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High pH-resistant, surface-bonded sol–gel titania hybrid organic–inorganic coating for effective on-line hyphenation of capillary microextraction (in-tube solid-phase microextraction) with high-performance liquid chromatography

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Abstract

Sol–gel titania–poly(dimethylsiloxane) (TiO_2–PDMS) coating was developed for capillary microextraction (CME) to perform on-line preconcentration and HPLC analysis of trace impurities in aqueous samples. A method is presented describing in situ preparation of the titania-based sol–gel PDMS coating and its immobilization on the inner surface of a fused silica microextraction capillary. To perform CME-HPLC, the sol–gel TiO_2–PDMS capillary was installed in the HPLC injection port as an external sampling loop, and a conventional ODS column was used for the liquid chromatographic separation. The target analytes were extracted on-line by passing the aqueous sample through this sampling loop. The sol–gel titania–PDMS coated capillaries were used for on-line extraction and HPLC analysis of polycyclic aromatic hydrocarbons, ketones, and alkylbenzenes. The extracted analytes were then transferred to the HPLC column using an organic-rich mobile phase followed by HPLC separation via gradient elution. To our knowledge, this is the first report on the use of sol–gel titania-based organic–inorganic material as a sorbent in capillary microextraction. The newly developed sol–gel titania-based CME coatings demonstrated excellent pH stability and enhanced extraction capability over the commercial GC coatings that are conventionally used for the same purpose. Extraction characteristics of a sol–gel titania–PDMS capillary remained practically unchanged after continuous rinsing with a 0.1 M NaOH solution (pH 13) for 12 h.

Keywords: Sol–gel; Capillary microextraction; In-tube solid-phase microextraction; Gradient elution; Titania–poly(dimethysiloxane); Polycyclic aromatic hydrocarbons; Ketones; Alkylbenzenes

1. Introduction

Solid-phase microextraction (SPME), a solvent-free sample preparation technique, was developed by Pawliszyn and co-workers [1–3] using a fused-silica fiber externally coated with a polymeric sorbent covering a small segment of it at one of the ends. Analytes present in the sample medium were directly extracted and preconcentrated by the coated sorbent in the process of reaching an extraction equilibrium with the sample matrix. The preconcentrated analytes were then desorbed into a GC instrument for analysis.

In conventional fiber-based SPME, still there exist a number of shortcomings that need to be overcome. These include inadequate thermal and solvent stability of conventionally prepared sorbent coatings [4], low sample capacity, difficulties associated with the immobilization of thick coatings, susceptibility of the fiber (especially the coated end) to mechanical damage [5,6], and technical difficulties

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associated with the hyphenation of fiber-based SPME with liquid-phase separation techniques [7,8].

Capillary microextraction (CME) [9] (also called in-tube SPME [10,11]) presents a convenient format for coupling SPME to HPLC and for automated operation of SPME-HPLC. Hyphenation of CME to HPLC is especially important for the analysis of a wide range of less volatile or thermally labile compounds [12] that are not amenable to GC separation. In the open tubular format of CME, a sorbent coating is applied to the inner surface of a capillary. This alternative format provides an effective solution to the problem associated with the mechanical damage of sorbent coating frequently encountered in conventional fiber-based SPME where the coating is applied on the outer surface of the fiber. In this new format of SPME, a segment of wall-coated capillary GC column is commonly used [10–12] for the direct extraction of organic analytes from an aqueous medium. To perform HPLC analysis, the extracted analytes are transferred to the HPLC column by desorbing them with an appropriate mobile phase.

Capillary microextraction has great prospects in liquid-phase trace analysis. However, to achieve its full analytical potential, the technology needs further improvements in a number of areas. First, segments of GC columns that are commonly used for sample preconcentration have thin coatings that limit the sorption capacity, and hence, the extraction sensitivity of in-tube SPME. Second, the sorbent coatings in such microextraction capillaries usually are not chemically bonded to capillary inner walls, which limits their thermal and solvent stabilities. Third, conventionally prepared GC coatings that are used in in-tube SPME capillaries inherently possess poor pH stability. This places serious limitations on the range of applications amenable to CME-HPLC analysis. Low pH stability of in-tube SPME coatings practically excludes the applicability of the technique to high-pH samples or analytes that require high-pH solvent systems for desorption from the microextraction capillary. Therefore, development of methodologies for the creation of high pH- and solvent-resistant sorbent coatings is an important area in the future development of in-tube SPME, and is expected to play a major role in effective hyphenation of this sample preconcentration technique with liquid-phase separation techniques that commonly use organo-aqueous mobile phases with a wide range of pH conditions [13].

Sol–gel chemistry has been recently applied to solid-phase microextraction [4,14–17] and capillary microextraction [9] to create silica-based hybrid organic–inorganic coatings. The sol–gel technique provided chemically bonded coatings on the inner surface of fused-silica capillaries, and easily solved the coating stability problems described above.

Although sol–gel technique helped overcome some significant shortcomings of SPME or in-tube SPME techniques by providing an effective means of chemical immobilization for sorbent coatings, an important problem inherent in silica-based material systems (commonly used in SPME or CME) still remains to be solved: silica-based materials possess a narrow window of pH stability [18]. In the context of SPME, it pertains to the stability of silica-based fibers and coatings. The development of alternative materials possessing superior pH stability and better mechanical strength should provide SPME with additional ruggedness and versatility.

Recently, titania has attracted interest in separation science due to its superior pH stability and mechanical strength compared with silica [19–23]. Several studies have been conducted on the application of titania in chromatographic separations. Tani and Suzuki [21] reported the preparation of titania-based packing materials for HPLC by sol–gel method, and investigated their properties. Tsai et al. [22] prepared silica capillaries coated with titania or alumina for capillary electrophoresis (CE) separation of proteins. Fujimoto [23] used a thermal decomposition technique to create titania coatings on the inner surface of fused-silica capillaries for capillary zone electrophoresis (CZE) and capillary electrochromatography (CEC) applications. The titania-coated capillaries were found to possess a bi-directional electroosmotic flow (EOF) and low solubility in aqueous solutions within a pH range of 3–12. Pesek et al. [24] reported the surface derivatization of titania with triethoxysilane to prepare titania-based stationary phases via silanization/hydrosilylation. Some other groups [25,26] reported preparations of silica-coated titania monolayers for faster and more efficient coating, which is important for further preparation of nanocomposites.

To date, very little (if any) research has been done on the development and application of titania-based coatings in analytical microextraction techniques. In this paper, we report the preparation of sol–gel TiO_2–PDMS coated capillaries and show the possibility of on-line CME-HPLC operation using sol–gel TiO_2–PDMS microextraction capillaries to provide a significant improvement in pH stability and extraction sensitivity.

2. Experimental

2.1. Equipment

On-line CME-HPLC experiments were carried out on a Micro-Tech Scientific (Vista, CA) Ultra Plus HPLC system with a variable wavelength UV detector (Linear UVIS 2000). A Nicolet model Avatar 320 FT-IR (Thermo Nicolet, Madison, WI) was used for FT-IR measurements. A reversed-phase ODS column (25 cm × 4.6 mm i.d., 5 μm d_p) was used for HPLC separation of the extracted analytes. A Fisher model G-560 Vortex Genie 2 system (Fisher Scientific, Pittsburgh, PA) was used for thorough mixing of the sol solutions. A Microcentaur model APO 5760 centrifuge (Accurate Chemical and Scientific Corp., Westbury, NY) was used for centrifugation of sol solutions. A Barnstead model 04741 Nanopure deionized water system (Barnstead/Thermodyne, Dubuque, IA) was used to obtain 16.0 MΩ cm water. On-line data collection and processing were done using

Chrom-Perfect (version 3.5 for Windows) computer software (Justice Laboratory Software, Denville, NJ).

2.2. Chemicals and materials

Fused silica capillary (250 and 320 μm i.d.) was purchased from Polymicro Technologies Inc. (Pheonix, AZ). A commercial polysiloxane-based GC column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used for comparison with sol–gel titania–PDMS-based microextraction capillary in pH stability studies. Titanium (IV) isopropoxide (99.999%), 1-butanol (99.4%+), poly(methylhydrosiloxane) (PMHS), 1,1,1,3,3,3-hexamethyldisilazane (HMDS), trifluoroacetic acid (TFA), polycyclic aromatic hydrocarbons (PAHs) (acenaphthylene, fluorene, phenanthrene, fluoranthene), ketones (butyrophenone, valerophenone, hexanophenone, heptanophenone), and alkylbenzenes (toluene, ethylbenzene, cumene, propylbenzene, butylbenzene, amylbenzene) were purchased from Aldrich (Milwaukee, WI). Hydroxy-terminated poly(dimethylsiloxane) (PDMS) was purchased from United Chemical Technologies Inc. (Bristol, PA). HPLC-grade solvents (acetonitrile, methylene chloride, and methanol) were purchased from Fisher Scientific.

2.3. Preparation of the sol solution

The sol solution was prepared by thoroughly vortexing the following reagents in a 2 mL polypropylene centrifuge tube: a sol–gel-active organic component (hydroxy-terminated PDMS, 50 mg), a sol–gel precursor (titanium (IV) isopropoxide, 50 μL), two solvents (methylene chloride and 1-butanol, 200 μL each), a mixture of two surface deactivation reagents (HMDS, 8 μL and PMHS, 2 μL), and a sol–gel chelating agent (27% TFA in H_2O, 18 μL). The content of the tube was then centrifuged for 5 min (at 13 000 rpm; 15 682 × *g*). Finally, the top clear solution was transferred to another clean vial by decantation, and was further used for coating the fused silica microextraction capillary.

2.4. Preparation of sol–gel TiO_2–PDMS coated microextraction capillaries

A 1 m long hydrothermally treated [27] fused silica capillary (250 or 320 μm i.d.) was installed on an in-house built gas pressure-operated capillary filling/purging device [28], and the capillary was filled with the prepared sol solution under 10 psi helium pressure. After filling, the sol solution was kept inside the capillary for 15 min to facilitate the creation of a surface-bonded coating due to sol–gel reactions taking place in the coating solution inside the capillary. Following this, the unbonded portion of the sol solution was expelled from the capillary under helium pressure (20 psi), and the capillary was further purged with helium for 30 min. The coated capillary was then conditioned in a GC oven by programming the temperature from 40 °C to 320 °C at 1 °C/min under helium purge. The capillary was held at 320 °C for 180 min. Finally, the capillary was cooled down to room temperature and rinsed with methylene chloride and methanol (3 mL each). Following this, the capillary was installed in the GC oven for drying and further thermal conditioning under temperature-programmed heating as described above, except that this time the capillary was held at the final temperature for 30 min.

2.5. Capillary microextraction (CME) and on-line CME-HPLC analysis

A schematic of the CME-HPLC setup for on-line capillary microextraction and HPLC analysis is presented in Fig. 1. An ODS column (25 cm × 4.6 mm i.d., 5 μm d_p) was previously installed in the HPLC system and pre-equilibrated with the mobile phase consisting of a mixture of acetonitrile and water (80:20, v/v). A 40 cm segment of the sol–gel TiO_2–PDMS coated microextraction capillary was mounted on the injection port as an external sampling loop. Analytes were preconcentrated in the sol–gel TiO_2–PDMS coating by passing the aqueous sample from a gravity-fed dispenser [9] through this sol–gel titania–PDMS coated microextraction capillary for 40 min. Using a syringe, the sampling loop was flushed out with deionized water to remove the sample matrix. The analytes extracted in the sol–gel TiO_2–PDMS coating of the sampling loop were then transferred into the HPLC column by desorbing with 100% acetonitrile for 30 s. This was accomplished by simply switching the injection valve from the "load" to "inject" position. The injected analytes were then separated on the ODS column under gradient elution conditions by programming acetonitrile composition in the organo-aqueous mobile phase from 80% (v/v) to 100% in 15 min.

2.5.1. Treatment of coated capillaries with 0.1 M NaOH solution

A 40 cm segment of the sol–gel TiO_2–PDMS coated capillary was directly installed on the gravity-fed sample dispenser, and continuously rinsed with 0.1 M NaOH solution (pH 13) for 12 h. The capillary was then flushed out with deionized water for 30 min, and mounted back on the HPLC injection port. The target analytes (PAHs) were extracted on-line for 40 min, followed by their HPLC analysis as described in Section 2.5.

Using the same procedure, a 40 cm segment of the commercial PDMS-based GC capillary was treated with a 0.1 M NaOH solution. CME performances of the used capillaries were evaluated both before and after the alkaline treatment to explore pH stability of the used coatings.

2.6. Safety precautions

The presented work involved the use of various chemicals (organic and inorganic) and solvent that might be environmentally hazardous with adverse health effects. Proper safety measures should be taken in handling strong bases

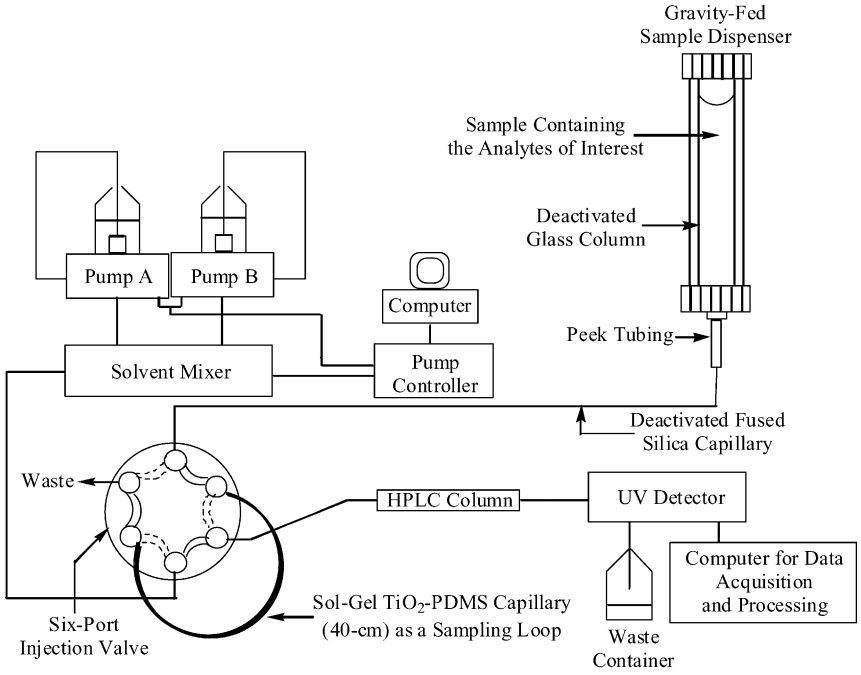


Fig. 1. Schematic diagram of the on-line CME-HPLC setup.

and organic solvents such as methanol, methylene chloride, and acetonitrile. All used chemicals must be disposed in the proper waste containers to ensure personnel and environmental safety.

3. Results and discussion

The goal of this research was to develop high pH-resistant, surface-bonded sol–gel titania coatings for capillary microextraction to facilitate effective hyphenation of CME with HPLC. Judicious utilization of unique attributes of sol–gel chemistry allowed us to create a surface-bonded hybrid organic–inorganic titania coating on the inner walls of a fused silica capillary providing an opportunity to exploit advanced material properties of titania-based sorbents [29,30] in capillary microextraction. Unlike the conventional multistep coating technologies [31–34], the sol–gel approach involves a single-step procedure to accomplish the sorbent coating, its chemical immobilization, and deactivation [35].

As sol–gel precursors, titanium alkoxides differ significantly from silicon alkoxides in terms of their chemical reactivity and complex-forming ability. These differences dictate the adoption of different strategies for the creation of titania-based sol–gel sorbents compared with those for silica-based analogs. While sol–gel reactions in a silica-based system are rather slow and often require the use of catalysts to accelerate the process [36], titania-based (transition metal oxide-based in general) sol–gel reactions are very fast. This is explained by the fact that titanium alkoxides are very reactive toward nucleophilic reagents like water [37]. They readily undergo hydrolysis, which results in a very fast sol–gel process. Because of this, titania-based sol–gel reactions need to be decelerated by a suitable means to allow for the sol–gel process to be conducted in a controlled manner. This is usually accomplished through the use of suitable chelating agents that form complexes with the sol–gel precursors (or replace the reactive alkoxy group with a less reactive group), thus hindering their participation in the sol–gel reactions. Without such a chelating agent, the gelation takes place instantaneously as the sol–gel solution ingredients are mixed together. Chelating agents such as acetic acid [38,39], trifluoroacetic acid [40], or metal β-diketonates [41] are often used for this purpose.

In the present work, sol–gel TiO_2–PDMS coated capillaries were prepared through hydrolytic polycondensation reactions performed within fused silica capillaries followed by thermal conditioning of the created coatings to achieve fine porous structures. Here, TFA served as a chelating agent [40], and decelerated the gelation process for the creation of TiO_2–PDMS coating. It has been shown by infrared spectra that the acetate ion can serve as a bidentate ligand (chelating and bridging) to the transition metal alkoxides, such as $Ti(OR)_4$ or $Zr(OR)_4$ [38,40,42].

Fig. 2 represents two scanning electron micrographs (SEM) showing the fine structural features of a 320 μm i.d. fused silica capillary with sol–gel TiO_2–PDMS coating on the inner surface. As is evident from these images, the sol–gel TiO_2–PDMS coating in the microextraction capillary acquires a porous structure, providing enhanced surface area and sorption ability. Based on the SEM data, the

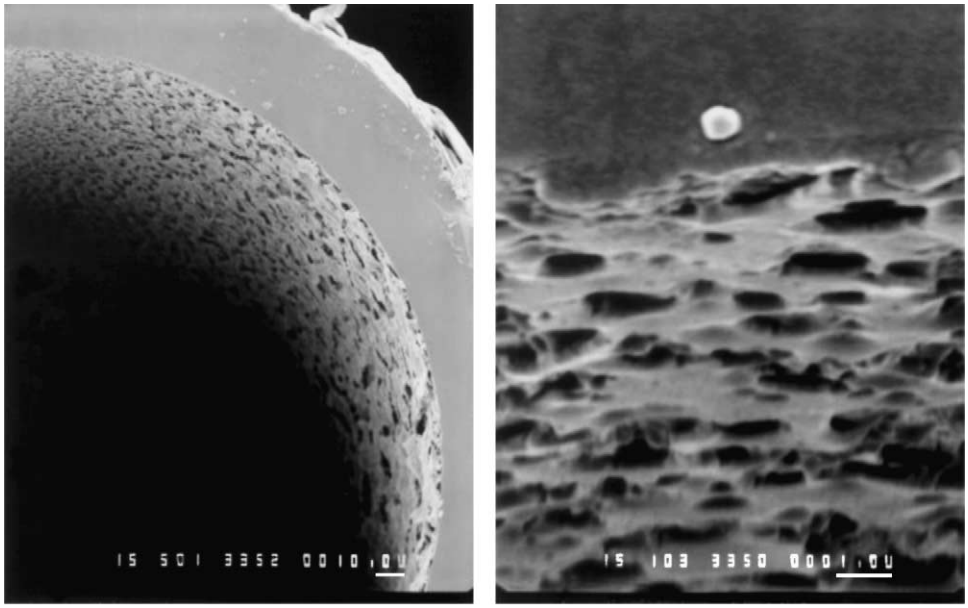


Fig. 2. Scanning electron microscopic images of a 320 μm i.d. fused silica capillary with sol–gel TiO_2–PDMS coating: (A) cross-sectional view (500×) and (B) surface view (10 000×).

thickness of the sol–gel TiO_2–PDMS coating was estimated at 0.5 μm.

The sol–gel process for the generation and chemical immobilization of the coating involves: (A) hydrolysis of the titanium alkoxide precursor [43], (B) polycondensation of the hydrolysis products into a three-dimensional sol–gel network [44,45], (C) chemical incorporation of hydroxy-terminated PDMS in the sol–gel network [46,47], and (D) chemical anchoring of the sol–gel hybrid polymer to the inner walls of the capillary [44,45]. Scheme 1 illustrates the hydrolysis and polycondensation reactions of the sol–gel precursor, titanium (IV) isopropoxide, and Scheme 2 represents the final structure of the sol–gel TiO_2–PDMS coating on the inner surface of a fused silica capillary.

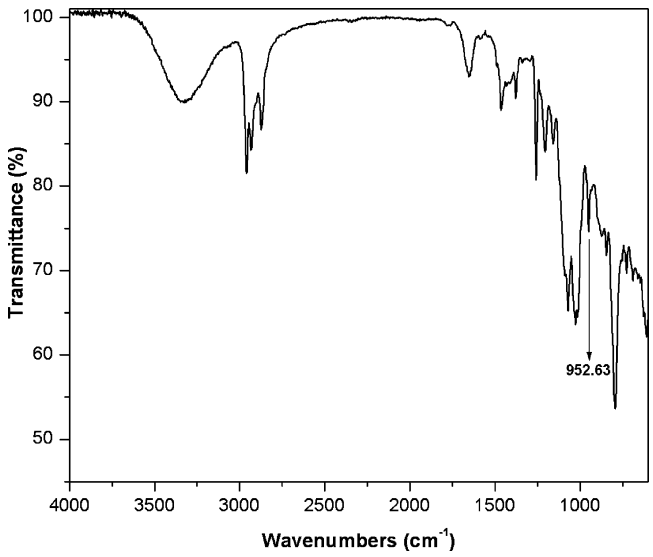


Fig. 3. FT-IR spectra of the sol–gel TiO_2–PDMS coating.

The formation of Ti–O–Si bonds in the prepared sol–gel sorbent was examined by FT-IR. The FT-IR experiments were performed by passing IR radiation through a thin layer of sol–gel titania coating material that was used in the fused silica capillary. This was done in separate experiments outside the fused silica capillary. It has been reported [48,49] that a characteristic IR band representing Si–O–Ti bonds is located at 940–960 cm^{-1}. Fig. 3 shows FT-IR spectra of the sol–gel TiO_2–PDMS coating with a specific band at 952.63 cm^{-1}. This is indicative of the presence of Si–O–Ti bonds in the sol–gel sorbent used in the fused silica microextraction capillaries to perform on-line CME-HPLC analysis.

Deactivation of the sol–gel coatings can be expected to take place mainly during thermal conditioning of the capillary, through derivatization of the free hydroxyl groups in the coating structure with HMDS [50] and PMHS [25,51] incorporated in the sol solution. To control the gelation time and to obtain a transparent gel, it was essential to find an optimum ratio (v/v) of HMDS and PMHS. In the present study, this ratio was found to be 4:1 (HMDS:PMHS, v/v).

Sol–gel technology is quite versatile, and allows for the control of coating thickness either by manipulating the reaction time or composition of the sol solution. Zeng et al. [16] has recently reported the preparation of 70 μm thick silica-based sol–gel coating on conventional SPME fiber. It should be possible to create such thick coatings (either silica-based or transition metal oxide-based) on the inner surface of fused silica capillaries as well. Use of thicker coatings should enhance the sample capacity and extraction sensitivity in CME with titania-based sol–gel coatings.

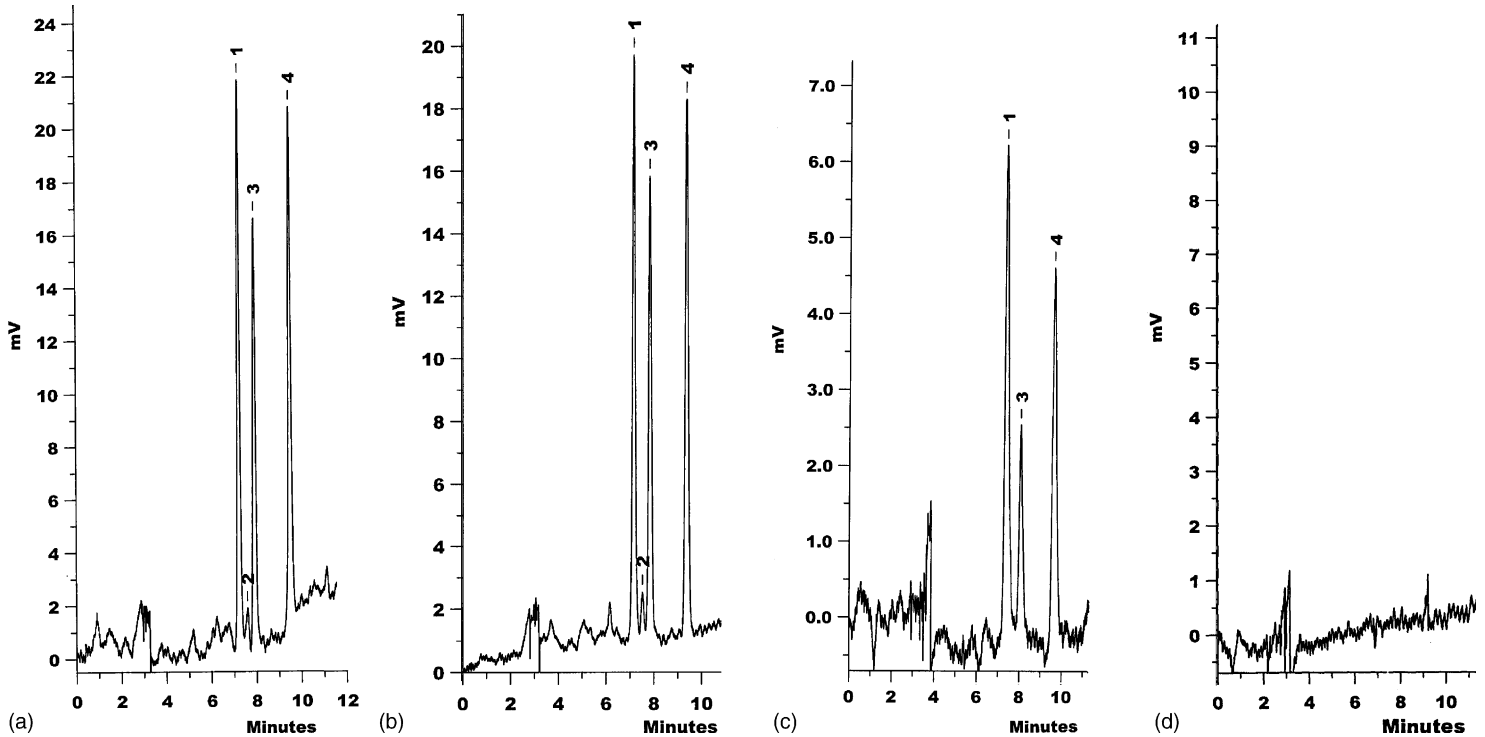


Fig. 4. Chromatograms representing capillary microextraction-HPLC analysis of PAHs using sol–gel titania–PDMS coated (a and b) and commercial PDMS-based GC (c and d) capillaries before (a and c) and after (b and d) rinsing the microextraction capillaries with a 0.1 M NaOH solution (pH 13) for 12 h. Extraction conditions: 40 cm × 0.25 mm i.d. × 0.25 μm sol–gel TiO_2–PDMS-coated capillary (a and b), and 40 cm × 0.25 mm i.d. × 0.25 μm commercial GC capillary (c and d); extraction time, 40 min (gravity-fed at room temperature). Other conditions: 25 cm × 4.6 mm i.d. ODS column (5 μm d_p); gradient elution with mobile phase composition programmed from 80:20 (v/v) acetonitrile/water to 100% acetonitrile for 20 min; 1 mL/min flow rate; UV detection at 254 nm; ambient temperature. Peaks: (1) acenaphthylene (500 ppb), (2) unknown, (3) phenanthrene (20 ppb), and (4) fluoranthene (100 ppb).

Table 1
Peak area repeatability and detection limit data for PAHs using a sol–gel TiO_2–PDMS-coated capillary treated with 0.1 M NaOH for 12 h[a]

Extracted PAHs	Peak area repeatability (n = 3)				Percent change in peak area ($\lvert(A_2 - A_1)/A_1\rvert \times 100\%$)	Detection limits (ppb) (S/N = 3)	
	Before rinsing		After rinsing			Before rinsing	After rinsing
	Mean peak area (A_1) (arbitrary unit)	R.S.D. (%)	Mean peak area (A_2) (arbitrary unit)	R.S.D. (%)			
Acenaphthylene	17.7	1.7	16.2	3.6	5.1	5.37	4.39
Phenanthrene	13.9	6.2	14.2	1.0	1.4	0.28	0.24
Fluoranthene	16.5	9.2	16.3	2.3	1.2	1.32	1.00

[a] Extraction conditions: 40 cm × 0.25 mm i.d. × 0.25 μm sol–gel TiO_2–PDMS-coated capillary; extraction time: 40 min; HPLC conditions: 25 cm × 4.6 mm i.d. ODS column (5 μm d_p); gradient elution 80:20 (v/v) ACN/water to 100% ACN for 20 min; 1 mL/min flow rate; UV detection at 254 nm.

The sol–gel titania–PDMS coatings demonstrated excellent pH stabilities over conventionally created coatings like those used in commercial GC capillary columns. Fig. 4 illustrates the CME performance of a TiO_2–PDMS coated microextraction capillary (250 μm i.d.) in CME-HPLC analysis of PAHs before (Fig. 4a) and after (Fig. 4b) rinsing the capillary with a 0.1 M NaOH solution (pH 13) for 12 h. Analogously obtained data for a piece of commercial PDMS-based GC column are presented in Fig. 4c and 4d, respectively. Chromatogram of Fig. 4b was obtained on the sol–gel TiO_2–PDMS coated microextraction capillary after it was thoroughly rinsed with deionized water. The extraction of PAHs was performed under the same set of conditions as in Fig. 4a. From the comparison of peak profiles and peak heights in Fig. 4a and 4b, it is evident that the sol–gel TiO_2–PDMS coating in the microextraction capillary remained unaffected even after the prolonged rinsing with 0.1 M NaOH solution of pH 13.

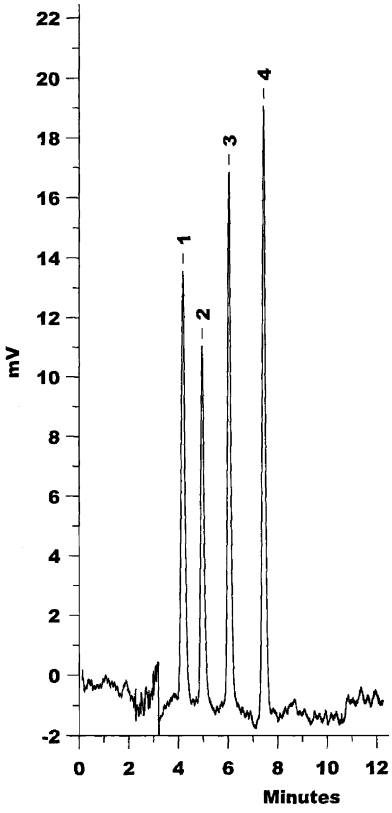


Fig. 5. Capillary microextraction-HPLC analysis of ketones. Extraction conditions: 40 cm × 0.32 mm i.d. × 0.5 μm sol–gel TiO_2–PDMS-coated capillary; extraction time, 40 min (gravity-fed at room temperature). Other conditions: 25 cm × 4.6 mm i.d. ODS column (5 μm d_p); gradient elution with mobile phase composition programmed from 80:20 (v/v) acetonitrile/water to 100% acetonitrile for 15 min; 1 mL/min flow rate; UV detection at 254 nm; ambient temperature. Peaks: (1) butyrophenone (1 ppm), (2) valerophenone (1 ppm), (3) hexanophenone (500 ppb), and (4) heptanophenone (300 ppb).

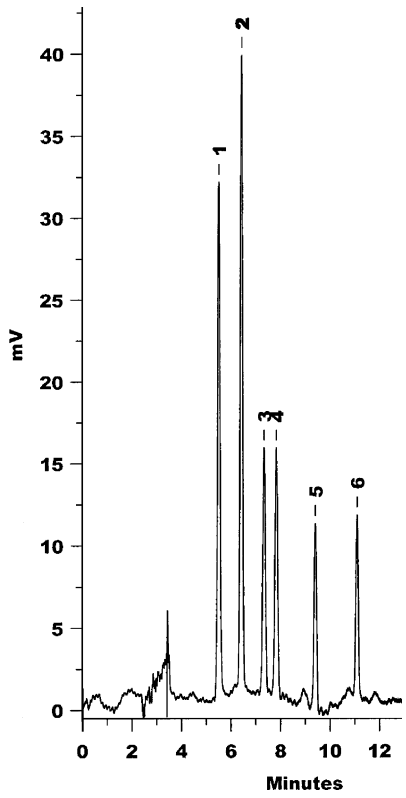


Fig. 6. Capillary microextraction-HPLC analysis of alkylbenzenes. Extraction conditions are the same as in Fig. 5. Other conditions: 25 cm × 4.6 mm i.d. ODS column (5 μm d_p); gradient elution with mobile phase composition programmed from 80:20 acetonitrile/water to 100% acetonitrile for 15 min; 1 mL/min flow rate; UV detection at 205 nm; ambient temperature. Peaks: (1) toluene (600 ppb), (2) ethylbenzene (200 ppb), (3) cumene (50 ppb), (4) propylbenzene (50 ppb), (5) butylbenzene (50 ppb), and (6) amylbenzene (50 ppb).

Table 2
Peak area repeatability and detection limit data for PAHs, ketones, and alkylbenzene in CME-HPLC using a sol–gel TiO_2–PDMS-coated microextraction capillary[a]

Chemical class	Name	Peak area repeatability (n = 3)		Detection limits (ppb) (S/N = 3)
		Mean peak area (arbitrary unit)	R.S.D. (%)	
PAH	Acenaphthylene	23.5	9.5	3.07
	Fluorene	12.2	8.9	1.40
	Phenanthrene	19.9	8.8	0.15
	Fluoranthene	21.4	9.7	0.84
Ketone	Butyrophenone	48.6	3.9	9.62
	Valerophenone	27.7	4.6	11.60
	Hexanophenone	27.9	3.5	4.35
	Heptanophenone	21.6	7.9	2.47
Alkylbenzene	Toluene	20.3	1.9	5.45
	Ethylbenzene	23.9	1.6	1.24
	Cumene	12.3	6.1	0.74
	Propylbenzene	13.6	4.5	0.65
	Butylbenzene	14.4	9.9	0.84
	Amylbenzene	9.4	7.4	1.07

[a] Extraction conditions: 40 cm × 0.32 mm i.d. × 0.5 μm sol–gel TiO_2–PDMS-coated capillary; extraction time: 40 min; HPLC conditions: 25 cm × 4.6 mm i.d. ODS column (5 μm d_p); gradient elution from 80:20 (v/v) ACN/water to 100% ACN for 15 min (20 min for PAHs); 1 mL/min flow rate; UV detection at 254 nm (at 205 nm for alkylbenzenes).

On the other hand, the PDMS-based stationary phase coating in the commercial GC capillary showed significantly less extraction sensitivity as is evident from peak heights in Fig. 4c. It also failed to survive the harsh conditions of rinsing with 0.1 M NaOH solution, which is evidenced by a dramatic decrease in the extraction sensitivity after the NaOH treatment (compare Fig. 4c and 4d). These results show that a sol–gel TiO_2–PDMS coated capillary possesses excellent pH stability and retains its extraction ability under extreme pH conditions, while conventionally prepared PDMS-based GC coatings were found to be unstable under such extreme pH conditions [52,53].

Table 1 shows repeatability and detection limit data for CME-HPLC analysis using sol–gel TiO_2–PDMS coated microextraction capillaries. For a 0.25 mm i.d. sol–gel titania–PDMS microextraction capillary, the R.S.D. value in peak area remained within 9.2%, and detection limits in the range of 0.25–5.37 ppb were achieved using UV-detection.

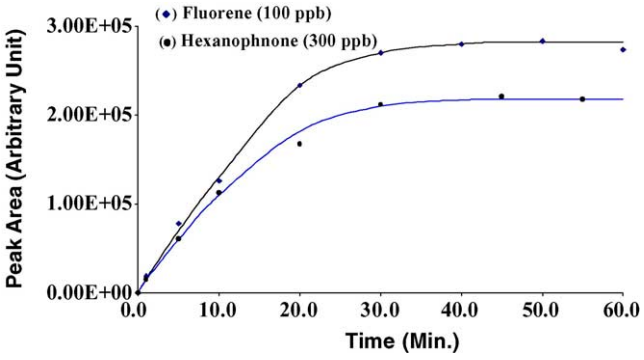
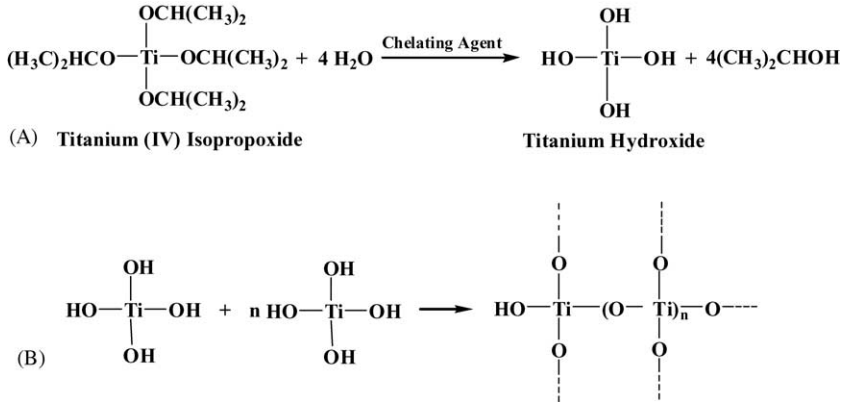


Fig. 7. Illustration of the extraction kinetics of fluorene (♦), and hexanophenone (●) obtained on a 40 cm × 0.32 mm i.d. × 0.5 μm sol–gel TiO_2–PDMS-coated capillary using 100 and 300 ppb aqueous solutions, respectively. Extraction conditions are the same as in Fig. 5. Other conditions: 25 cm × 4.6 mm i.d. ODS column (5 μm d_p); 85:15 (v/v), and 90:10 (v/v) acetonitrile/water (isocratic elution), respectively; 1 mL/min flow rate; UV detection at 254 nm; ambient temperature.

Fig. 5 presents a chromatogram illustrating CME-HPLC analysis of moderately polar aromatic ketones extracted from an aqueous sample using a 0.32 mm i.d. sol–gel coated TiO_2–PDMS capillary.

Compared to PAHs samples, ketones needed higher analyte concentrations (300 ppb–1 ppm) for CME-HPLC analysis. This may be explained by the nonpolar nature of the sol–gel TiO_2–PDMS coating, higher solubility of ketones in water due to higher polarity, and the working principles of UV detection. In this case, the run-to-run peak area repeatability was less than 8% R.S.D. Detection limits for the extracted ketones ranged between 2.47 ppb for heptanophenone to 11.60 ppb for valerophenone in conjunction with UV detection. From the presented results it is evident that sol–gel TiO_2–PDMS coating is able to extract both nonpolar and moderately polar analytes with good extraction sensitivity. Such an ability of the used sol–gel coating may be due to the presence of two different types of domains (a nonpolar organic domain based on an PDMS and a more polar inorganic domain based on sol–gel titania materials) in such coatings [54].

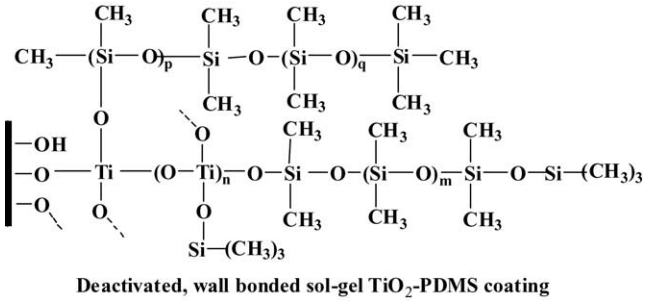
Fig. 6 illustrates on-line CME-HPLC analysis of alkylbenzenes using a TiO_2–PDMS coated capillary. Excellent detection limits were also achieved for these analytes (0.65–5.45 ppb), using UV detection. Like PAHs, alkylbenzenes are less polar analytes than aromatic ketones, and they are well extracted by a sol–gel TiO_2–PDMS extraction capillary with low-ppb and sub-ppb level detection limits. Table 2 summarizes the peak area repeatability and detection limit data for PAHs, ketones, and alkylbenzenes.



Scheme 1. (A) Hydrolysis of titanium (IV) isopropoxide, and (B) polycondensation of hydrolysis product, titanium hydroxide.

Fig. 7 illustrates the extraction kinetic profile for: (A) fluorene (nonpolar analyte) and (B) hexanophenone (moderately polar analyte) on a sol–gel TiO_2–PDMS coated microextraction capillary. Experimental data for these curves representing extraction kinetic profiles were obtained by individually performing capillary microextraction for each of the solutes. The microextraction experiments were performed using aqueous samples containing 100 and 300 ppb concentrations of fluorene and hexanophenone, respectively. A series of capillary microextraction experiments were conducted to vary the extraction time for each of the two analytes that were extracted from their standard solutions. Three replicate extractions of each analyte were performed for 1, 5, 10, 20, 30, 40, 50, and 60 min. The average peak area was then plotted against the extraction time to obtain Fig. 7. For both fluorene and hexanophenone, extraction equilibrium was reached within 40 min as is evidenced by the plateau on the extraction curve. Since PDMS has nonpolar characteristics, the TiO_2–PDMS coating tends to extract a nonpolar analyte, in this case fluorene, better than a more polar analyte, hexanophenone, which has higher affinity for the aqueous medium.

Further optimization of capillary preparation method and operation conditions may be necessary to exploit full analytical potential of the sol–gel titania coated extraction capillaries. It will be also interesting to use TiO_2–PDMS extraction capillary in CME-GC to achieve better detection limits, since CME-GC will allow for the use of highly sensitive flame ionization detector. Such an assumption stems from the fact that sol–gel TiO_2–PDMS coatings have already shown good extraction capabilities for CME-HPLC equipped with a UV detector, which is much less sensitive than the FID. The use of wider bore capillaries with thicker sol–gel coatings or monolithic extraction beds [55] should further enhance the extraction sensitivity.



Scheme 2. Final structure of the sol–gel TiO_2–PDMS coating.

4. Conclusions

To the best of our knowledge, this is the first report on the creation and use of a sol–gel TiO_2–PDMS coating in solid-phase microextraction. Sol–gel TiO_2–PDMS coated microextraction capillaries possess excellent pH stability and retain their extraction characteristics intact even after prolonged treatment with highly alkaline (pH 13) NaOH solution. Direct chemical bonding of the coating to capillary inner walls provides these coatings with excellent solvent resistance, and make sol–gel TiO_2–PDMS coated capillaries very much suitable for on-line sample preconcentration in CME-HPLC analysis. The newly developed sol–gel TiO_2–PDMS coating was effectively used for the extraction of different classes of analytes with good extraction sensitivity, and run-to-run repeatability. Low ppb and sub-ppb level (0.15–11.60 ppb) detection limits were achieved for PAHs, ketones, and alkylbenzenes in CME-HPLC analysis using the newly constructed sol–gel TiO_2–PDMS coated microextraction capillary in conjunction with UV detection. Through proper optimization of experimental conditions for sol–gel coating and the capillary microextraction processes it should be possible to further enhance the extraction sensitivity. For volatile and thermally stable analytes, use of sol–gel TiO_2–PDMS coated capillaries in CME-GC should provide significant enhancement in sensitivity.

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