

Analysis of Low Chlorinated PCDD/F - Isomer Specific Analysis of MCDF to T₃CDF on DB-5MS-Column and Some Aspects Regarding Air Sampling

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Introduction

Due to the high toxicity of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) substituted in 2,3,7,8-position¹, a lot of attention was paid to the isomer specific analysis of tetra- to octachlorinated dibenzo-p-dioxins and dibenzofurans in the last two decades^{2,3}.

Since, exclusively, the congeners substituted in all four 2,3,7,8-position exhibit the dioxin related toxicity, lower chlorinated congeners were not assigned with TEQ values and, therefore, not a lot of attention was paid to them.

However, the analysis of low chlorinated isomers seems interesting from several points of view. For the investigation of the mechanisms of PCDD/F formation, the low chlorinated compounds offer valuable additional information. For on-line measurement of PCDD/F in e.g. waste incineration, some recent research projects focused on estimating TEQ values by measurement of low chlorinated PCDD/F⁴. To establish this correlation, it seems important to measure not only the total amount of the low chlorinated homologues but to calculate and correlate specific isomers. Furthermore, the low chlorinated PCDD/F may give valuable information for environmental samples. The analysis of isomer distributions in environmental samples is the key to estimating the origin of dioxins and related compounds. Also in this field, many data are published for T₄CDD/F-OCDD/F, however, insufficient data are available for mono- to tri-chlorinated dioxin/furan.

In our previous paper, we did a complete assignment of MCDD/F to T₃CDD/F on SP-2331 column⁵. However, for e.g. cross-checking, it is advantageous to have an isomer specific analysis on several standard columns.

The aim of this study was to establish an assignment of MCDF to T₃CDF on DB5-MS. Additionally, we wanted to preliminarily evaluate whether the low chlorinated PCDD/F could be sampled together with T₄CDD/F-OCDF by a standard procedure for ambient air sampling.

Materials and Methods

Standards. All 74 congeners of the MCDD-T₃CDD and MCDF-T₃CDF were synthesised by pyrolysis of the respective chlorophenols or chlorobiphenyls. Additionally, all 23 commercially available isomers were obtained as authentic standard/mixtures for cross-checking the assignment.

GC/MS Analysis. The analysis was carried out using an HP 5890 II gas chromatograph connected to a JMS-700 mass spectrometer (JEOL Ltd. Japan) (operating at a resolution >10 000).

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Temperature program used for isomer specific separation of the MCDD/F- T_3 CDD/F on DB-5MS (60m, 0.32mm i.d., 0.2 μ m, J&W): 80°C, 1 min. isothermal; 20°C/min. to 150°C, 3°C /min. to 280°C. Quantification was carried out using 13 C-labelled 1,2,3,4- T_4 CDD as internal standard.

Evaluation of ambient air sampling method. For the assessment of the high volume air sampling method, polyurethane foam plug (PUF) for vapour phase sampling were tested for their adsorption ability of MCDD/F-OCDD/F. The high volume air sampler was equipped with a quartz micro fibre filter (QMF) (203 x 254mm) for particulate matter prior to the PUF plugs. The cylindrical PUF plugs (85mm diameter; 50mm height) were slightly larger in diameter than the internal diameter of the PUF holder cartridge. The QMF was spiked with 1000-2000pg 13 C-labelled MCDD/F- T_3 CDD/F (EDF-4955 Mix) and T_4 CDD/F-OCDD/F (EPA-1613 Mix). 1000 m³ of ambient air was passed through the sampling equipment during a 24-hour sampling period.

Results and Discussion

Figure 1 show the chromatogram of MCDF to T_3 CDF on the DB-5MS column. Due to the lower polarity of the DB-5MS column (5%phenyl 95% dimethylpolysiloxan), the isomers are less separated compared to the SP-2331 column⁵ (90%biscyanopropyl 10% phenylcyanopropyl). Therefore, the DB5-MS column is not effective for an isomer specific analysis of low chlorinated PCDF as it is requested e.g. for detailed mechanistic studies. On the other hand, the different homologues for PCDD and PCDF are separated on the DB5-MS column, decreasing the masses to be detected simultaneously in SIM mode and therefore increasing the sensitivity of the analysis. Together with the higher sensitivity of the non-polar DB-5MS columns compared to polar columns, this results in an increase in sensitivity for the GC/MS analysis.

Besides a isomer specific trace analysis, sampling is another crucial point in the process of environmental monitoring. For T_4 CDD/F-OCDD/F, the PUF foam method is widely used for ambient air sampling. We wanted to evaluate if this standard method can be used for a simultaneous sampling of MCDD/F to OCDD/F.

Figure 2 shows the recovery of MCDD/F to T_4 CDD/F for the PUF sampling train. Complete recovery were found for T_3 CDD/F and higher chlorinated PCDD/F within the measurement accuracy. T_3 CDD/F and T_4 CDD/F (and the higher chlorinated congeners) mainly adsorb on the first PUF segment+QMF. For DCDD/F and for MCDD/F, considerable parts were detected in the second and third PUF segment and more than 50% of MCDD/F passed the sampling train and were not recovered (Figure 2). This demonstrates molecular migration of low chlorinated PCDD/F at room temperature and the standard flow during ambient air sampling (1000 m³/24 hours) through the PUF. The increase in volatility due to a slightly lower boiling point (see Table 1)^{6,7} seems to have a significant impact on the adsorption strength. Therefore, for high sampling volume of 1000 m³, a part of MCDD/F and DCDD/F would be lost for analysis by the PUF standard sampling procedure and the actual amount of MCDD/F and DCDD/F would be underestimated. Reduced sampling volume or increased PUF volume should minimise the losses. Low chlorinated sampling spikes may be another option to compensate losses.

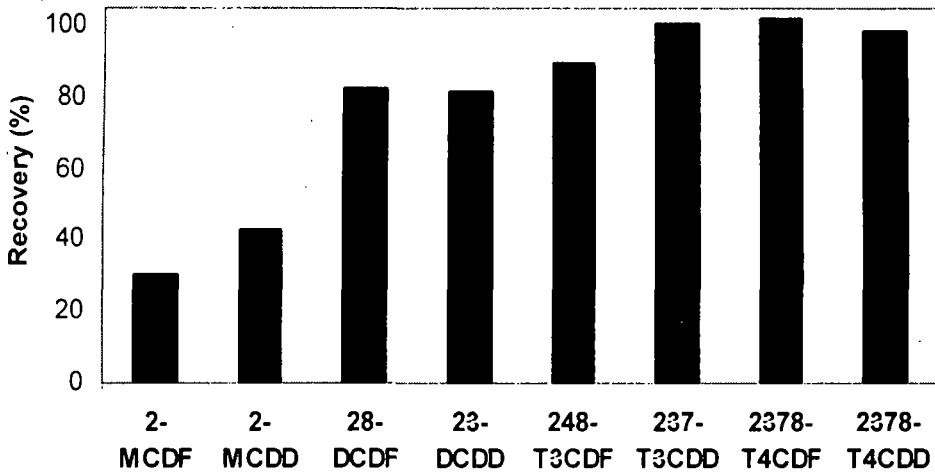


Figure 2: Recovery of spiked MCDD/F to T₄CDD/F in the PUF (24 hours sampling; 1000 m³)

Table 1: Boiling points of some PCDD and PCDF^{6,7}

PCDD	DD	23-D ₂ CDD	124-T ₃ CDD	2378-T ₄ CDD	123678-H ₆ CDD	H ₇ CDD	O ₈ CDD
boiling point (°C)	279	358	375	447	487	507	510
PCDF	DF	23-D ₂ CDF	238-T ₃ CDF	2378-T ₄ CDF	123678-H ₆ CDF	H ₇ CDF	O ₈ CDF
boiling point (°C)	287	375	408	438	488	507	537

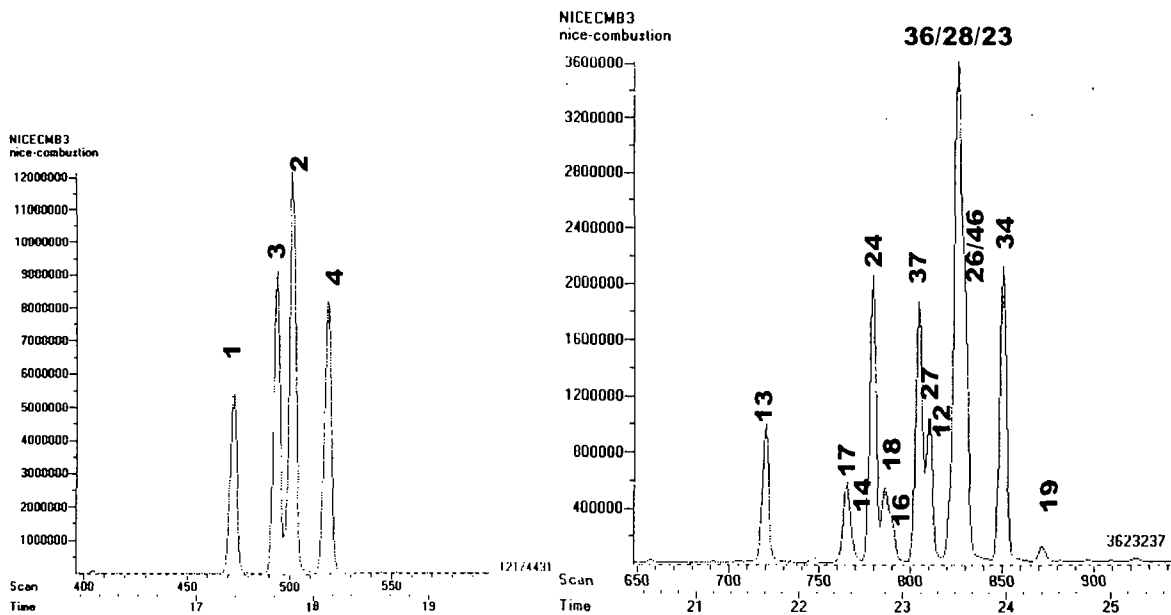
Acknowledgement

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ANALYSIS II - POSTER



NICE-CMB3
nice-combustion

236/234

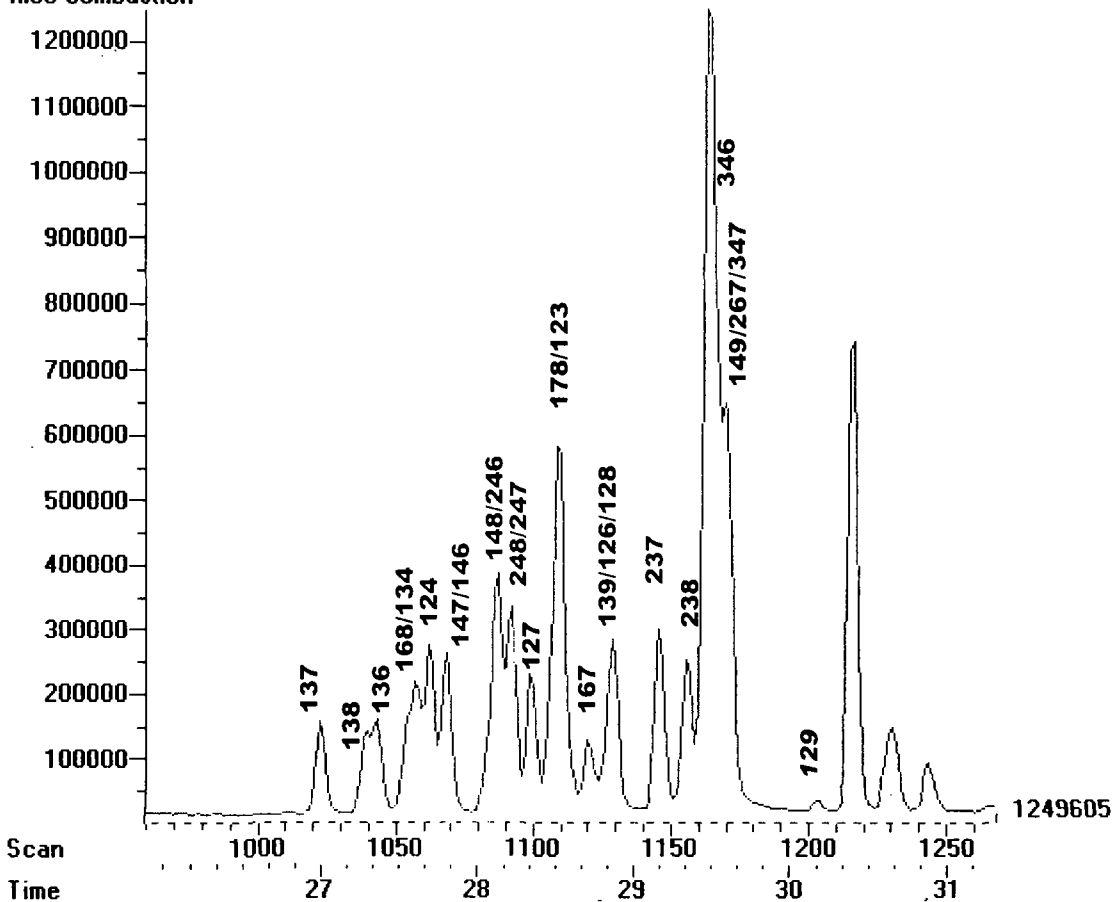


Figure 1: Chromatogram of MCD/F to T₃CDD/F on DB5-MS