Analysis of PCDD/Fs in fly ash using comprehensive two-dimensional gas chromatography with electron capture detection (GC×GC-μECD)

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Introduction

There are 49 polychlorinated dibenzo-*p*-dioxins (PCDDs) and 87 polychlorinated dibenzofurans (PCDFs) that are substituted with four to eight chlorines. Among these 136 congeners, the seven PCDDs and ten PCDFs with 2,3,7,8-substitution are considered as the most toxic PCDD/F congeners. The determination of PCDD/Fs is challenging since their concentrations often are down at ppt levels. Despite an efficient clean-up and fractionation, other classes of compounds and also other PCDD/Fs can interfere during analysis of the toxic 2,3,7,8-substituted PCDD/Fs. Today, the analysis of dioxins is costly, partly due to the tedious pre-treatment and clean-up but also due to the unavoidable use of gas chromatography - high-resolution mass spectrometry (GC-HRMS). There is indubitably a need for methods that can deliver results similar to GC-HRMS, but at a lower cost. An alternative technique that offers comparable selectivity is comprehensive two-dimensional GC (GC×GC) – a powerful technique that has been developed during the last decadeand recently has been evaluated for PCDD/F analysis in biological matrices[1]. In contrast to biological matrices where normally only the 2,3,7,8-substituted PCDD/Fs are present, other samples e.g. fly ash is much more complex and may contain every single PCDD/F congener. In this work, 2,3,7,8-substituted PCDD/Fs were separated from non-2,3,7,8 congeners and all 87 tetra-octa-CDFs and also the hexa-octa-CDDs were identified in a fly ash sample containing all of the 136 PCDD/F congeners with four to eight chlorines.

Materials and Methods

For identification of the PCDFs, 16 mixtures with 4 to 11 individual PCDF congeners in each[2] and a standard solution including all of the 87 PCDF congeners were used. The fly ash sample was collected in 1999 from a municipal solid waste incinerator located in Umea, Sweden. It was prepared as for traditional dioxin analysis with GC-HRMS[3], except that it was not fortified with ^{13}C labeled compounds, as the electron capture detector (ECD) can not differentiate between isotopes. At the time of sample preparation, no suitable internal standards had been evaluated for GC×GC-μECD, and the sample was thus not quantified with the GC×GC technique. However, the sample could still be used to assess whether the GC×GC technique is suitable for dioxin analysis of fly ash. Assignment of the HxCDD congeners was carried out by comparison with a chicken fat sample with known levels of each congener (GC-HRMS analysis) and the 2,3,7,8- substituted PCDD/F congeners have been assigned in a previous study[1]. As a first dimension column a 28 m x 0.25 mm x 0.25 μm DB-XLB (J&W Scientific) was employed, followed by a 0.9 m x 0.15 mm x 0.1 μm LC-50 (J&K Scientific) second dimension column. The temperature program used was: 90°C (2 min), 5°/min to 200°C, 1°C/min to 245°C, and 30°C/min to 270°C (16 min). Helium was used as carrier gas at a constant flow of 1.0 ml/min, and the detection was by an Agilent μECD operating at 300°C with a nitrogen make-up gas flow of 150 ml/min and a data acquisition rate of 50 Hz. A longitudinally modulating cryogenic system (LMCS) was used for modulation with a modulating period of 6 seconds.

Results and Discussion

The toxic congeners with chlorines in the 2,3,7,8 positions were well resolved from all other tetra-penta-CDD/Fs (Figure 1 and 2). To achieve a comparable separation with conventional GC-MS, injection on two columns with different polarity, such as DB-5 and SP 2330, is usually used[3]. Still, 2,3,7,8 -TCDF, 2,3,7,8-TCDD, and 1,2,3,7,8-PeCDF would not be completely separated from other PCDD/Fs assuming that every congener is at about the same level. The SP-2330 chromatograms from the GC-HRMS analysis of the same fly ash sample showed that, 2,3,7,8-TCDD partly coeluted with 1,4,7,8-TCDD (50 % valley) and 1,2,3,7,8-PeCDF was not resolved from 1,2,3,4,8-PeCDF, but would have been almost resolved on a DB-5 column with approximately a 10 % valley. The 2,3,7,8-TCDF was completely resolved on the SP-2330, but this was due to the very low concentration of the 1,2,6,9-TCDF, which otherwise would have interfered.

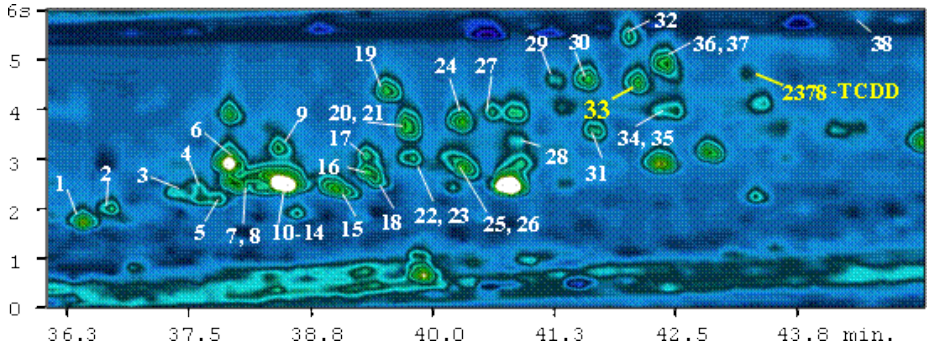

Figure 1. Contour plot of tetra-CDD/Fs in fly ash.

Table 1. Annotation for Figure 1, assignments of tetra-CDFs (2,3,7,8-congeners in bold).

No.	Substitution	No.	Substitution	No.	Substitution
1	1368	16	1237	29	1279
2	1468	17	1246	30	2347
3	1346	18	1369	31	2348
4	1478	19	1678	32	3467
5	2468	20, 21	1238, 2467	**33**	**2378**
6	1378	22, 23	1469, 1236	34,35	2346, 1269
7, 8	1347, 1348	24	1278	36, 37	2367, 1239
9	1379	25, 26	2368, 1349	38	1289
10-14	1467, 1367, 1247, 1268, 1248	27	1267		
15	1234	28	1249		

Although better separation is achieved on DB-XLB×LC-50 for above-mentioned congeners, the resolution of 1,2,3,7,8-PeCDD is not as good as on DB-5 and SP-2330 where it is completely resolved. The resolution between 1,2,3,7,8-PeCDD and 1,2,3,6,7-PeCDD in Figure 3 is calculated by using the expression for resolution in GC×GC: $R_s^2 = R_{s1}^2 + R_{s2}^2$. In this case, the two-dimensional resolution was calculated to 0.8 and a valley of 20 % was obtained by using the heights located at points x and y in Figure 3.

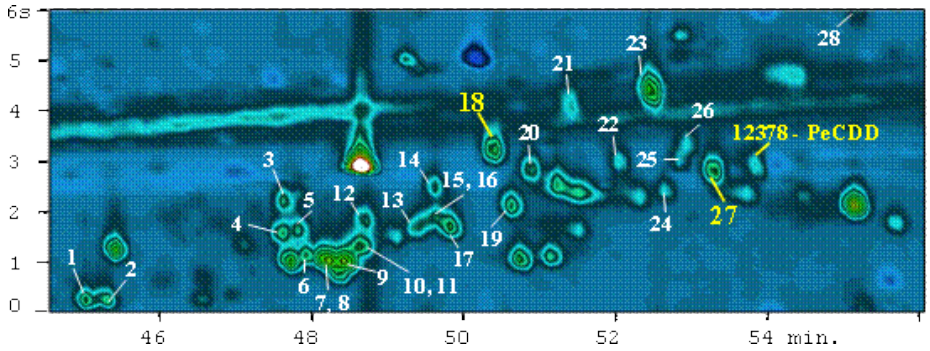

Figure 2. Contour plot of penta-CDD/Fs in fly ash.

Table 2. Annotation for Figure 2, assignments of penta-CDFs (2,3,7,8-congeners in bold).

No.	Substitution	No.	Substitution	No.	Substitution
1	13468	12	12346	22	12679
2	12468	13	12479	23	23467
3	12467	14	12347	24	12369
4	13467	15, 16	12469, 12348	25	12349
5	23469	17	23468	26	12489
6	13678	**18**	**12378**	**27**	**23478**
7, 8	13478, 12368	19	12678	28	12389
9	12478	20	12367		
10, 11	13469, 13479	21	12379		

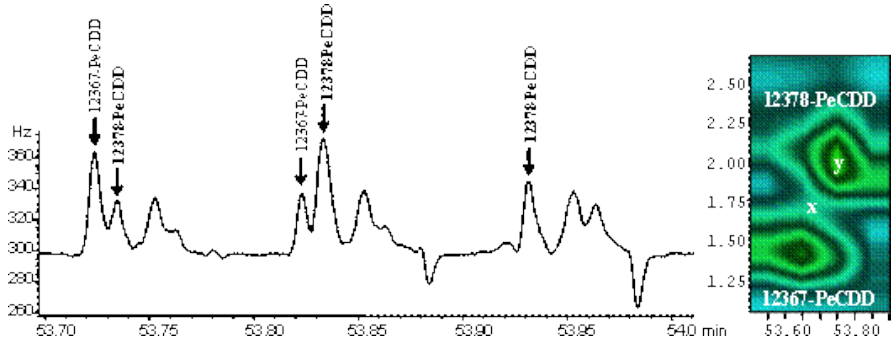

Figure 3. 1,2,3,7,8-PeCDD and 1,2,3,6,7-PeCDD in fly ash. Unconverted chromatogram (left) and contour plot (right).

On DB-XLB×LC-50, 1,2,3,4,7,8-HxCDF was resolved from all other HxCDFs but it partly coeluted with 1,2,3,4,6,8-HxCDD (R=0.4) and will thus be unresolved using the µECD (Figure 4). However, if the alternative detection technique GC×GC- time of flight mass spectrometer (TOFMS) is used, these two congeners will be separated by mass over charge (*m/z*). The only 2,3,7,8-substituted congener that won't be separated on DB-XLB×LC-50 –TOFMS is 2,3,4,6,7,8-HxCDF that is coeluting with 1,2,3,6,8,9-HxCDF. Consequently, a single injection on GC×GC-µECD will give a similar separation as GC-HRMS using both DB-5 and SP-2330, while a single injection on GC×GC-TOFMS will result in a better separation of 2,3,7,8- substituted congeners as compared to the two former alternatives.

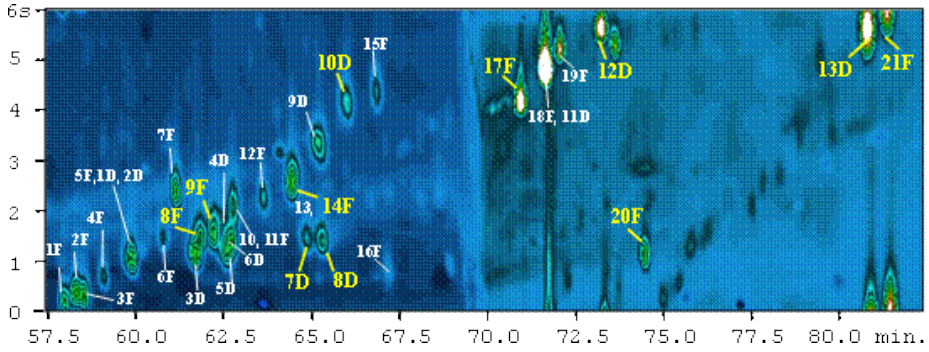

Figure 4. Contour plot of hexa-octa-CDD/Fs in fly ash.

Table 3. Annotation for Figure 4, assignments of Hexa-octa-CDDFs. F = Furane; D = Dioxin

No.	Substitution	No.	Substitution	No.	Substitution
1F	123468	13F, **14F**	123689, **234678**	5D	123469
2F	134678	15F	123489	6D	123689
3F	124678	**16F**	**123789**	**7D**	**123478**
4F	134679	**17F**	**1234678**	**8D**	**123678**
5F	124679	18F	1234679	9D	123467
6F	124689	19F	1234689	**10D**	**123789**
7F	123467	**20F**	**1234789**	11D	1234679
8F	**123478**	**21F**	**12346789**	**12D**	**1234678**
9F	**123678**	1D, 2D	124679, 124689	**13D**	**12346789**
10F, 11F	123479, 123469	3D	123468		
12F	123679	4D	123679		

The levels in the analyzed fly ash sample were between 33 pg/g (2,3,7,8-TCDD) and 3.9 ng/g (OCDD) for the 2,3,7,8-substituted PCDD/F congeners, resulting in an injected amount of 2,3,7,8-TCDD of 6 pg which is around 100 times higher than the instrumental detection limit for GC×GC-µECD and 10 times higher than for GC×GC-TOFMS. These results show that GC×GC-µECD with appropriate column combination has a large potential as the final and determinative step in a method aimed for the analysis of PCDD/Fs in fly ash samples. However, more work is needed before this technique can be used as a routine method. Validation of the method including analysis of fly ash samples with low dioxin content must be carried out, and an evaluation of appropriate software for faster and more reliable quantification is needed for a high sample throughput.

Acknowledgements

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References

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