Determination of PCDDs, PCDFs, Dioxin-like and Non-Dioxin-Like PCBs in Fish Samples – A Comparison between Pressurized Solvent Extraction and Soxhlet Extraction

S. Cleres, R. Hartmann, B. Mullis, BÜCHI Labortechnik AG, 9230 Flawil, Switzerland / S. Hamm, A. Maulshagen, mas GmbH, 48149 Münster, Germany

Abstract

The efficiency of pressurized solvent extraction (PSE) for the determination of 17 PCDD/Fs, 12 dioxin-like and 6 non dioxin-like PCBs in fish samples was investigated by comparing PSE (SpeedExtractor E-914) with Soxhlet extraction. The isolation of PCDD/Fs and PCBs was performed in fish samples with different fat content; eel and trout. After a multi-step chromatographic column clean-up, the extracts were analyzed by means of high resolution mass spectrometry (HRGC/HRMS). The results of the trout reference material showed an accurate reproduction of the data for both, PSE and Soxhlet. Values of reproducibility for analyzed compounds were excellent and PCDD/F and PCB data of the fish samples obtained with PSE were closely comparable to the Soxhlet results.

Introduction

The extraction process for the determination of PCDD/Fs and PCBs in fish samples is normally time and solvent consuming, especially if the classical Soxhlet method is applied. Pressurized Solvent Extraction (PSE) is a well-established alternative to the conventional Soxhlet method. PSE combines elevated pressures and temperatures, resulting in a more efficient extraction process. Thus, time and solvent are significantly reduced. The purpose of this study was to compare PSE results with those gathered by the application of the classical Soxhlet extraction method, and an interlaboratory round robin test, respectively.

Fig. 1: *SpeedExtractor*

Materials and Methods

PCDD/Fs, dioxin-like PCBs and non dioxin-like PCBs were extracted from fish samples with different fat content: eel (> 30%) and trout (~ 4%). In addition, a fish sample from a round robin test was extracted as reference material (Interlaboratory Comparison on Dioxins in Food 2010, Folkehelseinstituttet, Oslo, Norway). The samples were disembowelled, boned, scaled, washed, freeze-dried and homogenized. 8 to 19 g (dependent of the fat content) were mixed with diatomaceous earth and extracted with di-chloromethane/*n*-hexane (1:1/v:v). The extraction method of the SpeedExtractor E-914 is displayed in Table 1. Before extraction, 16 $^{13}C_{12}$-labeled PCDD/F standards and 18 $^{13}C_{12}$-labeled PCB standards were added to the sample material.

Tab. 1: *Extraction method of the SpeedExtractor E-914*

Speed Extractor E-914 (4 positions)	
Temperature	100°C
Pressure	100 bar
Cells	80 ml
Solvent	Di-chloromethane 50%, *n*-hexane 50%
Cycles	3
-Heat-up	5/1/1 min
-Hold	10 min
-Discharge	4 min
Flush with solvent	2 min
Flush with gas	10 min

Analysis

In each case, the extract was concentrated and purified by a multi-step chromatographic column clean-up: silica gel/sulfuric acid, alumina and Florisil. The determination of PCDD/Fs and PCBs was performed by HRGC/HRMS. A Thermo Scientific Trace-GC-Ultra coupled with a Thermo Scientific DFS high resolution mass spectrometer was used. The analytes were separated on a DB-5MS column (60 m x 0.25 mm x 0.25 µm). Concentrations of PCDD/Fs and PCB were determined by the isotopic dilution method.

Results

The concentrations of PCDD/Fs, dioxin-like and non dioxin-like PCBs obtained with the SpeedExtractor E-914 were very similar to those obtained by the Soxhlet method and showed also good comparability to the values of the reference material (Figures 2 and 3). The expenditure of time however, was a lot better for PSE as the total time used to extract 4 samples was one hour and 20 min compared to 16 hours for Soxhlet.

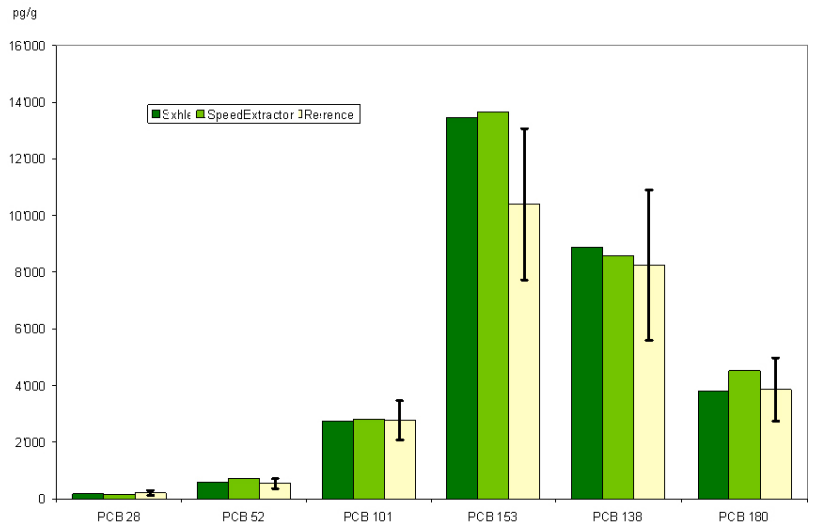

Fig. 2: *Concentrations of PCBs in pg/g Fresh Weight (FW) of the reference trout sample; Soxhlet and SpeedExtractor (n=1), Reference (n=62)*

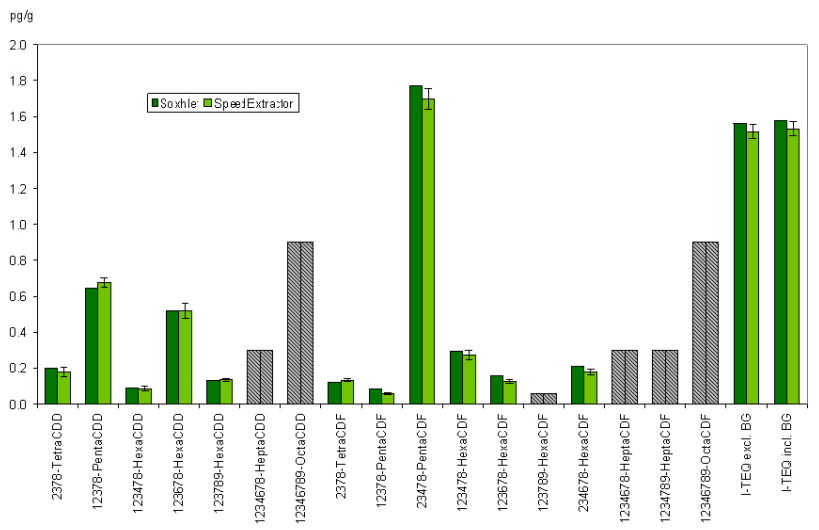

Fig. 3: *Concentrations of PCDD/Fs in pg/g FW of the eel sample (grey bars: results < LOQ); Soxhlet (n=1), SpeedExtractor (n=3)*

Relative standard deviations of three SpeedExtractor extractions were calculated for all 2,3,7,8-substituted PCDD/Fs and dioxin-like and non dioxin-like PCBs and ranged from 3 to 15% for PCDD/Fs and 1 to 10% for PCBs.
Blank samples indicated neither cross-contamination (parallel blank) nor carry over of PCDD/Fs and PCBs for subsequent extractions.

Conclusion

The SpeedExtractor delivered results similar to those obtained with the Soxhlet extraction method with a great advantage in terms of time savings and solvent consumption. This study demonstrated that PSE is the technique of choice regarding ecological and economical aspects.

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