Elution Profile of Tetra to Octa Chloro- Dibezo-*p*-dioxins and Dibenzofurans on a New GC Capillary Column

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1 Introduction

Polychlorinated dibenzo-p-dioxin (PCDDs) and Polychlorinated dibenzofurane (PCDFs) are persistent organic pollutants that are constantly monitored in various matrix including environmental and food matrix. While a 5% phenyl selectivity is commonly utilized for the analysis by GC/MS or GC/MS/MS, there are many critical pairs that needs better chromatographic resolution, which is not possible with a low polar 5% phenyl selectivity. ZB-Dioxin GC capillary column was developed to address separation of key components like high toxic congeners (2,3,7,8-TeCDD, 2,3,7,8-TeCDF) that are mentioned in EPA guidelines. The experimental data already proved high chromatographic resolution of 2,3,7,8-chlorine substituted isomers from 4 to 8 chlorinated congeners of PCDDs/DFs. However, the technical requirements for capillary columns used in the dioxin analysis at the Japanese industrial standards (JIS) for dioxin analysis[1), 2)] and official manual of dioxin analysis (ambient air , soil and sediment) on Ministry of the environment[3), 4), 5)], regulate that it is capable of separating 2,3,7,8-chloro-substituted isomers with high chromatographic resolution and it is clear on elution order of all congeners from 4 to 8 chlorinated substances in PCDDs/DFs. Furthermore, information of isomer composition in PCDDs/DFs are extremely important when analyzing sources and estimating pollution sources in environmental analysis. Therefore, it is an extremely important to study in the elution order of PCDDs/DFs. We reported the elution order, chromatographic profile of 4 to 8 chlorinated substances components of PCDDs/DFs using ZB-Dioxin.

2 Materials and Methods

ZB-Dioxin (Length 60m, I.D. 0.25mm, Film thickness 0.2µm) was used as the GC separation column. Standard solutions, tertra to octa chloro dibenzo-p-dioxins (49 congeners) and tertra to octa chloro dibenzofurans (87 congeners) distributed by Cambridge Isotope Laboratories, Inc., were used. Standard solution of each congener was diluted, and 2 to 4 congeners were mixed. Flyash certified reference material (Flyash II, National Institute for Environmental Studies, Japan) and was used to confirm all congeners of PCDDs/DFs. Flyash was extracted by ASE200 (Thermofisher scientific) and cleanup was performed by automatic sample preparation system (SPD-600GC, Kyoto Electronics Manufacturing Co., Ltd.). Incineration sample containing PCDE was performed with the same pretreatment. Measurement of PCDDs/DFs was performed by high-resolution GC/MS (GC: GC7890 (Agilent), MS: JMS-800D Ultra FOCUS (JEOL LTD.). The temperature program of GC oven was as follows: 130℃ (1 min) - 15℃/min - 210℃ - 3℃/min - 290℃ -10℃min-330℃ (4 min). Injection mode was splitless injection. Carrier gas was used to He and flow rate was 1ml/min in constant flow mode. The measurement conditions of MS were as follows: MS interface and ion source temperature were 280℃, accelerated voltage was 10kV, ionization voltage was 38 eV, resolving power was over 10000. Diok Ver4.2 (JEOL LTD.) was used for data analysis.

3 Results and Discussion

The elution order of TeCDDs to OCDD and TeCDFs to OCDF were determined by analysing standard solutions on the GC/MS. Chromatograms of Flyash II with elution order are shown in Fig.1 for PCDDs and in Fig.2 for PCDFs. The separation of 2,3,7,8-substituted isomers of PCDDs could be separated as single components (in Fig.1). But in PCDFs, some congeners could not separate single components as below: 2,3,4,7,8-PeCDF was co-eluted with 1,2,3,6,9-PeCDF and 1,2,4,8,9-PeCDF. 1,2,3,7,8,9-HxCDF was co-eluted with 1,2,3,4,8,9-HxCDF. 2,3,4,6,7,8-HxCDF was not well separation, because 1,2,3,6,8,9-HxCDF was appeared as shoulder peak of 2,3,4,6,7,8-HxCDF (in Fig.2). To accurately quantify these congeners, it is necessary, for example, to measure them on capillary columns

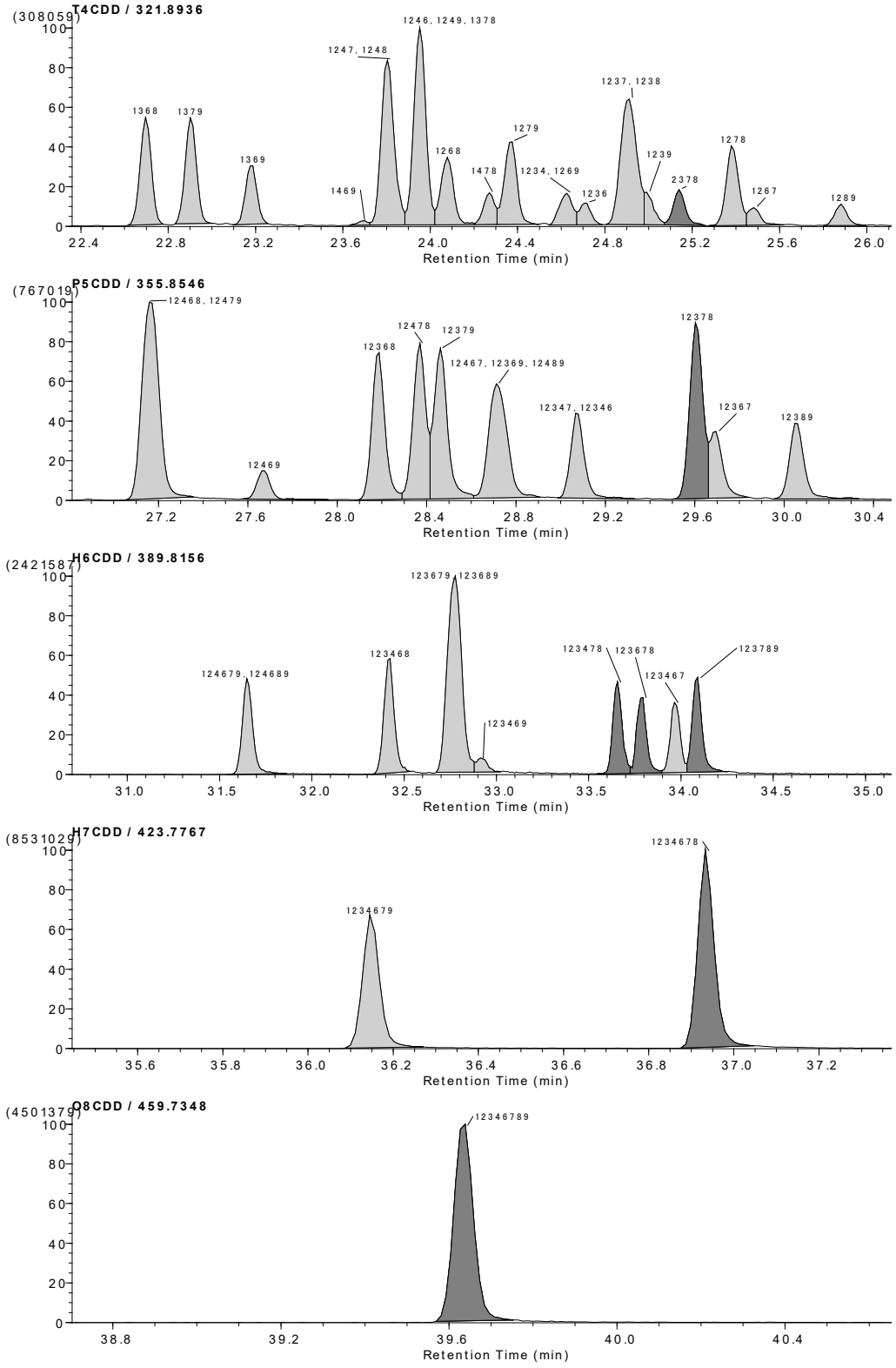

Figure 1: Chromatograms of PCDDs with isomer assignment in flyash certified reference material

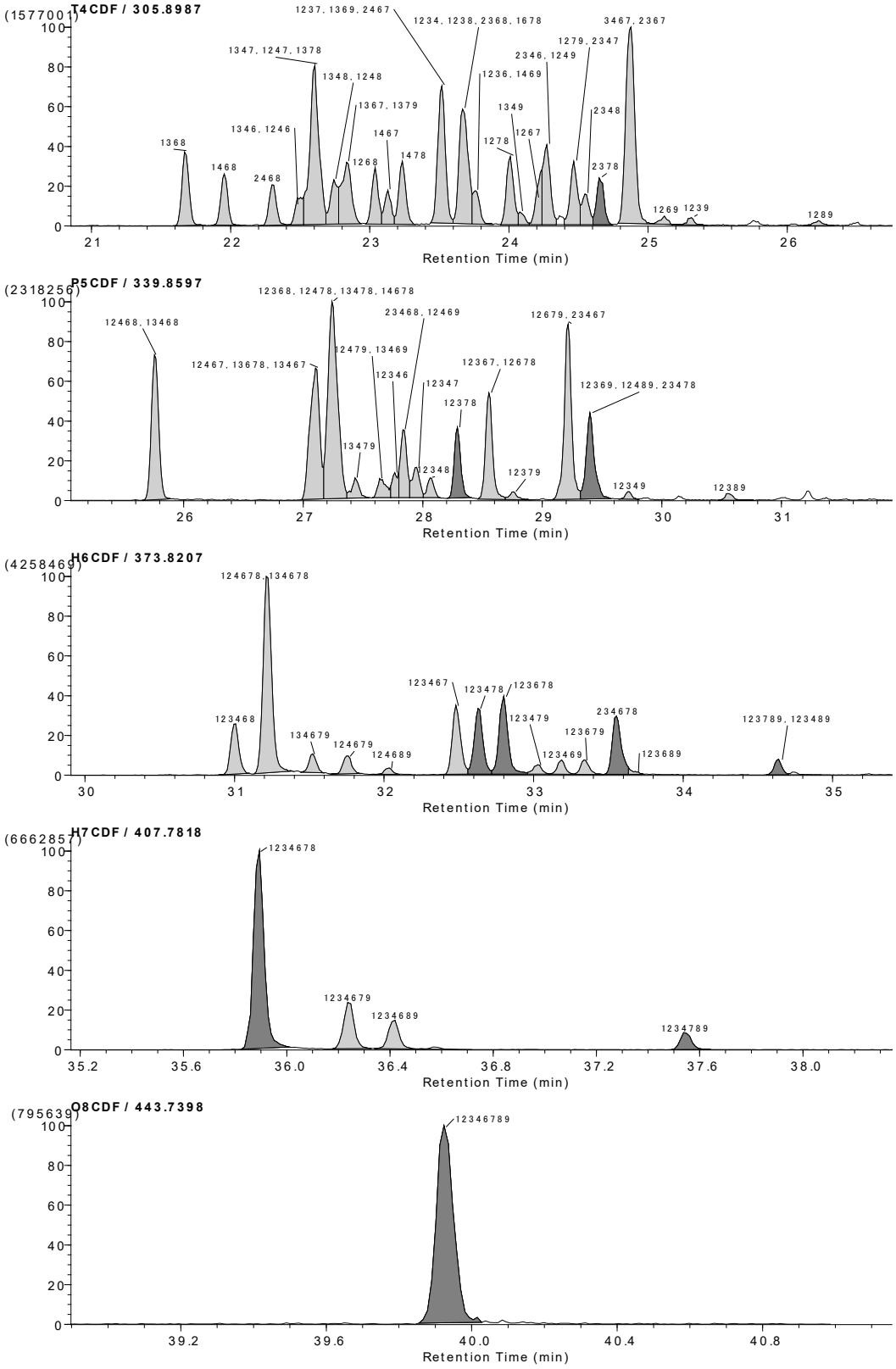

Figure 2: Chromatograms of PCDFs with isomer assignment in flyash certified reference material

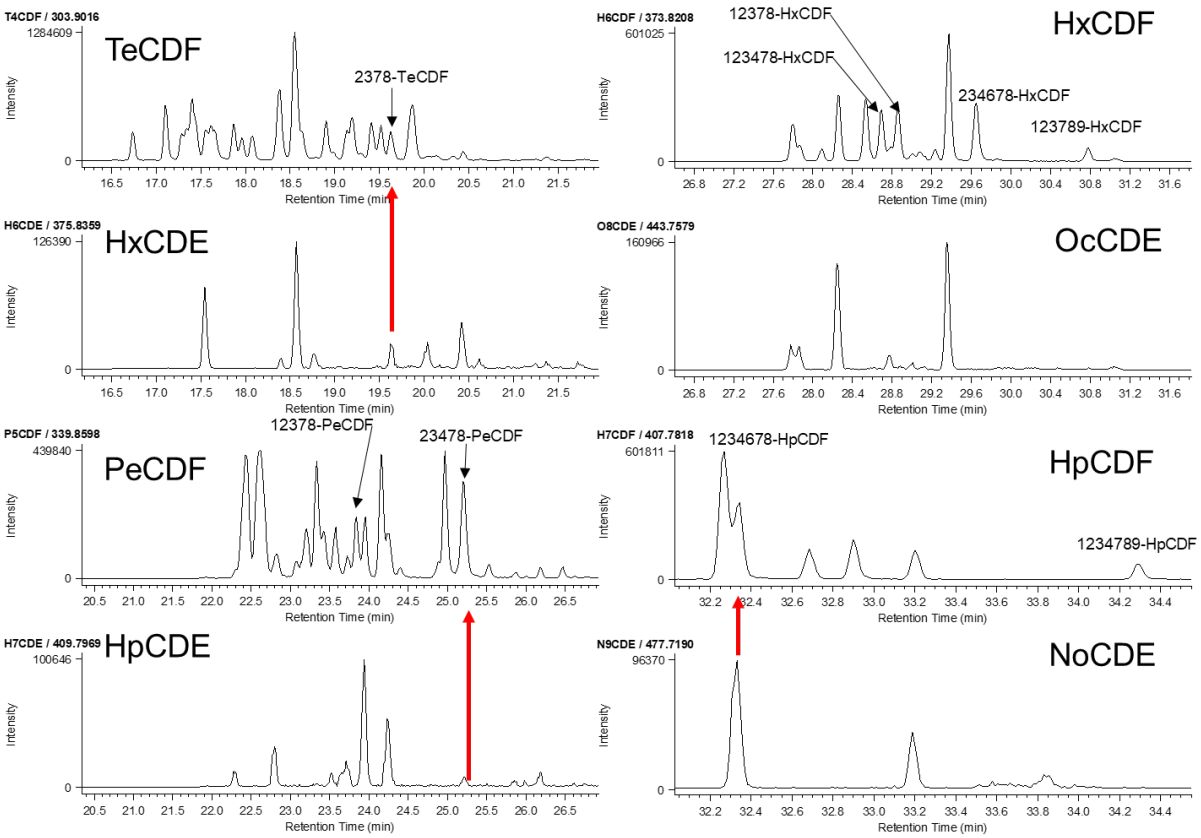

Figure 3: Chromatogram of PCDEs interfering with PCDFs (HxCDE: Hexachloro diphenylether, HpCDE: Heptachloro diphenylether, OcCDE: Octachloro diphenylether, NoCDE: Nonachloro diphenylether)

with different stationary phase polarity. Fig. 3 was shown the chromatograms of PCDFs and PCDEs to interfere with PCDFs quantification. For ZB-dioxin, HxCDE and HpCDE congeners were eluted near 2,3,7,8-TeCDF and 2,3,4,7,8-PeCDF under the temperature program in this study.

It is known that interference of PCDEs with PCDFs could be reduced by separating mono-*ortho* DL-PCBs fraction and PCDD/DFs fraction using alumina column chromatography or activated carbon-dispersed silica gel column chromatography in sample pretreatment. Therefore, the influence of PCDD/DFs on the quantification can be reduced by appropriate clean-up procedures. In further work, we will clarify the elution order for all congeners of PCBs that can be analyzed by ZB-Dioxin.

4 Conclusions

We have determined the elution order and peak profile of TeCDDs to OCDD congeners and TeCDFs to OCDF congeners on ZB-Dioxin GC capillary column. The results demonstrates that ZB-Dioxin enabled accurate isomer specific analysis for PCDDs/DFs.

5 References

1. Japan Standards Association (2020), JIS K0311:2020, Japanese industrial standards committee
2. Japan Standards Association (2020), JIS K0312:2020, Japanese industrial standards committee
3. Ministry of the Environment Government of Japan (2022), Manual on Determination of Dioxins in Ambient Air
4. Ministry of the Environment Government of Japan (2022), Manual on Determination of Dioxins in soil
5. Ministry of the Environment Government of Japan (2022), Manual on Determination of Dioxins in bottom sediment