Chemosphere 106 (2014) 51–56

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Trace analysis of hydrophobic micropollutants in aqueous samples using capillary traps

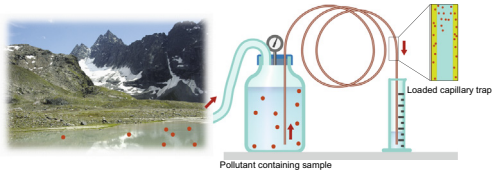
Pavlina Aneva Pavlova [a,b,c], Peter Schmid [a], Markus Zennegg [a], Christian Bogdal [d], Margit Schwikowski [b,c,e,*]

[a] Empa, Swiss Federal Laboratories for Materials Testing and Research, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
[b] PSI, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
[c] Oeschger Centre for Climate Change Research, University of Berne, Berne, Switzerland
[d] Institute for Chemical and Bioengineering, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland
[e] Department of Chemistry and Biochemistry, University of Berne, Berne, Switzerland

## HIGHLIGHTS

- A novel method for analysis of hydrophobic compounds in aqueous samples.
- PDMS coated open capillary trap for retention of the analytes.
- Interference-free, small sample volumes, resource-saving, easy-handling.
- Robust and widely applicable.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 2 September 2013
Received in revised form 18 December 2013
Accepted 30 December 2013
Available online 18 February 2014

*Keywords:*
PDMS
Micropollutants
POPs
Aqueous samples
GC–MS

## ABSTRACT

Studying the fate of persistent organic pollutants (POPs) in glacier environments scientist face the challenge of snow and ice samples, in which concentrations of these pollutants are at the ultra-trace level and the amount of sample available is often very limited. We have improved an extraction method for hydrophobic organic pollutants such as polychlorinated biphenyls (PCBs) in aqueous media to meet the requirements of these challenging samples. It is based on partitioning of the analytes from the water into the polydimethylsiloxane (PDMS) coating of an open tubular-fused-silica capillary. By comparison with conventional liquid-liquid extraction, we validated the method for six indicator PCBs, covering a wide range of polarity. The new method has very low detection limits of 10–20 pg/L for the investigated PCBs, a small uncertainty between 9% and 37%, depending on concentration, and requires a small sample volume of less than one liter. Further, it is characterized by easy handling and reduced organic solvents consumption. The method is comparatively insensitive to contamination, reproducible, and suitable for a wide range of applications.



## 1. Introduction

Persistent organic pollutants (POPs) represent a group of anthropogenic organic substances, including industrial chemicals, pesticides, as well as unintentional by-products of combustion processes and chemical reactions, which have been regulated by the UN Stockholm Convention since 2004. Due to their widespread use in the past, their resistance to environmental degradation, and potential for bioaccumulation, POPs became ubiquitous in the environment, even far away from their initial emission sources. Remobilization processes such as volatilization, erosion and leaching into water bodies lead to widespread distribution in the environment. Depending on the environmental compartment detection of these compounds may pose considerable analytical

* Corresponding author at: PSI, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland. Tel.: +41 56 310 41 10.
*E-mail address:* margit.schwikowski@psi.ch (M. Schwikowski).

http://dx.doi.org/10.1016/j.chemosphere.2013.12.092
0045-6535/

challenges. Whereas for certain matrices such as soil, sediment, and biological tissue extraction methods of hydrophobic compounds such as polychlorinated biphenyls (PCBs) are well established, determination in water is still a demanding task. Due to extremely low concentrations ultra-trace analytical methods require enrichment steps, which are prone to interferences of these compounds ubiquitous also in the laboratory environment.

The existing methodical approaches can be divided into liquid and solid phase extraction methods. The laborious liquid–liquid extraction (LLE), being the classical method for analysis of POPs in aqueous samples, usually requires large sample volumes (up to dozens of liters) and high amounts of organic solvents, leading to relatively high blank values, because of the extensive glass surfaces in contact with the sample. Still, LLE is appreciated for its robustness, wide range of application, and the relatively high analyte recovery rates, as well as the fact that both dissolved and particulate analytes are covered (Gregor and Gummer, 1989; Barra et al., 2005; Finizio et al., 2006). Solid phase extraction (SPE) is the alternative approach consisting in enrichment of the analytes on or in a solid extraction medium, from which they are subsequently released. The solid extraction phase may be a chromatographic packing material or a coating absorbing the analytes. SPE using packed cartridges is easy to perform, although, because of the vast surface of the adsorbent, it implies risks of adsorption losses and contamination (Carrera et al., 2001; Hermanson et al., 2005; Zhang et al., 2011).

Other SPE techniques are based on supports of different geometry coated with a stationary extraction phase such as polydimethyl siloxane (PDMS), which absorbs the analytes from the aqueous sample. The most common techniques used are solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE). SPME is based on partitioning of analytes between a coated fused silica fiber and the sample, following thermal desorption in the injector of a gas chromatograph (GC) (Pawliszyn, 1997). In SBSE a magnetic stir bar with a PDMS coating adsorbs the analytes from an aqueous sample (Baltussen et al., 1999; Nogueira, 2012). However, this technique requires specific instrumentation and, as reported by Lung et al., intensive continuous stirring enhances contact of the aqueous phase with the container walls, which may result in unaccounted adsorptive losses of the analytes (Lung et al., 2000).

Trap columns are short open tubular columns coated with immobilized PDMS, which absorbs hydrophobic analytes while purging the aqueous samples. Thermal desorption and detection of the analytes is conducted by mounting the trap in a GC as a pre-column to the analytical column and applying a chromatographic temperature program (Grob and Schilling, 1985; Russo et al., 2001; Nardi, 2003). In solid phase dynamic extraction (SPDE), which is based on the same principle, the aqueous sample is drawn into a syringe and expelled through a syringe needle coated with PDMS. The analytes are subsequently desorbed by injection of a flush gas at reduced pressure from the sampling syringe into the hot GC injector (Lipinski, 2001). All the above mentioned techniques are practicable for samples volumes up to 100 mL.

In an ongoing project on the behavior of POPs in glacier environments, selected POPs are to be determined in ice samples (Bogdal et al., 2009; Schmid et al., 2011). This calls for extraction methods suitable for limited sample volumes in the range of 1 L, for which the above mentioned techniques are inadequate. Furthermore, many environmental contaminants are characterized by their ubiquitous occurrence, which is a pitfall also for the sample handling in the laboratory. Thus, an optimal enrichment method should feature (i) low susceptibility to background contamination, (ii) minimal contact of aqueous samples with surfaces, (iii) capacity for sample volumes in the range of 1 L, (iv) easy handling, and (v) minimized consumption of resources in compliance with green analytical chemistry.

To meet these requirements, a new approach based on capillary traps was developed. Extraction was directly performed from the sample container, i.e. no sample transfer was necessary. In contrast to previously applied thermal desorption, target analytes are eluted by a suitable solvent directly into a GC sample vial avoiding any additional contact with potentially contaminated surfaces and enabling multiple analyses of the same sample by injection of aliquots.

## 2. Materials and methods

### 2.1. Chemicals and reference materials

All solvents used were of pesticide residue analysis grade. Reference indicator PCBs (i-PCBs, mixture of PCB 28, 52, 101, 138, 153, and 180) were purchased from AccuStandard Inc., New Haven, CT, USA. $^{13}C_{12}$-labeled i-PCBs and $^{13}C_{12}$-labeled PCBs 70 and 111 were from Cambridge Isotope Laboratories, Andover, MA, USA. The recovery standard mixture PCB ISS-H, Wellington Laboratories, contains $^{13}C_{12}$-labeled PCB 37, 79, 162 (see also Table 1, Supplementary data).

### 2.2. Preparation of trap capillaries

Fused silica tubing of 0.32 mm inner diameter (BGB, Boeckten, Switzerland) was coated with a film of vinyl terminated PDMS PS-255 (Fluka, Buchs, Switzerland). Coating of the capillary tubing and immobilization of the stationary phase using dicumyl peroxide as a cross-linker was based on methods described by Grob (1986). The degree of immobilization was measured gravimetrically in the eluate after rinsing the coated capillary with diethyl ether and dichloromethane. Starting from a target value of 2.5 μm an extractable loss of 18% of the phase resulted in a remaining film thickness of 2.1 μm.

Commercially available capillary fused silica GC columns coated with an immobilized PDMS stationary phase may be used as well. Based on the following considerations in Section 2.4. (calculation of PCB retention volumes in the capillaries), the thickness of the coating should be in the range of 2 μm and sufficient immobilization should previously be tested by rinsing as described above.

### 2.3. Preparation of glassware

Glassware was immersed in an alkaline bath (RBS35 5% Fluka, Buchs, Switzerland) for 12 h, subsequently washed in a glassware washer with RBS50 (Fluka, Buchs, Switzerland) and baked out at 450 °C in a muffle furnace overnight. Glass containers were rinsed with a solvent mixture (acetone, *n*-hexane, methanol 1:1:1 v/v) immediately before use.

### 2.4. Extraction of water samples

Hydrophobic analytes in a water sample partition into the PDMS coating (stationary phase) of a short open tubular column. Based on the assumption that the mobile phase (water sample) and the stationary phase are in equilibrium, retention can be described by the partition coefficient $K_{sm}$ between the two phases, which represents the ratio of the analyte concentrations in both phases (Eq. (1)).

$$K_{sm} = c_s/c_m \quad (1)$$

$c_s$ and $c_m$ are the concentrations of the analyte in the stationary and mobile phase, respectively. The retention of extracted analytes depends on the volumetric phase ratio $\beta$ (Eq. (2)).

$$\beta = V_m/V_s \quad (2)$$