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THE ANALYSIS OF DIOXINS AND RELATED POPs USING GC-HIGH RESOLUTION MS WITH THE AUTOSPEC-*ULTIMA* NT

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Presented at Dioxins Meeting, Krakow, Poland, 25th - 26th September 2002

INTRODUCTION

'Dioxins' refers to a group of chemical compounds that share certain similar chemical structures and biological characteristics. Several hundred of these toxic compounds exist and are members of three closely related families: the chlorinated dibenzo-p-dioxins (CDDs), chlorinated dibenzofurans (CDFs) and certain polychlorinated biphenyls (PCBs). CDDs and CDFs are not created intentionally, but are produced inadvertently by a number of human activities. Natural processes also produce CDDs and CDFs.

Over the past decade, regulatory environmental agencies and industry have worked together to dramatically reduce dioxin emissions. Because dioxins are extremely persistent compounds, levels of dioxins still exist in the environment from both man-made and natural sources and will take years to decline.

The detection of dioxins is a particularly demanding analysis due to the low level of regulatory exposure limits and the variety of complex sample matrices encountered. This analysis and analyses of related compounds are most often accomplished using Gas Chromatography (GC) coupled to high resolution magnetic sector GC-MS instruments, which provide the necessary high sensitivity, selectivity and wide dynamic range to address this application. The AutoSpec-*Ultima* NT is the market-leading GC-high resolution MS instrument.

Other 'Dioxin-like' analyses

A variety of other Persistent Organic Pollutants (POPs) provide the same analytical challenges and must be analysed in a similar fashion to dioxins and furans. The most important of these are Polychlorinated Biphenyls (PCBs) and Polybrominated Diphenylethers (PBDEs).

Analysis of Dioxins and Furans

Across the world there are many different legislative methods for dioxin and furan analysis including USEPA method 1613, European method EN1948, Canadian EPS1/RM/19 and other variants of these.
In the UK and across much of Europe, there is no specific legislative method for the analysis of dioxins and furans. In UK based laboratories, for example, methods using the extraction and clean-up processes of USEPA method 1613 and the labelled internal standard mixtures of USEPA method 23 are employed for the analysis of all environmental samples other than those obtained by air emission sampling.

The general common factor is the use of labelled internal standards for quantification and determination of recoveries, the use of resolutions in excess of 10,000 resolving power (5% height, 10% valley definition) coupled with a 60m GC column, either DB5, SP2331 or similar.
Figure 1 shows the Browser output from QuanLynx, the Application Manager for quantitation, for the hexa-furans. **Figure 2** is a calibration curve for 2,3,7,8-TCDD from CS1 to CS5 illustrating excellent quantitative linearity.

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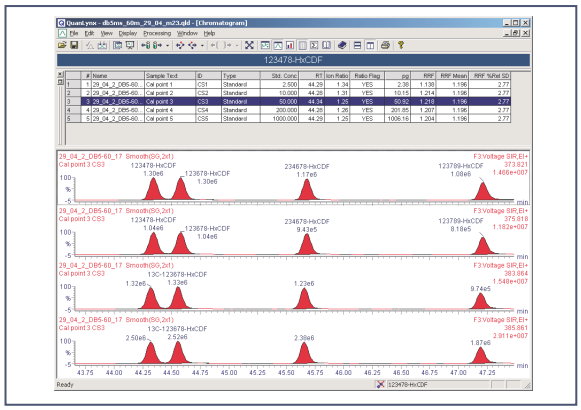

Figure 1.

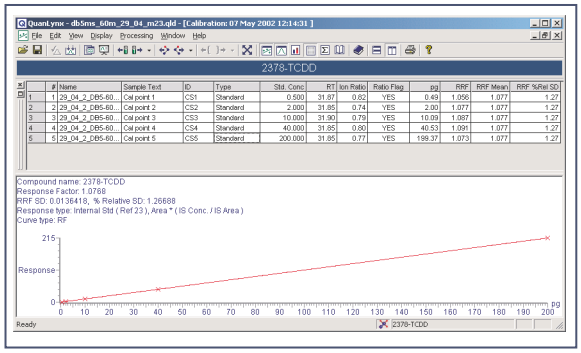

Figure 2.

Analysis of PCBs

PCBs of particular toxicological concern have been identified by the World Health Organisation, these are often described as the WHO-PCBs. Across the world there are many different methods (both legislative and non-legislative) for the analysis of PCBs e.g. USEPA method 1668(a).

In the UK and across much of Europe, there is no specific legislative method for the analysis of PCBs. For example UK-based laboratories use a variety of different extraction and clean-up methods, often employing the USEPA 1613 dioxin extraction and clean-up methods to isolate the PCBs from samples.

The general common factor in the various methods is the use of labelled internal standards for quantification and determination of recoveries, the use of resolution in excess of 10,000 resolving power (5% height, 10% valley definition) coupled with a 30m-60m GC column, either DB5(ms) type or SPB-octyl or similar.

Figure 3 shows a typical chromatogram for WHO-PCB analysis with the groups labelled. **Figure 4** is a calibration curve for the non-ortho PCB-81 illustrating excellent quantitative linearity.

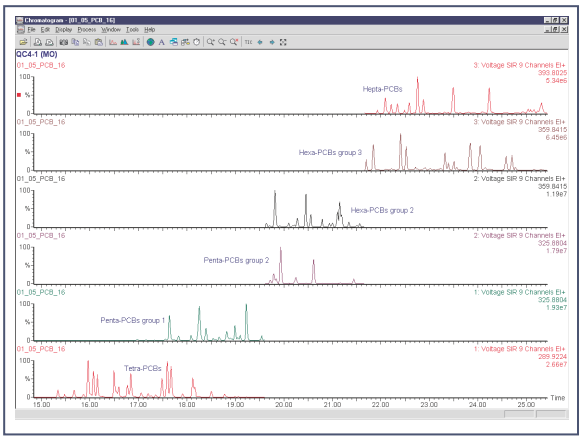

Figure 3.

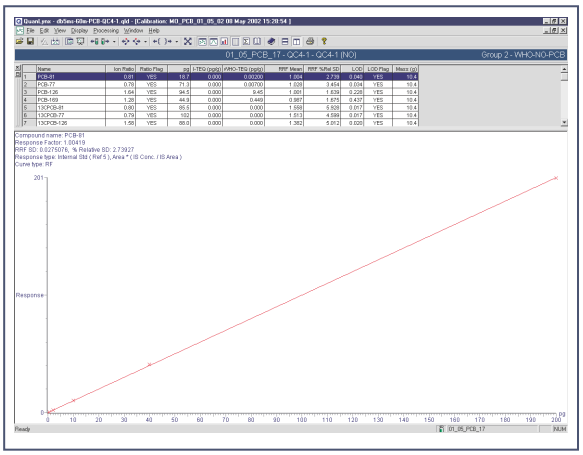

Figure 4.

Analysis of PBDEs - Brominated Flame Retardants

Brominated flame retardants (BFRs) are the largest group of organic flame retardants currently in use. Key constituents of these materials are PBDEs, polybrominated diphenyl ethers, which are added to plastics to decrease the likelihood and intensity of fire in a wide variety of products. PBDEs are both lipophilic (they concentrate in lipids, or fats) and extremely resistant to physical, chemical or biological degradation making them highly persistent in the environment and bio-accumulative. The most common BDE congeners found in biological samples are BDE-47 (2,2',4,4'-tetra BDE) and BDE-99 (2,2',4,4',5-penta-BDE), The penta brominated diphenyl ether (penta-BDE) formulation will be banned in the European Union (EU) in 2003.

High resolution GC-MS is the analytical method of choice for detection and quantification of PBDEs, elevated resolution being necessary to confirm the identity of individual ion clusters[1]. EI (electron impact) is the preferred ionisation method, giving characteristic mass spectra containing M^+, $M\text{-}Br^+$ and $M\text{-}Br2^+$ ions. Negative ion chemical ionisation (CI-) is a less favourable approach, as Br^- and HBr dominate PBDE spectra, thus reducing selectivity.

Figure 5 shows the extracted mass chromatograms for the analysis of mono- to hepta-brominated PBDEs. **Figure 6** is a calibration curve for BDE-99 from 25fg to 500pg illustrating the excellent sensitivity and linearity that can be obtained.

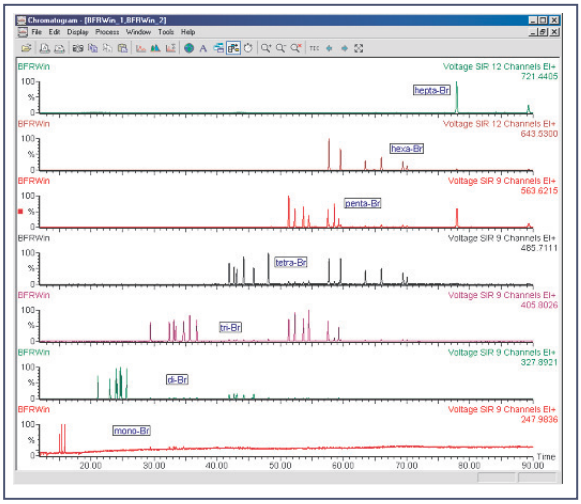

Figure 5.

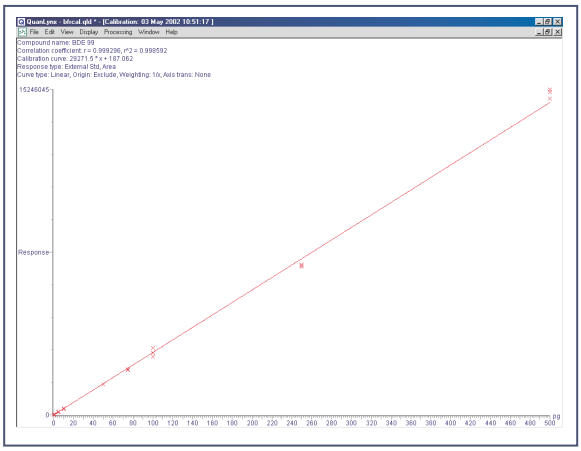

Figure 6.

CONCLUSIONS

Analysis of dioxins and other related POPs to low, regulatory levels, requires gas chromatography coupled with the selectivity, sensitivity and dynamic range of high-resolution mass spectrometry. The AutoSpec-*Ultima* NT provides unmatched performance for these types of analyses.

Please check the Micromass website at www.waters.com/micromass for details of other AutoSpec-*Ultima* NT GC-HRMS applications.

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REFERENCES

1. Alaee, M. *et al*, Determination of brominated diphenyl ethers in environmental matrices, Proc. 46th ASMS Conf. Mass Spectrom. Allied Topics, Orlando, FL, May 31-June 4, 1998, page 739

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