Selective Pressurized Liquid Extraction of Polychlorinated Biphenyls in Sediment

Rikard WESTBOM,* Sune SPORRING,** Louise CEDERBERG,* Lars-Ola LINDEROTTH,* and Erland BJÖRKLUND*,***†

*Department of Analytical Chemistry, Lund University, P. O. Box 124, SE-221 00 Lund, Sweden
**Department of Pharmaceutics and Analytical Chemistry, University of Copenhagen, Universitetsparken 2, DK-2100 Copenhagen, Denmark

A selective pressurized liquid extraction procedure (SPLE) was developed for a fast determination of polychlorinated biphenyls in sediment. The final method was performed at 100 °C with heptane/dichloromethane (90:10, v/v) as extraction solvent for 2 × 5 min. Sulfuric acid impregnated silica was placed downstream of the sample in the extraction cell to remove interfering components. This simultaneous extraction/clean-up was performed in 20 min, with an average congener recovery of 92% compared to a classical 24 h Soxhlet methodology and 2 h of external manual clean-up.

(Received September 11, 2007; Accepted January 11, 2008; Published April 10, 2008)

The utilization of pressurized liquid extraction (PLE) in environmental analyses of persistent organic pollutants (POPs) has recently changed from being solely a fast and exhaustive extraction technique1–6 to become a versatile sample preparation tool combining extraction and clean-up by integrating an adsorbent in the extraction cell.7–15

A promising new procedure is the inclusion of sulfuric acid impregnated silica in PLE cells, which efficiently removes fat and other interfering materials as demonstrated for the extraction of PCBs11,12 and dioxins10,11 from food and feed samples. This latter type of PLE applications are often termed selective PLE or SPLE. Even though PLE has been used with great success for the extraction of PCBs from sediments with conventional external clean-up4,5 and for the extraction of PCBs from food and feed with integrated clean-up11,12 no investigations have so far been conducted to apply selective PLE to sediments containing PCBs. This note, for the first time, reports on the possibility of integrating extraction and clean-up in SPLE to obtain a fast analysis of PCBs in sediments.

Experimental

Sediment sample

The study was conducted with a historically contaminated harbor sediment supplied by the National Institute for Standards and Technology (NIST, Gaithersburg, MD). This material originates from a large sediment batch of which a later part was used for the production of the certified reference material SRM 1939. The organic carbon content of the sediment is 3.8 ± 0.1% (w/w), as determined with a Leco CR-12 element analyzer (Leco Corp., MI), and the particle size is ≤45 μm, as stated by NIST.

Reagents and chemicals

Acetone D (for analysis of dioxins) and heptane (Pestanal grade) were obtained from Riedel-de-Haën, Seelze, Germany, who also supplied the sulfuric acid (H2SO4, analytical reagent grade, 95 – 97%). Dichloromethane (DCM, ≥99.8%), sodium sulfate (Na2SO4, puriss, analytical reagent grade ≥99%) and silica gel 60 were purchased from Fluka Chemie GmbH, Buchs, Switzerland. Sodium hydroxide pellets (NaOH, 95 – 100%) were purchased from Eka Nobel AB, Bohus, Sweden. The pellets were dissolved in water produced with a Milli-Q purification system (Millipore, Milford, MA) to obtain a 1 M NaOH solution. The Na2SO4 and silica gel 60 were baked at 400 °C for 10 h prior to use. Impregnated silica was prepared by heating silica gel 60 as mentioned above and adding it to the cold material H2SO4 or NaOH so that the impregnation became 40 and 33% (w/w), respectively. Glass microfiber filters GF/A came from Whatman International Ltd. (Maidstone, UK). The PCB solution used for calibration was NIST 2262 (NIST) while the PCB solution used as internal standard (IS), containing PCBs 35 (time reference) and 169 (quantification reference) was obtained from Larodan Fine Chemicals AB (Malmö, Sweden). Nitrogen (Quality 4.6 or Detektor OTC-50) and helium (Detector Quality) were all purchased from AGA Gas AB (Sundbyberg, Sweden).

Soxhlet extraction

Soxhlet extractions were performed in triplicate for 24 h using 125 ml of a mixture of heptane/acetone (1:1, v/v) with cellulose thimbles (Whatman International Ltd.) containing 1 g of sediment mixed with 1 g of Na2SO4. Fifty microliters of IS (PCB 35 and 169) were added, and the extracts were then concentrated to about 1.5 ml. Extracts were cleaned on a column packed with H2SO4 impregnated silica (40:60, v/v) and Na2SO4, eluted with 50 ml heptane and reduced to 1.5 ml prior to final analysis.

Pressurized liquid extraction

All extractions were performed on an ASE-300 system ( Dionex Corporation, Sunnyvale, CA). The extraction cells used had a volume of 33 ml. Each sample was mixed with

1 To whom correspondence should be addressed. E-mail: ejb@farma.ku.dk
NaSO\(_4\) which also was used to fill up the dead volume. The packing of the extraction cells can be seen in Fig. 1.

Extractions were performed at 100°C and 100 bars for 2 × 5 min. After each extraction cycle the cell was flushed with an solvent amount corresponding to 30% of the cell volume, giving a total flush volume of 60%. In the end, the cell was purged for 90 s using nitrogen. Fifty microliters of IS were added to the extracts before they were concentrated to about 1.5 ml. External clean-up of PLE extracts were performed as described for Soxhlet extracts. PLE extracts with integrated clean-up did not require additional cleaning.

**Chromatographic analysis**

Analyses were performed on an Agilent 6890 gas chromatograph connected to an Agilent 5973 network mass selective detector and a 7683 series autosampler and injector (Agilent, Palo Alto, CA). Injections of 2.0 μl were made on-column into a deactivated retention gap (5 m × 0.53 mm i.d., Agilent) connected to an HP-5 ms column (30 m × 0.25 mm, 0.25 μm 5% phenylmethylpolysiloxane, Agilent). Helium was used as carrier gas at an initial flow rate of 1.5 ml/min. The GC oven temperature programming was initialized with 2 min at 90°C followed by a ramp at 20°C/min to 175°C which was held for 7.5 min. After this a ramp at 3°C/min to 280°C was applied and this temperature was held for 10 min. The temperature of the quadrupole mass filter was 150°C and the ionization mode was electron ionization carried out at an electron energy of 70 eV. The temperatures of the ion source and transfer line were 230 and 280°C, respectively. The mass spectrometer was operated in selected ion monitoring (SIM) mode observing m/z, which are characteristic for PCBs (188, 222, 256, 292, 326, 360, 396, 428, 464, and 498).

**Results and Discussion**

**Soxhlet extraction with acetone/heptane**

PCB concentrations for 11 different congeners were determined to be 844 ng/g (PCB 52), 1019 ng/g (PCB 66), 1292 ng/g (PCB 101), 1418 ng/g (PCB 118), 928 ng/g (PCB 153), 555 ng/g (PCB 105), 1231 ng/g (PCB 138), 81 ng/g (PCB 187), 219 ng/g (PCB 128), 164 ng/g (PCB 180) and 118 ng/g (PCB 170), with RSD values typically around 10%. These concentrations served as reference values for all other extractions since Soxhlet is a widely utilized and accepted technique.

**SPLE with pure heptane**

Pure heptane has previously been used successfully to extract PCBs and dioxins from food and feed matrices using H\(_2\)SO\(_4\) impregnated silica inside the extraction cell.

Even though a polar solvent such as acetone was absent in these extractions, quantitative results were obtained in most cases. This is mainly believed to be caused by the increased extraction temperature in PLE, which should not be below 100°C. Even though it is well known that most environmental matrices require a polar component in the extraction of POPs, a few experiments were still performed to evaluate the effects using pure heptane in combination with the two types of integrated clean-up approaches, H\(_2\)SO\(_4\) and NaOH. The results are presented in Fig. 2.

The average recovery compared to Soxhlet for 11 investigated PCBs using heptane with external H\(_2\)SO\(_4\) clean-up was 72%, which demonstrates that extraction without a polar solvent component does not provide sufficient exhaustiveness despite the fact that an elevated temperature of 100°C was used. Even lower recoveries were obtained with internal clean-up using H\(_2\)SO\(_4\) and NaOH, with recoveries of 64 and 57%, respectively. The results show that SPE of sediments with pure heptane does not generate quantitative extractions and should be avoided.

**SPE with heptane/DCM**

Acetone is a commonly applied polar non-toxic solvent for extraction of e.g., PCBs in soils and sediments. However, acetone does not resist H\(_2\)SO\(_4\), so an alternative strategy had to be found. Even though DCM is a toxic compound, it is often
used in PLE of POPs from environmental matrices since it gives good recoveries. Furthermore, it can withstand both H$_2$SO$_4$ and NaOH. Therefore, 10% of DCM was added as a polar modifier to heptane to study the effects on PCB recoveries combined with various clean-up strategies, as seen in Fig. 3.

PLE with external clean-up resulted in quantitative recoveries compared to Soxhlet with an average recovery for the 11 investigated PCBs of 107%. This demonstrated that 10% DCM was suitable as a polar modifier in SPLE. When SPLE was performed with H$_2$SO$_4$ impregnated silica, good results were also obtained with an average recovery for the investigated PCBs of 92%. However when NaOH was utilized in SPLE, the recoveries were significantly reduced with an average recovery of 59%. It has been reported that KOH at 90°C degrades PCBs, especially higher congeners. In this study, a temperature of 100°C was used, furthermore, NaOH dissociates more easily than KOH because of the lower atomic number of Na. Therefore, it can be assumed that NaOH degrades PCBs under these conditions, causing significantly lower recoveries with this approach. In any case, NaOH is not recommended as a means to remove interfering components in SPLE. It should be mentioned that DCM is not an optimal solvent from an environmental perspective, however, it is an excellent solvent in releasing analytes for sediments during SPLE. By applying SPLE, the overall consumption of solvents is also greatly reduced since the PLE in itself uses less solvent than Soxhlet methodologies, and furthermore no external clean-up is necessary for the obtained extracts. Additionally as little as 10% of DCM in the extraction solvent mixture is sufficient to obtain quantitative recoveries.

Conclusions

With the developed SPLE methodology, solvent consumption and time spent on sample preparation, including extraction and clean-up, were drastically decreased. Replacement of classical methods such as Soxhlet and external clean-up approaches is therefore proposed as an efficient means to increase the performance of the analytical laboratory.

References