A Screening Method for Detection of OCDD/F in Textiles

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Abstract

A screening method based on analysis with GC/ECD was developed for detection of octachlorodibenzo-p-dioxin and octachlorodibenzofuran (OCDD/F) in textiles. The method was tested using commercially available textile samples. The results from the screening method were cross-checked using conventional analysis procedures for selected contaminated and uncontaminated samples and good agreement was found. About two thirds of the investigated cotton textiles contained low or non-detectable levels of OCDD/F. The concentrations in the remaining samples ranged from 60 pg/g up to 40 ng/g.

Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) are found ubiquitously in sewage sludge in Germany [1), 2)]. In an investigation of the origins of PCDD/F in sewage sludge it was shown that contaminated textiles were responsible for high concentrations of PCDD/F in washing machine effluents [3)]. PCDD/F from this source was estimated to make a considerable contribution to the contamination of sewage sludge [4)]. Levels of up to 300,000 pg/g (Σ PCDD/F) were found in cotton textiles [5)], and it was demonstrated that PCDD/F are transferred from contaminated textiles to human skin [4)]. Hence textiles are an important source of the PCDD/F in sewage sludge and may contribute to human exposure to these compounds.

The levels of PCDD/F in textiles were found to vary over more than 5 orders of magnitude, with a very small number of samples contributing the vast majority of the PCDD/F found in this matrix. As the analysis of PCDD/F is a time consuming procedure requiring specialized equipment, it would be prohibitively expensive to monitor textiles in order to identify contaminated material or even to conduct representative surveys. A simpler screening method would be very useful in this regard.

The PCDD/F homologue patterns found in the textiles in the initial study were in almost all cases dominated by OCDD and/or OCDF. Between 50 % and 90 % of the total PCDD/F-contamination of new textiles can be ascribed to ΣOCDD/F [6)]. Hence, it should be possible to identify contaminated samples by screening for OCDD/F. The development of an appropriate method using GC/ECD for detection was the purpose of this study.

Experimental

Sample Extraction

The textile samples (5 - 20 g) were cut in small pieces and subdivided into portions of 2 g for analysis. The material was sonicated three times for 15 minutes with n-hexane using about 50 ml of solvent per gram of sample. An internal standard was added to the sample directly before the extraction procedure. The 1,2,3,4,7,8,9-H_7CDF isomer, which was found only in very low concentrations in textile samples [1], was selected for this purpose. The extraction efficiency of this method was measured for several textiles and the method yielded 90 - 95 % of the OCDD/F obtained with the conventional soxhlet extraction in toluene. This was judged to be adequate for screening purposes.

Sample Clean-up

The cleaning efficiency of the mixed acid-base-silica gel column and the alumina column used in the comprehensive PCDD/F method [6] was tested using the textile extracts. It was found that the alumina column alone provided an adequately clean extract for analysis on the GC/ECD. No improvement was observed when the mixed acid-base-silica gel column was also employed, and this column was hence not included in the procedure. It was also possible to reduce the size of the alumina column and hence reduce the eluting time and the material costs without compromising the results. The final method was as follows:

A Glass-column (1 cm i.d.) was filled from the bottom with glass-wool, 5 g Al_2O_3 (ICN B - Super 1) and 4 g Na_2SO_4. The combined n-hexane extracts were evaporated to 1 ml and transferred to the column. Impurities were first eluted with 50 ml hexane/dichloromethane (98/2, v/v). The PCDD/F were then eluted with 50 ml hexane/dichloromethane (50/50, v/v). After evaporating almost to dryness under a slow nitrogen stream the extracts were brought to a final volume of 30 µl toluene.

Sample analysis

The samples were analyzed using a gas chromatograph (HP 5890) with electron capture detection. Approximately 1 µl of sample was injected in splitless mode onto a capillary column (DB 5-MS, J&W, length: 30 m, 0.25 mm i.d., 0.25 µm film thickness) with helium as carrier gas. The column head pressure was 15 psi, resulting in an initial gas flow of about 1 ml/min. The injector and detector temperatures were 280°C and 320°C, respectively. The oven temperature program was 130°C for 1 minute, 20°C/min to 240°C , 10°C/min to 300°C, holding for another 10 minutes.

Complete baseline separation of OCDD and OCDF was nearly achieved. The reproducibility of standard measurements and the constancy of response factors was good with deviations of less than 10%. The detection limit of the ECD-system was 0.2 pg for both OCDD and OCDF. Reliable quantification required concentrations of 0.5 pg/µl in standard solutions. In real samples coelutions from the matrix increased the quantification limit to about 2 pg/µl. This enabled a reliable detection of concentrations of 30 pg/g in the textiles.

HRGC/HRMS Analysis

Several samples were analyzed for comparison purposes using a comprehensive extraction and clean-up with HRGC/HRMS analysis. This method is described elsewhere [1].

Results and discussion

To date 68 new textile samples have been analyzed with the screening method. The samples were all 100% cotton and consisted mostly of T-shirts but also included socks and underwear. The results are summarized in Tables 1.

Table 1: Summary of the OCDD/F concentrations in 68 new cotton textiles

Conc. range (ΣOCDD/F)	Number of samples	Remarks
< 60 pg/g	42	quantification limit
60 pg/g - 200 pg/g	13	OCDF: n.d.
200 pg/g - 500 pg/g	9	OCDF: n.d.
> 500 pg/g	4	see Table 2

In order to check the method, all textile samples containing more than 500 pg/g ΣOCDD/F and some less contaminated textiles were also analyzed using a standard comprehensive PCDD/F method with HRGC/HRMS detection. The OCDD/F concentrations obtained with the screening method and with the comprehensive method were in good agreement, with maximum deviations of 40% (see Table 2).

Table 2: OCDD/F concentrations in selected textile samples in pg/g

Sample	screening method			comprehensive method		
	OCDD	OCDF	Sum	OCDD	OCDF	Sum
T-Shirt, blue-gray (10)	358	< 30	358	190	27	217
T-Shirt, green (12)	< 30	< 30	<60	19	1.5	20.5
T-Shirt, red (13)	< 30	< 30	<60	4.6	1.2	5.8
T-Shirt, green (23)	827	1,098	1,925	589	1,205	1,794
undershirt, blue (46)	28,867	2,097	30,964	40,400	1,800	42,200
undershirt, gray (47)	810	< 30	810	631	42	673
T-Shirt, white (55)	856	< 30	856	1,177	14	1,191

In this context it should be pointed out that the contamination of the samples was not necessarily homogenous, and that this may partly explain the observed deviations. ECD-chromatograms were normally almost free of any coelutions of other detectable compounds. Samples 12 and 13, however, were clearly contaminated with at least 4 unidentified substances in the concentration range of 1 ng/g up to 1,000 ng/g. However, the coelutions did not significantly influence the detection of OCDD/F, as was confirmed by HRGC/HRMS analysis.

It can be seen from Table 1 that little or no PCDD/F was found in about 2/3 (42) of the samples. The levels in the remaining samples ranged up to about 40 ng/g. If the level of action for OCDD/F contamination in textiles were set at 1 ng/g, only 3 of the 68 samples would have been relevant. Hence the results both confirm the presence of high levels of PCDD/F in some textiles and emphasize the need for an inexpensive screening method.

The method presented here is a first step in this direction. No expensive labeled PCDD/F standards are required and the PCDD/F congeners employed in the method have a comparatively low toxicity. A relatively inexpensive GC/ECD is employed in the place of the complex GC/MS instrumentation. The extraction and clean-up procedure has been significantly simplified, reducing the technician hours per sample by at least 80%. Testing of the method is continuing.

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