Special Instrumental Techniques and Pattern Recognition (Ana 3)

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The session on special instrumental techniques and pattern recognition includes 19 papers, of which 8 orals and 11 posters. In two papers (Haglund et al., and Van Loco et al.) results from the European research project DIFFERENCE (Dioxins in food and feed – reference methods and new certified reference materials) are presented. Both show rapid developments in comprehensive two-dimensional gas chromatography (GCxGC). In several interlaboratory studies results of dioxin analyses by this technique (with electron capture detection (ECD)) are completely comparable those of analyses of the same samples by GC/HRMS. Although there is a need for better software and further automation of the integration of the three-dimensional chromatograms, there seems to be no doubt that within one or two years this technique, which requires much lower investments than GC/HRMS, will be a very attractive alternative for dioxin laboratories. Even below the very low maximum residue levels (MRLs) for dioxins, furans and PCBs set in the EU for food and animal feed GCxGC-ECD was still fully comparable with GC/HRMS. Combination with pressurized liquid extraction (PLE or ASE) can bring the analysis costs even further down. The addition of fat retainers to the extraction cell is essential as with that at least one clean-up step will become redundant. Van Loco et al. show that in addition to GCxGC-ECD also GC/LRMS/MS can serve as an alternative for GC/HRMS, provided conditions are optimal. This was confirmed by the work of Sobrado et al. who also compared GC/LRMS/MS with GC/HRMS for routine monitoring of dioxins in the fish industry. Haglund et al. show that there are other possibilities in hyphenation that may be useful in some occasions such as LC-LC-GC-ECD. A third paper, related to the DIFFERENCE project, by Korytar et al. shows very powerful separations not only of PCBs, dioxins and furans, but also and in the same run of polybrominated diphenylethers and biphenyls, polychlorinated diphenylethers, polychlorinated naphthalenes, polychlorinated dibenzothiophenes, organochlorine pesticides, toxaphene, polychlorinated terphenyls and polychlorinated alkanes. In this way a very large dataset is obtained from only one GC run. Combination with Time-of-Flight MS instead of ECD would result in an enormous amount of data. A two-dimensional GC system but now combined with a combustion chamber and an isotope ratio MS is presented by Hori et al. This instrument is made to be used in compound-specific carbon isotope analysis (CSIA) of man-made chemicals such as PCBs and PCNs in order to find sources of these compounds in the environment. Stable carbon isotope ratio analysis is also presented by Vetter et al. for comparison of technical mixtures of toxaphene.

As regards screening methods for dioxin analysis, Van Loco et al. also studied the CALUX bioassay. The use of an internal standard is emphasized. This assay can be validated as a screening technique, according to EU standards, but care should be taken where to set the cut-off limit and a more precise quantification of the TEQ values may not be expected. Bassonpierre et al. present another type of screening method. This is

again based on GC, but now in combination with a flame ionization detector (FID). This method is based on the correlation of TEQ levels in fish with fatty acid profiles. The method is cost-effective and only requires the use of chemometric software. You et al. have studied correlation between TEQ levels and possible indicator isomers. Based on correlation coefficients of 0.9999 and 0.9991 they propose 1,2,3,6,7,8-HxCDF and 2,3,4,7,8-PeCDF as indicators for incinerator and ambient air, respectively. Feshin et al. propose a perchlorination method as a simplification of the PCB analysis. Although the method may make use of different chemicals, it is unclear if this method would take away objections against perchlorination methods published in the 1970 which showed a considerable risk for overestimation and false positive results. Shin et al. propose a total PCB measurement by GC-ECD after saponification. The approach is certainly not new but may be useful for a cost-effective determination of high Aroclor levels in transformer oil. Riesbeck et al. present a simple method for air monitoring of PCBs. The so-called Twister (Stir Bar Sorptive Extraction), already in use for monitoring of organic compounds in water is optimized for PCB measurements in air.

A much more complicated method is presented by Suzuki et al. The use of Vacuum ultra-violet light ionized ion trap time-of-flight MS (VUV analyzer) for on-line monitoring of pentachlorodibenzofuran and trichlorobenzene was tested. This analyzer helps to estimate the amount of dioxin precursors at the outlet of a furnace which is useful and can be used for adjusting combustion conditions. Sun et al. have optimized microwave assisted extraction (MAE) to analyse PCBs and chlorobenzenes in fly ash. Comparison with Sohxlet extraction shows that MAE results in ca. 10% higher recoveries and a reduction of time and solvent volumes. Jones et al. describe a modification of an existing magnetic sector MS system by introducing a new ion detection system at the rear of the instrument. This new system enables a better characterization of unresolved mass interferences.

Two papers are dealing with brominated flame retardant (BFR) analysis. The one of Schlummer et al. presents two methods for the analysis of bromine and phosphorus based flame retardants in polymers, one using HPLC/UV, the other using gel permeation chromatography (GC) coupled to HPLC/UV. The first method can be applied for the analysis of 15 different technical flame retardants. The second one can be used as a screening method. Yoshida et al. present a new method for the analysis of tetrabromobisphenol-A (TBBP-A) based on a fluorimetric determination after derivatisation with 4-(1-pyrene)butanoyl chloride.

Zencak et al. addresses the analysis of the highly complex mixtures of polychlorinated alkanes (chlorinated paraffins). The use of chloride enhance atmospheric pressure chemical ionization (APCI) combined with ion trap MS offers a number of advantages compared to the GC analysis.

There are clearly two trends visible. One focuses on simplification and the development of cost-effective measurements, possibly based on indicator compounds or pattern recognition. The other one shows the development of more and more complicated, often hyphenated techniques that are able to solve technically highly difficult problems such as monitoring in waste incinerators. At the same time, hyphenated techniques such as GCxGC may serve as relatively cheap alternatives for the HRMS analysis of dioxins. Both trends show that the analysis of dioxins and other halogenated contaminants is possible at a progressively lower level.