



## Design and testing of a new sampler for simplified vacuum-assisted headspace solid-phase microextraction<sup>☆</sup>



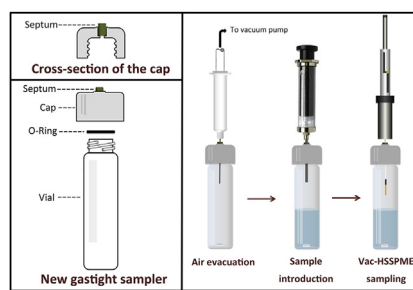
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### HIGHLIGHTS

- We describe a new, low-cost and simplified gastight sampler for Vac-HSSPME.
- All Vac-HSSPME operations are performed through the septum of one port.
- The device is tested for the water analysis of polychlorinated biphenyls.
- Very good sensitivity achieved within short sampling times and mild conditions.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The design and testing of a new and low-cost experimental setup used for vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME) is reported here. The device consists of a specially designed O-ring seal screw cap offering gas-tight seal to commercially available headspace vials. The new polytetrafluoroethylene (PTFE) cap was molded by a local manufacturer and had a hole that could tightly accommodate a septum. All operations were performed through the septum: air evacuation of the sampler, sample introduction and HSSPME sampling. The analytical performance of the new sampler was evaluated using 22 mL headspace vials with 9 mL water samples spiked with polychlorinated biphenyls (PCBs). Several experimental parameters were controlled and the optimized conditions were: 1000 rpm agitation speed; 30 min extraction time; 40 °C sampling temperature; polydimethylsiloxane-divinylbenzene (PDMS-DVB) fiber. The lack of accurate Henry's law constant ( $K_H$ ) values and information regarding how they change with temperature was a major limitation in predicting the phase location of evaporation resistance during Vac-HSSPME. Nevertheless, the combined effects of system conditions indicated the increasing importance of gas phase resistance with increasing degree of PCBs chlorination. Stirring enhancements were not recorded for the higher chlorinated PCBs suggesting that the hyperhydrophobic gas/water interface was the preferred location for these compounds. Analytically, the developed method was found to yield linear calibration curves with limits of detection in the sub ng L<sup>-1</sup> level and relative standard deviations ranging between 5.8 and 14%. To compensate for the low recoveries of the higher chlorinated PCB congeners in spiked river water the standard addition methodology was applied. Overall, the compact design of the new and reusable sample container allows efficient HSSPME sampling of organic analytes in water within short extraction times and at low sampling temperatures compared to other published HSSPME methods.

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## 1. Introduction

Introduced in the early 1990s, solid-phase microextraction (SPME) proved to be a simple, sensitive, time-efficient and solvent less sample preparation technique that established the basis for the development of many subsequent equilibrium-based methods [1–3]. In SPME, the extraction phase can be exposed directly to the sample media (direct immersion, DI) or to its headspace (HS); the latter being advantageous for complex matrices and/or analytes characterized by high Henry's law constants ( $K_H$ ) [2]. Different strategies exist so as to enhance HSSPME extraction kinetics of less volatile analytes and/or compounds with lower  $K_H$  values, and these include: applying agitation, ensuring a large sample/headspace interface, increasing the sampling temperature and/or, ultimately, heating the sample and cooling the extraction phase at the same time (cold fiber HSSPME approach) [2–6].

Next to these strategies, applying reduced pressure conditions during the non-equilibrium stage of HSSPME sampling was also found to dramatically improve extraction kinetics for organic compounds having a low  $K_H$  value [7–14]. By using the two-film theory and the assumption that the overall resistance to mass transfer results from resistances through the two thin films (gas and liquid) adjacent to the gas/liquid interface, we have postulated that for compounds close or below the reported threshold values for low  $K_H$  solutes (i.e.  $1.2 \cdot 10^{-5}$  atm m<sup>3</sup> mol<sup>-1</sup> for low  $K_H$  compounds and  $1.6 \cdot 10^{-4}$  atm m<sup>3</sup> mol<sup>-1</sup> for solutes where gas and liquid phase resistances are approximately equal (1 atm =  $1.01 \cdot 10^5$  Pa)), mass transfer resistance in the thin gas-film adjacent to the gas/sample interface controls evaporation rates and reducing the total pressure will result in a faster overall extraction process [11,12]. At the same time, sampling under reduced pressure conditions is not expected to improve extraction rates compared to regular HSSPME when equilibrium conditions are readily attained or when sampling high  $K_H$  compounds in which case mass transfer resistance is located in the thin liquid-film adjacent to the gas/sample interface and as such is independent of the pressure conditions in the headspace [11].

The first sampler used for HSSPME under reduced pressure conditions used a 20 mm polytetrafluoroethylene (PTFE)-coated silicone rubber septum to seal a 100 mL screw-neck conical flask and all operations (sample introduction followed by air evacuation of the sample container and HSSPME sampling) were performed through the silicone rubber septum [7]. Reduced pressure HSSPME sampling at room temperature of volatiles from either raw turkey homogenate or aqueous standards using this device resulted in a remarkable enhancement in chromatograms compared to atmospheric pressure. Nonetheless, the authors reported a slight increase in pressure after a 30 min sampling. The effect was reported as quite reproducible but was not quantified and other analytical figures of merit were not investigated most probably because it was not a central aim of this work [7]. A later report dealing with the effect of reduced pressure conditions on HSSPME sampling used a modified 50 mL conical flask with a welded glass tube on the side to allow air evacuation of the device and a welded open vial at the top to allow sealing with a PTFE-coated silicone rubber septum and HSSPME sampling [8]. Based on the extraction time profiles of butyl and phenyltin compounds presented in these studies we assume that sampling conditions were not constant for extraction times longer than 15 min when using this extraction setup. In another report, reduced pressure HSSPME sampling of fixed surfaces and at room temperature was possible with a device referred to as field vacuum extractor consisting of a modified 30 mL plastic syringe capable of creating an enclosed volume over solid surfaces [9]. More recently, a home-designed manually operated cylinder chamber and piston device (total volume 600 mL) was used to

sample the volatile components of a solid sample (cigarette tobacco leaves) and a liquid sample (fresh mulberry juice) and demonstrated the remarkable improvement in HSSPME sensitivity under reduced pressure conditions compared to atmospheric [10].

Introducing aqueous samples into pre-evacuated sample containers followed by HSSPME sampling was first reported in 2012 [11]. At the time, the so-called vacuum-assisted HSSPME (Vac-HSSPME) used a 1000 mL commercially available sample container equipped with three ports (two high vacuum glass stopcocks and a port with a half-hole cylindrical septum compatible with the needle of the SPME device) to ensure constant reduced pressure conditions for HSSPME sampling times up to 150 min. Vac-HSSPME sampling was performed in the static mode since the small openings of the three ports did not allow the introduction of magnetic stir bars that could lead to efficient sample agitation. To overcome agitation restrictions imposed by the commercially available 1000 mL sampling chamber, custom-made glass sample containers (500 mL and 1000 mL) were then constructed having a high vacuum glass stopcock for connecting to the vacuum pump, a port equipped with septum used for introducing the SPME device and an auxiliary gas-tight port offering additional access to the sampling chamber and easy handling of the magnetic stir bar [12]. In a subsequent report, the extraction device for HSSPME sampling under reduced pressure conditions was downsized for the first time to 22 mL [13]. The custom-made gas-tight sample container was built from a 20 mL headspace rounded bottom glass vial, further modified to accommodate on the top part two gas-tight ports: one high vacuum glass stopcock and one glass port equipped with a septum for introducing the SPME device. Downsizing Vac-HSSPME enabled practical and effortless application of the method and allowed efficient sampling of aqueous and solid samples [13,14]. In addition, for those analytes that reach equilibrium within a reasonable amount of time, reducing the size of the sample container and accordingly the volume of the headspace also increased the final amount of analyte extracted by the fiber as predicted by the theory [13].

This contribution reports the design and testing of a new and breakthrough experimental setup for Vac-HSSPME, consisting of a specially designed O-ring seal screw cap with a hole that can accommodate a half-hole cylindrical septum. The cap is made of PTFE and offers gas-tight seal to commercially available screw thread 22 mL headspace vials. All operations are performed through the septum of the screw cap: air evacuation of the sample container, sample introduction and HSSPME sampling. The performance of this new, simple and reusable sample container was tested using polychlorinated biphenyls (PCBs) as model compounds. Several experimental parameters were controlled and optimized and the results were compared to those obtained with regular HSSPME. The contributions of system conditions and analyte properties on Vac-HSSPME were used to discuss and evaluate the results. Finally, the performance of the resulting method was assessed and matrix effects upon extraction were evaluated.

## 2. Materials and methods

### 2.1. Chemicals

An analytical standard solution containing 10 mg L<sup>-1</sup> of 2,4,4'-PCB (PCB-28), 2,2',5,5'-PCB (PCB-52), 2,2',4,5,5'-PCB (PCB-101), 2,2',3,4,4',5-PCB (PCB-138), 2,2',4,4',5,5'-PCB (PCB-153) and 2,2',3,4,4',5,5'-PCB (PCB-180) in iso-octane was obtained from Sigma-Aldrich (Steinheim, Germany). Working standard solutions were prepared by evaporating an aliquot of the analytical standard solutions under a gentle stream of nitrogen gas. After evaporation the volume was completed with acetone to a final concentration of

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