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Sol–gel-coated oligomers as novel stationary phases for solid-phase microextraction

Chanbasha Basheer, Subbiah Jegadesan, Suresh Valiyaveettil *, Hian Kee Lee *

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

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Abstract

Amphiphilic and hydrophilic oligomers were synthesized and coated on fused silica capillaries using a sol–gel technique. Sol–gel-coated capillaries were evaluated for the solid-phase microextraction and preconcentration of a wide variety of non-polar and polar analytes. Both types of coatings were stable under high temperature (up to 280 °C). The extraction efficiency of the sol–gel coatings was evaluated for the extraction of both non-polar and polar analytes, including organochlorine pesticides, triazine herbicides, estrogens and alkylphenols (APs) and bisphenol-A (BPA). Compared with commercially available solid-phase microextraction (SPME) adsorbents such as poly(dimethylsiloxane)-divenylbenzene and polyacrylate, the new materials showed comparable selectivity and sensitivity towards both non-polar and polar analytes. The new coatings gave good linearity and detection limits. For example with triazines, a detection limit of <0.005 $\mu l\,l^{-1}$, precision from 5.0 to 11.0% ($n = 6$) and linearity of the calibration plots (0.5 to 50 $\mu l\,l^{-1}$) were obtained. The sol–gel coated SPME capillaries were used for the determination of triazine herbicides in reservoir water samples collected in Singapore.

Keywords: Solid-phase microextraction; Sol–gel; Herbicides; Pesticides and alkylphenols; Bisphenol-A

1. Introduction

Since solid-phase microextraction (SPME) was introduced by Belardi and Pawliszyn [1] in 1989, the technique has developed very rapidly in the past decade. SPME uses polymer-coated fibers to extract analytes from aqueous or gaseous samples. After extraction, the analytes are either desorbed thermally by exposing the fiber in the injection port of a gas chromatograph (GC) or chemically desorbed and analysed by liquid chromatography [2]. This convenient and solvent-free extraction method is sensitive, inexpensive and portable, and has been successfully applied to the analyses of many complicated samples, such as milk, sludge [3], soil [4], blood and urine [5].

Up to now, only seven types of SPME coatings are commercially available: polydimethylsiloxane (PDMS), PDMS–divinylbenzene (DVB), polyacrylate (PA), carboxen–PDMS, carbowax (CW)–DVB, carbowax–templated resin, and DVB–carboxen–PDMS (StableFlex) [6]. The PDMS is a non-polar phase, which is commonly used for extracting non-polar analytes, such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls and polybrominated biphenyls [7–9]. The PA fiber is used for phenols [10,11], estrogens [12], fatty acids [13] and organophosphorous pesticides [14]. The PDMS–DVB fiber is used for moderately polar compounds such as triazine herbicides [15–17]. The CW–DVB fiber is more polar, but its low temperature stability (265 °C) limits its application range.

Commercial SPME sorbent coatings have generally good extraction properties; however, some aspects of their performance can be improved. For example, incomplete sample desorption that causes carry-over problems and a reduction of the lifetime of the fibers due to direct extraction of higher salt content samples and complex matrices, have been reported in the literature [11,18]. The latter problem arises due to the physical deposition of the polymer on the fiber. In terms of durability, chemical bonding of the sorbent material is recommended [19].

* Corresponding authors. Tel.: +65 6874 4327; fax: +65 6779 1691.
E-mail addresses: chmsv@nus.edu.sg (S. Valiyaveettil), chmleehk@nus.edu.sg (H.K. Lee).

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Malik and co-workers [20–22] established a simple and convenient pathway for surface coatings using sol–gel technology. Sol–gel chemistry can provide efficient incorporation of organic components into inorganic polymeric structures in solution under mild thermal conditions [21,22]. The major inherent advantages of sol–gel technology are: (a) low costs, (b) high thermal stability, (c) porous structure of coating and (d) strong adhesion of the coating to the substrate due to chemical bonding. For example, sol–gel-coated PDMS fiber can be used up to 320 °C; whereas the conventional PDMS coating starts to decompose at 200 °C [23]. Additionally, the fiber coating thickness plays an important role to determine fiber capacity. Analytical sensitivity can be increased with increased thickness of the coating [11]. The sol–gel coating procedure permits control of the thickness more effectively and is suitable for the preparation of SPME coatings [19–22].

Amphiphilic oligomers/polymers provide advantages towards the extraction of the mixture of both polar and non-polar compounds than conventional polymers. They have dual (polar and non-polar) functional groups and work more efficiently for mixed target analyte mixtures. In this work, amphiphilic and hydrophilic oligomers coated-SPME fibers were prepared using a sol–gel procedure. The oligomer coated-SPME fibers were evaluated for the analysis of a wide range of polar and non-polar organic pollutants from environmental samples. Extraction parameters, with specific reference to triazine herbicides, such as extraction temperature, time, pH, and extraction efficiency were investigated.

2. Experimental

2.1. Materials and reagents

Silicon capillary tubes (77 μm I.D. and 194 μm O.D.) were purchased from Polymicro Technologies (Phoenix, AZ, USA) for sol–gel coating. The SPME holder for manual sampling was obtained from Supelco (Bellefonte, PA, USA). The SPME fiber holder and fibers (PDMS–DVB and PA) were used without modification and used for comparison with the prepared oligomer coated-capillaries. Before extraction, the fibers were conditioned in the GC injection port based on the manufacturer's recommended procedure. Tetraethoxysilane (TEOS) and ammonium hydroxide were purchased from Aldrich (Allentown, PA, USA). All solvents used in this study were of analytical-reagent grade. Organochlorine pesticides (PolyScience, Niles, IL, USA), triazine herbicides (Dr. Ehrenstorfer GmbH, Augsburg, Germany), estrogens (Sigma–Aldrich, St. Louis, MO, USA), and alkylphenols (APs) and bisphenol-A (BPA) (Wako, Tokyo, Japan), were used for evaluating the extraction efficiency of oligomer-coated fibers. Triazine herbicides were considered for the quantitative analysis of aqueous samples. In the qualitative study, comparisons were made between the commercial sorbent coating materials with our sol–gel-coated sorbent fibers. Ultrapure water was prepared on a Milli-Q (Millipore, Milford, MA, USA) system. A standard stock solution of 50 μg ml^{-1} of each analyte was prepared in acetone and diluted to 1 μg ml^{-1} of each analyte for analysis.

2.2. Instrumentation

Sample analyses were carried out using a Shimadzu (Tokyo, Japan) QP2010 gas chromatography–mass spectrometry (GC–MS) system equipped with a Shimadzu AOC-20i auto sampler and a DB-5 fused silica capillary column 30 m × 0.32 mm I.D., film thickness 0.25 μm (J&W Scientific, Folsom, CA, USA). Helium (purity 99.9999%) was used as the carrier gas at a flow rate of 1.5 ml min^{-1} and a split ratio of 20. Samples (2 μl) were injected in splitless mode with an injection time of 2 min. For the analysis of OCPs and triazine herbicides, the GC–MS conditions were optimized. The injection temperature was set at 250 °C and the interface temperature at 280 °C. The GC–MS temperature programme used was as follows: initial temperature of 60 °C was held for 2 min, then increased to 250 °C at a heating rate of 30 °C min^{-1}, followed by another ramp of 30 to 280 °C min^{-1}. The later temperature was held for 2 min. For phenols, pressure programming was used to resolve the peaks. The pressure programme was as follows: carrier gas pressure 40 kPa (for 5 min), then increased by 2 kPa min^{-1} to 70 kPa, held for 7 min. All standards and samples were analysed in selective ion monitoring (SIM) mode with a detector voltage of 1.5 kV and a mass scan range of *m*/*z* 50–500.

2.3. Synthesis of amphiphilic and hydrophilic oligomers

The hydrophilic (**1**) and amphiphillic (**2**) oligomers were synthesized as described in Fig. 1. The palladium (Pd)-catalyzed aryl-aryl cross coupling between boronic acid and bromine functional groups provided the oligomers 3,5′,3″-trisbenzyloxy-2′-dodecyloxy-[1,1′;4′,1″]terphenyl and 2′,5′-bisbenzyloxy-[1,1′;4′,1″]terphenyl (Fig. 1). Then debenzylation of these oligomers **6** and **9** was carried out using 10% Pd/C as catalyst. The oligomers were purified via recrystallization from acetone.

2.4. Preparation of SPME fiber

Before coating the stationary phase on a silica capillary tubes, the protective polyimide layer was removed from the silica capillary by dipping it in acetone for several hours. This was followed by the immersion of fiber in 1 M NaOH solution for 1 h to form silanol groups on the surface of the capillary. The capillary was then cleaned with water and placed in a 0.1 M HCl solution for 20 min to neutralize the excess NaOH, rinse with water and dried. The sol–gel was prepared as follows: 14 mg of the oligomer was weighed and dissolved in 300 μl of tetrahydrofuran. To this solution, 100 μl of TEOS was added, followed by 36 μl of distilled water and 200 μl of ammonium hydroxide as catalyst to initiate the hydrolysis. This mixture was sonicated for 5 min to accelerate the gela-

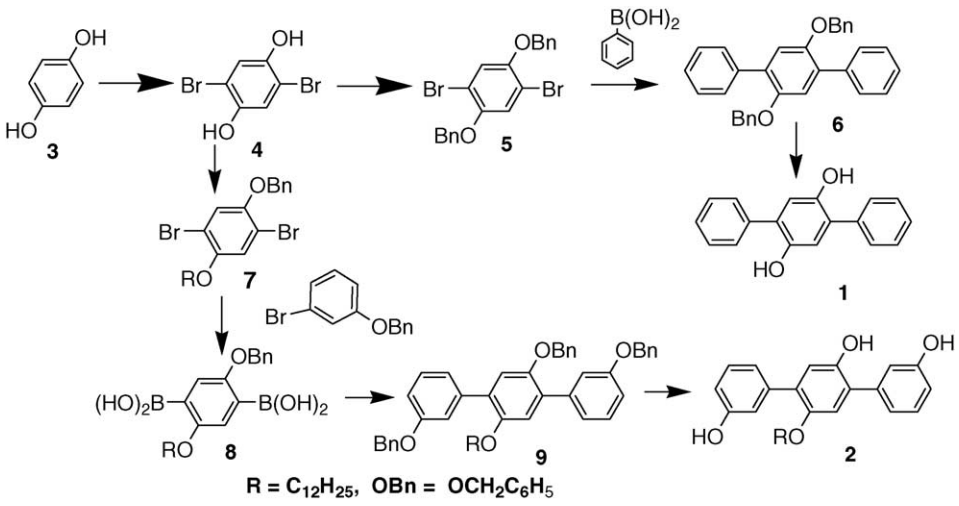

Fig. 1. Synthetic scheme for hydrophilic oligomer **1** and amphiphillic oligomer **2**.

tion process and centrifuged at 1300 rad s^{-1} for 6 min. The white precipitate at the bottom of the tube was removed and the clear sol solution was used for capillary coating.

In our sol–gel coating procedure, previously treated capillaries were dipped into the sol solution for 20 min. The capillary was removed and dried in air for 5 min. A thin layer of oligomer coating was formed on the outer surface of the capillary. To improve the uniformity of the coating, longer dipping time (2 h) was used. This coating process is highly reproducible. The coated capillary was then removed and placed in a desiccator at room temperature for 24 h, then conditioned at 260 °C in the GC injection port for 2 h. The capillary was cooled to room temperature and rinsed with water followed by dichloromethane to clean it. The thickness of the fiber was measured using scanning electron microscopy (SEM) and found to be ca. 5–7 μm.

Fig. 2A and B show the comparative scanning electron micrographs of the oligomer coated-capillary and commercial PA fiber before extraction and after 50 analyses. As seen clearly from Fig. 2, a thin layer of the oligomer was coated on the capillary.

2.5. Characterizing the oligomer coated capillaries

A useful lifetime of the coating is important for practical SPME applications. Injection port temperature and sample

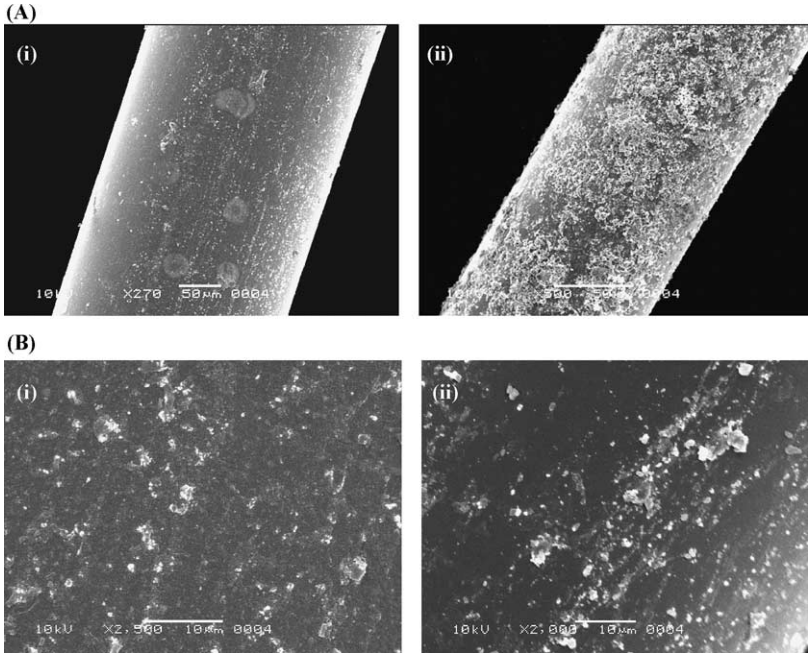

Fig. 2. Scanning electron microscope images of: (A) commercial PDMS–DVB-coated fiber (i) and amphiphillic sol–gel-coated capillary (ii). (B) Comparison of the surface morphology of PDMS–DVB fiber (i) and sol–gel-coated capillary (ii) after 50 analyses.

matrix effects are the main sources of coating damage. In HPLC applications, desorption solvents were also an important factor for damaging the sorbent materials. Generally, sol–gel-coated capillaries show high thermal and solvent stability [20–22]. Our sol–gel coated capillaries were conditioned between 250 and 290 °C for 1 h and found that the coatings were stable up to 280 °C. This allowed their use at a maximum temperature of 280 °C for estrogen analysis.

2.6. SPME procedure

SPME was carried out on various groups of analytes using the stated commercial fiber and the sol–gel-coated fiber prepared in this work.

2.6.1. Organochlorine pesticides

Extraction of organochlorines pesticides from aqueous samples, choice of the fibers and fiber conditioning process have already been reported in the literature [24,25]. Similar conditions were used in the present work. Briefly, 3 ml of aqueous sample (pH and ionic concentration were not adjusted) was magnetically agitated at 105 rad s^{-1} string speed. The analytes were extracted by direct immersion of PA or sol–gel coated fiber in the aqueous sample for 45 min at 60 °C. Thermal desorption in the injection port of the GC was at 250 °C for 5 min. Analysis was carried out in the splitless mode.

2.6.2. Triazine herbicides

Extraction of herbicides in aqueous samples was carried out using other sol–gel coated fiber or the PDMS–DVB fiber by direct immersion of the fiber into the sample [5 ml, 30% (w/v) NaCl] contained in a 8-ml clean glass vial under magnetic stirring (105 rad s^{-1}) for 60 min. Desorption of herbicides was carried out at 240 °C for 5 min in the spilitless injector.

2.6.3. Estrogens

Extraction of estrogens was performed using a previously validated procedure [26]. The PA fiber was used for comparing the efficiency of extraction with the sol–gel coated fibers. A 10 ml of sample (spiked at 20 μg l^{-1} of individual analyte) with added salt (30%, w/v) and an adjusted pH of 6, was extracted by direct immersion and equilibrium was established after 160 min. After extraction, the adsorbed analytes were derivatized by exposure to the headspace of 1.5 ml containing 50 μl of bis(trimethylsilyl) trifluoroacetamide (BSTFA). On-fiber derivatization was carried out for 30 min at 60 °C and the analytes were desorbed in the injection port for 5 min at 280 °C.

2.6.4. Analysis of alkylphenols (APs) and bisphenol-A (BPA)

APs and BPA were extracted by direct immersion using the PA and the sol–gel coated fibers [27] from a 10-ml sample solution (pH and salt concentration were adjusted to 2 and 30% (w/v), respectively) spiked at 20 μg l^{-1} of individual analytes. Equilibrium was established within 90 min. After extraction, the fiber was placed in the headspace of a 3-ml GC autosampler vial containing 50 μl of BSTFA in 1 ml of acetone at 60 °C for 20 min and desorption was carried out for 10 min at 250 °C.

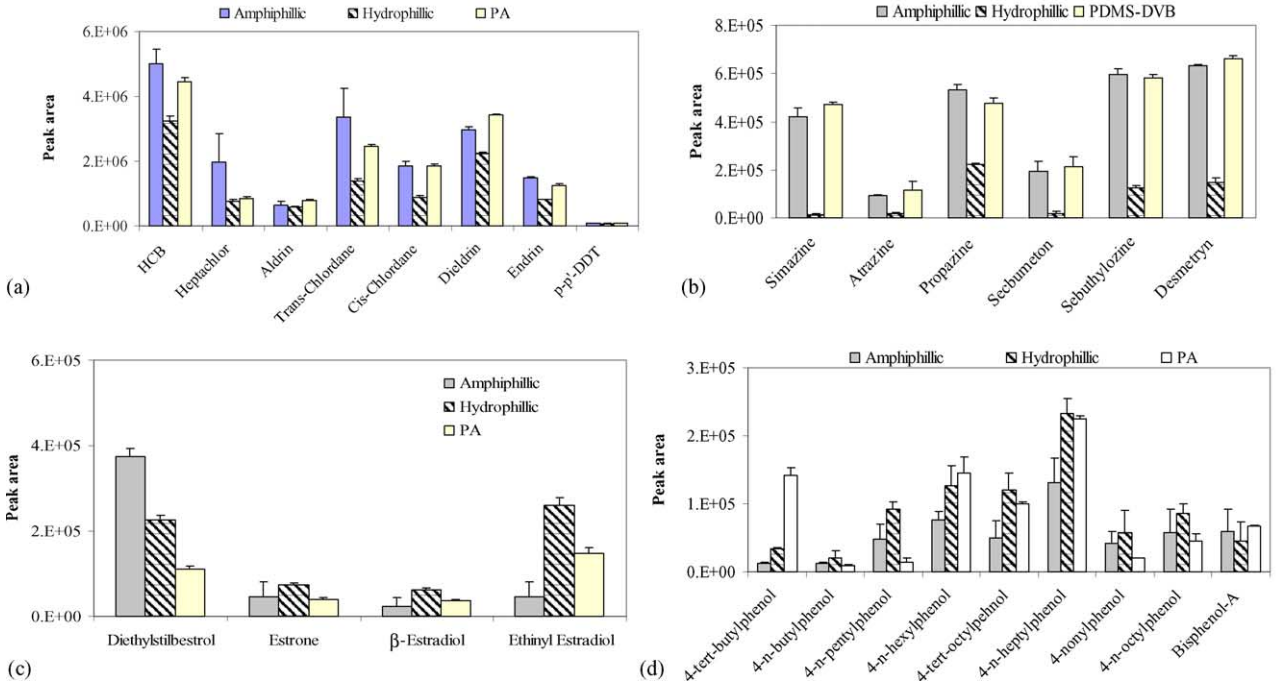

Fig. 3. Extraction efficiency of sol–gel coated capillaries with commercial SPME fiber: (a) OCPs; (b) triazine; (c) estrogens; and (d) APs and BPA. Extraction conditions are given in the text.

Fig. 3 shows the extraction efficiency of sol–gel coated SPME capillaries with commercial SPME fibers (PDMS–DVB and PA) for OCPs, triazines, estrogens, APs and BPA from samples spiked at the same concentrations. The results clearly show that comparable (in some cases, superior) extraction efficiencies could be achieved using sol–gel-coated capillary. The extraction efficiency for triazine herbicides using the coating of the amphiphillic oligomer appears significantly better than those obtained by the commercial PDMS–DVB coated fiber. Thus, further optimization of the extraction parameters for these analytes was performed.

3. Results and discussion

3.1. Method optimization of triazine extraction

The development of the SPME procedure required the optimization of a series of variables including extraction time, sample ionic strength, pH and desorption of the analytes as discussed in several publications [28–30]. All our experiments were carried out in triplicates. Once the optimum conditions were determined for the sol–gel coated capillaries, quantitative data were obtained for precision, linearity range, and limits of detection.

Extraction time profiles were obtained at various extraction times ranging from 5 to 60 min by extracting an aqueous solution containing 20 $\mu g\,l^{-1}$ of each analyte at 105 $rad\,s^{-1}$ stirring speed. Fig. 4 shows that the analytical signals increase up to 60 min of extraction time. SPME is a process dependent on equilibrium rather than exhaustive extraction. Generally, the equilibrium time is selected as extraction time. Taking the high extraction efficiency of this technique into account, an extraction time of 60 min was deemed to be sufficient for subsequent experiments.

pH plays an important role in the extraction of ionisable compounds such as herbicides [24]. Thus, the influence of extraction pH on sol–gel coated SPME over the range of 2–12 was investigated. Triazine herbicides are basic herbicides and higher extraction efficiency was achieved at a moderately high pH of 10. However, above pH 10, there is slight decrease in the extraction efficiency, attributed to hydrolysis of these compounds under alkaline conditions. [31].

Addition of salt enhances the extraction efficiency of some organic compounds in SPME. Since ionic strength increases retention of analytes on the fiber coating especially for non-polar compounds, extraction of fungicides was carried out using PDMS–DVB fiber [32]. However, ionic strength also decreases the lifetime of the coating material and complete removal of coating has been observed after 15 analyses [33].

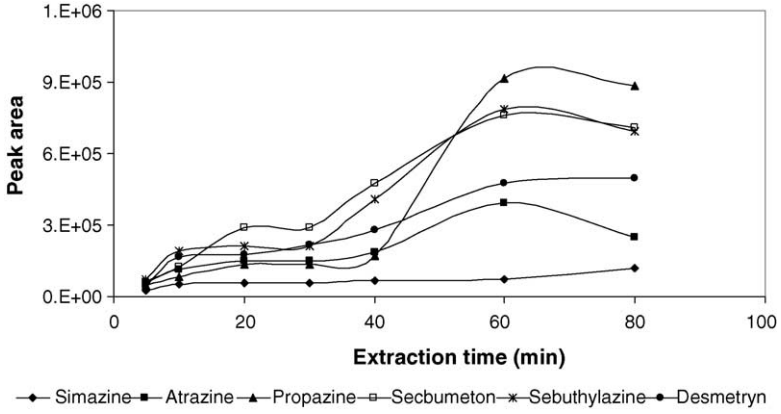

Fig. 4. Effect of extraction time on sol–gel-coated SPME capillary (ionic content and pH was not adjusted) at constant stirring speed of 105 $rad\,s^{-1}$.

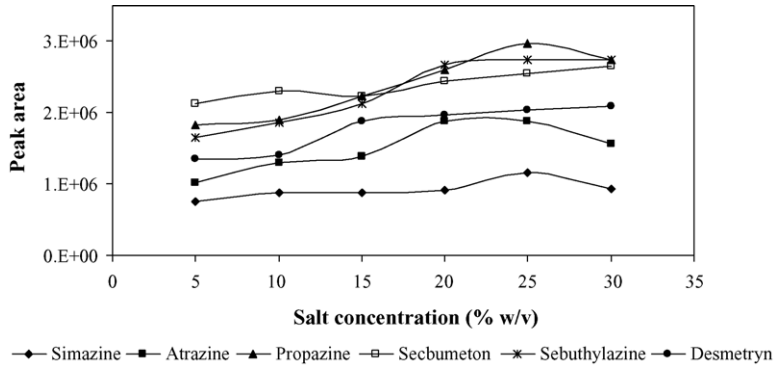

Fig. 5. Effect of salt addition on sol–gel-coated SPME. Extraction time 60 min at pH 10, stirring speed 105 $rad\,s^{-1}$.

Table 1
Linearity, precision and limits of detection (LODs) of triazine herbicides using sol–gel-coated SPME. Precision data for PDMS–DVB-coated fiber are also shown

Analyte	Sol–gel coated SPME			
	Correlation coefficient*	RSD (%, $n=6$)	LOD ($\mu g\,l^{-1}$)	RSD (%, $n=6$) PDMS–DVB
Simazine	0.9966	9.6	0.005	7.7
Atrazine	0.9937	5.0	0.004	7.9
Propazine	0.9930	8.3	0.001	6.8
Secbumeton	0.9988	9.0	0.002	5.4
Sebuthylazine	0.9990	6.6	0.002	8.3
Desmetryn	0.9977	11.0	0.003	10.6

* Linear range 0.5–50 $\mu g\,l^{-1}$.

Table 2
Quantitative results for reservoir sample spiked at 5 $\mu g\,l^{-1}$ ($n=3$)

Analytes	Reservoir water spiked at 5 $\mu g\,l^{-1}$			
	Relative recovery (%) (PDMS–DVB)	RSD (%)	Relative recovery (%) (amphiphillic)	RSD (%)
Simazine	93.8	4.4	106.2	10.3
Atrazine	84.3	11.2	98.6	6.9
Propazine	107.4	7.8	93.3	7.1
Secbumeton	95.4	9.2	93.2	10.0
Sebuthylozine	97.1	7.5	101.3	6.7
Desmetryn	95.5	7.0	105.9	9.9

The addition of salt to the sample was tested (5–30%, w/v) with sol–gel coated capillary. Fig. 5 shows the mean peak areas of triazine herbicides increasing with increasing salt addition. The coating appeared to be stable, even after 50 analyses similar to the PDMS–DVB fiber (Fig. 2).

3.2. Quantitative information

Linearity, repeatability, precision, and limits of detection (LODs) have been evaluated in order to assess the performance of SPME with sol–gel-coated capillary. The calibration study was performed using spiked ultrapure water samples. The correlation coefficient (r) values were >0.999 for all the analytes in the concentration range of 0.5–50 $\mu g\,l^{-1}$, so a directly proportional relationship between the extracted amount of compounds and the initial concentration in the sample was demonstrated. LODs were calculated by progressively decreasing the analyte concentration in the spiked sample such that GC–MS-SIM signals were clearly discerned at S/N of 3 at the final lowest concentration. LODs were from 0.001 to 0.005 $\mu g\,l^{-1}$ (Table 1). The precision of the procedure was also evaluated at 5 $\mu g\,l^{-1}$ spiked concentration levels by calculating the relative standard deviation RSD ($n=6$). The RSD values were between the range of 5.0 and 11.0% for sol–gel coating and from 5.4 to 10.6% for PDMS–DVB coated fibers (Table 1).

4. Real water analysis

Natural water from a local reservoir was used as samples for evaluating the sol–gel coated SPME capillary and commercial PDMS–DVB SPME fiber. The natural reservoir water was found to be free from triazine contamination. They were spiked with 5 $\mu g\,l^{-1}$ of triazine standards to assess matrix effects. Results of relative recoveries and RSDs are shown in Table 2. The data show that for all triazines, the relative recoveries were higher than 84% and RSD less than 11%. These results clearly demonstrate the absence of significant matrix effects on the efficiency of SPME.

5. Conclusion

The oligomers prepared in this work are suitable for the sol–gel technique owing to their good solubility in solution. Sol–gel coated fibers showed excellent SPME characteristics for the extraction of both non-polar and polar organic compounds. The sol–gel coated capillaries also exhibited longer application lifetime, thermal stability (up to 280 °C), and improved selectivity towards different organic compounds (non-polar or polar). Quantitative results obtained from these capillaries exhibited precision at LOD values comparable with commercial coating materials [33]. Therefore, sol–gel coating of amphiphillic oligomers offers an alternative to existing commercial coatings with high operational temperatures along with better analytical performance and longer lifetimes.

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