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IDENTIFICATION OF POLYCHLORINATED DIBENZOFURAN ISOMERS IN FLY ASH AND PCB PYROLYSES

Hans Rudolf Buser and Hans-Paul Boeshardt
Swiss Federal Research Station
CH - 8820 Wädenswil, Switzerland

and

Christoffer Rappe and Roger Lindahl
Department of Organic Chemistry, University of Umea
S - 901 87 Umea, Sweden

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Introduction

Fly ash and flue gases of municipal incinerators and of an industrial heating facility were shown to contain the hazardous polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in addition to other chlorinated compounds.[1,2] The fly ash from two different facilities in Switzerland showed a remarkably similar distribution of the PCDD isomers.[3] The major PCDD isomers found in samples from both facilities were those formed in the pyrolytic dimerization of the most common chlorophenates, namely the 2,4-di-, 2,4,6-tri-, 2,3,4,6-tetra- and pentachlorophenate, suggesting these commonly used products as precursors to the PCDDs. The known toxic PCDD isomers, such as 2,3,7,8-tetra-, 1,2,3,7,8-penta-, 1,2,3,6,7,8- and 1,2,3,7,8,9-hexa-CDD were present as minor components.

In addition to PCDDs, the fly ash from both facilities showed the presence of PCDFs at a similar level as the PCDDs.[2] In all, 135 positional isomers exist for the PCDFs, and some of these are about equally toxic or biologically active as the most toxic PCDDs.

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This is especially true for the 2,3,7,8-tetra-, 1,2,3,7,8- and 2,3,4,7,8-penta-CDF.[4,5]

Commercial chlorophenols have been found to contain PCDDs and PCDFs in the range of tens to hundreds of ppm.[6] PCDFs have been involved in a serious intoxication in Japan in 1968, called the Yusho disease,[7,8] and they have been associated with polychlorinated biphenyls (PCBs) in which they are usually present as trace impurities at the ppm level.[9] PCBs are industrial chemicals of wide use; they have been associated with a world-wide contamination. Recently, actions were taken to reduce or ban their use.

In a previous paper, we showed that pyrolysis of PCBs can result in the formation of PCDFs at the percent level.[10] Since a large portion of the used PCBs may be disposed by incineration, this formation of PCDFs may have environmental significance.

In addition to PCBs, polychlorinated diphenylethers (PCDPEs) could come into consideration as possible precursors of PCDFs. We have shown that the thermal conversion of PCDPEs into PCDFs is of the same order of magnitude as that from PCBs.[11] For the present, we consider PCBs as a more probable source for the hazardous PCDFs due to the much larger production volume of the PCBs as compared to the PCDPEs.

In this paper, we report the analysis of PCDFs in two fly ash samples. Although we do not give the complete structure of all isomers present, we show by high-resolution gas chromatography and mass spectrometry that most of the major PCDFs in these fly ash samples were also formed in the pyrolysis of commercial PCBs (Aroclor 1254 and 1260). This finding gives strong support to the assumption that the PCDFs found in fly ash are originating from the uncontrolled burning of PCBs.

Experimental

Extraction and purification of fly ash samples

The extraction and purification procedure used has been previously described.[3] The same sample extracts were used in this study as for the identification of the PCDD isomers.[3]

Micropyrolysis of PCBs

Aroclor 1254 and 1260 (100 μg each) were pyrolyzed at 600°C in separate quartz mini-ampoules. The exact pyrolysis conditions and the clean-up procedure used have been

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described.[10] Extracts of previously pyrolyzed 2,4,5,2',4',5'- and 2,4,6,2',4',6'-hexachlorobiphenyl were analysed for comparison.

Standard and reference PCDF isomers

The following PCDF isomers were obtained: 2,3,7,8-tetra- and 2,3,4,7,8-penta-CDF as gifts from Dr. J.D. McKinney, and 1,2,3,7,8-penta-CDF as a gift from Dr. A. Poland. The 1,2,3,4,8-penta-CDF was prepared from the corresponding PCDPE by a Pd-catalyzed cyclization.[12] In addition, a mixture of 2,3,4,6,8-penta-, 2,3,4,6,7,8-hexa- and 1,2,3,4,6,7,8-hepta-CDF was obtained by chlorination and deamination of 3,7-diaminobenzofuran.[12] This mixture contained a minor amount of 1,2,4,6,7,8-hexa-CDF as well.

GC-MS Analysis

A Finnigan 4000 quadrupole GC-MS instrument equipped with electron-impact ion source and a Finnigan 6111 data system was used. The samples were analyzed on a 50 m 0.37 mm ID OV-17 glass capillary column coupled to the mass spectrometer via a glass-lined stainless steel tube of low internal diameter (0.3 mm ID). In a first phase, complete mass spectra of individual PCDFs were recorded (1.4 sec/scan, m/e 35-470) using the data system. The column conditions were as follows: 120°, 2 min isothermal, 20°/min to 180°, 5°/min to 250°C. In a second phase, the samples were reanalyzed with optimal isomer separation using mass specific detection (mass fragmentography) of PCDFs by monitoring molecular ions at m/e 270, 304, 338, 372 and 406 for the tri- to heptachloro compounds. The column conditions this time were: 100°, 2 min isothermal, 20°/min to 160°, 2°/min to 250°C. Individual PCDFs were found to elute in the retention time ranges indicated in Figure 1 and 2. Isomers in the extracts were identified by co-chromatography with the reference compounds.

In the pyrolysis and fly ash samples minor quantities of polychlorinated naphthalenes (PCNs) were observed at levels of one tenth to one fifth of the PCDFs. These compounds give a response at the m/e values listed above due to M^++6 isotope peaks, e.g. penta-CN (M^+-298) at m/e 304. Most of the PCNs observed elute prior to the retention time ranges of the corresponding PCDFs. A differentiation between these compounds is easily achieved by observation of their complete mass spectra (presence of M^+, number of Cl's as determined from the isotope cluster and the typical fragmentation with formation of M^+-COCl for PCDFs

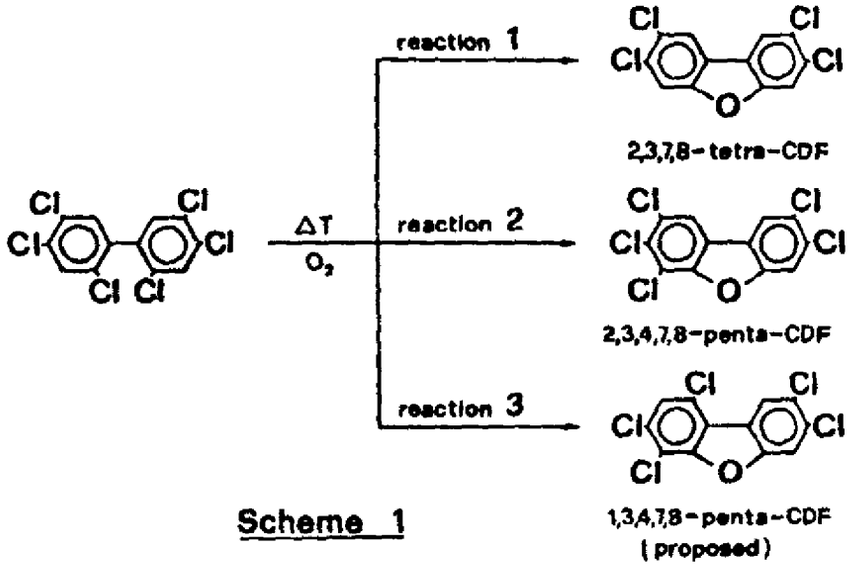
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and M^+-Cl_2 for PCNs). PCDPEs were not observed in the cleaned-up extracts.

Results and Discussion

Formation of PCDFs from the pyrolysis of individual PCB isomers

In the previous paper we reported the formation of PCDFs from the pyrolysis of 3 individual PCB isomers.[10] 2,4,5,2',4',5'-Hexachlorobiphenyl, one of the major hexachlorobiphenyls found in commercial PCBs, formed one tetra- and two penta-CDF isomers. The tetra-CDF was the 2,3,7,8- substituted isomer resulting from the formal loss of Cl_2 by reaction 1 (Scheme 1). The formation of two penta-CDFs means that one of these isomers must be formed in a rearrangement reaction. It was now shown, by comparison to an authentic standard on a high-resolution glass capillary column, that one of the penta-CDFs formed is the 2,3,4,7,8-substituted isomer. This isomer is formed by the formal loss of HCl and a rearrangement involving a 2,3-chlorine shift (reaction 2). The second penta-CDF (earlier eluting isomer) is expected to be the 1,3,4,7,8-penta-CDF resulting from the loss of HCl without rearrangement according to reaction 3. The proposed reaction pathways for the formation of PCDFs from the pyrolysis of PCBs are illustrated below for the 2,4,5,2',4',5'-hexachlorobiphenyl.



Scheme 1

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The quantifications given in the previous paper[10] indicate, that the three reaction mechanisms have about equal probability in case of the 2,4,5,2',4',5'-hexachlorobiphenyl.

2,4,6,2',4',6'-Hexachlorobiphenyl is an isomer not usually found in commercial PCBs.[13] Pyrolysis of this compound resulted in the formation of a tetra- and a penta-CDF in about equal amounts. The tetra-CDF expected is the 1,3,7,9-substituted isomer formed by reaction 1. The formation of a penta-CDF has to involve a rearrangement; this isomer could be the 1,3,4,7,9-penta-CDF formed by reaction 2 or another penta-CDF isomer formed in another rearrangement. The formation of a penta-CDF without any rearrangement according to reaction 3 is not possible and no additional penta-CDF was observed.

2,6,2',6'-Tetrachlorobiphenyl did yield a di- and a tri-CDF. The di-CDF is most likely the 1,9- substituted isomer formed according to reaction 1, the tri-CDF is expected to be the 1,4,9- substituted isomer formed by a rearrangement (reaction 2). A tri-CDF formed by reaction 3 is not possible, and the elution of an additional isomer was not observed.

Very few PCDF standards are presently available. However, micro-pyrolysis of individual, synthetically available PCB isomers in quartz mini-ampoules could be a very helpful and convenient way of preparing small amounts of PCDF isomers for use as qualitative reference compounds in analyses of various samples. We are currently involved in such a program, where the structure of the products from the pyrolyses are studied by comparison with PCDFs prepared by other known methods.

Formation of PCDFs from the pyrolysis of commercial PCBs

Commercial PCBs (Aroclors, Clophens, Phenoclors, Kanechlors) consist of a multitude of individual PCB isomers; theoretically there exist 209 isomers, in practice up to 100 have been observed in commercial PCBs.[13,14] In the present investigation, we have studied the pyrolysis of two commercial PCBs, Arocolor 1254 and 1260. Aroclor 1254 mainly consists of tri- to heptachlorobiphenyls and from these we can expect the formation of mono- to hexa-CDFs according to reactions 1,2 and 3, Scheme 1. Aroclor 1260 has penta- to octachlorobiphenyls as the major constituents and from these we can expect the formation of tri- to hepta-CDFs.

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In Figure 1, mass fragmentograms show the elution of tri- to hepta-CDFs in the pyrolyzed Aroclors. With Aroclor 1254 (Figure 1a), mono- to penta-CDFs were formed (elution of the mono- and di-CDFs not shown) at a total level of approx. 2% relative to the PCB; with Aroclor 1260 (Figure 1b), tri- to hepta-CDFs formed at a similar level. In case of the major isomers, the discrete PCDFs could be identified in both samples by running complete mass spectra.

Significant quantities of tri-CDFs were formed from Aroclor 1254 and the elution of up to 17 isomers can be observed. Aroclor 1254 did also produce mono- and di-CDFs.

In case of the tetra-CDFs, significant quantities were formed from both Aroclors. Similar patterns with the same major tetra-CDF isomers were observed in these two pyrolysates. One of the major tetra-CDFs in both cases is the extremely toxic 2,3,7,8-tetra-CDF (peak 44) as shown by co-chromatography with the authentic standard. This PCDF is most likely formed from 2,4,5,2',4',5'-hexachlorobiphenyl (a major constituent of these Aroclors) by reaction 1 or from 2,4,5,3',4'-pentachlorobiphenyl (also present in these Aroclors) by reaction 3. 2,3,7,8-Tetra-CDF was not completely resolved on this column from another tetra-CDF (peak 43). With pyrolyzed Aroclor 1254, 6 major and about 15 minor tetra-CDFs were observed. Most of these isomers were also formed with Aroclor 1260 but some in reduced amounts, notably the peaks 34, 47 and 48. The tetra-CDF (peak 27) formed from 2,4,6,2',4',6'-hexachlorobiphenyl and tentatively identified as the 1,3,7,9-tetra-CDF could only be present as a minor component.

Again, similar patterns were observed for the penta-CDFs in both pyrolysis samples. One of the major isomers (peak 53, not separated from peak 54) in both cases has an identical retention time as one of the penta-CDFs formed from 2,4,5,2',4',5'-hexachlorobiphenyl; it is presumably the 1,3,4,7,8-substituted isomer formed by reaction 3. Both, the very toxic 1,2,3,7,8- and 2,3,4,7,8-penta-CDF (peak 60 and 68, respectively) were present in these samples at significant levels. The former could be a product from 2,3,4,2',4'5'-hexachlorobiphenyl resulting via reaction 3, the latter from 2,4,5,2',4',5'-hexachlorobiphenyl via reaction 2 or from 2,3,4,5,2',4',5'-heptachlorobiphenyl via reaction 1. These hexa- and heptachlorobiphenyls have been reported as constituents in commercial PCBs.[14] The 2,3,4,6,8- and the 1,2,3,4,8-penta-CDF (peak 61 and 62, respectively) were present as minor components

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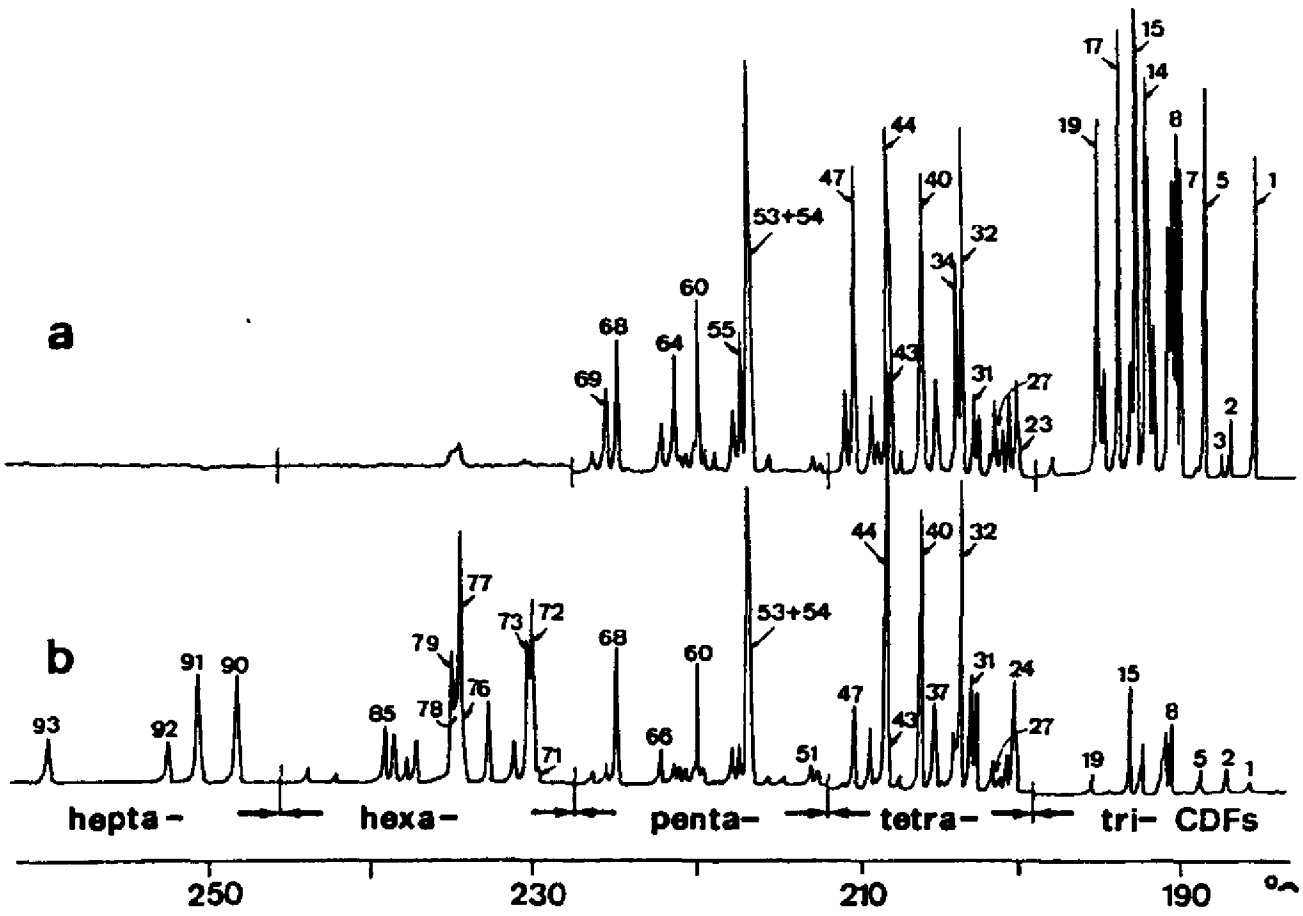


Figure 1: Mass fragmentograms (50 m OV-17, m/e 270, 304, 338, 372 and 406) showing elution of tri- to hepta-CDFs in a) pyrolyzed Aroclor 1254 and b) pyrolyzed Aroclor 1260. Peak identifications see text. Sensitivities: 0.1 to 2 V f.s.

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only. Aroclor 1254 shows the presence of another major penta-CDF (peak 55). This isomer did co-chromatograph with the penta-CDF formed in the pyrolysis of 2,4,6,2',4',6'-hexachlorobiphenyl and could be the 1,3,4,7,9-penta-CDF. However, the source or identity of this penta-CDF is not completely clear because 2,4,6,2',4',6'-hexachlorobiphenyl was not found to be present in these Aroclors,[13] and all other major PCBs in the Aroclors do not yield this PCDF isomer in reactions 1, 2 or 3, Scheme 1. Pyrolyzed Aroclor 1260 showed reduced levels of the penta-CDFs eluting as peaks 64 and 69.

Hexa-CDFs were formed at a significant level only with Aroclor 1260. In this case, over 10 isomers were observed; 2,3,4,6,7,8-hexa-CDF (peak 85) was one of the minors only. Additionally, all 4 hepta-CDFs (peak 90-93) and octa-CDF were observed in the pyrolysis of Aroclor 1260. The elution of octa-CDF is not shown in the mass fragmentogram in Figure 1.

PCDFs in fly ash

Fly ash samples from two facilities in Switzerland were analyzed. The two samples were from an industrial heating facility near Aarau and a municipal incinerator in Zürich. The same samples have been analyzed for the PCDD isomers,[3] and have been more accurately described in that paper. Both samples showed the presence of PCDFs at a level of 0.3 and 0.1 ppm, respectively. This is about one third to one half of the level of the PCDDs present. In addition, these samples also showed the presence of PCBs at about the same level as the PCDFs. PCNs were present in smaller amounts as well as other chlorinated compounds.

In Figure 2, mass fragmentograms show the elution of tri- to hepta-CDFs in both fly ash samples. The same peak numbering was applied as for the pyrolyzed PCB samples in Figure 1. As can be seen from Figure 2, both samples show remarkable similarities in the pattern of the PCDF isomers, pointing to a common source for these compounds.

In case of the tri-CDFs, up to 18 isomers can be observed. The same isomers were found as the major tri-CDFs in both samples (peaks 7, 10 and 17). With the exception of 3 minor peaks, all were found in the Aroclor 1254 pyrolysis as well.

Among the tetra-CDFs, again very similar patterns were found for both of the samples and the elution of up to 21 isomers can be observed. The very toxic 2,3,7,8-tetra-CDF (peak 44) is the major isomer of this group in both samples. Most of the tetra-CDF isomers

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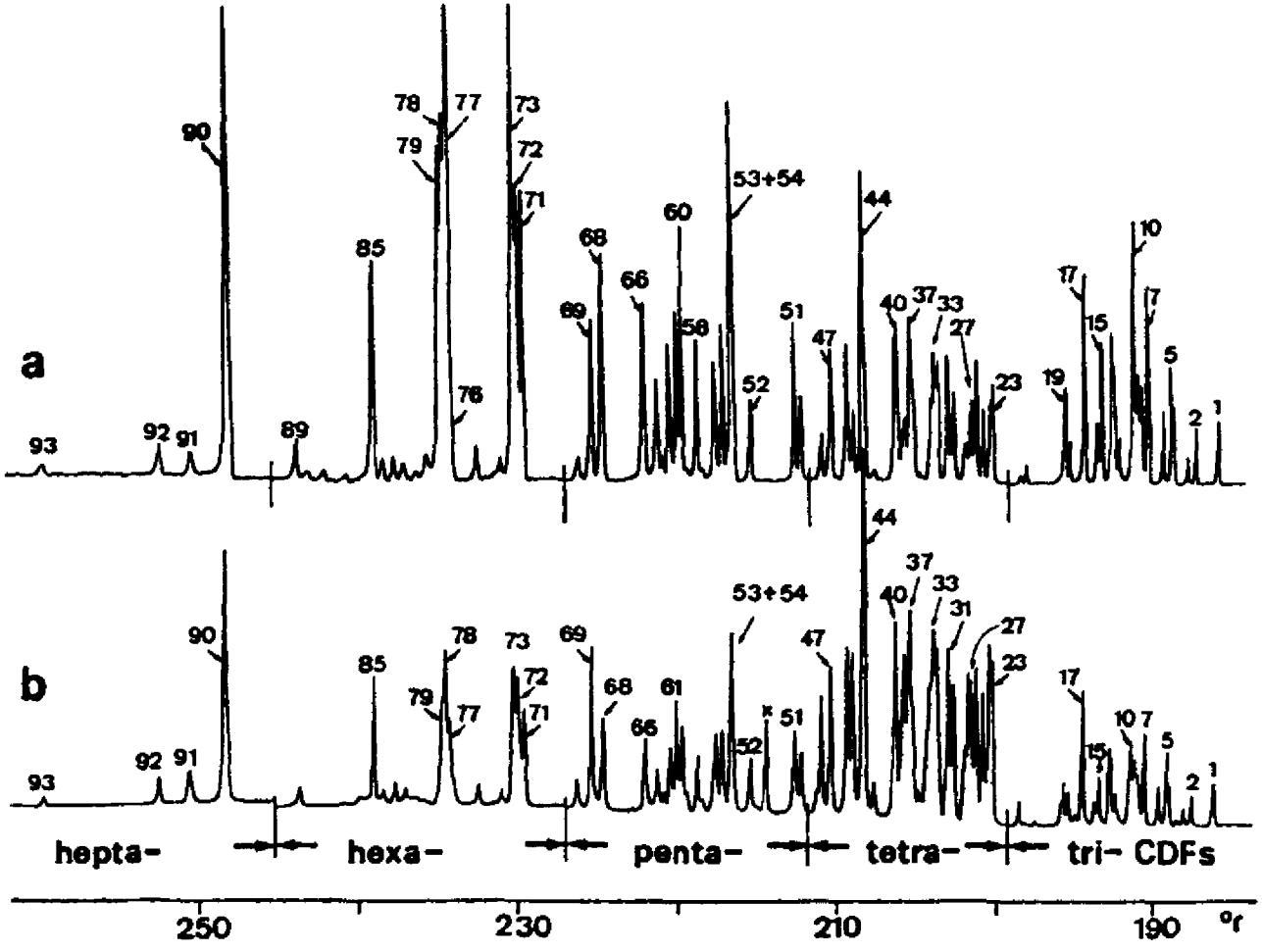


Figure 2: Mass fragmentograms showing elution of tri- to hepta-CDFs in the fly ash of a) an industrial heating facility near Aarau and b) a municipal incinerator at Zürich. Conditions and peak numbering as in Figure 1. Sensitivities: 0.2 to 2 V f.s.

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found in these fly ash samples were also present in the Aroclor 1254 and 1260 pyrolyzates, although in somewhat different proportions.

In case of the penta-CDFs, up to 17 different isomers were found to be present in both samples. Note that one of the peaks (marked x) in the fly ash from Zürich is not a penta-CDF but a hexa-GN (M^++6-338) eluting in this temperature range. As in the Aroclor pyrolyses, the major components here again are the isomers eluting as peaks 53 and 54; the former is a pyrolysis product of 2,4,5,2',4',5'-hexachlorobiphenyl, tentatively identified as 1,3,4,7,8-penta-CDF. Again, the toxic 1,2,3,7,8- and 2,3,4,7,8-penta-CDF (peak 60 and 68, respectively) are present. In addition, both fly ash samples show the presence of 2,3,4,6,8- and 1,2,3,4,8-penta-CDF (peak 61 and 62, respectively) that were minor constituents in the pyrolysed Aroclors. The fly ash samples also show increased amounts of the penta-CDF isomers eluting as peaks 50, 51, 58 and 66.

Among the hexa-CDFs, we can see the same 7 major isomers in both fly ash samples. Compared to the Aroclor 1260 pyrolyzate, the fly ashes show increased amounts of the isomers eluting as peaks 71, 78 and 85 and a somewhat reduced amount of the isomer eluting as peak 75; otherwise, very similar patterns of the hexa-CDF isomers were observed. The isomer eluting as peak 85 is the 2,3,4,6,7,8-hexa-CDF; peak 71 could correspond to the 1,2,4,6,7,8-hexa-CDF, present as a minor impurity in one of our standards.

Whereas in the pyrolysis of Aroclor 1260 similar amounts of the 4 individual hepta-CDFs were formed, we see a clear preference of the first eluting isomer (peak 90) in both fly ash samples. This isomer did co-elute with 1,2,3,4,6,7,8-hepta-CDF of our standard mixture.

Conclusions

Fly ash and flue gases were shown to contain PCDDs and PCDFs.[1,2] Previously, we have shown that commercial chlorophenates are potential precursors to the PCDDs, and that the most toxic PCDDs were only minor constituents.[3] The present investigation, using high-resolution GC and MS, has shown that the same PCDF isomers were present in the fly ash of such different facilities as an industrial heating facility and a municipal incinerator. Most of these isomers were also formed in laboratory pyrolyses of commercial PCBs. This gives strong support to the assumption that the PCDFs in the fly ash were, to a significant

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extent, due to the uncontrolled burning of PCBs. Contrary to the PCDDs, in case of the PCDFs, we found the most toxic isomers to be the major constituents in fly ash as well as in the PCB pyrolyzates. Consequently, the disposal of PCBs by incineration should be carefully controlled in order to minimize environmental and occupational exposure to the hazardous PCDFs.

Acknowledgements

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