Extraction method for PCDD/F and PCB analysis in consumer products using pressurized fluid extraction

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1 Introduction

The determination of PCDD/F and PCB in environmental and food/feed matrices are already well described, regulated, and international methods has been established [1-3]. For consumer products and raw materials there were no regulation nor method established yet, so analytical laboratories needed to develop methods for this kind of matrices. The sample preparation step, where matrix effects usually have the biggest influence in PCDD/F and PCB analysis, is the extraction method. Different techniques for the extraction are available to create valid results for PCDD/F and PCB in different matrices. One technique is the pressurized fluid extraction (PFE). This technique is used by the extraction device "X-Traction" from LCTech, where application notes for environmental, food, and feed samples are already existing [4-6], but not for consumer products and raw materials.
Aim of this study was to set up a single method for extraction different consumer products and raw materials using the "X-Traction" instrument for sample extraction by LCTech.

2 Materials and Methods

The work has been carried out using the LCTech X-Traction device for extraction of the samples, using all 17 2,3,7,8-substituated PCDD/F, and all 12 WHO-PCB as $^{13}C_{12}$-labelled internal standards. Afterwards the extract cleanup was performed by LCTech DEXTech16, equipped with a three-column setup ("Universal column", "alumina column" and "carbon column" from LCTech). Evaporation was done by a Buchi rotary evaporator and SuperVap from FMS Inc. After evaporation, before injection, a recovery standard using four $^{13}C_{12}$-labelled PCDF and three $^{13}C_{12}$-labelled PCB has been added. The measurement of the final extract for PCDD/F and PCB was performed by Agilent 7010B triple quadrupole GC/MS. For the measurement of PCDD/F a VF-Xms column from Agilent was used and for the PCB the HT8 from Trajan. All used standard solutions (native and $^{13}C_{12}$-labelled) have been prepared by different ready to use mixtures from Wellington and CIL.
During the different extraction tests different solvents and mixtures of toluene, n-hexane, acetone, and isopropanol has been used.
Different sample materials with different natural PCDD/F congener pattern were used during the method development. The materials were two synthetic nonwoven fabric, one diaper, two textile samples, and one mixed material that is also used as an internal quality control material.
The number of extraction cycles were set to 3 and the temperature was set to a value above the boiling point of the used solvent and solvent mixtures.

3 Results

For the development of the extraction method five different solvents and solvent mixtures has been tested. An overview of the solvents, the solvent mixtures and the used extraction temperatures is given in Table 1.

Table 1: Overview of used solvent mixtures and extraction temperatures

Number	1	2	3	4	5
Solvent	n-hexane	n-hexane/toluene	toluene	toluene/acetone	toluene/isopropanol
Abbr.	n-hex	n-hex/tol	tol	tol/ace	tol/iso
Mixture (v/v)	-	1/1	-	1/1	7/3
Temperature [°C]	85	105	150	100	105

Not all combinations of extraction solvent mixture and sample materials has been tested, as some of the solvent mixtures has been sorted out early during the tests, due to a low extraction efficiency or due to matrix interactions, that disqualified the solvent for the general use of all the different matrices.
The PCDD/F and PCB results of the different consumer product matrices, generated with the used solvent mixture, are shown in Table 2 to Table 7. There are also shown the results of a reference value that was created using the GALAB standard operation procedure (cold extraction using n-hexane in acid environment) for the specific matrix

type, in addition to an upper and lower acceptance limit. Only results above LOQ are listed. All results within the limits are marked green, below the reference limits marked with red numbers and above ae marked orange.

Table 2: Result table for GALAB internal QC material "REF 9029"

	Ref value	lower limit	upper limit	n-hex/tol	tol	tol/ace	tol/iso
	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDF	**0.762**	0.317	1.207	0.277	0.707	0.802	0.616
1,2,3,7,8-PeCDF	**1.040**	0.533	1.546	0.35	0.944	0.936	0.959
1,2,3,4,7,8-HexCDF	**4.295**	1.637	6.952	1.109	3.473	3.530	3.159
1,2,3,6,7,8-HexCDF	**0.616**	0.234	0.997	0.174	0.516	0.484	0.450
1,2,3,7,8,9-HexCDF	**1.303**	0.507	2.099	0.382	1.169	1.156	1.295
1,2,3,4,6,7,8-HepCDF	**0.597**	0.262	0.931	0.174	0.511	0.502	0.376
1,2,3,4,6,7,8-HepCDD	**0.858**	0.488	1.228	0.295	0.837	0.654	0.591
1,2,3,4,7,8,9-HepCDF	**1.260**	0.556	1.964	0.282	1.064	1.023	0.964
OCDD	**3.676**	1.895	5.458	0.946	3.879	3.249	2.076
PCB 126	**4.143**	1.016	7.270	3.447	3.385	4.403	7.156
PCB 77	**136**	52.8	219	122	131	141	174
PCB 81	**5.456**	2.270	8.643	5.003	5.614	6.058	7.156

Table 3: Result table for diaper sample A

	Ref value	lower limit	upper limit	n-hex	n-hex/tol	tol/iso
	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
OCDF	**0.367**	0.220	0.514	0.808	0.912	0.984

Table 4: Result table for nonwoven fabric sample A

	Ref value	lower limit	upper limit	n-hex	n-hex/tol	tol	tol/ace
	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
OCDD	**0.971**	0.582	1.359	0.739	0.994	n.a.	n.a.
OCDF	**3.726**	2.236	5.217	3.282	3.565	n.a.	n.a.

Table 5: Result table for nonwoven fabric sample B

	Ref value	lower limit	upper limit	n-hex	n-hex/tol	tol	tol/ace
	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDF	**0.243**	0.146	0.341	0.206	0.267	n.a.	n.a.
1,2,3,7,8-PeCDF	**0.188**	0.113	0.263	0.150	0.201	n.a.	n.a.
2,3,4,7,8-PeCDF	**0.071**	0.043	0.099	0.067	0.083	n.a.	n.a.

Table 6: Result table for textile sample A

	Ref value	lower limit	upper limit	n-hex/tol	tol	tol/ace	tol/iso
	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDF	**2.360**	1.416	3.305	0.966	2.240	3.184	2.799
1,2,3,7,8-PeCDF	**3.525**	2.115	4.935	1.603	3.440	4.811	4.123
2,3,4,7,8-PeCDF	**0.982**	0.589	1.375	0.351	0.808	1.314	1.136
1,2,3,4,7,8-HexCDF	**17.455**	10.473	24.437	6.020	12.024	18.307	15.000
1,2,3,6,7,8-HexCDF	**1.184**	0.710	1.658	0.861	1.640	2.469	2.279

Table 6: Result table for textile sample A

	Ref value	lower limit	upper limit	n-hex/tol	tol	tol/ace	tol/iso
	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,4,6,7,8-HexCDF	**0.258**	0.155	0.361	0.078	0.141	0.228	0.203
1,2,3,7,8,9-HexCDF	**4.709**	2..826	6..593	1.848	4..134	5..860	5..758
1,2,3,7,8,9-HexCDD	**0.107**	0.064	0.149	0.103	0.132	0.176	0.162
1,2,3,4,6,7,8-HepCDF	**2.179**	1.308	3.051	0.725	1.197	1.959	1.656
1,2,3,4,7,8,9-HepCDF	**5.681**	3.409	7.954	1.602	3.530	5.560	4.546
1,2,3,4,6,7,8-HepCDD	**1.685**	1.011	2.358	1.099	1.570	1.975	1.717
OCDD	**3.27**	1.960	4.573	2.19	2.81	3.61	3.17
OCDF	**1.50**	0.898	2.095	0.53	0.88	1.61	1.39
PCB 77	**5.688**	3.413	7.963	4.331	7.247	6.266	4.931
PCB 81	**0.329**	0.197	0.461	0.228	0.479	0.415	0.369
PCB 126	**0.261**	0.157	0.365	0.186	0.308	0.358	0.282
PCB 169	**0.234**	0.141	0.328	0.138	0.191	0.251	0.252

Table 7: Result table for textile sample B

	Ref value	lower limit	upper limit	n-hex	n-hex/tol	tol/iso
	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDF	**0.771**	0.385	1.156	<LOQ	0.098	0.480
1,2,3,7,8-PeCDF	**0.486**	0.243	0.729	<LOQ	0.103	0.373
2,3,4,7,8-PeCDF	**0.344**	0.172	0.515	<LOQ	0.034	0.112
1,2,3,4,7,8-HexCDF	**3.862**	1.931	5.793	0.068	0.423	2.123
1,2,3,6,7,8-HexCDF	**0.357**	0.179	0.536	<LOQ	0.051	0.180
2,3,4,6,7,8-HexCDF	**0.191**	0.095	0.286	<LOQ	0.027	0.168
1,2,3,7,8,9-HexCDF	**1.783**	0.891	2.674	<LOQ	0.237	1.501
1,2,3,6,7,8-HexCDD	**0.557**	0.278	0.835	0.049	0.108	0.303
1,2,3,7,8,9-HexCDD	**0.446**	0.223	0.669	<LOQ	0.122	0.369
1,2,3,4,6,7,8-HepCDF	**1.236**	0.618	1.853	<LOQ	0.109	0.581
1,2,3,4,7,8,9-HepCDF	**4.134**	2.067	6.201	0.478	0.335	2.148
1,2,3,4,6,7,8-HepCDD	**10.69**	5.346	16.038	<LOQ	1.69	6.01
OCDD	**22.72**	11.359	34.078	1.07	3.11	12.16
OCDF	**1.117**	0.558	1.675	<LOQ	0.123	0.542
PCB 77	**5.000**	2.500	7.501	0.042	2.059	3.163
PCB 81	**0.273**	0.136	0.409	<LOQ	0.126	0.256
PCB 126	**0.683**	0.342	1.025	0.263	0.159	0.533
PCB 169	**1.389**	0.695	2.084	0.084	0.225	1.100

4 Discussion

All results were compared by checking the extraction efficiency and the usability of the solvent mixtures for the different matrices. An overview of the extraction solvents with an assessment of the extraction efficiency and possible matrix restrictions is shown in Table 8.

The extraction performed with pure n-hexane and n-hexane/toluene 1/1 (v/v) mixture showed lower results compared with the results from the reference method for the textile samples and the GALAB inhouse QC material (see Table 2, Table 6 and Table 7). For the extraction of the nonwoven fabric material an extraction using the solvents pure toluene, or a mixture of toluene/acetone 7/3 (v/v) did not lead to usable results (see Table 4 and Table 5). Some parts of the material dissolved in the extraction cell and flocculated again in the final extract, respectively

blocked the tubing's of the extraction device. The extraction with n-hexane and n-hexane/toluene 1/1 (v/v) was sorted out due to low extraction efficiency. Toluene and toluene/acetone 7/3 (v/v) were skipped because they couldn't be used for all matrices.
The solvent mixture toluene/isopropanol 7/3 (v/v) was selected as a compromise method, as it showed acceptable results compared with the reference method and was applicable with all consumer products that have been tested during this study.

Table 8: Overview of solvents, extraction efficiency and matrix restrictions

Solvent	Extraction efficiency	Matrix restriction
n-hexane	Lowest	Non
n-hexane/toluene 1:1 (v/v)	Low	Non
Toluene	Very good	Yes
toluene/acetone 7:3 (v/v)	Very good	Yes
toluene/isopropanol 7:3 (v/v)	Good	Non

5 Conclusions

The extraction method using the mixture of toluene/isopropanol 7/3 (v/v) showed acceptable results for all tested consumer product matrices. If contaminations of PCDD/F and PCB were present in the sample, the method was always able to extract at least an acceptable amount of the residues. Depending on the analytical question the selected compromise extraction method can be used, if a sample generally shows a contamination of PCDD/F and PCB. For a "true" value another extraction solvent may lead to better, more reliable results.

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7 References

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