrupole MS/MS for the analysis of PBDE. The loss of COBr or Br₂ was monitored. Quantitative results for fish tissue were in good agreement with HRMS.

Petersen et al. (525) present an GC-MS and HPLC-MS method for the determination of hexabromocyclododecane in soil and water. In opposite to GC, HPLC is able to separate the α , β and γ -isomers. The total concentrations obtained by both techniques were well comparable.

An interesting method is presented by Kawaguchi et al. (64) for the determination of chlorophenols in water. They use stir bar sorptive extraction combined with in-situ derivatisation by acylation followed by GC-MS.

The use of HRMS combined with electron capture negative ion ionisation is proposed by Matsukami (512) for the determination of toxaphenes in air and fish. Besides a complete clean-up scheme, instrumental conditions and optimisation are presented.

Wylie et al. (17) show that a rapid simultaneous analysis of a large number of pesticides and endocrine disruptors (in total 567) is possible, even if these are not completely separated by HRGC. A deconvoluting software allows to obtain pure mass spectra enabling a proper compound identification and quantification within a much shorter time. Chandramouli et al. (554) demonstrates that a combination of HRGC-HRMS and HPLC-MS/MS allow to screen a list of 250 pesticides in water and soft drinks. In this way both lipophilic and rather polar thermolabile compounds can be detected.

In summary, this session shows that there are enough problems left to be solved to improve routine analysis, though instrument progress may have reached a level of consolidation. Method improvements are as important as a spectacular breakthrough in instrument performance and are essential for an easier daily life in the laboratory.