PCDD/F IN THE DRY-CLEANING PROCESS

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Summary

The reactions of chloroorganic compounds at high temperature (1,2) indicated that PCDD/F may be formed during the distillation process in dry-cleaning machines. For that reason the distillation residues of dry cleaning shops, industrial dry-cleaners and dry-cleaning machines of textile factories were analysed. All samples contained PCDD and PCDF in relative large amounts (ppb) and a similar distribution type, were H_7CDD and OCDD dominated. 2,3,7,8-TCDD was detected in almost every sample (3,4,7,8). Some further samples were taken from other parts of the "PER-circle" to find out whether the PCDD/F came only from the distillation process or also from other sources. The results indicated the distillation process to be the main source, but showed that other ways of a PCDD/F entry are possible.

Introduction

Within the framework of this research program series of a different tests were carried out. At first, a survey was made on the concentrations of polyhalogenated dioxins and furans in distillation residues. The sludges of seven different dry cleaning shops, two industrial dry-cleaners and two textile factories were examined (3).

To clarify the origin and formation of the PCDD/F more samples from other points of a dry-cleaning machine - run on perchloroethylene - were taken and analysed. Using a sweater the influence of the cleaning process on the clothing and the input was examined.

Figure 1 shows the scheme of a dry-cleaning machine; the numbers indicate where samples were taken (see also table 3).

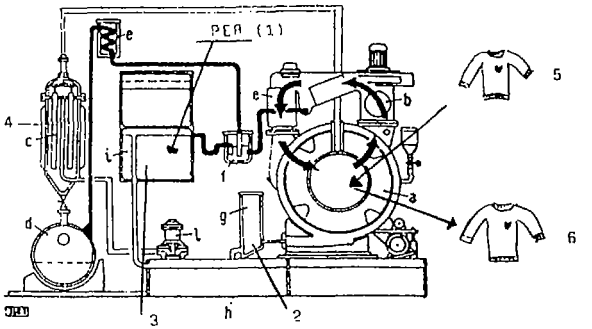


Fig. 1: Scheme of a dry-cleaning machine (5)
a cage, b air circle, c filter, d still, e cooling coils, f water separator, g button trap, h main solvent tank, i pure solvent tank

Experimental

Samples

The distillation residues of the different dry-cleaners are of variable consistence as a function of the distillation parameters (solid-liquid). In the seven dry cleaning shops only normal clothing was cleaned, in the industrial dry-cleanings also working cloth, carpets etc. were treated, while the textile factories only dry-clean their own new products. Perchloroethylene-sensitive materials and garments like leather, suede, plastic beads and trimmings were treated with chlorofluorohydrocarbons (as trichlorotrifluoroethane R113 or trichloromonofluoromethane R11) as solvent (5,6). For this reason a fluorocarbon-distillation sludge was analysed as well.

Sample extraction and clean up

The ensuing method was used for the clean up of samples from the dry-cleanings:

1) Quantification: The sample was spiked with an ^{13}C-labeled internal standard mixture, containing TCDD/F-OCDD/F standards

2) Extraction: liquid samples were extracted 48hrs with toluene in a soxhlet apparatus; liquid organic samples were applied directly on the column

3) Cleanup procedure: The cleanup was made by liquid column chromatography, with several adsorbents. The following columns were used generally in various combinations.

   -acid-silica-column: Each sample was applied to a column of 20 g washed silica and 350 g 44% H_2SO_4/silica, prewashed with 250 ml hexane. After sample application the column is eluted with 400 ml hexane.

   -acid/basic silica-column: This column is filled from bottom to top with 5,6 g 33% NaOH/silica; 0,5 g activated silica; 7,3 g 44% H_2SO_4/silica; 1 g 22% H_2SO_4/silica; the concentrated solution of the sample (ca 10 ml) was applied to the column and eluted with 60 ml hexane.

   -alumina-column: 50 g activated alumina oxide; 40 g Na_2SO_4; prewashed with hexane. After application of the sample dissolved in benzene the column eluted with a) 160 ml benzene; b) 400 ml hexane/dichloromethane 98:2; c) 300 ml hexane/dichloromethane 1:1.

   If the cleaning was insufficient, the columns were used with the double quantity of adsorbents and solvent. In some cases additional columns were necessary.

GC/MS Analysis

For the GC/MS analysis, a mass selective detector, Mod. 5970 HP directly coupled with a Mod. 5890 gaschromatograph (HP) was used. The GC conditions were as follows: 12.5 m ultra 2 capillary column; injector 280°C split/splitless 1.5 min; program: oven temp. 100°C for 2 min isotherm, then 20°C/min to 180°C, 5°C/min to 320°C, 7 min isotherm. Carrier gas Helium: 0.5 bar.

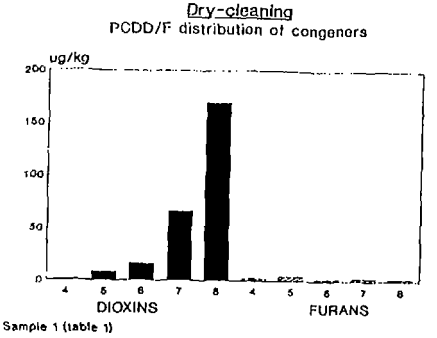
For isomeric specification a high resolution GC/MS system was used: gaschromatograph Varian 3400, MS Finigan MAT 8200, Datensystem 55300. Gaschromatographic conditions: 60 m capillary column SP 2331 (Supelco); Gerstel cold injection system: final temperature 280°C, oven temp. 100°C, 1 min isotherm, 20°C/min to 180°C, 5°C/min to 320°C, 7 min Isotherm.Carrier gas Helium: 0.5 bar.

Results and Discussion

The results of the analysis are illustrated in tables 1-3.

Figure 2 shows a typical PCDD/F congener pattern found in dry-cleaning residues. The ratio of dioxins and furans is on the average 10:1. Nearly in all cases the residues contained 2,3,7,8-TCDD; nevertheless the large I-TEF-values results from a large contribution of the H_7CDD and OCDD, depending on the extremely increase from TCDD to OCDD. In dry cleaning shops the amount of PCDD/F is in general lower than in industrial dry-cleanings and textile factories.

Fig. 2



The congener distribution and the high concentration of PCDD/F in textile factories (where only new products were cleaned) demonstrate that the PCDD/F found in the dry-cleaning wastes cannot be attributed to absorption of automobile exhaust components in clothing.

In order to draw conclusions about the origin of the PCDD/Fs, several samples were examined from other points of the dry-cleaning machines and from clothing (dyed cotton) before and after treatment (30 times) in a PER-machine. The analysis of the new garment show a concentration in the ppt-range, that may result from conservation of the cotton, dressing or dyes. After dry-cleaning only the distribution has changed, not the I-TEF value.

Detailed tests about the formation of dioxins and furans are in progress.

Acknowledgement

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Table 1. PCDD/F in distillation residues of dry cleaning shops (µg/kg)

	1	2	3	4	5	6	7
Tetra-CDD, sum	1.155	0.134		0.191	0.095	5.151	0.468
2,3,7,8	0.007	0.018		0.006	0.003	0.040	0.003
Penta-CDD, sum	8.435	0.266		0.073	0.546	16.603	4.079
1,2,3,7,8	0.117	0.022		0.019	0.016	0.339	0.052
Hexa-CDD, sum	16.129	2.611	0.610	0.319	2.196	18.989	55.271
1,2,3,4,7,8	0.163	0.036	0.067	0.014		0.242	0.209
1,2,3,6,7,8	1.229	0.296	0.268	0.133	0.180	2.492	8.427
1,2,3,7,8,9	0.511	0.113	0.127	0.043	0.059	1.216	2.430
Hepta-CDD, sum	66.572	29.323	2.818	3.059	31.723	55.877	190.295
1,2,3,4,6,7,8	39.521	13.724	1.457	1.938	1.852	34.304	124.430
Octa-CDD	169.977	187.577	14.388	21.604	214.961	66.538	175.743
Tetra-CDF, sum	2.108	0.444	0.260	0.103	0.643	3.868	1.347
2,3,7,8/2,3,4,8	0.059	0.051	0.017	0.017	0.087	0.151	0.092
Penta-CDF, sum	4.108	0.732	0.635	0.097	0.919	4.605	2.382
1,2,3,7,8/1,2,3,4,8	0.057	0.043	0.029	0.023	0.060	0.384	0.087
2,3,4,7,8	0.058	0.038	0.028	0.009	0.052	0.922	0.029
Hexa-CDF, sum	1.763	2.042	0.796	0.280	0.851	4.360	1.260
1,2,3,4,7,8/1,2,3,4,7,9	0.080	0.108	0.079	0.034	0.090	0.197	0.165
1,2,3,6,7,8	0.094	0.132	0.074	0.055	0.189	0.060	0.748
1,2,3,7,8,9	0.015	0.058	0.020		0.011	0.019	0.011
2,3,4,6,7,8	0.153	0.208	0.099	0.014	0.039	0.234	0.045
Hepta-CDF, sum	2.241	8.247	1.295	0.321	4.032	4.977	1.902
1,2,3,4,6,7,8	1.540	5.539	1.091	0.302	2.012		1.074
1,2,3,4,7,8,9	0.038					0.293	
Octa-CDF	1.655	4.365	0.365	0.458	8.701	5.566	2.944
sum PCDD/F	274.143	235.741	21.168	26.502	264.700	186.534	435.691
I-TEQ	0.908	0.535	0.131	0.096	0.372	1.571	2.694

Table 2: PCDD/F in distillation residues from industrial dry-cleanings and textile factories (µg/kg)

	PER-distillation	PER-distillation	fluorocarbon-distillation	textile factory 1	textile factory 2
Tetra-CDD, sum	0.088	7.058			0.013
2,3,7,8	0.011	0.015			0.002
Penta-CDD, sum	1.621	36.538	0.029	0.044	0.103
1,2,3,7,8	0.729	0.658	0.019	0.011	0.016
Hexa-CDD, sum	8.315	31.997	1.774	6.138	5.942
1,2,3,4,7,8	0.214	3.847	0.029	0.055	0.061
1,2,3,6,7,8	2.961	0.657	0.136	0.929	0.945
1,2,3,7,8,9	1.545		0.082	0.268	0.364
Hepta-CDD, sum	32.378	211.596	2.867	166.800	161.465
1,2,3,4,6,7,8	31.782	130.231	1.369	93.350	85.782
Octa-CDD	99.480	345.588	26.645	1176.990	355.603
Tetra-CDF, sum	0.132	6.174	0.017	0.237	0.204
2,3,7,8/2,3,4,8	0.042	0.107		0.018	0.021
Penta-CDF, sum	0.941	9.584	0.087	0.400	0.347
1,2,3,7,8/1,2,3,4,8	0.045	0.162	0.027	0.078	0.029
2,3,4,7,8	0.203	0.642		0.015	0.301
Hexa-CDF, sum	3.709	2.289	0.067	2.287	2.019
1,2,3,4,7,8/1,2,3,4,7,9	0.506	0.186	0.025	0.078	0.082
1,2,3,6,7,8	1.740	0.087	0.018	0.951	0.837
1,2,3,7,8,9	0.216	0.012	0.007	0.170	0.253
2,3,4,6,7,8	1.112	0.203		0.069	0.120
Hepta-CDF, sum	2.717	4.045	0.566	43.530	29.656
1,2,3,4,6,7,8	1.082	1.532	0.278	20.606	13.802
1,2,3,4,7,8,9	0.350	0.125			
Octa-CDF	2.610	3.045	0.528	32.623	32.133
sum PCDD/F	152.000	659.914	32.560	1428.849	587.485
I-TEQ	1.748	2.834	0.077	2.623	1.820

Table 3. PCDD/F in samples from the dry-cleaning circle (see Fig. 1) (ng/kg)

	pure PER (1)	PER from circle (2)	PER from pure solvent tank (3)	PER + silicafilter (4)	new garment (5)	dry-cleaned garment (6)
Tetra-CDD, sum		0.57		1.358	2.868	4.004
2,3,7,8		0.134		0.100	0.029	0.025
Penta-CDD, sum		8.58	1.93	37.853	0.836	2.301
1,2,3,7,8		0.972	0.07	0.410	0.370	0.338
Hexa-CDD, sum		24.33	4.77	31.306	1.404	5.178
1,2,3,4,7,8		0.606		0.344	0.074	0.119
1,2,3,6,7,8		3.640		2.235	0.302	0.593
1,2,3,7,8,9		2.422	1.23	0.685	0.179	0.231
Hepta-CDD, sum	9.35	150.611	29.51	154.241	9.488	21.769
1,2,3,4,6,7,8	6.19	69.956	18.59	77.556	4.181	10.836
Octa-CDD	30.90	616.47	136.05	1315.430	194.324	73.920
Tetra-CDF, sum		8.56		54.498	2.093	4.118
2,3,7,8/2,3,4,8		1.512		0.510	0.106	0.240
Penta-CDF, sum		16.32	2.44	71.997	1.248	4.355
1,2,3,7,8/1,2,3,4,8		0.774		0.807	0.092	0.090
2,3,4,7,8		0.895	0.30	5.650	0.090	0.139
Hexa-CDF, sum		22.14	5.10	42.712	2.920	2.244
1,2,3,4,7,8/1,2,3,4,7,9		1.177		1.302	0.124	0.183
1,2,3,6,7,8		1.884		3.382	0.043	0.069
1,2,3,7,8,9		0.256	0.46	1.381	0.108	0.060
2,3,4,6,7,8		0.411		5.685	0.060	0.119
Hepta-CDF, sum	4.35	36.35	14.35	70.563	13.167	3.995
1,2,3,4,6,7,8	2.89	22.742	8.30	56.634	8.267	2.231
1,2,3,4,7,8,9	0.84	2.569	1.86	0.778	0.191	0.107
Octa-CDF	8.99	38.675	22.78	38.482	18.309	2.259
sum PCDD/F	53.59	922.506	216.93	1810.438	246.657	124.143
I-TEQ	0.130	4.125	0.800	7.447	0.702	0.637