Stir Bar Sorptive Extraction (SBSE) Applied to the Analysis of PPT Traces of Polychlorinated Biphenyls (PCBs) in Human Sperm

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1. INTRODUCTION
The increasing amount of estrogenic chemicals in the environment has become a major issue of concern. Exposure to these compounds has already been associated to the observed decrease in human sperm quality in some parts of the world. The demand for precise, reliable and accurate determination of ultra-trace concentrations of estrogenically active compounds has, therefore, increased tremendously over the last several years. Recently, a novel and promising approach for sample enrichment, i.e. stir bar sorptive extraction (SBSE), was developed. In SBSE a glass-lined metal bar is covered with a thick layer of polydimethylsiloxane (PDMS), which acts as enrichment phase. After enrichment the stir bar is thermally desorbed and the compounds analysed. In this contribution SBSE, combined with thermodesorption (TD-GC-MS), is validated for the determination of PCBs in human sperm.

2. EXPERIMENTAL
- PCB Standard: Di-Deuterated PCB (Augsburg, Germany);
- Stir Bar: 15 mm, 6.0 mm, 0.5 mm d, from PDMS;
- GC: HP-6890 (Agilent Tech., Little Falls, DE, USA);
- Oven: 40 °C (2.5 min) to 150 °C @ 25 °C/min to 280 °C (3 min)
- @ 10 °C/min, splitless time 2.5 min
- TD: TDS2 system (Gerstel, M uhlheim a/d Ruhr, Germany);
- Sample inlet: 10 mm L, 2 mm I.d, of PDMS;
- GC-MS: HP-6890 (Agilent Tech., Little Falls, DE, USA);
- Detector: HP 5973 MSD;
- Oven: 20 °C (1 min) to 350 °C @ 20 °C/min to 370 °C (3 min)
- @ 10 °C/min, splitless time 2.5 min
- TCD-2 °C (1 min) to 325 °C (10 min) @ 60 °C/min;
- TCEA-150°C (0.5 min) to 500°C (5 min) @ 12 °C/min, empty liner

3. RESULTS AND DISCUSSION
3.1 Sampling
Sampling conditions were developed using Mill-Q water, which was spiked with the standard mixture containing the seven 'Bichlorinated' PCBs. Concentrations ranged from 100 fg to 10 pg in 10 mL. Octachloronaphthalene (1 ng) was used as internal standard.

The main problem in PCB analysis in aqueous solutions is glass adsorption, caused by their apolar nature. A simple but effective way to minimize this effect is to add MeOH to the solutions. Increasing percentages, however, negatively influence PCB recovery, due to polarity changes in the sample. The optimal MeOH percentage was determined. The influence of recovery for PCBs 28 and 180 is given in Figure 1. Each data point is the average of 5 analyses. %RSDs were determined (error bars).

The increase amount of estrogenic chemicals in the environment increased tremendously over the last several years. Exposure to these compounds has, therefore, become a major issue of concern. The demand for precise, reliable and accurate determination of ultra-trace concentrations of estrogenically active compounds has increased tremendously over the last several years. Recently, a novel and promising approach for sample enrichment, i.e. stir bar sorptive extraction (SBSE), was developed. In SBSE a glass-lined metal bar is covered with a thick layer of polydimethylsiloxane (PDMS), which acts as enrichment phase. After enrichment the stir bar is thermally desorbed and the compounds analysed. In this contribution SBSE, combined with thermodesorption (TD-GC-MS), is validated for the determination of PCBs in human sperm.

3.2 Matrix effect
An extra adsorptive contribution was expected from the biological matrix. Calibration graphs in aqueous solution and in sperm are depicted in Figure 2. For the sperm analyses 1 mL of sperm was spiked in human sperm. Two ions per compound were monitored. Linearities were measured in the concentration range from 10 fg up to 10 pg.

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