Identification of Polybrominated Diphenylethers as Possible Interferences in Dioxin Analysis by HRGC-HRMS.

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1. Introduction.

The standard analytical methodology for dioxin analysis utilizes HRGC-HRMS after an extensive clean-up procedure. Despite the use of alumina and multi-layer silica columns in the clean-up procedure, it is still possible to observe interferences in some samples. Identification of these interferences can yield valuable information on their suspected sources and/or indicate possible alternative clean-up strategies.

An alternative mode of HRGC-HRMS acquisition, mass peak profile monitoring (MP)[1,2] can be employed to furnish information on the accurate masses and isotope ratios of components in the sample. In combination with scanning HRGC-HRMS analysis, tentative identification of the interfering species can be made.

We have previously published data on interferences observed in routine dioxin analysis[2,3]. This paper reports the identification of polybrominated diphenylethers as interferences to heptachlorinated dibenzofurans (and also pentachlorinated biphenyls) in the analysis of routine environmental samples.

2. Materials and Methods.

Samples described were collected as part of monitoring activities, and included urban air, shredded waste and household dust. After solvent extraction with toluene, a portion of the extract was spiked with $^{13}C_{12}$-labelled PCDF/PCDD internal standards and subjected to a column chromatographic clean-up procedure. This consisted of a multi-layer silica column (silica, 10% $AgNO_3$/silica, 22%- & 44%-H_2SO_4/silica, silica, 2% KOH/silica, silica) and an alumina column. This was the standard clean-up regime used for all samples. After the identity of the interferences was known, a further carbon clean-up stage (HPLC porous graphitic carbon) was added[4].

HRGC-HRMS was performed on a Kratos Concept mass spectrometer fitted with a Shimadzu GC14A GC. Both SP-2331 (Supelco) and DB-17 (J&W) capillary columns were used for the separation. The mass spectrometer was operated in standard peak top selected ion monitoring mode (SIM) at a resolution ≥10,000 for routine analysis. Additionally, MP acquisitions at high resolution (≥10,000) and low resolution scanning were performed to identify the interferences.

3. Results and Discussion.

Figure 1 shows the HRGC-HRMS SIM chromatograms for H7CDF (native and $^{13}C_{12}$-labelled internal standard) of a sample of dust accumulated on a window ledge in a room on the ground floor of an office building.

This sample was also analysed by the mass peak profile monitoring method (MP) using a resolution of 10,000 and an ESA sweep of 250ppm (2.5 times the nominal ion peak width) over each monitored ion. The accurate mass data obtained for the interferences were very close to that of the H7CDFs, but the isotope ratios were different. This suggests that the interferences may be polychlorinated or polybrominated compounds. In order to investigate further the identity of the interferences, a low resolution scanning acquisition was performed.

Figure 2 shows the mass spectrum for one of the interferences obtained from the low resolution scanning GC-MS acquisition. Although the spectrum is weak and also contains major ions at m/z

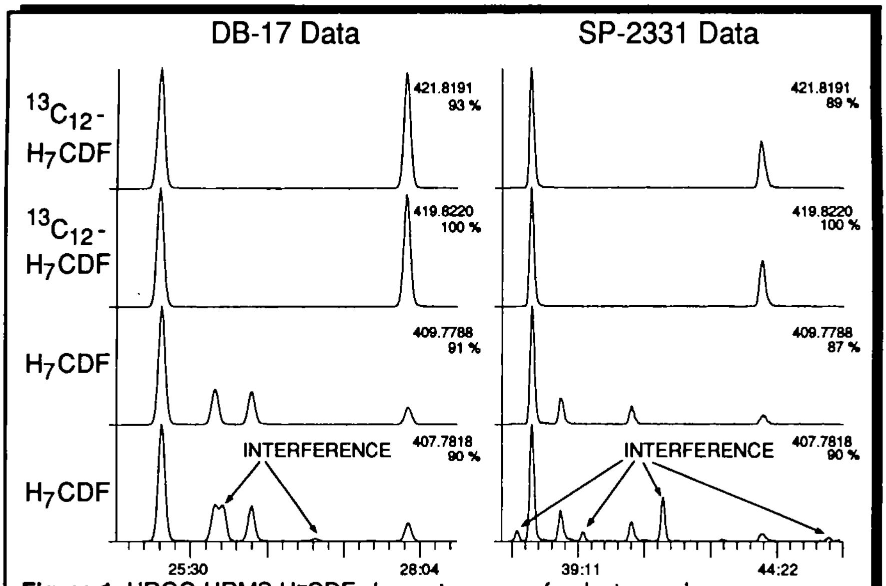


Figure 1. HRGC-HRMS H7CDF chromatograms of a dust sample.

311 & 346 thought to be from another co-eluting species, it shows two sets of ions at m/z 406, 484 and 564. The isotope ratios indicate that the observed interference is probably a pentabrominated compound, but the ion intensities are too weak to make a positive identification. The major use of brominated compounds in Japan is as flame retardants. A major class of brominated flame retardants, polybrominated diphenyl ethers, could give rise to ions ($C_{12}H_7OBr_3$ M^+ of Br_3DPE & $C_{12}H_5OBr_3$ M-Br_2 of Br_5DPE) that would interfere with H7CDFs. Although the mass spectrum favours the identification of Br_5DPE as the interference, a further MP acquisition was performed in which additional ions were monitored in order to be able to differentiate between these two possibilities.

Figure 3 shows the MP data obtained for H7CDFs and the interferences, together with their observed accurate masses. Inspection of the observed accurate masses and the isotope ratios for the interfering ions indicates that the interfering ions have a molecular formula of $C_{12}H_5OBr_3$. Although this formula could correspond to tribromodibenzofuran, the low levels of brominated furans and dioxins usually seen in this type of sample make it unlikely that this is the interfering species. This leads to the tentative identification of the interference as a pentabrominated diphenylether (Br_5DPE).

Samples containing these interferences were then subjected to an extra HPLC clean-up step with a porous graphitic carbon (PGC) column [4]. The effectiveness of these further clean-up step in removing these interferences can be seen in Figure 4, where H7CDF chromatograms for the same sample before and after the PGC HPLC clean up are shown.

Recently, we have observed components in shredded waste that give a strong response in the chromatograms for pentachlorinated biphenyls, but which elute after the last P_5CB isomer on a DB-5 column. Similar analysis to that described above indicates that these interferences may be tetrabromodiphenyl ether, with the interfering ions being M-Br_2.

Organobromine compounds have mainly been used as flame retardants in Japan and their level of usage was reported as 49,000 tonnes in 1991. The main organobromines used (and their usage in 1991) are tetrabromobisphenol A (24,500t), decabromodiphenylether (9,800t), octabromodiphe-

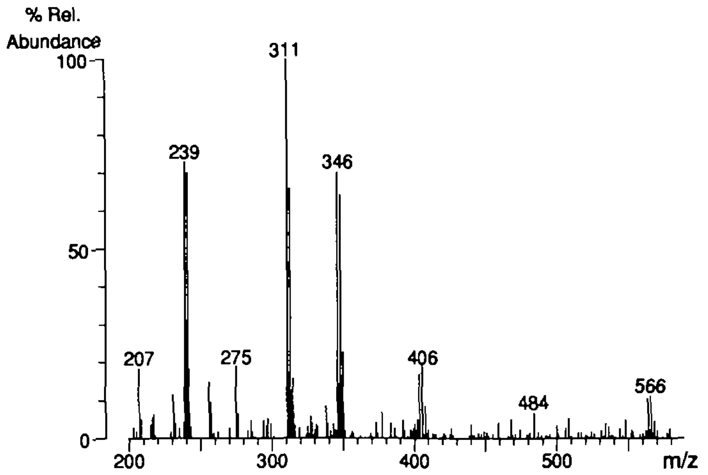
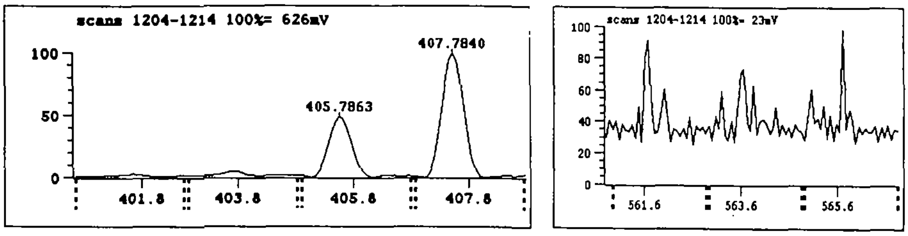
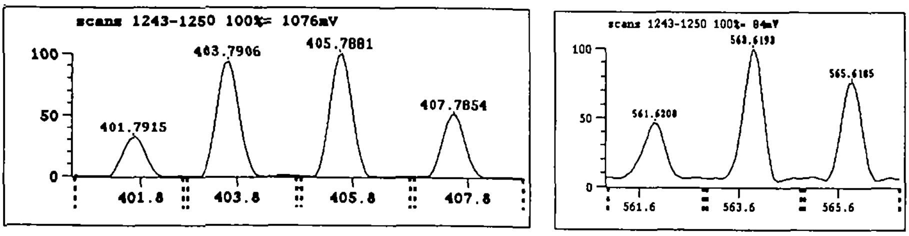


Figure 2. Mass spectrum of the interference.

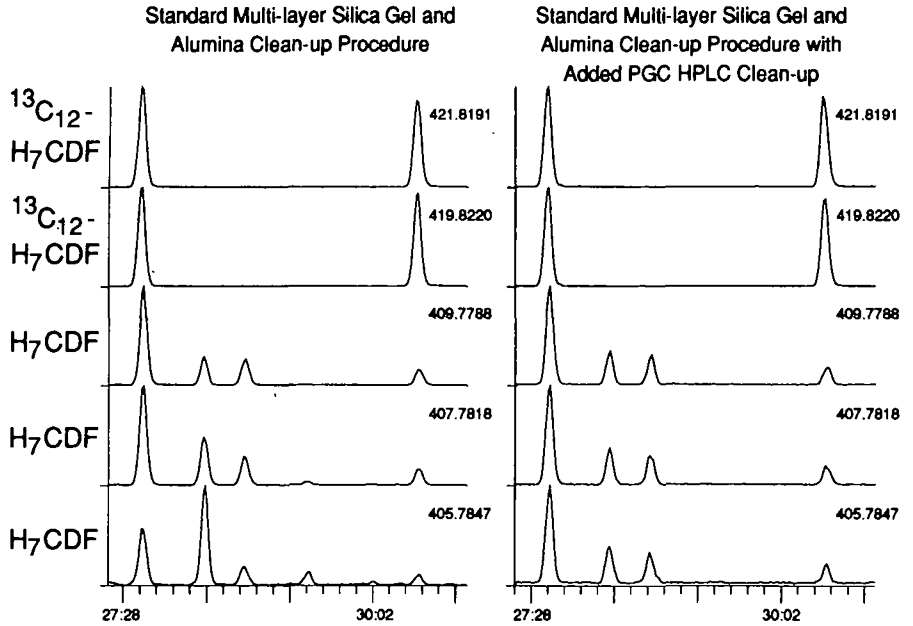


Data for first eluting H7CDF peak..



Data for largest eluting interference peak.

Figure 3. MP data of H7CDF and the interference.
Sweeps over seven ions are shown for the two peaks eluting from the GC. The left hand set of four ions correspond to the responses in the molecular ion region of H7CDF (M-4, M-2, M & M+2). The right hand set of three ions correspond to responses seen in the molecualr ion region of Br5DPE (M+2, M+4 & M+6).



Standard Multi-layer Silica Gel and Alumina Clean-up Procedure

Standard Multi-layer Silica Gel and Alumina Clean-up Procedure with Added PGC HPLC Clean-up

Figure 4. SIM chromatograms of H7CDF and the interference for a shredded waste sample with standard clean-up (left) and standard & PGC HPLC clean-ups (right).

nylether (1,500t), & tribromodiphenol (1,500t)[5]. These compounds have been detected in environmental samples such as fish, and river and marine sediments in Japan[6]. The main use of these flame retardants has been in the manufacture of plastics, and it is possible that this is the source of these compounds in the environment.

The fate of these compounds in the environment is also of interest as sunlight can cause photochemical debromination. Additionally, these compounds exhibit a "pre-dioxin" structure. Therefore continuous monitoring is desirable for these compounds as well as dioxins and furans. In this respect, further investigation into the levels of brominated diphenyl ethers in environmental samples is being performed.

References.

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