Identification of Chlordane Related Compounds as Potential Interferences to PCDFs in the Analysis of Ambient Air Sample in Japan by HRGC/HRMS

Takasuga, T., Inoue, T., Ohi, E.
Shimadzu Techno-Research Inc., 2-4, Nishinokyo-Sanjo Bocho, Nakagyo-ku, Kyoto 604, JAPAN

Current methodology for dioxin analysis utilizes high resolution capillary gas chromatography coupled with high resolution mass spectrometry at 10,000 resolution to obtain highest sensitivity, selectivity and specificity. As the samples are often in the complex matrices containing many potential interferences at much higher levels, an extensive clean-up procedure also precedes the HRGC/HRMS analytical step. Even with the use of such a method, some of interferences can still be present. Identification of these interferences can yield valuable information on their suspected source and/or indicate alternative clean-up strategies. This presentation focuses on the identification of potential interferences in Dioxin analysis of ambient air sample by HRGC/HRMS.

Air samples were collected every 24hrs in summer and/or winter season at several industrial cities in the western part of Japan using high volume air sampler fitted with quartz microfiberfilter and polyurethane foam(PUF) plugs adsorbents. The samples were soxhlet extracted with toluene and acetone for filters and PUFs respectively. The sample extracts were spiked with a mixture of $^{13}C_{12}$-labelled PCDDs/PCDFs internal standards and purified by clean-up procedures consisting of multilayer silica column chromatography (silica, 10% AgNO$_3$/silica, 22% & 44% H$_2$SO$_4$/silica, 2% KOH/silica, silica), alumina column chromatography and carbon column chromatography. To investigate interferences, the extracts of three clean-up steps, raw extract, before and after carbon column chromatography respectively were also applied to GC/MS analysis.

The HRGC/HRMS instrument used in this study was a Kratos Concept 32 1S coupled with a Shimadzu GC 14A fitted by either a SP-2331(Supelco) or DB-5(J&W) capillary columns. In the analysis of HRGC/HRMS-SIM both standard peak top method(PT) and mass peak profile monitoring(MP)[1] were used to investigate the presence and identification of interferences. The M.S. resolution used was 10,000(10% valley definition), with full details of MS and GC conditions reported elsewhere[2]. Also low resolution scanning analysis were used to acquire mass spectra and structual informations of interferences.

Figure 2 shows HR-SIM chromatograms for PeCDFs(native & $^{13}C_{12}$-labelled) of a typical air sample in Japan on an SP-2331 capillary GC column. The presence of extra interfering peaks are indicated in this chromatogram by comparing with the elution pattern of typical fly ash samples of PeCDFs under same conditions. The mass peak profiles(Figure 3) by MP method with 10,000 resolution and a 200ppm sweep over each ion obtained for four components are also shown. From the mass peak profiles and accurate

masses calculated from profiles two types of interferences appear to be present, one at lower mass than the PeCDFs(A1) and two at higher mass than the PeCDFs(C1, C2), indicating the limitation of HR-SIM PT method in which false positives may occur due to interferences that produce responses having isotope ratio within the specified limit. **Figure 4** shows mass spectra corresponding to A1 and C1 probably. From the mass spectrum of the interference A1, it was easy to identify A1 as chlordane which was reported to be of higher concentration in ambient air sample in Japan. The other interferences(C1, C2, ..), appear to be chlordane related compounds.

To investigate interferences in detail, the comparative analysis of extracts from various clean-up steps of air sample with technical chlordane standard was made (**Figure 5, 6, 7**) and most of interferences were identified as chlordane related compounds, γ(*trans*)-chlordane (peak A1), α(*cis*)-chlordane(peak A2) and *trans*-nonachlor(peak B1). Also from the comparison of relative abundance ratio, relative retention time and mass spectra of technical chlordane on non polar GC column already reported[3], the interferences were identified as dihydroheptachlor(peak C1, C2, C3) and octachlordane (peak C5). And the relative abundance of these interferences in an air sample were similar to technical chlordane. Although those ions which interfere with PCDFs ions were quite minor in intensity in flagment ion cluster of chlordane related compounds, they could easy to interfere with PCDFs because of their very high concentrations in ambient air in Japan (several hundreds pg/m^3 for chlordane).

Isomers of dihydroheptachlor which were first identified in ambient air sample, were obtained not only by photodechlorination of chlordane and nonachlor, but also found to be obtained by dechlorination of chlordane and nonachlor in dioxin sample clean-up procedure. For example peak C1(1-*exo*, 2-*endo*, 4, 6, 7, 8, 8-4, 7-heptachloro-3a, 4, 7, 7a-tetrahydro-4, 7-metanoindane) is obtained by dechlorination[-Cl(R_5)] of trans-chlordane and dechlorination[-Cl$_2$(R_5 & R_3)] of trans-nonachlor.

The interferences of chlordane related compounds in ambient air sample could be almost removed from PCDFs ions after carbon column chromatography except for summer season samples containig higher concentrations of chlordane related compounds. Thus great care should be taken in the isomer specific analysis for the PCDFs to avid the possible interferences of chlordane related compounds.

Figure 1. General structure of chlordane

trans-chlordane	Cl(R_1, R'_2, R_5, R_6)
cis-chlordane	Cl(R_1, R_2, R_5, R_6)
trans-nonachlor	Cl(R_1, R'_2, R_3, R_5, R_6)
C1 dihydroheptachlor	Cl(R_1, R'_2, R_6)
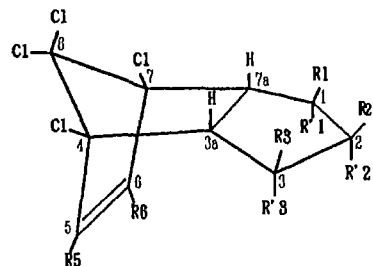
1. Takasuga T, Ireland P, Inoue T, Takeda T, Experience with Mass Peak Profile Monitoring in Dioxin Analysis by HRGC/HRMD-SIM. *DIOXIN'92 EXTENDED ABSTRACTS* Volume 8, 153-156 (1992).
2. Takasuga T, Inoue T, Ohi E, Evaluation of a High-resolution Gas Chromatography/High-resolution Mass Spectrometry Method for the Determination of Dioxin and Related Compounds. *Journal of Environmental Chemistry*, 2, 599-613 (1992).
3. Dearth M. A, Hiteds R. A, Complete Analysis of Technical Chlordane Using Negative Ionzation Mass Spectrometry. *Environ. Sci. Technol.*, 25, 245-254 (1991).
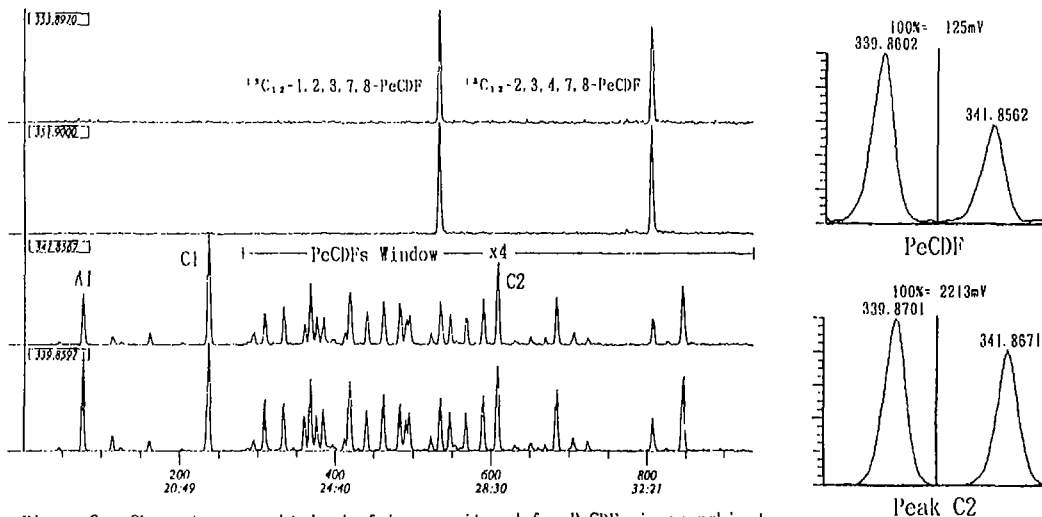
Figure 2. Chromatograms obtained of ions monitored for PeCDFs in an ambient air sample by standard peak top SIM at 10,000 resolution with an SP-2331 capillary column. The presence of extra, interfering peaks are indicated by comparison of typical fly ash under the same conditions.
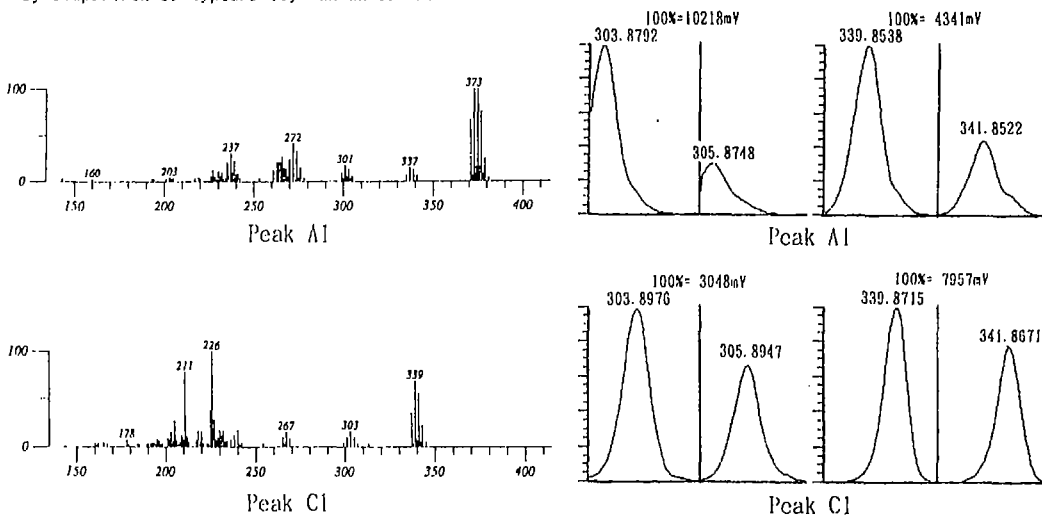

Peak A1

Peak C1

Figure 4. Mass spectra corresponding to peak A1 and C1. From library search peak A1 was identified as chlordane.

Peak A1

Peak C1

Figure 3. Mass peak profiles for two or four ions monitored for PeCDFs or TCDFs & PeCDFs in an air sample by the mass peak profile method with a 200ppm sweep over each ions at 10,000 resolution.
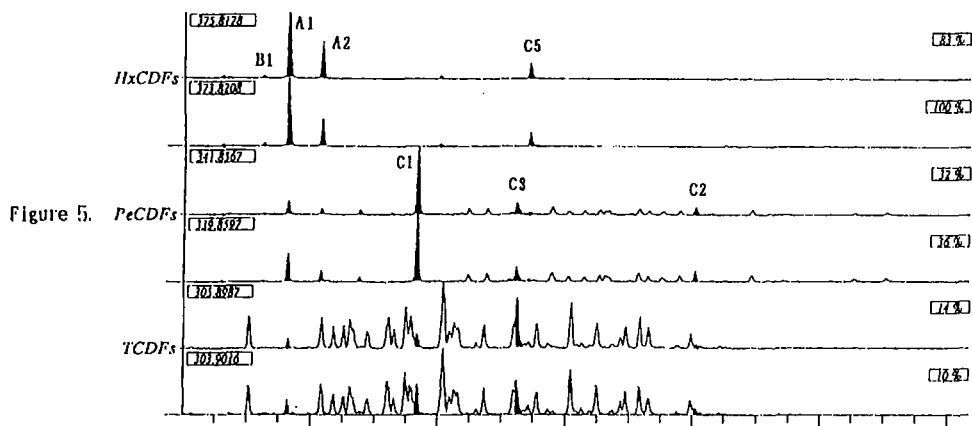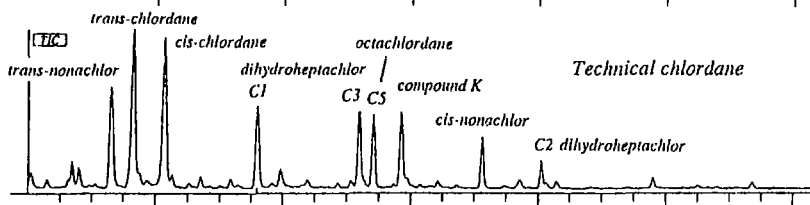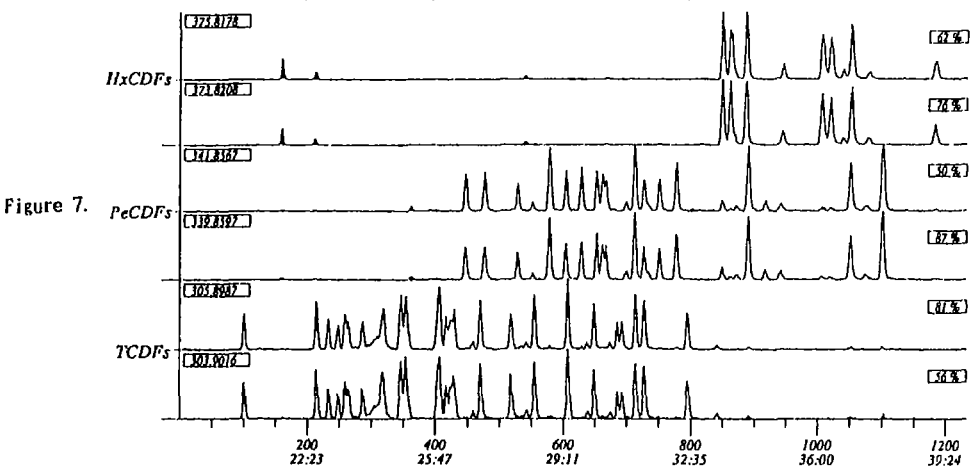
ANA

Figure 5. HR-SIM chromatogram for native Tetra/Penta/HexaCDFs ions in an ambient air sample before carbon column chromatography with an SP-2331 capillary column. The presence of extra, interfering peaks are also indicated.

Figure 6. Total ion chromatogram (m/z 50~550) of technical chlordane on SP-2331 capillary column. The GC conditions are same as Figure 5.

Figure 7. HR-SIM chromatograms for Tetra/Penta/HexaCDFs ions of an ambient air sample after carbon column chromatography. The air sample and GC conditions are the same as Figure 5.