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Polyelectrolyte coatings prevent interferences from charged nanoparticles in SPME speciation analysis

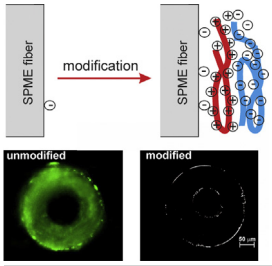
Katarzyna Zielińska *, Herman P. van Leeuwen

Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703HB Wageningen, The Netherlands

HIGHLIGHTS

- For the first time SPME fiber is coated with polyelectrolyte layer.
- Sorption of nanoparticles on the solid phase surface is prevented.
- Polyelectrolyte-modified fiber enables extraction of free analyte in presence of sorbing nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we present a new approach for protection of the fiber in solid phase microextraction (SPME) from interfering charged particles present in the sample medium. It involves coating of commercial poly (dimethylsiloxane) extraction phase with polyelectrolyte layer composed of poly(diallyldimethylammonium chloride), and poly(sodium 4-styrenesulfonate). The modified fiber provides reproducible, convenient and fast extraction capabilities toward the model analyte, triclosan (TCS). A negatively charged polyelectrolyte coating prevents sorbing oxidic nanoparticles from both partitioning into the PDMS phase and aggregation at its surface. The results for the TCS/nanoparticle sample show that the polyelectrolyte layer-modified solid phase extracts just the free form of the organic compound and enables dynamic speciation analysis of the nanoparticulate target analyte complex.

1. Introduction

Since its introduction by Artur and Pawliszyn [1], solid phase microextraction (SPME) gained a lot of attention as a solvent-free, fast and simple sampling/preconcentration technique [2,3]. It is based on the partitioning of freely dissolved organic molecules between the sample solution and a polymer solid phase. The amount of extracted analyte is analyzed by an appropriate analytical technique, usually one of the common chromatographic methods, e.g., gas chromatography [4–6] or high-performance liquid chromatography [7,8] and then related back to their respective concentrations in the sample via an appropriate calibration method. In the case of complex samples, containing both free and bound forms of the target analyte, the equilibrium analyte concentration in the solid phase is correlated with the freely dissolved form [9–11]. The latter form is often considered to associate with the accumulation in organisms and hence it is important from pharmacological and toxicological points of view [6,10,12]. In connection with this, time-dependent SPME has been further developed [13,14] as a tool for dynamic speciation analysis of organics in complex samples.

It has already been shown that the presence of sorbing entities may influence the accumulated analyte concentration (since only the free form is accumulated) and change extraction kinetics (e.g., by labile complexes which contribute to the analyte transport) [9,14]. Another complication may ensue from sample components like proteins [10], humic acids [9], and nanoparticles [15], that not only form complexes with the target analyte but also partition into

* Corresponding author. Tel.: +48 696917406.
E-mail address: kzielinska@gmail.com (K. Zielińska).

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the solid phase and/or are sorbed at its surface (often denoted as "fouling" [10,12]). Therefore, a substantial number of studies have been devoted to search for ways to improve the performance of SPME in complex samples. Solutions like sample pretreatment and clean-up, preparation of new biocompatible extraction phases [16,17] and employment of a protective membrane around the solid phase [18] have been suggested.

Herein we propose a new method for modification of the commercial SPME fiber element in order to make it suitable for straightforward speciation analysis of organics in the presence of charged, sorbing nanoparticles. Our approach involves the deposition of a polyelectrolyte coating with a negative top layer which prevents negatively charged particles in the sample medium to approach the solid phase. Such polyelectrolyte-modified fibers are tested in the SPME analysis of the model organic compound triclosan, in the presence of its negatively charged complexes with SiO_2 nanoparticles.

2. Experimental

2.1. Chemicals and materials

Triclosan (TCS, purity>97%), Ludox LS silica nanoparticles (mean radius of 7.5 nm [19], molar mass M computed as ca. 200,000 [13]), poly(sodium 4-styrenesulfonate) (PSS, 30% in water, M ~70,000), poly(diallyldimethylammonium chloride) (PDDA, 20% in water, M ~150,000), sodium chloride (≥99%), hydrogen peroxide (30 wt.% in H_2O), hydrogen chloride (≥99%), nitric acid (≥69%), acetone (for HPLC, ≥99.9%), ethanol (for HPLC, ≥99.9%), and LC–MS grade methanol were obtained from Sigma–Aldrich. Spherical SiO_2 nanoparticles with a radius of 10 nm (labeled with covalently bound fluorescein isothiocyanate) were purchased from Corpuscular Inc., cylindrical poly(dimethylsiloxane), PDMS fibers (with a glass core) were obtained from Poly Micro Industries (Phoenix, AZ). The PDMS layer had inner and outer diameters of 110 and 210 μm, respectively. Both polyelectrolytes (10 mol m^{-3} with respect to the monomer unit) were dissolved in ultrapure water (resistivity >18 MΩ cm, Millipore). NaCl was added to a final concentration of 2×10^2 mol m^{-3} and the pH was set at 6.5. The obtained solutions were passed through a 0.45-μm syringe filter.

2.2. Modification of PDMS surface

The scheme of the modification procedure is presented in Fig. 1. The commercial PDMS fibers were cut to a length of 2 cm and cleaned with methanol. They were oxidized in a mixture of H_2O/H_2O_2/HCl (volume ratio of 5:1:1) for 5 min and rinsed with Millipore water [20]. Then the PDMS solid phase was precoated with a cationic polyelectrolyte layer by placing it for 10 min in PDDA solution. These pretreatment steps are essential in obtaining good adherence of the negative outer layer. The excess of unbound PDDA was removed by rinsing with Millipore water. Next an anionic polyelectrolyte PSS layer was adhered to the PDDA-covered PDMS surface, thus completing the cycle of building an alternate polycation/polyanion coating. In the course of optimizing the procedure we varied parameters like polyelectrolyte type as well as salt content and pH. For details see the Supporting Information.

2.3. Confocal laser scanning microscopy (CLSM)

In order to verify the effectiveness of the proposed solid phase modification, polyelectrolyte-coated and unmodified fibers were exposed to SiO_2 nanoparticles with covalently bound fluorescence label (pH 5.0, ionic strength 1 mM, nanoparticles concentration of 8.2×10^{-3} mol m^{-3}). After 3 h of exposure, confocal laser scanning microscopy (CLSM) images were acquired using a Zeiss Axiovert 200M microscope (Carl Zeiss, Germany) equipped with an argon laser set at 488 nm (detailed procedure in Ref. [15]). In order to check whether any release of dye from fluorescent-labelled SiO_2 NPs occurs, the nanoparticle suspension was transferred to a dialysis cell (cut-off 50,000 Da, Spectra/Por Dialysis) and dialyzed for 2 days against ultrapure water. The fluorescence intensity of the dialysate was measured (CLSM Zeiss Axiovert 200M, excitation wavelength 488 nm) every 2 h and no free dye was detected at any time of experiment.

2.4. SPME measurements

Sample solutions of the test analyte triclosan (TCS) were prepared by spiking Millipore water with TCS dissolved in methanol and adding aliquots of a standard Ludox LS nanoparticles dispersion. Using nitric acid, the dispersions were adjusted to pH 5.0 as a compromise between sufficient negative charge on the nanoparticles (increasing with increasing pH) and sufficient sorption affinity for triclosan (increasing with decreasing pH). Each individual polyelectrolyte-modified PDMS was exposed to 10 cm^3 sample, containing triclosan (3.4×10^{-2} mol m^{-3}) or to TCS/SiO_2 nanoparticle dispersion (nanoparticle concentration 8.2×10^{-3} mol m^{-3}), under mild stirring on a rock-and-roller shaker (Meettech, NL) at ambient temperature in the laboratory (20 ± 2 °C). Fibers were floating freely in the sample medium and after varying times they were removed and rinsed in Millipore water. Each fiber was used just once. The amount of TCS accumulated by the solid phase was determined by means of

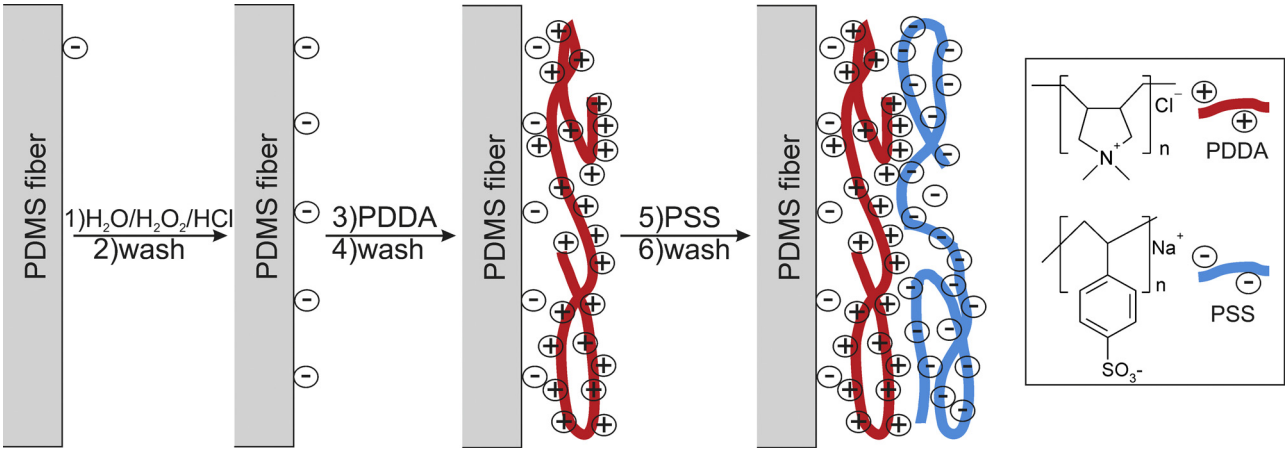

Fig. 1. The modification procedure of the PDMS extraction phase.