Experiences with Mass Peak Profile Monitoring in Dioxin Analysis by HRGC/HRMS-SIM.

Takasuga, T.[A], **Ireland, P.**[B], **Inoue, T.**[A], **Takeda, T.**[C]

[A] Shimadzu Techno-Research Inc., & [C] Shimadzu Corp., Kyoto 604, Japan.
[B] Kratos Analytical Ltd., Manchester M31 2LD, U.K.

Dioxin analysis is a demanding analysis that requires high sensitivity, high selectivity and high specificity. Currently, the analytical method of choice is HRGC/HRMS using the SIM method after extensive column clean-up. The high resolution MS method typically consists of monitoring the peak tops of two isotopic ions for each congener at 10,000 resolution; the peak top being monitored to obtain maximum sensitivity, the high resolution to exclude as many interferences as possible, and the two isotopic peaks to check for the presence of interferences and ensure that the target compounds are correctly identified. Even with the use of such a method, the presence of interferences is often indicated by extra peaks in the chromatogram, poor isotope ratios, and/or abnormal isomer patterns. Additionally, false positives may occur due to interferences that produce responses having an isotope ratio within the limits specified. However, it is not always possible to prove the presence of, let alone identify, interferences by the "peak top SIM" method (PT). Such interference effects are typically seen with samples from complex matrices, such as biological samples, fly ash, sludges, *etc.* Improvements in the clean-up step, changes in the GC separation, use of higher mass resolution of the M.S., use of MS/MS or use of negative CI instead of EI may help to overcome these problems, but is difficult to determine which alternative to choose when little is known about the interference. An alternative that has been proposed[1,2] is to use mass peak profile, in which a sweep is performed over each ion detected, rather than monitoring the peak top. This presentation will focus on the use of a commercially available mass peak profile system[3] to investigate interferences that were indicated in the course of analysing samples by the standard peak top SIM method.

As already mentioned, with the mass peak profile method (MP) a user-defined sweep is performed over each chosen ion, rather than switching the ESA to monitor the peak top alone (PT). The use of this sweep has two main consequences for MP in comparison to PT: a reduction in sensitivity, and a reduction in the effective mass resolution if data for all the sweep is used. As the MP method has been used here to investigate the presence, and identity, of interferences the loss in sensitivity can be tolerated, and the second problem of loss of effective resolution can be overcome with the post-acquisition data handling capabilities. The information that has become available by use of MP can be summarised as: a) ability to check that the

response observed with PT is due to one component, b) target compound confirmation, c) confirmation of the presence, and possible identification, of interferences, d) from the results of c) the success of the clean-up step can be gauged and improvements proposed, and, e) the instrument stability can be checked. Data has been obtained that illustrates each of these advantages.

The instrument used in this study was a Kratos Concept 32 IS fitted with a Shimadzu GC14A and coupled by either a DB-5 (J&W) or SP-2331 (Supelco) capillary columns. The M.S. resolution used and sweep for each experiment are indicated with the relevant data sets.

Figure 1 shows a portion of the relevant chromatograms of the two ions monitored for the native PentaCDDs of a dirty fly ash sample by the standard PT method. Peak B1 and three others have no corresponding response in the trace for 355.8546 and are clearly interferences. Figure 2 is the data for the same fly-ash sample analysed by the MP method with 10,000 resolution, but also a 200ppm sweep over each ion. The chromatograms in Figure 2 are the summed intensity responses for each sweep, and thus correspond to a chromatogram with an effective resolution of 5,000 (200ppm). The extra peaks (*e.g.* Z2) seen in Figure 2 compared to Figure 1 are a result of the lower effective resolution of this chromatogram.

The mass peak profiles obtained for three of the components (A2, Z2 & B2) in Figure 2 are shown in Figures 3 to 5. From the accurate mass of component B2 (Figure 4), it appears that this interference may be due to hexachlorobiphenyl [M^+=355.8444]. Likewise, the accurate mass and isotope ratio of the ions in Figure 5 (Z2), enables this interference to be tentatively identified as hexachlorobiphenylene (or, less probably, hexachloroacenaphthylene) [M^+=355.8287 and $(M+2)^+$=357.8258].

It is also possible to centroid any ion found in each sweep and process this centroided data to produce chromatograms for each component identified. Figure 6 shows the chromatograms that correspond to hexachlorobiphenylenes, hexachlorobiphenyls and Penta-CCDs.

By using the MP method we have investigated other problems relating to the clean-up step, and have identified a problem with hexachlorobiphenyl which co-elutes with the 1,2,3,7,8-PentaCDD isomer when a DB-5 column is used. Additionally, unusual isomer patterns observed when an SP-2331 column was used for Tetra-CDFs and Penta-CDFs in a polyurethane foam air sample, and extra responses in the $^{13}C_{12}$-TetraCDF trace for a fish sample, have been found to be due to the presence of unidentified interferences, which gave similar isotope ratios to the target compounds with the PT method.

The MP acquisition method requires a high degree of instrument control, large memory and fast post-acquisition data processing, all of which are now available. As can be seen from the examples given above, a wide variety of information, including target compound confirmation, intereference identification, and an indication of the efficiency of the clean-up step, can be obtained from a single analysis. It is expected that this method of acquisition will be a useful and necessary technique in the determination of trace amounts of other target compounds in complex environmental and biological samples when, as with dioxin analysis, a high degree of confidence is required in the data.

1. H. Y. Tong, D.E. Giblin, R.L. Rapp, S.J. Monson, and M.L. Gross. Mass Profile Monitoring in Trace Analysis by Gas Chromatography/Mass Spectrometry. *Anal. Chem.*1991, 63, 1772-1780

2. H. Tong, D. Giblin, S. Monson, and M. Gross. HRGC/MS with Mass Profile Monitoring in

Analysis of Dioxin and Related Compounds. *DIOXIN '91 Abstracts*, 1991, p.8.
3. H. Wight, J. Moncur, and G. Warburton. Peak Profile Acquisition in Dioxin Analysis. *Kratos Analytical Application Note*, N0. A475-1191, 1991.

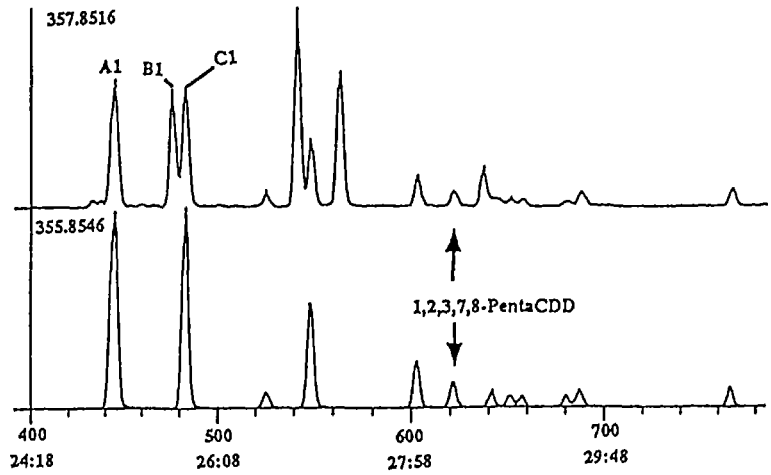

Figure 1. Chromatogram obtained for the pentachlorinated native dibenzo-p-dioxins (PentaCDDs) of a dirty fly ash sample using standard peak top monitoring SIM (PT) at 10,000 resolution and an SP-2331 column.

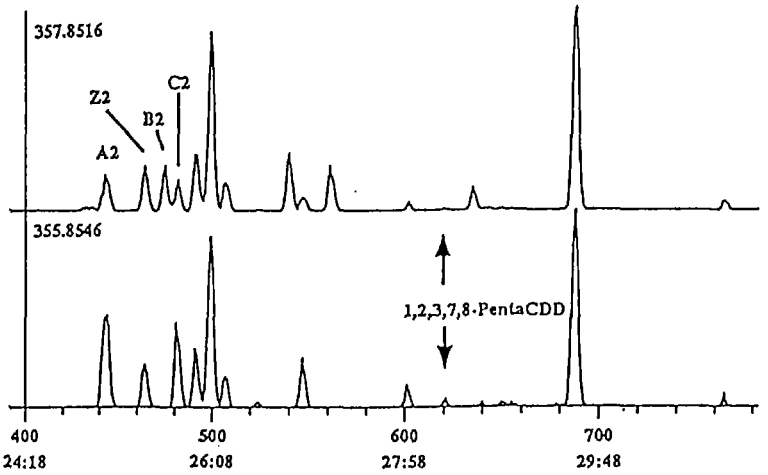

Figure 2. The summed responses for the two ions monitored for PentaCDDs using a resolution of 10,000 and a sweep of 200ppm in mass peak profile method (MP). The fly ash sample, GC column (SP-2331), and GC conditions same as Figure 1.

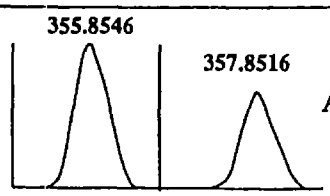

Figure 3. Mass peak profile for A2 (1,2,4,6,8- and 1,2,4,7,9- PentaCDD) from Figure 2. Isotope ratio calculated from areas of each ion is 65.8% (theoretical 64.8%, M+4/M+2)

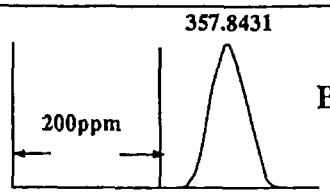

Figure 4. Mass peak profile for B2 (probably hexachlorobiphenyl) from Figure 2. Deviation of observed mass from theoretical is 3.6ppm.

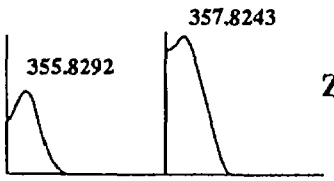

Figure 5 Mass peak profile for Z2 (probably hexachlorobiphenylene) from Figure 2. From peak heights isotope ratio is 59.7% (theoretical 51.4%, M/M+2), and deviations of observed mass from theoretical are 1.2 & -4.2ppm.

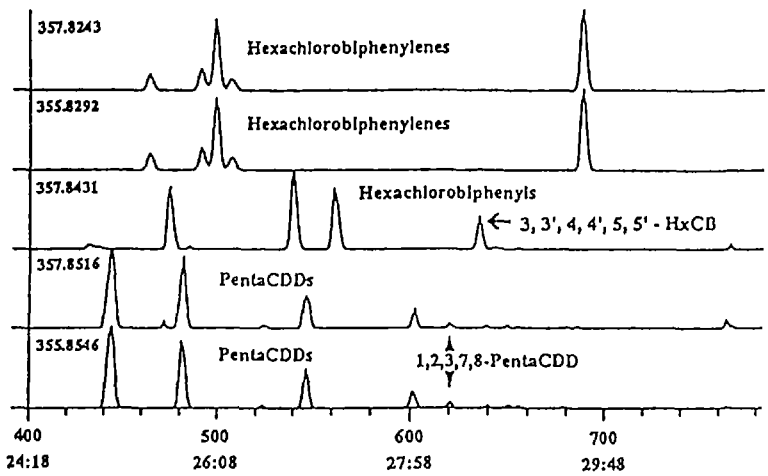

Figure 6. Chromatograms produced for PentaCDDs and tentatively identified interferences after centroiding the data for each individual sweep.