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Optimization of selective pressurized liquid extraction for extraction and in-cell clean-up of PCDD/Fs in soils and sediments

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HIGHLIGHTS

- ▶ SPLE for large scale screening of PCDD/Fs in soils/sediments.
- ▶ Extraction was optimized using experimental design.
- ▶ Temperature is the most important factor.
- ▶ The TEQ accuracy was ⩽11%.
- ▶ Diethyl ether may substitute hazardous dichloromethane.

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ABSTRACT

This paper describes the development of methods for selective extraction of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from soils and sediments, using pressurized liquid extraction with in-cell clean-up (SPLE). Two binary solvent mixtures, *viz.* dichloromethane/*n*-heptane (DCM/Hp), and diethylether/*n*-heptane (DEE/Hp), were evaluated. The SPLE extraction conditions were optimized using central composite face (CCF) design. Three factors were investigated: extraction temperature (60–160 °C), number of extraction cycles (1–3) and time per cycle (2–18 min). The results showed that DCM/Hp (1/1, v/v) and DEE/Hp (1/2, v/v) were the best extraction solvent compositions and that the extraction temperature was a critical factor that needed careful optimization to achieve high extraction efficiency without co-extraction of sulfuric acid. Under the optimal conditions, the SPLE methods provided results with good accuracy and precision. For the sandy soil certified reference material (CRM-529) the quantification results ended up in the range 82–110% as compared to the concentrations obtained by a reference method based on Soxhlet extraction and external column clean-up. Furthermore, for a clay soil (CRM-530) and a sediment reference material (WMS-01), the accuracy (trueness) of the TEQ values were +11% (DCM/Hp) and +8% (DEE/Hp) for CRM-530, +8% and −7% for WMS-01, respectively. The individual congener concentrations also agreed well with the certified values. These findings show that SPLE is a promising method for combined extraction and clean-up of PCDD/Fs in soil/sediment samples.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are well-known environmental contaminants that have shown a wide range of toxic effects in humans and the environment (Nording et al., 2006; Van den Berg et al., 2006). The 2,3,7,8-substituted PCDD/Fs have been assigned toxic equivalent factors (TEFs) by the World Health Organization (Van den Berg et al., 2006). These TEFs can be used to calculate total toxic equivalents (TEQs) of all PCDD/Fs quantified in the samples. The group of PCDD/Fs comprises 210 different congeners that are formed as unintentional by-products during incineration and various industrial processes. The PCDD/Fs are ubiquitous in the global environment today (Bernes, 1998). Although the levels are often low, they may be elevated at certain industrial sites. These sites may constitute a direct risk for humans and the environment, but may also act as secondary sources of pollution to the surrounding environment. The contaminants may enter the food web *via* uptake by terrestrial organisms, (Matscheko et al., 2002) or, after leaching to the aquatic environment, *via* uptake by various aquatic species (Yasuhara and Katami, 2007). Hence, there is an urgent need to assess the risk and remediate these contaminated sites. However, this is often hampered by costly and labor intensive dioxin analyses, which generally involves

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several time-consuming steps, e.g., Soxhlet extraction, multi-column clean-up followed by gas chromatography/high resolution mass spectrometry (GC/HRMS) analysis (EPA, 1994, 2007). Thus, alternative cost-efficient methods with high sample throughput need to be developed (Focant et al., 2004). One promising approach combines extraction and clean-up in the same step, using Pressurized Liquid Extraction (PLE) with in-cell clean-up (Björklund et al., 2006; Ghosh et al., 2011).

PLE utilizes organic solvent at elevated temperature and pressure to extract organic pollutants from solid matrices. The technique has gained considerable interest over the last decade as it saves both time and solvent during the sample preparation process. In addition, PLE has proven to be more flexible and efficient than Soxhlet extraction (van Leeuwen and de Boer, 2008; de Koning et al., 2009). In conventional PLE, the extraction cell is packed solely with sample material and a dispersant. This generally enables an exhaustive extraction process with high recovery of the analytes. However, like Soxhlet extraction, the selectivity of this process is limited and the resulting extract contains a multitude of co-extracted materials that need to be removed by an extensive clean-up procedure (Camel, 2001). In 1996, Dionex described a new approach in which alumina was added into the PLE cell to eliminate fat from biota samples (Dionex, 1996). Subsequently, several publications have shown the possibilities of combining the PLE extraction with integrated clean-up, so called selective PLE (SPLE). For examples, Sporring and Björklund (2004), Sporring et al. (2006) used sulfuric acid impregnated silica gel to remove lipids from food and feed samples during PCB extraction. This method significantly reduced time and solvent cost, and provided fat-free extracts that could be directly analyzed by GC and electron capture detection. Chuang et al. (2009) developed a SPLE strategy to detect PCDD/Fs in sediments and soils. The samples were extracted with dichloromethane (DCM) at 100 °C, passed through different layers of H_2SO_4–silica, 10% $AgNO_3$–silica, and alumina to retain the matrices. The cleaned extracts were analyzed by enzyme-linked immunosorbent assays (ELISAs). The method allows high sample throughput. However, there are some potential drawbacks with the Chuang's procedure. A low extraction temperature (100 °C) and the use of a sole solvent (DCM) are potentially insufficient for extraction of dioxins from solid samples (Kiguchi et al., 2006); moreover ELISA gives no information about the relative contribution of individual congeners.

The aim of the present study was to develop and optimize a SPLE procedure for congener specific GC/HRMS analysis of PCDD/Fs in highly contaminated soil/sediment samples. The development and optimization was divided into three steps: (i) choice of sulfur removal procedure; (ii) binary solvent mixture evaluation and screening of a less toxic polar solvent alternative to DCM due to environmental and health concerns over the chlorinated solvent (Westbom et al., 2008); and (iii) optimization of extraction parameters for efficient extraction and bulk matrix removal. Experimental design was used during the third step to optimize the influences of temperature, number of extracting cycles and time per cycle on the extraction efficiency of PCDD/Fs. The performance of the extraction procedure was evaluated using certified reference materials (CRMs).

2. Materials and methods

2.1. Chemicals and standards

DCM and tetradecane (⩾99.5%) were obtained from Fluka, Buchs, Germany. Tetrahydrofuran, potassium hydroxide and *n*-heptane were purchased from VWR International, France. Acetone, methanol, diethylether (DEE), toluene, sulfuric acid (H_2SO_4, 95–97%) were purchased from Merck, Darmstadt, Germany, who also supplied silica gel 60 (70–230 mesh) and anhydrous sodium sulfate (Na_2SO_4). Activated carbon AX-21 originated from Norit Company, Amersfoort, The Netherlands. Methyl *t*-butyl ether (MTBE), 1,2-dimethoxyethane, 2-methyl tetrahydrofuran, Celite 545, fine powder copper (−200 mesh, 99%) and granule copper (−10 + 40 mesh, 99.9%) were purchased from Sigma–Aldrich, Steinheim, Germany. The copper was activated based on the Battelle standard operating procedure (SOP) #5-192-05 before use (Battelle, 2001).

Native and labeled standards were obtained from Cambridge Isotope Laboratories, Andover, MA, USA and Wellington Laboratories, Guelph, ON, Canada. Internal standard (IS) containing seventeen ^{13}C-labeled 2,3,7,8-PCDD/Fs was spiked to each sample before the extraction; whereas recovery standard (RS) was added prior to GC/HRMS analysis. RS contained a mixture of 1,2,3,4-TCDD; 1,2,3,4,6-PeCDF; 1,2,3,4,6,9-HxCDF and 1,2,3,4,6,8,9-HpCDF. The same volumes of IS and RS were added to the blank samples and to a quantification standard (QS) containing seventeen native 2,3,7,8-PCDD/Fs.

2.2. Samples

Three CRMs, two soils and one lake sediment, were used in the study. The soil CRMs were supplied by the Institute for Reference Materials and Measurements, Geel, Brussels; CRM-529 is a sandy soil and CRM-530 is a clay soil. Both soils are contaminated with PCDD/Fs as a result of industrial processes. The lake sediment WMS-01 is naturally contaminated with PCDD/Fs and was purchased from Wellington Laboratories, Canada. CRM-529 was used during method development and validation, while CRM-530 and WMS-01 were only used for validation.

2.3. Reference method

Reference data of CRM-529 was generated by Soxhlet extraction and open column chromatography clean-up. In brief, the extraction was performed with toluene for 20 h. The extracts were concentrated and loaded to multilayer silica columns, followed by active carbon column according to the method of Liljelind et al. (2003).

2.4. SPLE

In this study, all SPLE experiments were performed on a Dionex ASE®200 system (Sunnyvale, CA, USA) equipped with 22 mL stainless steel extraction cells. The extraction conditions were constant at 14 MPa, 100% flush and 90 s purge. The extraction cells were emptied and rinsed with water and acetone immediately after the extractions to avoid potential corrosion problems (no corrosion observed after >200 extractions).

2.4.1. Solvent evaluation

Five solvents: DEE, tetrahydrofuran, 2-methyl tetrahydrofuran, dimethoxy ethane, and methyl *t*-butyl ether considered to be similar physico-chemical properties as DCM but less toxic (Suchan et al., 2004; Zhang et al., 2010) than DCM were chosen. The solvents were evaluated by extracting six SPLE cells containing Celite and 40% H_2SO_4–silica under 3 cycle × 5 min at 100 °C. Following extraction the cell contents were carefully removed and inspected for indications of reactions between solvent and H_2SO_4 such as color alterations.

DEE was the best solvent after the evaluation. The next evaluation was to find the best DCM/Hp and DEE/Hp proportions that extracted the highest amount of PCDD/Fs with the lowest amount of co-extracted material. Six solvent mixtures, DCM/Hp (1/10, 1/4, 1/1, v/v) and DEE/Hp (1/10, 1/4, 1/1, v/v) were prepared, and used to