EXTRACTION EFFICIENCY ON THE ANALYSIS OF "NON-DIOXIN-COMPOUNDS" BY THE EN 1948 METHOD

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Abstract
The European EN 1948 standard procedure provides good extraction efficiencies performing PCDD/F analyses of exhaust gas samples. Good recoveries are also stated for other organic trace contaminants but not yet verified. This paper reports about some data on the extraction efficiencies by the EN 1948 procedure for PCBs, PAHs, PCBzs, PCPhs, PCNs and Lindane.

Introduction
The basics of sampling and analysis of polychlorinated dibenzo(p)dioxins and dibenzofurans (PCDD/F) in exhaust gas from stationary sources are layed down in the European standard EN 1948.[1] Part 1 describes the sampling while parts 2 and 3 are dealing with the extraction, the clean-up procedure and the analysis by HRGC/HRMS.

The EN 1948 points out that the described methods are also valid to collect and analyse for more volatile compounds e.g. dioxin-like PCBs (12 non-ortho and mono-ortho polychlorinated biphenyls as specified by the WHO), although there are no performance characteristics available yet. Above this, compounds like polycyclic aromatic hydrocarbons (PAHs), polychlorinated benzenes (PCBzs), polychlorinated phenols (PCPhs), polychlorinated naphthalines (PCNs) and Lindane (γ-hexachloro-cyclohexane) in practice are as well collected and analysed within the same sample. Of course, the respective analytical procedures are substance specific.

Since the relevant ranges of concentrations of these "Non-Dioxin-Compounds" are, as a rule, significantly higher than the PCDD/F concentrations, always small amounts of the sample extracts (10 %) are used for clean-up and analysis. For the same reason internal standards of these compounds are not added until the raw extract has been divided. This procedure obviously excludes the direct control of the extraction efficiency. On the other hand the recovery rates of the routinely determined PCDD/F extraction standards provide a principal evidence for a directive-concurring procedure.

The herewith described investigations shall serve as a verification for the extraction efficiency of compounds "beyond" dioxins but according to the extraction procedure given in EN 1948, part 2.

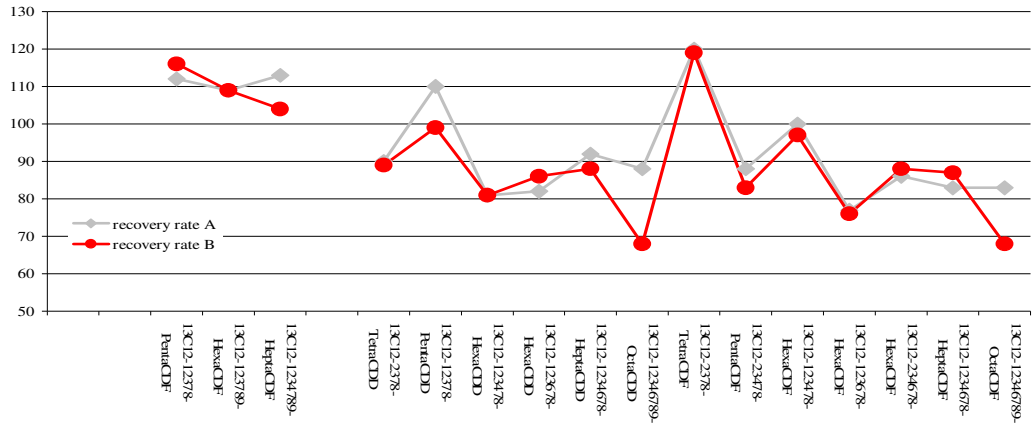
Materials and Methods
Two collection units (A and B) were used for the tests, each consisting of

- filter cartridge plugged with quartz wool
- cartridge filled with XAD resin (30 g) and a plane filter inlet
- cartridge filled with XAD resin (30 g)

Prior to extraction each collection unit was spiked with $^{13}C_{12}$-labelled PCDD/F-standards acc. to EN 1948 and D8-Naphthalene. In addition the units were spiked with defined amounts of native standards of all substance classes regarded here. The sample preparation and extraction was performed according to the EN 1948 method as well as the clean-up and analysis of the PCDD/F. Variations have been made for the clean-up procedure of the other substance classes according to validated and accredited in-house methods. All components were identified and quantified by means of GC/HRMS (Thermo Finnigan MAT 95 XP : PCDD/Fs and PCBs) resp. GC/LRMS analysis (Thermo Finnigan Trace GC Ultra : others).

Results and Discussion
The following tables and figures summarize the results of the recoveries of the native compounds by which the collection units have been spiked prior to sample preparation and extraction.

Fig 1 : PCDD/F-recovery rates of the sampling standards and the extraction internal standards in two samples A and B (spiked amount of $^{13}C_{12}$-labelled PCDD/F: 800 ng/sample for Hepta-/OctaCDD/F, 400 ng/sample for others)



Tab 1 : PCB-recovery rates for the two samples A and B spiked with native PCBs

Sample	**Added amount** of the native PCB [ng/sample] A/B	**Analytically detected amount** of the native PCB [ng/sample] A	B	**Recovery rate** of the native PCB [%] A	B
Non-ortho PCB					
PCB 77	400	390	381	**98**	**95**
PCB 81	400	396	372	**99**	**93**
PCB 126	400	374	347	**94**	**87**
PCB 169	400	379	351	**95**	**88**
Mono-ortho PCB					
PCB 105	400	402	379	**101**	**95**
PCB 114	400	401	389	**100**	**97**
PCB 118	400	359	355	**90**	**89**
PCB 123	400	406	373	**102**	**93**
PCB 156	400	376	350	**94**	**88**
PCB 157	400	384	359	**96**	**90**
PCB 167	400	421	373	**105**	**93**
PCB 189	400	401	386	**100**	**97**

Tab 2 : PAH-/PCBz- and Lindane-recovery rates for the two samples A and B spiked with native compounds

Sample	**Added amount** of the native compound [ng/sample] A/B	**Analytically detected amount** of the native compound [ng/sample] A	B	**Recovery rate** of the native compound [%] A	B
PAH compounds					
D_8-Naphthalene	5000	4632	4576	**93**	**92**
Acenaphthylene	800	776	800	**97**	**100**
Acenaphthene	800	824	999	**103**	**125**
Fluorene	800	945	990	**118**	**124**
Phenanthrene	800	815	917	**102**	**115**
Anthracene	800	795	804	**99**	**101**
Fluoranthene	800	894	1063	**112**	**133**
Pyrene	800	792	810	**99**	**101**
Benzo(a)anthracene	800	780	789	**98**	**99**
Chrysene	800	788	800	**99**	**100**
Benzo(b/j)fluoranthene	800	784	800	**98**	**100**
Benzo(k)fluoranthene	800	785	796	**98**	**100**
Benzo(a)pyrene	800	774	767	**97**	**96**
Dibenzo(a,h/a,c)-anthracene	800	819	810	**102**	**101**
Benzo(g,h,i)perylene	800	827	804	**103**	**101**
Indeno(1,2,3-c,d)-pyrene	800	789	819	**99**	**102**
Chlorobenzenes					
1,3,5-Trichlorobenzene	800	668	694	**84**	**87**
1,2,4-Trichlorobenzene	800	984	920	**123**	**115**
1,2,3-Trichlorobenzene	800	908	854	**114**	**107**
1,2,3,5-Tetrachlorobenzene	800	806	799	**101**	**100**
1,2,4,5-Tetrachlorobenzene	800	832	840	**104**	**105**
1,2,3,4-Tetrachlorobenzene	800	908	873	**114**	**109**
1,2,3,4,5-Pentachlorobenzene	800	803	823	**100**	**103**
1,2,3,4,5,6-Hexachlorobenzene	800	823	831	**103**	**104**
Lindane	1000	1024	1015	**102**	**101**

Tab 3 : PCPh- and PCN-recovery rates for the two samples A and B spiked with native compounds

Sample	**Added amount** of the native compound [ng/sample] A/B	**Analytically detected amount** of the native compound [ng/sample] A	B	**Recovery rate** of the native compound [%] A	B
Chlorophenols					
2,4,6-Trichlorophenol	1000	1013	1041	**101**	**104**
2,3,6-Trichlorophenol	1000	945	962	**95**	**96**
2,3,5-Trichlorophenol	1000	957	937	**96**	**94**
2,4,5-Trichlorophenol	1000	994	965	**99**	**97**
2,3,4-Trichlorophenol	1000	1057	994	**106**	**99**
3,4,5-Trichlorophenol	1000	988	968	**99**	**97**
2,3,5,6-Tetrachlorophenol	1000	916	1030	**92**	**103**
2,3,4,6-Tetrachlorophenol	1000	1018	1068	**102**	**107**
2,3,4,5-Tetrachlorophenol	1000	1087	1125	**109**	**112**
Pentachlorophenol (PCP)	448	462	476	**103**	**106**
PCN compounds					
2-MonoCN	1000	967	1036	**97**	**104**
1-MonoCN	1000	1051	1026	**105**	**103**
1,4-DiCN	1000	945	924	**95**	**92**
1,5-DiCN	1000	990	959	**99**	**96**
2,7-DiCN	1000	969	917	**97**	**92**
1,2-DiCN	1000	1024	876	**102**	**88**
2,3-DiCN	1000	1020	898	**102**	**90**
1,8-DiCN	1000	1032	909	**103**	**91**
1,2,7-TriCN	1000	1023	1028	**102**	**103**
1,2,3,4-TetraCN	1000	906	781	**91**	**78**
1,2,3,6,7-PentaCN	1000	1265	1022	**126**	**102**
1,2,3,4,6,7/1,2,3,5,6,7-HexaCN	2000	2518	2333	**126**	**117**
1,2,3,4,5,6,7-HeptaCN	1000	1228	1151	**123**	**115**
OctaCN	1000	1235	1239	**124**	**124**

The recoveries for PCDD/Fs are in the range of the required percentage with 76 to 120 % for Tetra- through HexaCDD/F and 68 to 92 % for Hepta- through OctaCDD/F. All other organic components show high recovery rates mostly between 90 and 110 %. This confirms that the extraction procedure acc. to the EN 1948 standard provides high extraction efficiency for other organic trace compounds as well.

References

1. DIN EN 1948, *Stationary Source Emissions*, Part 2: Extraction and clean-up, Ref.-No. EN 1948-2:2006 D