

## Determination of PCDD/PCDF in PCP-contaminated leather samples

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### INTRODUCTION

The contamination of pentachlorophenol (PCP) with polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) is well documented (e.g. review: lit. 1). Depending on the commercially available product, different levels of PCDD/PCDF were detected. PCP-Na had considerably lower amounts of PCDD/PCDF than PCP. Generally, OCDD is the predominant congener (2).

In our institute, leather products were examined in 1990-1992 for PCP-contamination (3). From 93 samples of 1992, 25 exceeded the tolerance level of 5 mg PCP/kg. With respect to the PCDD/PCDF-contamination of PCP-products, 11 leather samples were analyzed to find out whether there was a correlation between the PCP- and the PCDD/PCDF-concentration. In the literature, the results of a single analysis of a leather glove with a PCDD/PCDF-amount of 17.4 pg TEQ/g were reported (corresponding PCP-amount not mentioned) (4).

### EXPERIMENTAL

The basic steps of the analysis were presented earlier (5, 6). It is worth mentioning that the whole procedure does not use any halogenated solvents or benzene for protection of the analyst and the environment and to avoid problems of discharging the waste. The procedure is optimized in a way that we can generally recycle about 70 - 80 % of the solvent waste and reuse it. The procedure leather samples contains the following steps:

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- Soxhlet extraction of at least 10 g small pieces of leather (homogenous and representative for the whole sample) with cyclohexane/toluene (1+1)
- spiking of a small aliquot (depending on the predetermined PCP-amount in the range between 20 mg and 1 g) with all <sup>13</sup>C-labeled PCDD/PCDF-congeners
- removal of lipophilic and oxidizable substances on a column with layers of silica gel/sulfuric acid, silica gel/NaOH and silica gel (deactivated with 5 % water).
  - for low contaminated samples (aliquot of 1 g): From the bottom to the top: 5 g silica gel, 10 g silica gel/ NaOH (mixture of 100 g silica gel + 30 g 1 m NaOH), 5 g silica gel, 30 g silica gel/sulfuric acid (mixture of 100 g silica gel + 24 ml 96 % sulfuric acid), 5 g silica gel, 35 g silica gel/NaOH (mixture of 100 g silica gel + 30 g 1 m NaOH). Elution with 150 ml cyclohexane/toluene (1+1).
  - for high contaminated samples (aliquot of 20 mg): the same chemicals in the same order, but in reduced amounts (2 g silica gel, 3 g silica gel/NaOH, 2 g silica gel, 10 g silica gel/sulfuric acid, 2 g silica gel, 10 g silica gel/NaOH. Elution with 100 ml cyclohexane/toluene (1+1).
- gelchromatographic separation
- separation of PCB, chlorinated pesticides, chlorobenzenes, chlorinated biphenylethers and chlorophenols on a florisil column (deactivated with 3 % water; 6 g florisil; prewash for removal of disturbing substances with 50 ml hexane; elution of PCDD/PCDF with 60 ml toluene)
- Carbopack C/celite-clean up (0.4 g of mixture of 0.36 g Carbopack C and 1.64 g Celite; prewash with 2 ml hexane; elution of PCDD/PDCF with 50 ml toluene)
- addition of <sup>13</sup>C-labeled 1234-TCDD
- concentration to a final volume of 40 µl toluene
- GC/MS on a VG Autospec at 10000 resolution using a 60 m DB5-MS-column. The AS 200 autosampler injected 5 µl into the Multiinjector of a Carlo Erba Mega GC. The injector had a glassliner with silanized glass wool and was operated in the mode "cold split/splitless with solvent split purge": split of solvent for 10 s at 100 °C, then splitless transfer of PCDD/F onto the capillary at 330 °C.
- With every acquisition sequence, a 5 point-calibration curve was acquired in duplicate (5 points before and 5 points after the samples). The calibration curve covered the ranges between 0.025 to 2.0 pg/µl for PCDD/F which were expected in a lower concentration range (e.g. 2378-TCDD and 2378-TCDF) and 0.5 to 40 pg/µl for OCDD. Using the above conditions, the injection of the lowest concentrated standard with 12.5 fg TCDD/µl gave a

signal to noise of at least 10:1 (with +/- 2 standard deviations about the mean noise; theoretically according to specification and achievable in the daily routine: 15:1).

- All results were confirmed on a 60 m DB-Dioxin column.

### RESULTS AND DISCUSSION

Table 1 gives the results of the determination of PCDD/PCDF in 11 samples with PCP-amounts between 0.17 and 550 mg/kg.

| PCP-amount<br>(mg/kg) | pg I-TEQ/g | Sample No.<br>(1992) | Sort of leather         |
|-----------------------|------------|----------------------|-------------------------|
| 0.17                  | 3.1        | 9859                 | money bag <sup>1)</sup> |
| 0.21                  | 3.1        | 4972                 | money bag <sup>1)</sup> |
| 10.20                 | 29.3       | 8664                 | money bag <sup>1)</sup> |
| 10.30                 | 56.7       | 8662                 | money bag <sup>1)</sup> |
| 11.30                 | 1210.8     | 4962                 | shoe lining leather     |
| 11.60                 | 26.2       | 8665                 | money bag <sup>1)</sup> |
| 16.00                 | 28.8       | 8588                 | shoe leather uppers     |
| 130.00                | 425.3      | 8521                 | money bag <sup>1)</sup> |
| 220.00                | 243.9      | 4966                 | money bag <sup>1)</sup> |
| 246.00                | 353.3      | 4923                 | shoe lining leather     |
| 550.00                | 6388.1     | 4930                 | shoe lining leather     |

<sup>1)</sup> money bag worn around the neck

Table 1. Results of determination of PCDD/PCDF in leather products with different PCP amounts

The results prove a clear increase of PCDD/PCDF-contamination with raising amounts of PCP, although there is no strict linear correlation. Sample no. 4962 with its striking high PCDD/PCDF-contamination was repeatedly confirmed (determination of the PCP-amount in duplicate and of PCDD/PCDF-amount in triplicate). It is unclear whether here is another PCDD/PCDF-source the cause for this high contamination.

According to the German law, any goods exceeding 5 mg PCP/kg are

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prohibited from selling on the market. The two samples with about 0.2 mg PCP/kg resemble the background contamination. All other samples exceed the PCP tolerance level.

Up to now, there are no specific regulations for PCDD/PCDF in leather products. Anyhow, the consumer is protected sufficiently by the PCP-regulations.

## REFERENCES

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