Air monitoring of PCB with Gerstel-Twister

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Introduction

In recent years, there has been an increasing interest in developing new analytical tools for atmospheric monitoring of organic pollutants[1,2]. In general, sample preparation and conventional column chromatographic clean-up methods are labour-intensive and time-consuming. Therefore it is necessary to develop sensitive, easy to handle methods, which allow an automation of the analytical process. Especially for immission and effluent monitoring it is useful to have fast analytical techniques at hand, that e.g. make a high sample throughput and routine analytics at the sampling day possible.

To establish a new sampling and assay technique, tests with Gerstel-Twister were carried out. Gerstel-Twister offer the possibility to analyse organic compounds from aqueous matrices and were used only as aqueous media passive samplers so far.[3,4] But it is also supposed that Gerstel-Twister are capable of atmospheric sampling.

Materials and Methods

Gerstel-Twister: The operation principle of the sampling device Gerstel-Twister is based upon the Stir Bar Sorptive Extraction (SBSE), first introduced by Baltussen et al.[5,6] and similar to the Solid Phase Micro Extraction[7]. Commercially available Twister resemble magnetic stirring bars, coated with a layer of polydimethylsiloxane to selectively enrich nonpolar compounds from aqueous matrices. The accumulated substances can be directly chromatographed after thermodesorption. Figure 1 shows the structure of such a stir bar and a picture of the used air sampling cage.

Air Sampling: To research the characteristics of reception, Gerstel-Twister were exposed to air at two different sites by variation of the duration of exposure. Twister at sampling site A were placed inside a container, in which the gaseous effluents of combustion experiments had been passed in. Site B is located on an outdoor area and therefore exposed to cleaner air. The sampling period varied between two days and three months. The exposed Twister were frozen in glass vessels for storage.

Equipment: The used thermodesorption unit (TDU, Gerstel) was connected to a programmed-temperature vaporisation injector (CIS 3, Gerstel) and coupled to a gas chromatograph (5890 SERIES II, Agilent Technologies) high-resolution mass spectrometer (MAT 95, Thermo Finnigan). The GC was equipped with a high-resolution column and a multipurpose autosampler (MPS 2, Gerstel). Twister can be conditioned in a special tube-conditioner (TC 1, Gerstel).

Results and Discussion

Method Optimization: Factors affecting desorption were evaluated to ensure the optimum analyte transfer from the stirring bars to the column. Each Twister was thermal desorbed twice in order to verify complete analyte desorption. Best results for the PCB desorption (desorption temperature = 300 °C; desorption time = 6 min; cryofocussing temperature = -30 °C) were obtained by testing various set-up conditions. Different desorption He-flow rates (70ml/min, 90 ml/min) were compared and indicated no detectable difference. The desorption temperature has the most important effect on desorption so that a relative high temperature of 300 °C was chosen although siloxane bleeding from the PDMS-coat can occur. Twister were washed with water before desorption to remove dust and pollen. Table 1 shows the tested set-up conditions.

Quantification: Quantification was carried out by the isotopic dilution method. 13C-PCB-standards were put on the respective stir bar with the help of a 1µl syringe before thermal desorption. Calibration curves, displayed in Figure 2, show linear desorption properties for concentrations up to 1000 pg per Twister for high-volatile PCB. For the more difficult-to-volatilize PCB linearity is obtained up to 800 pg per Twister.

Exposure pilot test: The rapid TD-HRGC-HRMS method, combining some outstanding state-of-the-art techniques, made it possible to detect PCB adsorbed on Twister by atmospheric sampling. Under the established desorption conditions, good repeatability and high analyte recoveries were received. Figure 3 shows the amount of some selected Ballschmiter PCB in dependence on exposure time. Site A Twister accumulate obviously higher amounts of PCB and show more fluctuations than the Twister at site B. This is because of the occasional combustion experiments at site A, during which the Twister were taken out off the container.

Thermal desorption, chromatography and detection take directly place and no labour-intensive sample clean-up is required. Fast analysis, high sample throughput, no solvent consumption and a high sensitivity support further investigations in the field of air sampling.

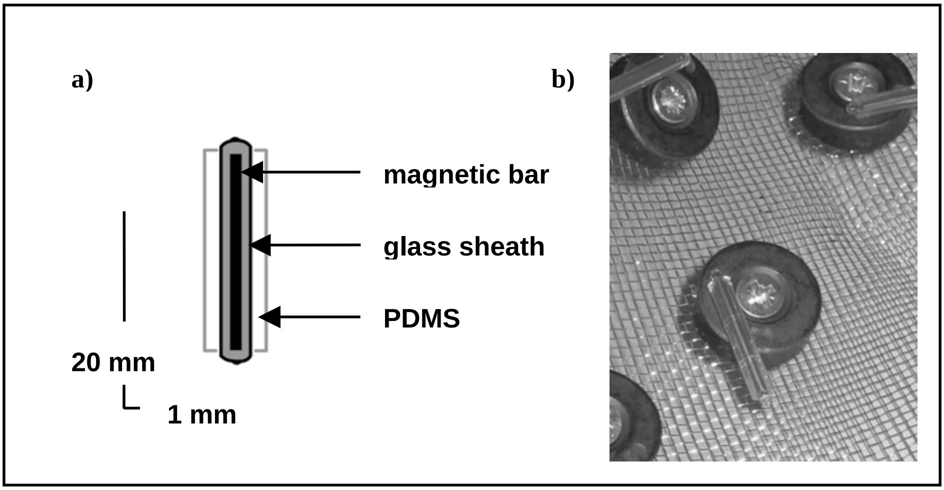

Figure 1: a) Schematic sketch of a stir bar Twister coated with a 1mm thick layer of polydimethylsiloxane. **b)** For exposition Twister were deposed in wire cages. The picture shows some Twister fixed on magnetic disks inside a wire net.

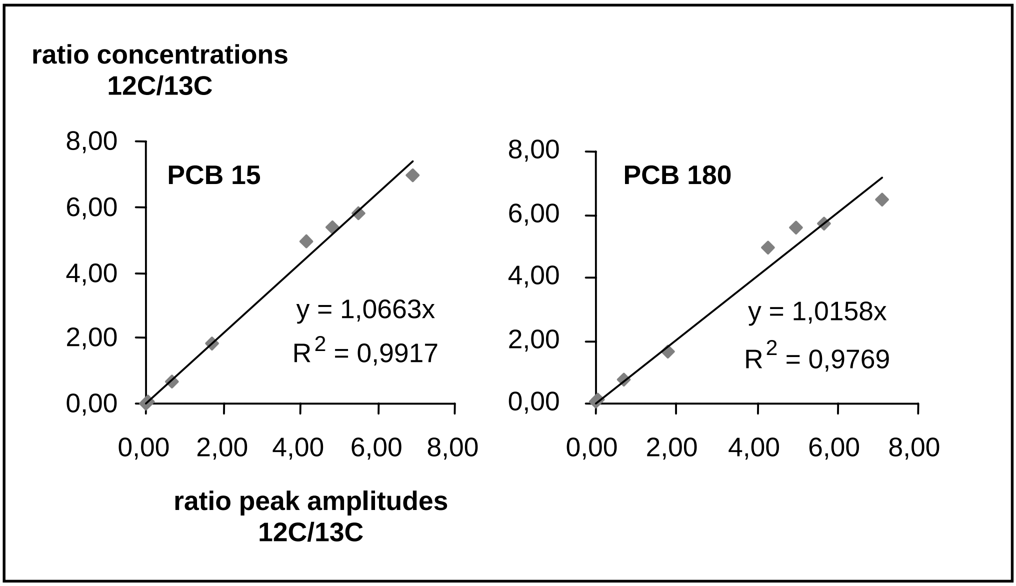

Figure 2: The graphics show exemplary the calibration curves for PCB 15 and PCB 180 (Ballschmiter No.).

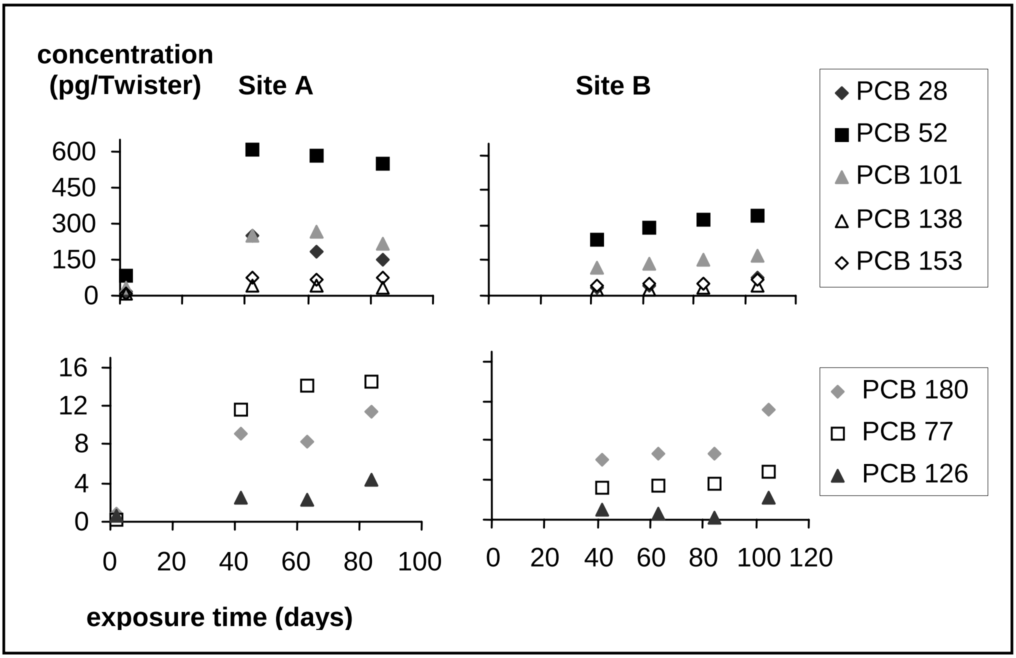

Figure 3: The diagram shows the thermal desorbed amount of some selected PCB (Ballschmiter No.) in dependance on duration of exposure and sampling site.

desorption temperature	280°C		**300°C**	
desorption time	3min	5min	**6min**	8min
cryofocussing temperature	-100°C	**-30°C**	0°C	20°C
desorption He-flow	**70ml/min**		90ml/min	

Table 1: Tested PCB desorption conditions; bold-typed data yield best analyte transfer and were chosen for future experiments. The difference between 6min and 8min desorption time is negligible so that the shorter time-saving and PDMS-preserving value was selected.

References

1. Petty, J.D., Huckins J.N., and Zajicek, J.L. (1993) Chemosphere 27(9), 1609.
2. Ockenden, W.A., Corrigan, B.P., Howsam, M., and Jones, K.C. (2001) Environ. Sci. Technol. 35, 4536.
3. Vercauteren, J., Pérès, C., Devos, C., Sandra, P., Vanhaecke, F., and Moens, L. (2001) Anal. Chem. 73, 1509.
4. León, V.M., Álvarez, B., Cobollo, M.A., Muñoz, S., Valor, I. (2003) J. Chromatogr. A 999, 91.
5. Baltussen, E., Sandra, P., David, F., and Cramers, C.A. (1999) J. Microcol. sep. 11(10), 737.
6. Baltussen, E., Cramers, C.A., and Sandra, P. (2002) Anal. Bioanal. Chem. 3, 373.
7. Arthur, C.L. and Pawliszyn, J. (1990) Anal. Chem. 62, 2145.