

Mixed chlorinated fluorinated Dibenzodioxins, Dibenzofurans, Biphenyls: Synthesis, Analysis and Formation

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1. Introduction

In all processes investigated so far (municipal waste incineration (MWI), pyrolysis of Freons, production of aluminum and combustion of polyfluorinated carbon) no polyfluorinated dioxins (PFDDs), furans (PFDFs), or biphenyls (PFBs) have been found [1].

This might be due to the instability of fluorinated aromatic systems (e.g. polyfluorinated benzenes are highly inflammable). The question was, whether mixed polychlorinated/fluorinated dioxines (PCFDDs), furans (PCFDFs) and biphenyls (PCFBs) are more likely to be formed.

These compounds should be more stable and the stability should increase with increasing degree of chlorination.

First investigations of the metabolism of PCFDD/PCFDF in mouse liver homogenates indicates a higher toxic relevance of this class of compounds than of PFDDs/PFDFs (For further information see poster presented in toxicology section).

For a first estimation of occurrence and formation, fly ashes from MWI, samples from the aluminum producing industry and from a commercial mixed chlorinated fluorinated phenol were investigated in order to find mixed chlorinated/fluorinated dioxins, furans or biphenyls. Also the formation of these compounds during pyrolysis of Freons (R11, R12, R13) was tested.

2. Material and Methods

Synthesis of polychlorinated fluorinated biphenyls:

Decafluorobiphenyl was heated in a sealed glass ampoule (7 cm, 1 cm i.d.) at 360°C with CaH₂ under N₂ 50 hours. After cooling to room temperature the ampoule was opened carefully. The reaction product was dissolved in toluene by treatment in a ultrasonic bath for 15 minutes and subjected to clean up on an alumina column. After removal of the solvent the mixture of fluorinated biphenyls was chlorinated in a glass ampoule with CuCl₂ at 360°C for 15 h.

Synthesis of chlorinated/fluorinated dibenzodioxins and dibenzofurans

a.) Mixtures of PFDDs or PFDFs obtained by condensation of fluorophenols [1,2] were chlorinated in a glass ampoule with CuCl₂ at 360°C for 15-40 h.

b.) PCFDD were also obtained directly by condensation of fluorinated phenols in the presence of CuCl₂ in a glass ampoule at 370°C for 2 hours.

The samples were treated in the same way as described above.

Condensation of 3-chloro-4-fluorophenol

40 mg 3-chloro-4-fluorophenol was heated in a glass ampoule under N₂ at 380°C for 2 hours. The resulting congeners were separated on an alumina column (50g Alumina B-Super1, ICN) with 180 ml heptane/dichloromethane (87,5:12,5) followed by 240 ml heptane/dichloromethane

(80:20). From the second fraction 24 separate samples were collected. These 24 samples were analyzed via GC/MS. Fractions containing the same congener were combined. By this method the 2,3,7,8 substituted congeners can be isolated or at least strongly concentrated even from complex mixtures.

Extraction of samples from the aluminum production and fly ashes

100 g of the sample were extracted for 8 h under reflux with a mixture of 600 ml toluene, 100 ml ethoxyethanol and 20 ml conc. HCl. The clean up was carried out on an alumina column.

Analysis of phenols on PCFDD, PCFDF

1 g phenol was dissolved in 200 ml toluene and extracted three times with NaOH Solution (2N). The organic layer was dried over Na₂SO₄ concentrated and cleaned up on an alumina column.

Pyrolysis of Freons

R11, R12 and R13 were pyrolyzed under variation of temperature (300-800°C), matrix (model fly ashes based on Al₂O₃/SiO₂ containing different amounts of Fe, Cu and Zn), concentrations of oxygen (the Freons were mixed with 0-100% technical air), addition of water and flow (conducting 0,1 mol Freon within 3-45 min) in a tube of nickel (30 cm, 0,7 cm i.d.), glass (60 cm, 1,0 cm i.d.) or quartz (30 cm, 2 cm i.d.). Products were adsorbed on active alumina followed by an adsorption bottle filled with toluene.

HRGC/LRMS Detection

The analysis was carried out with a HP 5890 gaschromatograph coupled directly to a HP 5970 mass selective detector.

A DB-5 fused silica column (30 m, 0,32 mm i.d., 0,25 µm film thickness, J&W) was used for the separation of the complex mixtures.

For isomer-specific separation a CP-SIL 88 column (50 m, 0,25 mm i.d., 0,2 µm film thickness, CHROMPACK Frankfurt) was used.

Sample aliquots (1 µl) were injected splitless (injector temperature 260°C) and the temp. program for DB-5 was programmed as following: 100°C, 1,5 min. isothermal; 10°C/min. to 200 °C, 5 min. isothermal; 5°C/min. to 300°C, 10 min. isothermal. Carrier gas was helium at a head pressure of 110 kPa. Temp. program for CP-SIL 88: 120°C, 3 min. isothermal; 6 °C/min. to 180°C, 4 min. isothermal; 10°C/min. to 220°C, 5 min. isothermal; 20°C/min. to 245°C, 15 min. isothermal. Carrier gas was helium at a head pressure of 160 kPa.

3. Results and discussion

Synthesis of the chlorinated/fluorinated compounds

For the synthesis of the PCFBs, commercial decafluorobiphenyl is chlorinated with CuCl₂ under substitution of fluorine. By this reaction perhalogenated mixed chlorinated/fluorinated biphenyls were obtained. For the synthesis of chlorinated/fluorinated/hydrogenated biphenyls the decafluorobiphenyl is first hydrogenated with CaH₂ and then chlorinated with CuCl₂. If this process is not carried out under exclusion of oxygen or water, dibenzofurans will also be formed.

To synthesize the furans it is better to chlorinate PFDF mixtures, which can be obtained by condensation of fluorophenols [1]

The PCFDD can be obtained by chlorination of PFDD with CuCl₂ analogous to the PCFDF. They can also be synthesized directly by condensation of fluorophenols in the presence of CuCl₂. Applying this method, chlorination of the phenol is more rapid than the competing reactions of condensation to dioxin and subsequent chlorination of the dioxin ring system.

Chlorinated/fluorinated benzenes and phenols are obtained by chlorination of the partially fluorinated benzenes and phenols.

Single PCFDD/PCFDF congeners, needed for toxicological investigations, can be synthesized by direct condensation of a chlorinated/fluorinated phenol. Thus 3-chloro 4-fluorophenol yields a mixture of 2,8-difluoro3,7-dichloro/1,9-dichloro2,8-difluoro/1,7-dichloro2,8-difluorodibenzofuran which can be separated on an alumina column.

Extraction, enrichment, and clean up procedures

For the mixed chlorinated/fluorinated compounds the same methods employed for the extraction, enrichment, and clean up of chlorinated dioxins, furans and biphenyls can be applied.

For the lower chlorinated compounds (mono-trichloro) the high volatility must be considered analogous to the fluorinated compounds.

For the clean up on different columns the substitution of chlorine by fluorine results in no significant changes in the clean up procedure. Thus the mixed 2,3,7,8 substituted dioxins and furans can be separated together with the 2,3,7,8 TCDD/TCDF on an alumina column from the non 2,3,7,8 substituted congeners or at least strongly enriched.

Substitution of chlorine in ortho position by fluorine in biphenyls apparently does not lead to a switch from the "coplanar" to the "non coplanar" elution fraction.

HRGC/LRMS separation and detection

To separate the complex mixtures, the DB-5 column was chosen from the three columns tested (DB-5, DB-DIOXIN, CP-SIL 88). The DB-5 separates the mixtures according to the degree of chlorination [Fig.1]. Given a certain degree of chlorination, the substitution of hydrogen by fluorine has hardly any effect on the retention time. These fluorine substituted congeners usually eluate slightly faster [Fig.2].

In order to separate single congeners of the same degree of chlorination the CP-SIL 88 column was chosen. This column was used for the separation and determination of the isomer mixtures which were obtained by the condensation of the chlorofluorophenols.

The detection by mass spectrometry and the identification is carried out analogous to the chlorinated compounds with the isotope ratios. According to the degree of chlorination two ions (M^+ , $(M+2)^+$, or $(M+4)^+$) are detected.

The mass spectrometric fragmentation is analogous to the PCDD/PCDF. While COCl cleavage ($M-63)^+$ can be seen, no COF ($M-47$) fragmentation is observed as for the PFDD/PFDF [Fig.3], [1].

First investigation regarding occurrence and formation of chlorinated/fluorinated dioxins, furans and biphenyls

The pyrolysis of Freons (R11, R12 R13) leads to the formation of highly chlorinated benzenes and biphenyls, and according to the conditions also highly chlorinated furanes and dioxins rather than the expected fluorinated dioxins and furans. In addition, small amounts of monofluoropolychloro benzenes, biphenyls and furans and difluorotetrachlorobenzene were found. For all conditions of pyrolysis investigated, the ratio of the monofluoropolychloro:polychloro aromatic systems never exceeded 1:50.

Also in a first investigation of samples from the aluminium production the same chlorinated fluorinated compounds could be detected. The ratio here was 1:10.

No mixed chlorinated/fluorinated aromatic compounds were detected in fly ash from MWI.

For commercial 3-chloro 4-fluoro phenol used for the synthesis of the mixed chlorofluorofurans, chlorinated fluorinated biphenyls and biphenylether were found in the ppm range. PCFDD and PCFDF were detected only in ppb range.

4. References

- 1) R. Weber, D. Schrenk, H.-J. Schmitz, A. and H. Hagenmaier, Chemosphere, Vol. 30, 629 (1995).
- 2) U. Haffer, W. Rotard, W. Mailahn, G. Schulze, Organohalogen Compounds, Vol. 11, 87 (1993)

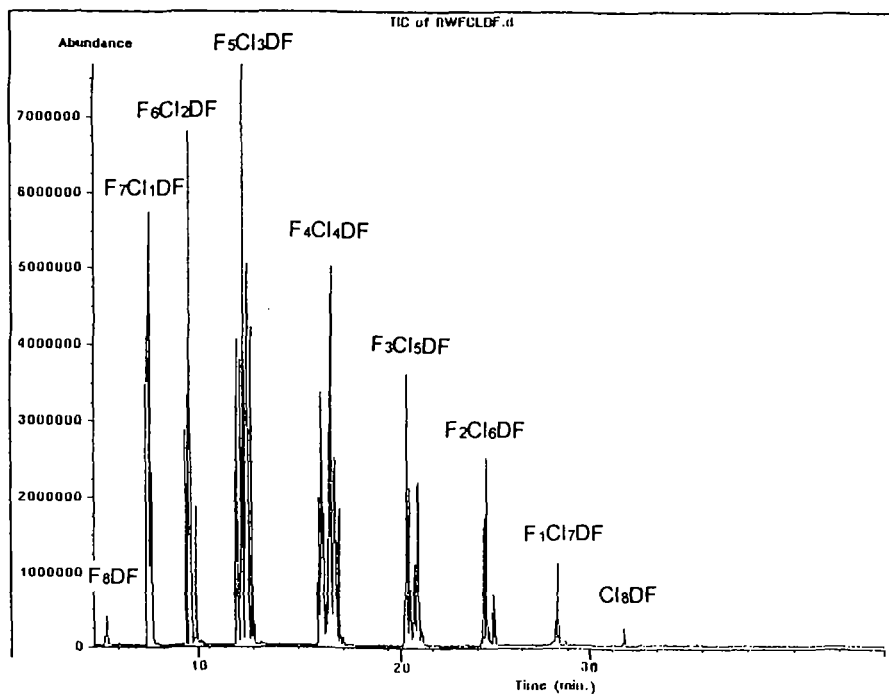


Figure 1: Mass fragmentogram of the perhalogenated chlorinated /fluorinated dibenzofurans (On DB-5)

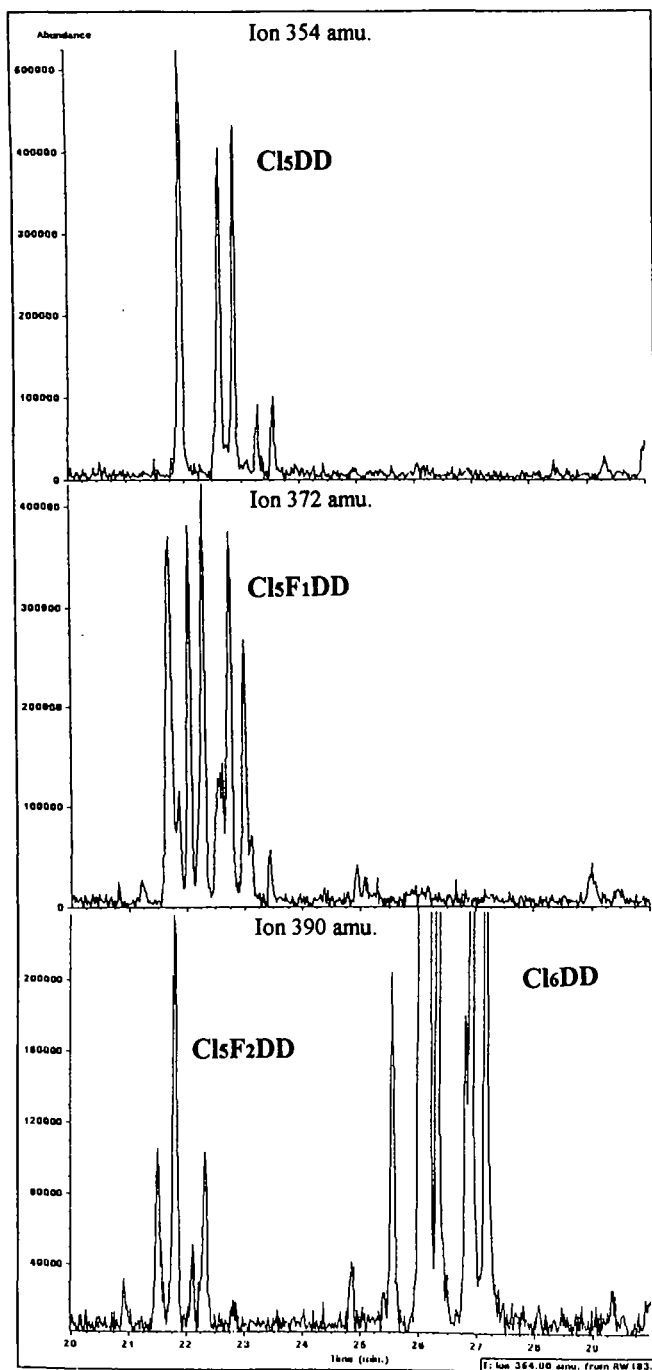


Figure 2:
 Mass fragmentograms of
 pentachloromonofluoro- and
 pentachlorodifluoro-
 dibenzodioxins in comparison
 to P₅CDD and H₆CDD
 (On DB-5)

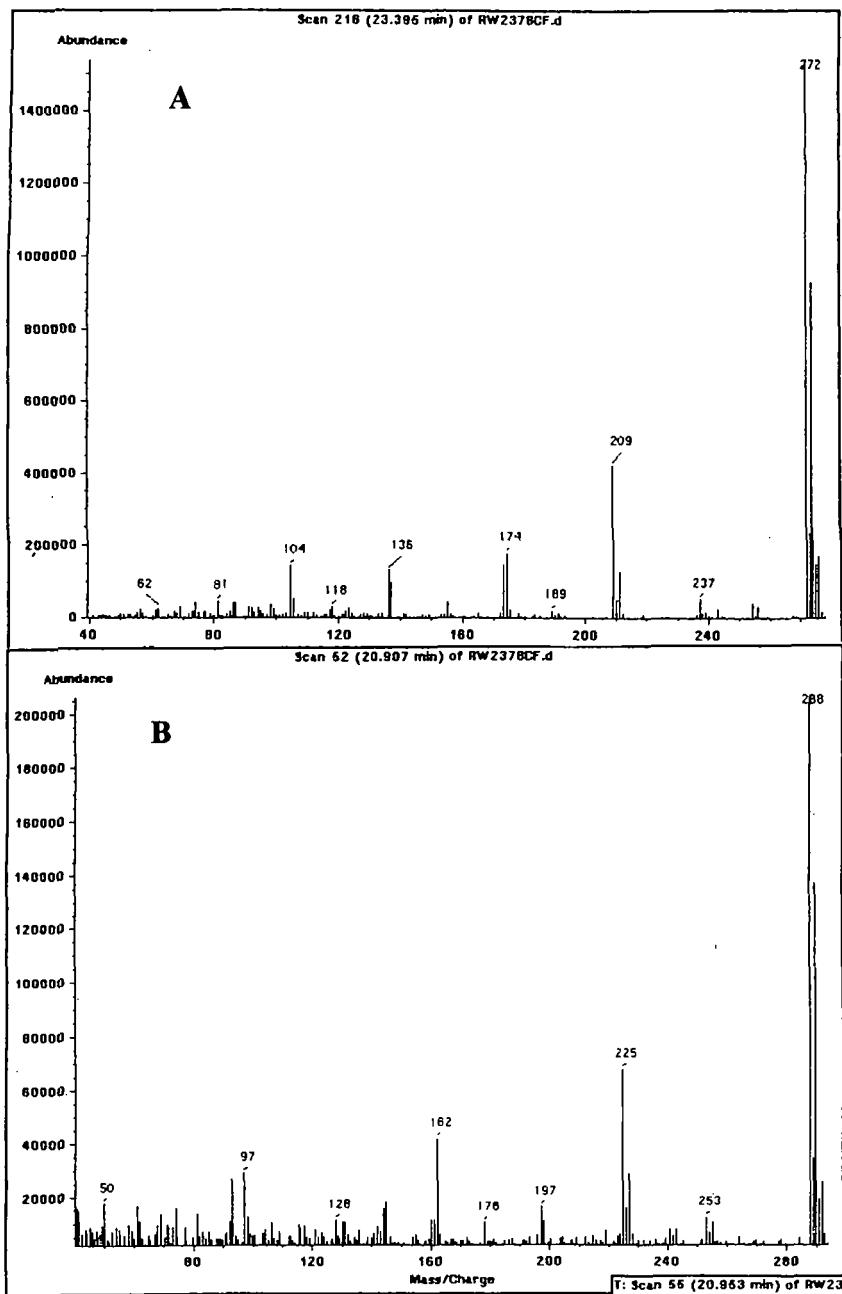


Figure 3: Mass spectra of 2,8 difluoro-3,7 dichlorodibenzofuran (A) and 2,7 dichloro-3,8difluorodioxin (B)