ANALYSIS OF LOW CHLORINATED PCDD/F - ISOMER SPECIFIC ANALYSIS OF MCDD/MCDF TO T_3CDD/T_3CDF ON DB-DIOXIN-COLUMN

Takeshi Nakano[1] and Roland Weber[2,*]

[1]Hyogo Prefectural Institute of Public Health and Environmental Sciences, 3-1-27 Yukihira-cho, Suma-ku, Kobe 654-0037 Japan
[2] Institute of Organic Chemistry, University of Tuebingen, D-72076 Tuebingen, Germany
*(Current address) Environmental Process Development Department, IHI Co., Ltd., Isogo-ku, Yokohama 235-8501, Japan

Introduction

Due to the high toxicity of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) substituted in 2,3,7,8-position[1], 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/F as surrogates.[4] 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 T_4CDD/F-OCDD/F, however, insufficient data are available for mono- to tri-chlorinated dioxin/furan.

In our previous papers, we did a complete assignment of MCDD/F to T_3CDD/F on SP-2331column[5] and MCDF to T_3CDF on DB-5-MS column[6]. However, for e.g. crosschecking, it is advantageous to have an isomer specific analysis on several standard columns. The DB-Dioxin column is widely used as standard column in analytic laboratories. The aim of this study was to establish an assignment of MCDF/MCDD to T_3CDF/T_3CDD on DB-Dioxin column to provide the possibility for a reasonable analysis of MCDD/MCDF to OCDD/OCDF with one injection on this standard column.

Materials and Methods

Standards

All 74 congeners of the MCDD-T_3CDD and MCDF-T_3CDF 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).

ANALYSIS II

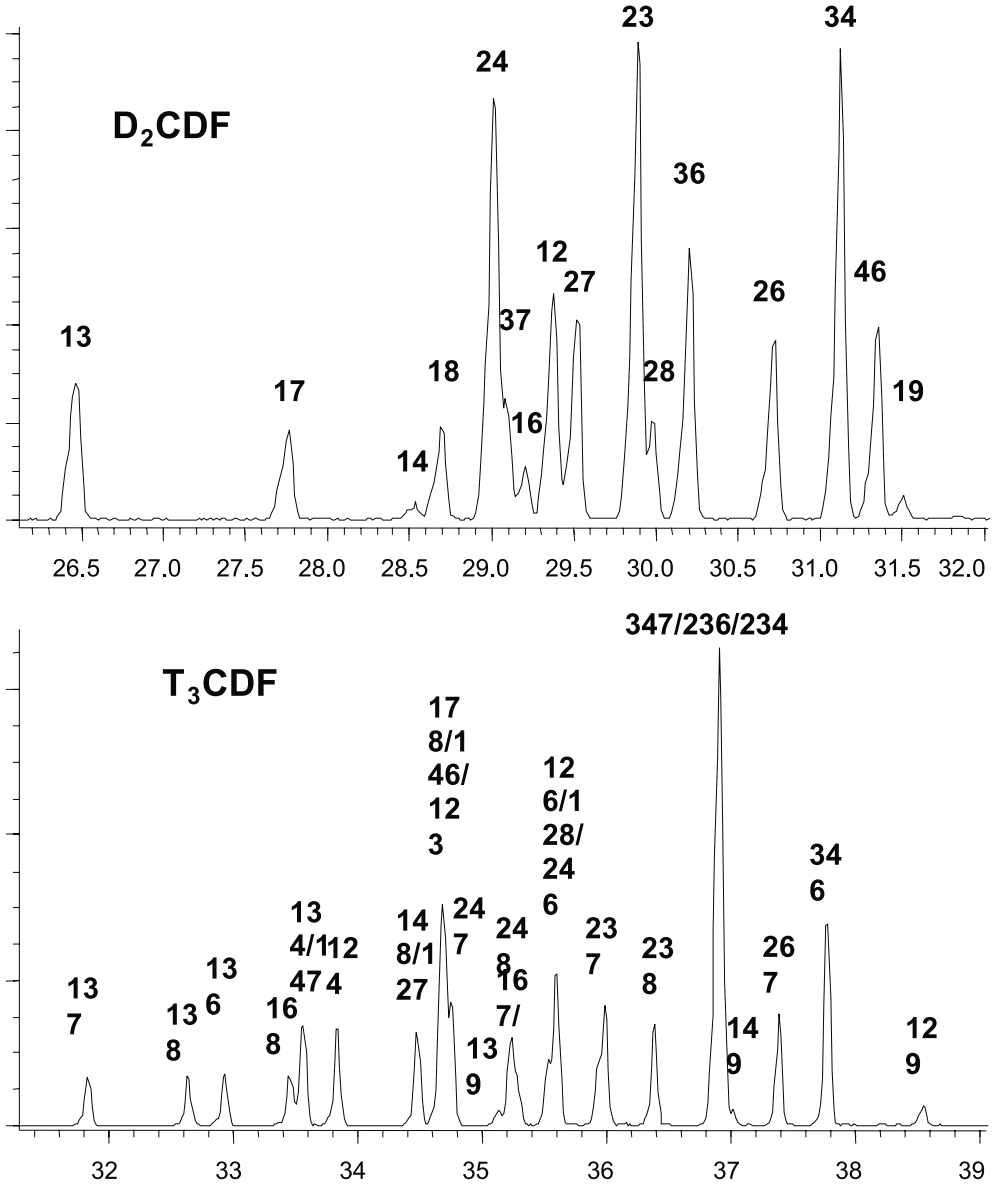

Figure 1. Chromatogram of D_2CDF and T_3CDF on DB-Dioxin column 60 m, 0.25 mm i.d., 0.15 um; 50 °C (1 min.), 20 °C/min. to 150 °C, 3 °C /min. to 270 °C (14 min); He 1.0 mL/min.

Temperature program used for isomer specific separation of the MCDD/F-T_3CDD/F on DB-Dioxin (60 m, 0.25 mm i.d., 0.15 µm, J&W): 50 °C, 1 min. isothermal; 20 °C/min. to 150 °C, 3 °C /min. to 270 °C, 14 min. isothermal. Carrier gas flow rate : He 1.0 mL/min.

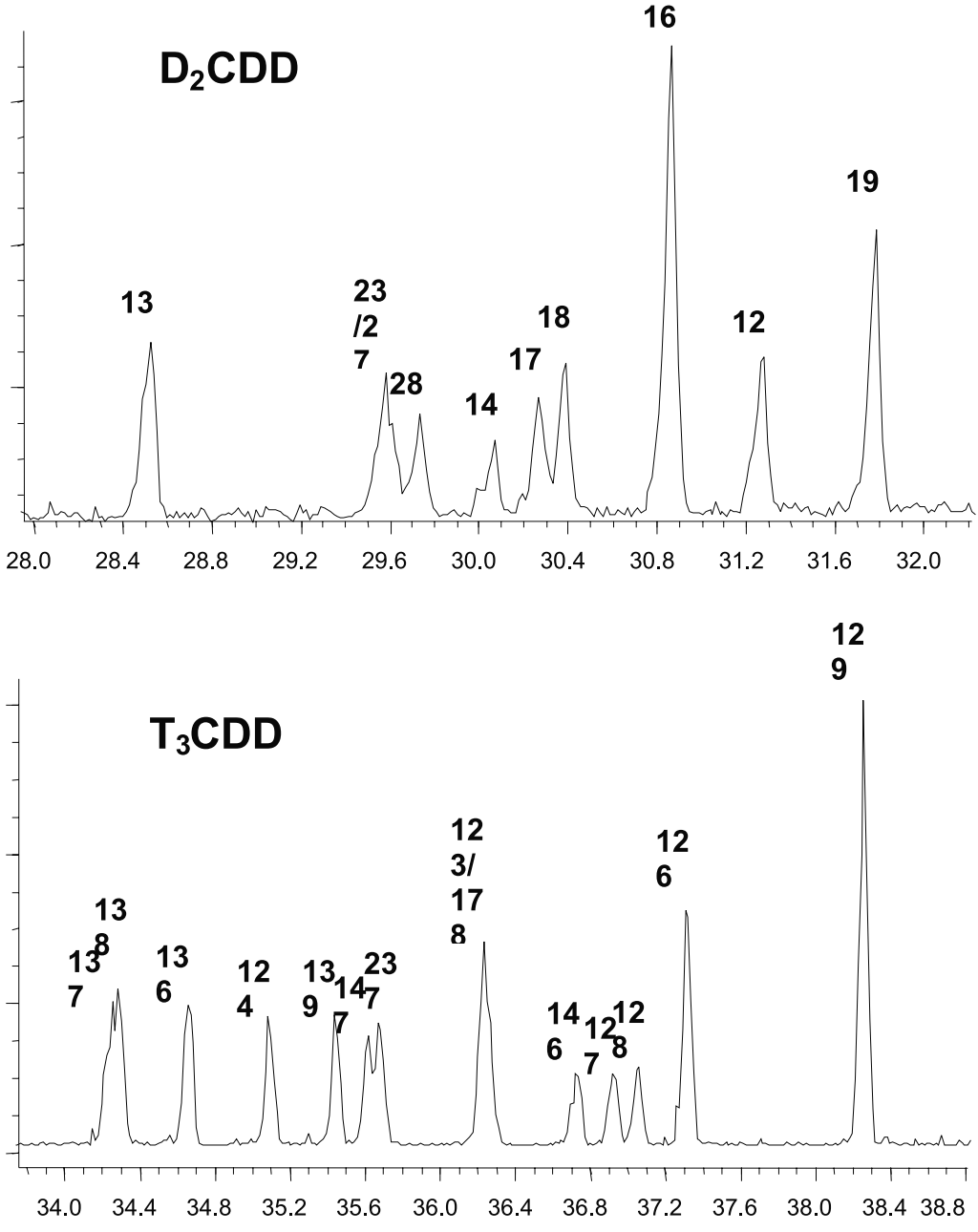

Figure 2. Chromatogram of D_2CDD and T_3CDD on DB-Dioxin column 60 m, 0.25 mm i.d., 0.15 um; 50 °C (1 min.), 20 °C/min. to 150 °C, 3 °C /min. to 270 °C (14 min); He 1.0 mL/min.

Results and Discussion

Figure 1 show the chromatogram of D_2CDF and T_3CDF on the DB-Dioxin column and Figure 2 show the chromatogram of D_2CDD and T_3CDD on the DB-Dioxin column. The DB-Dioxin column is effective for an isomer specific analysis of low chlorinated PCDF as it is requested e.g. for detailed mechanistic studies. Due to the lower polarity of the DB-Dioxin column (44 % methyl, 28 % phenyl, 20 % cyanopropyl and 8 % polyoxyethylene), the isomers are slightly less separated compared to the SP-2331 column[5] (90 % biscyanopropyl 10 % phenylcyanopropyl). The different homologues for PCDD are separated on the DB-Dioxin column, decreasing the masses to be detected simultaneously in SIM mode and therefore increasing the sensitivity of the analysis (Table 1). Together with the higher sensitivity of mid polar DB-Dioxin columns compared to polar columns, this results in an increase in sensitivity for the GC/MS analysis.

Table 1. Retention time of MCDD/F to T_3CDD/F congeners on DB-Dioxin column (60 m, 0.25 mm i.d., 0.15 um; 50 °C (1 min.), 20 °C/min. to 150 °C, 3 °C /min. to 270 °C (14 min); He 1.0 mL/min)

MCDD		TrCDD		MCDF		DCDF		TrCDF		TrCDF	
2	23.76	137	34.18	1	22.57	23	29.87	124	33.80	238	36.33
1	24.69	138	34.24	3	23.09	28	29.96	127	34.43	347	36.88
DCDD		136	34.61	2	23.56	36	30.16	148	34.43	236	36.88
13	28.51	124	35.07	4	24.51	26	30.69	123	34.63	234	36.88
27	29.57	139	35.40	DCDF		34	31.09	146	34.65	149	36.98
23	29.57	147	35.60	13	26.43	46	31.31	178	34.65	267	37.37
28	29.73	237	35.63	17	27.71	19	31.46	247	34.75	346	37.73
14	30.05	123	36.19	14	28.48	TrCDF		139	35.08	129	38.49
17	30.26	178	36.24	18	28.65	137	31.77	248	35.22		
18	30.39	146	36.65	24	28.96	138	32.58	167	35.23		
16	30.85	127	36.86	37	29.08	136	32.87	126	35.48		
12	31.26	128	37.00	16	29.28	168	33.44	128	35.48		
19	31.77	126	37.31	12	29.34	134	33.52	246	35.58		
		129	38.21	27	29.49	147	33.52	237	35.94		

Acknowledgement

The authors would like to express their thanks to Dr. Brian Gullett (US-EPA) for donating some standards, to Terry Humphries for critical reading of the manuscript.

References

1. Van den Berg M., De Joung J., Poiger H. and Olson J. R. (1994) Crit. Rev. Toxicol. 24, 1.
2. Buser H.R. and Rappe C. (1984) Anal. Chem. 56, 442.
3. Ryan J.J., Conacher H.B.S., Panopio L.G., Lau B.P.Y., Hardy J.A. and Masuda Y., (1991) J. Chromatogr. 541, 131.
4. Gullett B.K. and Wikstroem E. (1998) Organohalogen Compounds 36, 179.
5. Nakano T. and Weber R. (2000) Organohalogen Compounds 46, 558.
6. Nakano T. and Weber R. (2001) Organohalogen Compounds 50, 198.