Emission of Polyhalogenated Dibenzodioxins and Dibenzofurans from Combustion - Engines

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Summary

Halogenated compounds entering the combustion chamber of combustion motors cause emission of polyhalogenated dibenzodioxins (PHDD) and dibenzofurans (PHDF) resulting from incomplete combustion. Emissions of PHDD and PHDF were measured with motors run on leaded gasoline, unleaded gasoline with and without catalytic converters and for diesel engines. Due to the use of chlorinated and brominated scavengers in leaded gasoline the emissions from engines run on leaded gasoline were highest. Unleaded gasoline contained only trace amounts of brominated and chlorinated compounds and consequently showed much lower PHDD/PHDF emissions. Still lower were the emissions measured after catalytic gas cleaning. The PHDD/PHDF emissions for diesel engines were in the same range as found with catalytic converters.

In the course of this investigation an analytical procedure was developed, which allows the analysis not only of the chlorinated dibenzodioxins and dibenzofurans but also the determination and quantification of brominated and mixed halogenated compounds. The method was compared and validated by the two analytical laboratories involved in this study. In addition to the commonly analysed tetra- to octachlorodibenzodioxins and -dibenzofurans, brominated and mixed halogenated dibenzodioxins and particulary dibenzofurans were found in rather high concentrations in exhaust gases of combustion motors.

Introduction

Dioxin emissions from automobiles have been reported /1,2,3,4,5/. It is difficult to use these data from mainly single measurements under sometimes unrealistic conditions for an estimate of the dioxin input into the environment from this source. Especially analyses of automobile exhaust gases for mixed halogenated dioxins and dibenzofurans have sofar not been reported. The actual dioxin input by automobiles can reliabily be determined only by emission measurements under realistic conditions. In the course of a joint project between the Universities of Bayreuth, Stuttgart and Tübingen, several samplings were collected at various motor conditions. In this paper we present an overview of the results, reporting the data of only four characteristic samples: leaded gasoline, unleaded gasoline with and without catalytic exhaust gas cleaning and diesel fuel. The publication of the complete data set is in preparation.

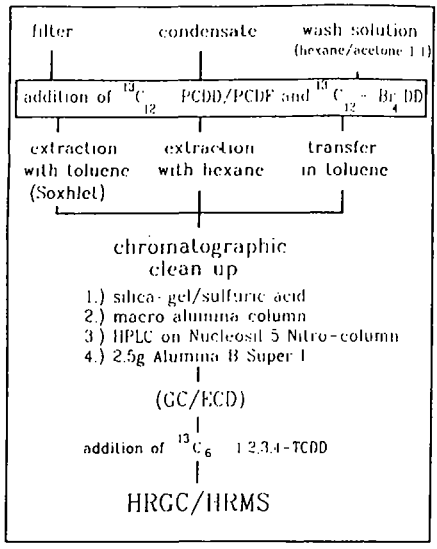

Figure 1: Extraction and clean-up of automobile exhaust gas samples

Sampling

For sampling the method of Grimmer (sampling of undiluted exhaust gas) was chosen/6,7/. The sampling train consists of a large glass condensor and a non impregnated filter of fiber-glass. In general the filter contains the main portion of PCDD/PCDF.

The experiments were carried out as stationary motor tests. The total emission of the motor was sucked through the sampling train by a pressure controlled blower. For the Otto-motor the following motor conditions were selected: n=1800 rpm and torque=50 Nm (63 km/h, 3% incline). These conditions are comparable to the FTP-cycle.

Analytical procedure

The extraction and clean-up scheme is shown in Figure 1. The quantification of the tetra- to octaCDD/F was carried out with ^{13}C-labelled internal PCDD/PCDF-standards. The PHDD/F were quantified by external standardization with numerous unlabelled single compounds synthesized by Hutzinger and co-workers/8,9/ and ^{13}C-labelled Tetrabromodibenzodioxin taking into account the response factors for the native standard compounds. Analysis of the samples was carried out with HRGC/MS and HRGC/HRMS. Capillary columns with a non polar GC-phase (J&W-DB-5, HP-ULTRA 2) were used for the analysis of brominated and mixed halogenated compounds. Capillary columns with a polar GC-phase (CP-SIL 88, SP 2331) were used for the isomer-specific analysis of tetra- to octaCDD/CDF.

Results and discussion

The results for the analysis of PHDD and PHDF for the four conditions are shown in Table 1. Here the total amount for the homologue groups detected are summarized. Only 41 out of the 88 possible homologues could be detected in at least one of the samples. The following conclusions can be drawn from the total concentrations of polyhalogenated dibenzodioxins and the total concentrations of polyhalogenated dibenzofurans in table 1:

1) Leaded gasoline (DIN 51600, Cl-content 48 mg/kg, Br-content 94 mg/kg): Under the experimental conditions mainly mixed halogenated and brominated dioxins (PHDD/PHDF) were detected. The total emission reached several 1000 ng/m^3. Mainly PHDD/PHDF substituted with 1 to 4 chlorine and/or bromine atoms were detected. The toxicologically more relevant tetra- to octaCDD/F represented only a relative small fraction of the total emitted PHDD/PHDF (1/100-1/1000).

2) Unleaded gasoline (DIN 51607, Cl-content <1 mg/kg, Br-content <1 mg/kg): In the exhaust of motors run on unleaded gasoline polyhalogenated dioxins could also be detected. The concentrations of PHDD/PHDF were substantially lower than with leaded gasoline (1-10%) and could be traced to contaminations of the unleaded gasoline with halogenated scavengers. The halogenated scavengers were actually detected in the unleaded gasoline used for the test. One can conclude therefore that the most of the dioxins found in the exhaust gases of Otto-motors are due to the use of chlorine and bromine containing compounds as scavengers.

3) Catalytic exhaust gas cleaning further reduces the emissions of PHDD/PHDF. Table 1 shows for this sample also the comparison of the analytical results from the two laboratories involved in this investigation (University of Tübingen and University of Bayreuth). Considering the complexity of the analytical procedure, especially the quantification procedure, finally a very good agreement between the two laboratories was obtained. This was the result of intensive joint validation studies. The higher differences of some homologue groups are mainly due to the lack of labeled mixed halogenated standards.

4) Diesel motor (DIN 51601): mixed halogenated dibenzodioxins and dibenzofurans were also detected in the diesel exhaust. The concentrations were in the same range as found with the Otto-motor run on unleaded gasoline and equipped with catalytic gas cleaning. The origin of the bromine and chlorine for the PHDD/PHDF formation was not entirely clear in this case.

Table 2 shows the results of the isomer specific analysis of tetra- to octaCDD/CDF for the four samples. The mass fragmentograms obtained resemble closely those found in emissions of PCDD/PCDF from other "thermal sources" e.g. municipal waste incinerators. The calculated TCDD-equivalents (TEQ) are also shown in Table 2. The emission concentrations of the chlorinated dioxins calculated in TCDD-equivalents werein the range of 0.1 ng/m^3 for leaded gasoline, 0.01 ng/m^3 for unleaded gasoline and 0.001 ng/m^3 for diesel fuel and unleaded gasoline with catalytic gas cleaning.

If one calculates the PHDD/PHDF emissions not on the basis of the exhaust gas volume but on the basis of fuel volume the relative emissions for the Otto-motor remained more or less the same. In table 2 the emissions of tetra- to octaCDD/CDF are also calculated as TEQs on the basis of fuel volume (leaded gasoline 1080 pg/l, unleaded gasoline 51 pg/l, unleaded gasoline with catalytic converter 7 pg/l). For the diesel motor this is different, however, due to the difference in air/fuel ratio. On this basis the emissions in pg TEQ/l for the diesel engine (24 pg/l) were in between the emissions for unleaded gasoline with and without catalytic converter. On the basis of emissions per fuel volume the dioxin input from motor vehicles into the environment can best be estimated.

In Figure 2 the relative concentrations of total PHDD/PHDF are compared with the concentrations of the tetra- to octaCDD/CDF. One can see that especially for the dibenzofurans, the tetra- to octachlorinated compounds comprise only a minor fraction of the total halogenated compounds determined. The lower the emitted concentration in total PHDD/PHDF, the higher the tetra- to octaCDD/CDF fraction. This reflects mainly the different detection limits for the isomer specific analysis of the tetra- to octaCDD/CDF and the analysis of the mixed halogenated and brominated dioxins and furans.

The main portion of dioxin emissions from motor vehicles is due to emissions from cars run on leaded gasoline, containing halogenated scavengers. In the Federal Republic of Germany 35 to 40% of the total gasoline used is still leaded gasoline. The current production of chlorinated tetra- to octadibenzodioxins and -furans is estimated to about 50 g TEQ/a compared to 400 g TEQ/a from municipal waste incinerators. In the future the dioxin input from municipal waste incinerators will be reduced to less than 1/100 of this value.

	Sample 1	Sample 2	Sample 3		Sample 4
			A	B	
	ng/cbm	ng/cbm	ng/cbm	ng/cbm	ng/cbm
Monobromodibenzodioxins	103.2	3.80	<0.005	<0.010	0.409
Monochlorodibenzodioxins	37.2	3.38	0.007	<0.010	0.535
Dibromodibenzodioxins	13.2	1.23	0.012	0.035	0.091
Monobromo-monochlorodibenzodioxins	38.9	1.78	0.003	0.021	0.097
Dichlorodibenzodioxins	6.8	1.48	0.004	0.019	0.089
Tribromodibenzodioxins	1.1	0.06	0.001	<0.034	<0.013
Dibromo-monochlorodibenzodioxins	4.7	0.14	0.005	<0.034	<0.013
Dichloro-monobromodibenzodioxins	6.5	0.29	0.002	<0.034	<0.013
Trichlorodibenzodioxins	1.5	0.11	0.001	<0.034	<0.013
Tetrabromodibenzodioxins	1.0	0.04	0.004	n.a.	n.a.
Monochloro-tribromodibenzodioxins	0.7	0.08	0.003	n.a.	n.a.
Dibromo-dichlorodibenzodioxins	1.8	0.11	0.002	n.a.	n.a.
Monobromo-trichlorodibenzodioxins	2.0	0.02	0.001	n.a.	n.a.
Tetrachlorodibenzodioxins	0.6	0.08	0.004	0.004	0.002
Pentachlorodibenzodioxins	0.4	0.09	0.003	0.003	0.001
Hexachlorodibenzodioxins	0.2	0.06	0.003	0.003	0.001
Heptachlorodibenzodioxins	0.2	0.02	0.005	0.002	0.004
Octachlorodibenzodioxin	0.1	0.03	0.022	0.054	0.022
Total Tetra- to Octachlorodibenzodioxins	**1.5**	**0.3**	**0.04**	**0.07**	**0.03**
Total PHDD	**220**	**12.8**	**0.08**	**0.14**	**1.25**
Monobromodibenzofurans	2 931.6	6.81	0.027	0.084	i
Monochlorodibenzofurans	1 296.0	10.95	0.079	<0.010	i
Dibromodibenzofurans	275.0	5.68	0.182	0.254	0.349
Monobromo-monochlorodibenzofurans	791.6	3.54	0.125	0.177	0.650
Dichlorodibenzofurans	86.0	6.52	0.073	0.018	0.422
Tribromodibenzofurans	7.8	0.44	0.023	0.305	<0.013
Dibromo-monochlorodibenzofurans	141.7	2.74	0.011	0.335	0.066
Dichloro-monobromodibenzofurans	161.1	1.99	0.092	0.266	0.066
Trichlorodibenzofurans	6.6	0.37	0.107	0.156	0.030
Tetrabromodibenzofurans	13.8	0.10	0.043	<0.034	n.a.
Monochloro-tribromodibenzofurans	94.0	0.18	0.022	<0.034	n.a.
Dibromo-dichlorodibenzofurans	289.3	0.47	0.070	<0.034	n.a.
Monobromo-trichlorodibenzofurans	20.3	0.19	0.010	<0.034	n.a.
Tetrachlorodibenzofurans	6.6	0.11	0.017	0.016	0.004
Pentabromodibenzofurans	0.4	<0.02	0.003	n.a.	n.a.
Monochloro-tetrabromodibenzofurans	<0.1	<0.02	<0.003	n.a.	n.a.
Dichloro-tribromodibenzofurans	11.4	<0.02	0.007	n.a.	n.a.
Dibromo-trichlorodibenzofurans	11.5	0.02	0.011	n.a.	n.a.
Monobromo-tetrachlorodibenzfurans	3.2	<0.02	<0.005	n.a.	n.a.
Pentachlorodibenzofurans	1.5	0.18	0.008	0.007	0.002
Hexachlorodibenzofurans	0.8	0.07	0.007	0.003	0.001
Heptachlorodibenzofurans	0.7	0.09	0.002	0.002	0.004
Octachlorodibenzofuran	<0.1	0.02	0.005	0.003	0.005
Total Tetra- to Octachlorodibenzofurans	**9.6**	**0.5**	**0.04**	**0.03**	**0.02**
Total PHDF	**6 151**	**40.5**	**0.92**	**1.61**	**1.6**

n.a.: not analysed ; i: not analysed because of interferences; cbm: standard cubicmeter

Table 1: Results from analyses of automobile exhaust samples for chlorinated, mixed chlorinated-brominated and brominated dioxins and furans. The samples were obtained under the following condtions:

Sample 1: leaded gasoline; 63 km/h, incline 3%,

Sample 2: unleaded gasoline; 63 km/h, incline 3%,

Sample 3: unleaded gasoline with catalytic converter; 63 km/h, incline 3%; (**A** analyzed at Univ. of Tübingen, **B** analyzed at Univ. of Bayreuth),

Sample 4: diesel fuel; 63 km/h, incline 3%.

	Sample 1 pg/cbm	Sample 2 pg/cbm	Sample 3 pg/cbm	Sample 4 pg/cbm
Tetrachlorodibenzodioxins	595	84	3.7	1.9
Pentachlorodibenzodioxins	436	93	3.3	1.0
Hexachlorodibenzodioxins	244	59	3.4	1.2
Heptachlorodibenzodioxins	152	18	5.0	4.5
Octachlorodibenzodioxin	65	34	21.9	22.4
Total Tetra- to Octachlorodibenzodioxins	**1 492**	**287**	**37.3**	**31.0**
Tetrachlorodibenzofurans	6 628	110	6.8	3.9
Pentachlordibenzofurans	1 514	180	6.9	2.0
Hexachlorodibenzofurans	824	73	4.3	1.3
Heptachlorodibenzofurans	737	92	3.5	4.1
Octachlorodibenzofuran	30	23	3.6	4.8
Total Tetra- to Octachlorodibenzofurans	**9 733**	**478**	**25.1**	**16.1**
2,3,7,8-Tetrachlorodibenzodioxin	16.7	0.5	0.21	0.40
1,2,3,7,8-Pentachlorodibenzodioxin	55.5	3.7	0.21	0.46
1,2,3,4,7,8-Hexachlorodibenzodioxin	24.5	3.2	0.31	<0.26
1,2,3,6,7,8-Hexachlorodibenzodioxin	27.1	3.3	0.45	<0.26
1,2,3,7,8,9-Hexachlorodibenzodioxin	24.5	3.4	0.40	<0.26
1,2,3,4,6,7,8-Heptachlorodibenzodioxin	65.7	7.8	1.97	2.24
2,3,7,8-Tetrachlorodibenzofuran	201.4	8.5	0.55	1.04
1,2,3,7,8-Pentachlorodibenzofuran	141.2	8.6	0.43	<0.26
2,3,4,7,8-Pentachlorodibenzofuran	58.4	4.0	0.31	0.36
1,2,3,4,7,8-Hexachlorodibenzofuran	111.8	8.1	0.62	0.33
1,2,3,6,7,8-Hexachlorodibenzofuran	111.8	4.1	0.81	0.34
1,2,3,7,8,9-Hexachlorodibenzofuran	<10.0	7.3	0.02	<0.26
2,3,4,6,7,8-Hexachlorodibenzofuran	35.7	10.5	0.59	<0.26
1,2,3,4,6,7,8-Heptachlorodibenzofuran	529.2	5.4	2.11	2.07
1,2,3,4,7,8,9-Heptachlorodibenzofuran	<10.0	3.2	<0.02	0.43
TEQ BGA	**197.5**	**12.6**	**0.99**	**0.96**
TEQ NATO/CCMS	**141.5**	**9.8**	**0.93**	**1.20**
TEQ NATO/CCMS (pg/l)	**1 083.3**	**50.7**	**7.20**	**23.60**

cbm: standard cubicmeter

Table 2: Isomerspecific analyses for chlorinated tetra- to octadibenzodioxins and -dibenzofurans.

For sample identification see table 1.

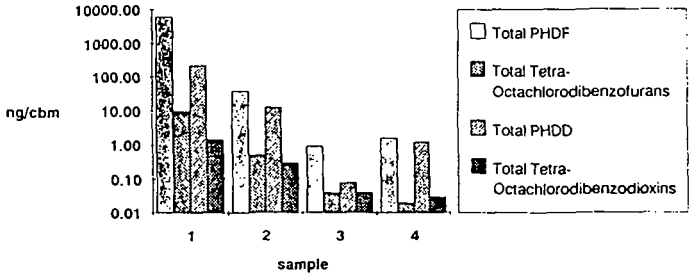

Figure 2: Relativ concentrations of total PHDD/PHDF and tetra- to octaCDD/CDF.
For sample identification see table 1

Still no satisfactory answer can be given regarding the ecotoxicological relevance of the rather high emission concentrations of mainly lower hologenated dioxins and furans from cars run on leaded gasoline. To minimize the production of PHDD/PHDF by automobiles the use of chlorine and bromine containing scavengers and additives should be abandoned. In Germany legislation in this direction is under discussion.

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