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Sol–gel approach to in situ creation of high pH-resistant surface-bonded organic–inorganic hybrid zirconia coating for capillary microextraction (in-tube SPME)

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Abstract

A novel zirconia-based hybrid organic–inorganic sol–gel coating was developed for capillary microextraction (CME) (in-tube SPME). High degree of chemical inertness inherent in zirconia makes it very difficult to covalently bind a suitable organic ligand to its surface. In the present work, this problem was addressed from a sol–gel chemistry point of view. Principles of sol–gel chemistry were employed to chemically bind a hydroxy-terminated silicone polymer (polydimethyldiphenylsiloxane, PDMDPS) to a sol–gel zirconia network in the course of its evolution from a highly reactive alkoxide precursor undergoing controlled hydrolytic polycondensation reactions. A fused silica capillary was filled with a properly designed sol solution to allow for the sol–gel reactions to take place within the capillary for a predetermined period of time (typically 15–30 min). In the course of this process, a layer of the evolving hybrid organic–inorganic sol–gel polymer got chemically anchored to the silanol groups on the capillary inner walls via condensation reaction. At the end of this in-capillary residence time, the unbonded part of the sol solution was expelled from the capillary under helium pressure, leaving behind a chemically bonded sol–gel zirconia-PDMDPS coating on the inner walls. Polycyclic aromatic hydrocarbons, ketones, and aldehydes were efficiently extracted and preconcentrated from dilute aqueous samples using sol–gel zirconia-PDMDPS coated capillaries followed by thermal desorption and GC analysis of the extracted solutes. The newly developed sol–gel hybrid zirconia coatings demonstrated excellent pH stability, and retained the extraction characteristics intact even after continuous rinsing with a 0.1 M NaOH solution for 24 h. To our knowledge, this is the first report on the use of a sol–gel zirconia-based hybrid organic–inorganic coating as an extraction medium in solid phase microextraction (SPME).

Keywords: Capillary microextraction; In-tube SPME; Sol–gel extraction media; Sol–gel technology; Sol–gel zirconia poly(dimethyldiphenylsiloxane) coating; pH stability; Sample preconcentration; Gas chromatography; Hyphenated techniques; Polycyclic aromatic hydrocarbons; Aldehydes; Ketones

1. Introduction

Solid phase microextraction (SPME) was developed in 1989 by Belardi and Pawliszyn [1] to facilitate rapid sample preparation for both laboratory and field analyses. It provided a simple and efficient solvent-free method for the extraction and preconcentration of analytes from various sample matrices.

In SPME, a sorptive coating (either on the outer surface of a fused silica fiber or on the inner surface of a fused silica capillary) serves as the extraction medium in which the analytes get preferentially sorbed and preconcentrated. Polymeric surface coatings are predominantly used in conventional fiber-based SPME [1–4] as well as in the more recently materialized in-tube SPME [5–8] also referred to as capillary microextraction (CME) [9]. A number of new polymeric coatings have recently been developed [10]. Besides polymeric coatings, SPME fibers have also been prepared by using nonpolymeric materials [11] or by gluing reversed-phase high-performance liquid chromatography (HPLC) particles

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onto SPME fiber surface [12]. The sorbent coating plays a fundamentally important role in the SPME analysis, and further development and growth of SPME will greatly depend on new breakthroughs in the areas of sorbent development and coating technology [13].

Sol–gel chemistry offers an effective methodology for the synthesis of macromolecular materials under extraordinarily mild thermal conditions (typically at room temperature). The room temperature operation, inherent in sol–gel chemistry, facilitates the material synthesis process by easing the operational requirements on equipment specification and laboratory safety. This greatly simplifies the job to carry out and/or control sol–gel reactions within small-diameter fused silica capillaries. The sol–gel approach provides a facile mechanism to chemically bind an in situ created sol–gel coating to the inner walls of the capillary made out of an appropriate sol–gel-active material. Thanks to this chemical bonding, sol–gel coatings possess significantly higher thermal and solvent stabilities [14] compared with their conventional counterparts. The sol–gel approach can be applied to create silica-based as well as the newly emerging transition metal oxide-based sorbents. Furthermore, sol–gel chemistry provides an opportunity to create advanced material systems to achieve enhanced performance and selectivity in analytical separations and sample preconcentration [10,15].

Sol–gel organic–inorganic hybrid materials provide desirable sorptive properties that are difficult to achieve by using either purely organic or purely inorganic materials. Because of this unique opportunity to achieve enhanced selectivity, hybrid sol–gel materials have created a great deal of interest in the field of microcolumn separations and sample preparation. In the recent past, silica-based organic–inorganic hybrid stationary phases have been developed in the form of surface coatings [16–18] and monolithic beds [19]. In 1993, Dabrio and co-workers [20] developed a procedure for the preparation of a thin layer of silica gel with chemically bonded C_{18} moieties on the inner walls of fused-silica capillaries for use as open tubular columns in reversed-phase high-performance liquid chromatography. Colon and Guo [21] used sol–gel technology to prepare stationary phase coatings for open-tubular liquid chromatography and electrochromatography. Malik and co-workers introduced sol–gel coated columns for capillary GC [22] and sol–gel coated fibers for solid-phase microextraction [13,23]. Subsequently, other groups also got involved in sol–gel research aiming at developing novel sorbents for solid-phase microextraction [24–28] and solid-phase extraction [29,30]. Compared with conventional fibers, sol–gel SPME fibers demonstrated superior performance by exhibiting high thermal stability (up to 380 °C) [24] and solvent stability [25]. This enhanced stability of sol–gel coated fibers is attributed to the chemical bonding between the sol–gel coating and the fiber surface. Compared with the conventionally prepared fibers, in many instances, sol–gel SPME fibers showed better selectivity and extraction sensitivity, [26] less extraction time, [27] and extended lifetime [26]. Recently, sol–gel capillary microextraction was reported by Malik and co-workers [9]. In this format, also known to as in-tube SPME, sample extraction was accomplished using a sol–gel coating created on the inner surface of a fused silica capillary.

The sol–gel microextraction sorbents reported to date are predominantly silica-based. In spite of many attractive material properties (e.g., mechanical strength, surface characteristics, catalytic inertness, surface derivatization possibilities, etc.), silica-based materials have some inherent shortcomings. The main drawback of silica-based sorbents is the narrow range of pH stability. Under extreme pH conditions, silica-based materials become chemically unstable, and their sorptive properties may be compromised. For example, silica dissolves under alkaline conditions, and their dissolution process starts at a pH value of about 8 [31]. Under highly acidic pH conditions, silica-based bonded phases become hydrolytically unstable [32]. Therefore, developing sorbents with a wide range of pH stability is an important research area in contemporary separation and sample preparation technologies. Transition metal oxides (zirconia, titania, etc.) are well known for their pH stability [33], and appear to be logical candidates for exploration to overcome the above-mentioned drawbacks inherent in silica-based materials.

Zirconia possesses much better alkali resistance than other metal oxides, such as alumina, silica, and titania. It is practically insoluble within a wide pH range (1–14) [36–39]. Zirconia also shows outstanding resistance to dissolution at high temperatures [40,41]. Besides the extraordinary pH stability, excellent chemical inertness and high mechanical strength are two other attractive features that add value to zirconia for being used as a support material in chromatography [34] and membrane-based separations [35].

Extensive research work has been done on zirconia particles and their surface modifications for use as HPLC stationary phases [42,43]. A number of reports have also recently appeared in the literature on the use of zirconia-modified fused silica capillaries in capillary electrophoresis (CE) [44–48]. However, the excessive chemical inertness of zirconia particles remains a difficult hurdle to creating surface-bonded stationary phases.

We approached this problem from a sol–gel chemistry point of view. We took into consideration the fact that contrary to the high inertness of zirconia particles that have already been formed and attained highly stable structural characteristics, zirconium alkoxides are highly reactive sol–gel precursors for zirconia. By using appropriate conditions, it should be possible to utilize the reactivity of such zirconia precursors to create organic–inorganic zirconia materials with covalently bonded organic ligands. In this paper, we report the preparation of zirconia-based hybrid organic–inorganic sol–gel sorbents from a highly reactive precursor, zirconium butoxide, and a sol–gel-active organic polymer (hydroxy-terminated PDMDPS). The covalent bonding of the organic ligand to the sol–gel zirconia network structure was accomplished via condensation reaction in the course of controlled hydrolytic polycondensation reactions taking place in the sol

solution. Here, we demonstrate the outstanding performance of the in situ created sol–gel zirconia-PDMDPS coating in capillary microextraction in hyphenation with open-tubular gas chromatography (CME-GC).

2. Experimental

2.1. Equipment

All CME-GC experiments were performed on a Shimadzu Model 14A capillary GC system equipped with a flame ionization detector (FID) and a split-splitless injector. On-line data collection and processing were done using ChromPerfect (version 3.5) computer software (Justice Laboratory Software, Denville, NJ). A Fisher Model G-560 Vortex Genie 2 system (Fisher Scientific, Pittsburgh, PA) was used for thorough mixing of various sol solution ingredients. A Microcentaur model APO 5760 microcentrifuge (Accurate Chemical and Scientific Corp., Westbury, NY) was used to separate the sol solution from the precipitate (if any) at 13,000 rpm (15,682 × *g)*. A Nicolet model Avatar 320 FTIR instrument (Thermo Nicolet, Madison, WI) was used to acquire infrared spectra of the prepared sol–gel materials. A Barnstead Model 04741 Nanopure deionized water system (Barnstead/Thermodyne, Dubuque, IA) was used to obtain ∼16.0 MΩ water. Stainless steel mini-unions (SGE Inc., Austin, TX) were used to connect the fused silica capillary GC column with the microextraction capillary, also made of fused silica. An in-house-designed liquid sample dispenser (Fig. 1) was used to facilitate gravity-fed flow of the aqueous sample through the sol–gel microextraction capillary. A homebuilt, gas pressure-operated capillary filling/purging device [49] was used to perform a number of operations: (a) rinse the fused silica capillary with solvents; (b) fill the extraction capillary with the sol solution; (c) expel the sol solution from the capillary at the end of sol–gel coating process; and (d) purge the capillary with helium after treatments like rinsing, coating, and sample extraction.

2.2. Chemicals and materials

Fused-silica capillary (320 and 250 μm, i.d.) with a protective polyimide coating was purchased from Polymicro Technologies Inc. (Phoenix, AZ). Naphthalene and HPLC-grade solvents (methylene chloride, methanol) were purchased from Fisher Scientific (Pittsburgh, PA). Hexamethyldisilazane (HMDS), poly (methylhydrosiloxane) (PMHS), ketones (valerophenone, hexanophenone, heptanophenone, and decanophenone), aldehydes (nonylaldehyde, *n*-decylaldehyde, undecylic aldehyde, and dodecanal), polycyclic aromatic hydrocarbons (PAHs) (naphthalene, acenaphthene, fluorene, phenanthrene, pyrene, and naphthacene), were purchased from Aldrich (Milwaukee, WI). Two types of silanol-terminated poly(dimethyldiphenylsiloxane) (PDMDPS) copolymers

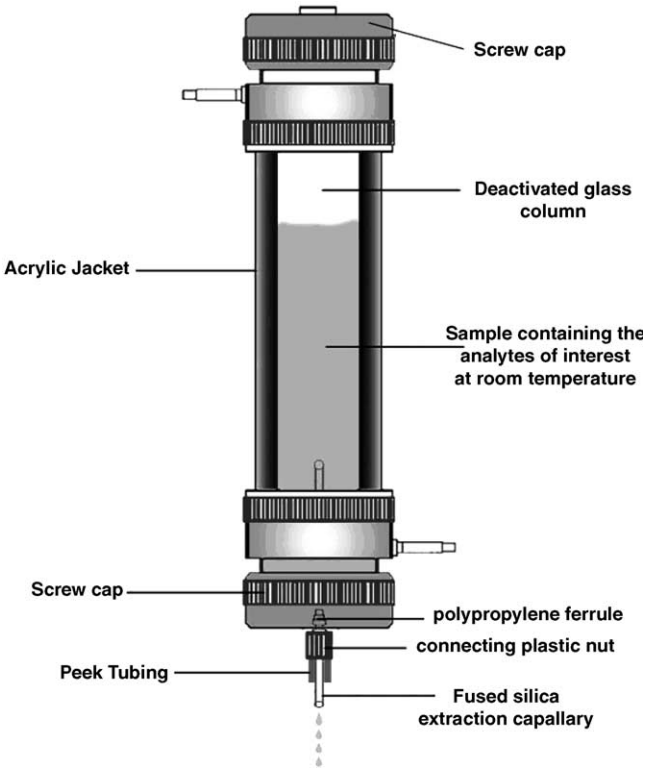


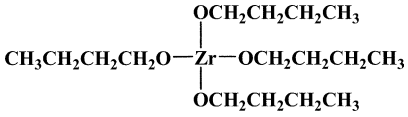
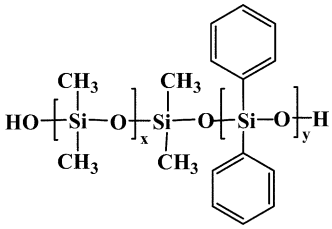
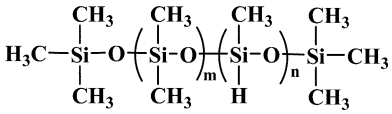
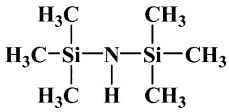
Fig. 1. Gravity-fed extraction system for capillary microextraction.

(with 2–3% and 14–18% contents of the diphenyl-containing component) were purchased from United Chemical Technologies Inc. (Bristol, PA).

2.3. Preparation of sol–gel zirconia-PDMDPS coating

A carefully designed sol solution was used to create the coating. The key ingredients of the sol solution used are listed in Table 1. The sol solution was prepared in a clean polypropylene centrifuge tube by dissolving the following ingredients in mixed solvent system consisting of methylene chloride and butanol (250 μL each): 10–15 μL of zirconium(IV) butoxide (80% solution in 1-butanol), 85 mg of silanol-terminated poly(dimethyldiphenylsiloxane) copolymer, 70 mg of poly(methylhydrosiloxane), 10 μL of 1,1,1,3,3,3-hexamethyldisilazane, and 2–4 μL of glacial acetic acid. The dissolution process was aided by thorough vortexing. The sol solution was then centrifuged at 13,000 rpm (15,682 × *g*) to remove the precipitate (if any). The top clear sol solution was transferred to a clean vial and was further used in the coating process. A hydrothermally treated fused silica capillary (2 m) was filled with the clear sol solution, using pressurized helium (50 psi) in the filling/purging device [49]. The sol solution was allowed to stay inside the capillary for a controlled period of time (typically 15–30 min) to facilitate the formation of a sol–gel coating, and its chemical bonding to the capillary inner walls. After that, the free portion of the solution was expelled from the capillary, leaving behind a surface-bonded sol–gel coating

Table 1
Names, and chemical structure of the coating solution ingredients for sol–gel capillary

Ingredient	Function	Chemical structure
Zirconium(IV) butoxide	Sol–gel precursor	
Silanol-terminated poly (dimethyldiphenylsiloxane)	Sol–gel-active organic component	
Methylene chloride	Solvent	CH_2Cl_2
Acetic acid	Chelating reagent	CH_3COOH
Poly(methylhydrosiloxane)	Deactivating reagent	
1,1,1,3,3,3-Hexamethyldisilazane	Deactivating reagent	

within the capillary. The sol–gel coating was then dried by purging with helium. The coated capillary was further conditioned by temperature programming from 40 to 150 °C at 1 °C/min and held at 150 °C for 300 min. Following this, the conditioning temperature was raised from 150 to 320 °C at 1 °C/min and held at 320 °C for 120 min. The extraction capillary was further cleaned by rinsing with 3 mL of methylene chloride and conditioned again from 40 to 320 °C at 4 °C/min. While conditioning, the capillary was constantly purged with helium at 1 mL/min. The conditioned capillary was then cut into 10 cm long pieces that were further used to perform capillary microextraction.

2.4. Preparation of the samples

PAHs, ketones, and aldehydes were dissolved in methanol or tetrahydrofuran to prepare 0.1 mg/L stock solutions in silanized glass vials. For extraction, fresh samples with ppb level concentrations were prepared by diluting the stock solutions with deionized water.

2.5. Gravity-fed sample dispenser for capillary microextraction

The gravity-fed sample dispenser for capillary microextraction (Fig. 1) was constructed by in-house modification of a Chromaflex AQ column (Kontes Glass Co., Vineland, NJ) consisting of a thick-walled glass cylinder coaxially placed inside an acrylic jacket. The inner surface of the thick-walled cylindrical glass column was deactivated by treating with a 5% (v/v) solution of HMDS in methylene chloride followed by overnight heating at 100 °C. The column was then cooled to ambient temperature, thoroughly rinsed with methanol and liberal amounts of deionized water, and dried in a helium flow. The entire Chromaflex AQ column was subsequently reassembled.

2.6. Sol–gel capillary microextraction-GC analysis

To perform capillary microextraction, a previously conditioned sol–gel zirconia-PDMDPS coated microextraction capillary (10 cm × 320 μm i.d. or 10 cm × 250 μm i.d.) was vertically connected to the bottom end of the empty sample dispenser (Fig. 1). The aqueous sample (50 mL) was then placed in the dispenser from the top, and allowed to flow through the microextraction capillary under gravity. While passing through the extraction capillary, the analyte molecules were sorbed by the sol–gel zirconia-PDMDPS coating residing on the inner walls of the capillary. The sample flow through the capillary was allowed to continue for 30–40 min for an extraction equilibrium to be established. After this, the microextraction capillary was purged with helium at 25 kPa for 1 min and connected to the top end of a vertically placed two-way mini-union connecting the microextraction capillary with the inlet end of the GC column. Approximately, 6.5 mm of the extraction capillary remained tightly inserted into the connector, as did the same length of GC column from the opposite side of the mini-union facing each other within the connector. The installation of the capillary was completed by providing a leak-free connection at the bottom end of the GC injection port so that top 9 cm of the extraction capillary remained inside the injection port. The extracted

analytes were then thermally desorbed from the capillary by rapidly raising the temperature of the injector (up to 300 °C starting from 30 °C). The desorption was performed over a 8.2 min period in the splitless mode allowing the released analytes to be swept over by the carrier gas into the GC column held at 30 °C during the entire desorption process. Such a low column temperature facilitated effective solute focusing at the column inlet. Following this, the column temperature was programmed from 30 to 320 °C at rate of 20 °C/min. The split vent remained closed throughout the entire chromatographic run. Analyte detection was performed using a flame ionization detector (FID) maintained at 350 °C.

3. Result and discussion

Capillary microextraction [9] uses a sorbent coating on the inner surface of a capillary, and thereby overcomes a number of deficiencies inherent in conventional fiber-based SPME such as susceptibility of the sorbent coating to mechanical damage due to scraping during operation, fiber breakage, and possible sample contamination. In CME, the sorbent coating is protected by the fused silica tubing against mechanical damage. The capillary format of SPME also provides operational flexibility and convenience during the microextraction process since the protective polyimide coating on the outer surface of fused silica capillary remains intact. Inner surface-coated capillaries provide a simple way to perform extraction in conjunction with a gravity-fed sample dispenser (Fig. 1), and thus avoid typical drawbacks of fiber-based SPME, including the need for sample agitation during extraction as well as the sample loss and contamination problems associated with this.

The sol–gel process is a straightforward route to obtaining homogeneous gels of desired compositions. In recent years, it has received increased attention in analytical separations and sample preparations due to its outstanding versatility and excellent control over properties of the created sol–gel materials that proved to be promising for use as stationary phases and extraction media.

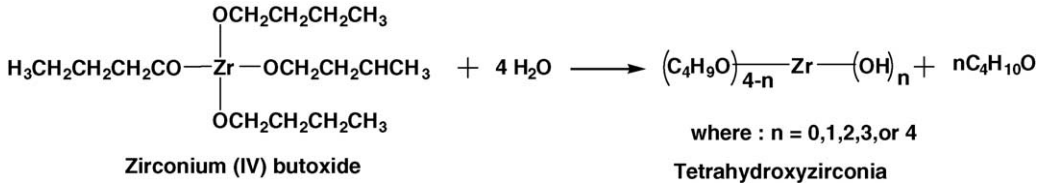
A general procedure for the creation of sol–gel stationary phase coating on the inner walls of fused silica capillary GC columns was first described by Malik and co-workers [22]. In the present work, a judiciously designed sol solution ingredients (Table 1) was used to create the sol–gel zirconia-PDMDPS coating on the fused silica capillary inner surface. Zirconium(IV) butoxide (80% solution in 1-butanol) was used as a sol–gel precursor and served as a source for the inorganic component of the sol–gel organic–inorganic hybrid coating.

The sol–gel Zirconia-PDMDPS coating presented here was generated via two major reactions: (1) hydrolysis of a sol–gel precursor, zirconium(IV) butoxide; and (2) polycondensation of the precursor and it hydrolysis products between themselves and with other sol–gel-active ingredients in the coating solution, including silanol-terminated PDMDPS. The hydrolysis of the zirconium(IV) butoxide precursor is represented by Scheme 1 [50].

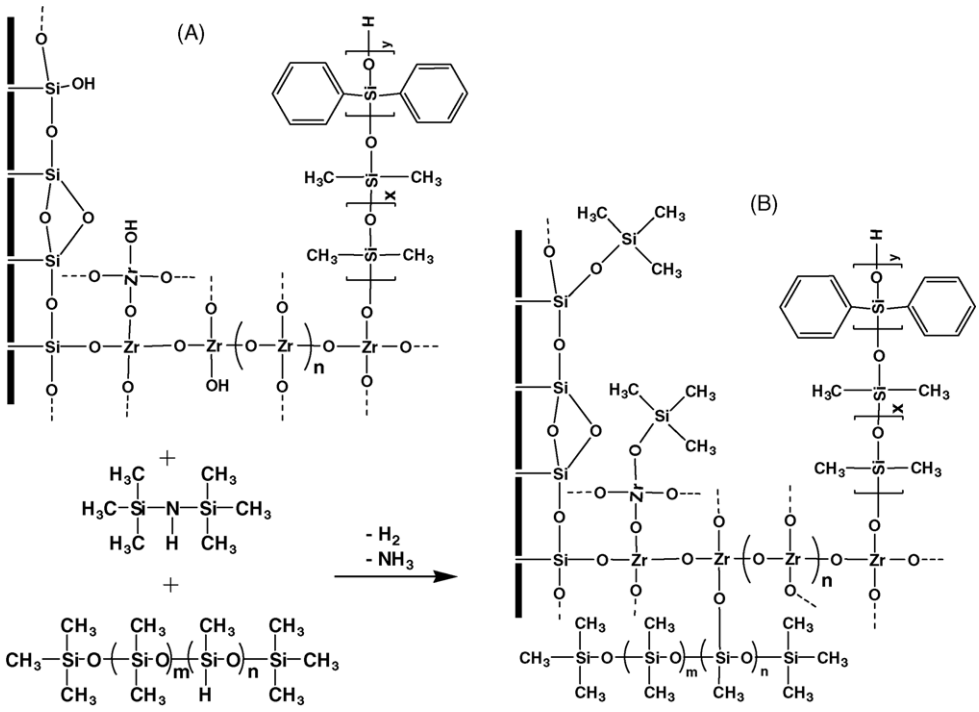
Condensation of the sol–gel polymer growing in close vicinity of the capillary walls with silanol group on the capillary surface led to the formation of an organic–inorganic coating chemically anchored to the capillary inner walls (Scheme 2A).

A major obstacle to preparing zirconia-based sol–gel materials using zirconium alkoxide precursors (e.g., zirconium butoxide) is the very rapid sol–gel reaction rates for these precursors. Even if the solution of zirconium alkoxide is stirred vigorously, the rates of these reactions are so high that large agglomerated zirconia particles precipitate out immediately when water is added [51]. Such fast precipitation makes it difficult to reproducibly prepare zirconia sol–gel materials. Ganguli and Kundu [52] addressed the fast precipitation problem by dissolving zirconium propoxide in a non-polar dry solvent like cyclohexane. The hydrolysis was performed by exposing the coatings prepared from the solution to atmospheric moisture. Heating to 450 °C was necessary to obtain transparent films. The hydrolysis rates of zirconium alkoxides can also be controlled by chelating with ligand-exchange reagents. Acetic acid [53,54], valeric acid [55], β-diketones [56–58], triethanolamine [59], and 1, 5-diaminopentane [56] have been used as chelating reagents for zirconia sol–gel reactions. In general, chelation occurs when the added reagent replaces one or more alkoxy groups forming a strong bond. The formation of this bond reduces the hydrolysis rate by decreasing the number of available alkoxy groups [60].

In the present work, we controlled the hydrolysis rate of zirconium butoxide by using glacial acetic acid [61] as a chelating agent as well as a source of water released slowly through the esterification with 1-butanol [62,63]. Two Silanol-terminated poly (dimethyldiphenylsiloxane) copolymers (with 2–3% and 14–18% diphenyl-containing blocks) were used as sol–gel-active organic components to be chemically incorporated in the sol–gel network through polycondensation reactions with the zirconium butoxide



Scheme 1. Hydrolysis of zirconium(IV) butoxide precursor.



Scheme 2. Deactivation and shielding of sol–gel zirconia-PDMDPS coated surface using PMHS and HMDS.

precursor and its hydrolysis products. An IR spectrum of the pure co-polymers (the one with 2–3% phenyl-containing block) is presented in Fig. 2A where a small stretching at 3068 cm^{-1} indicates the presence of phenyl groups.

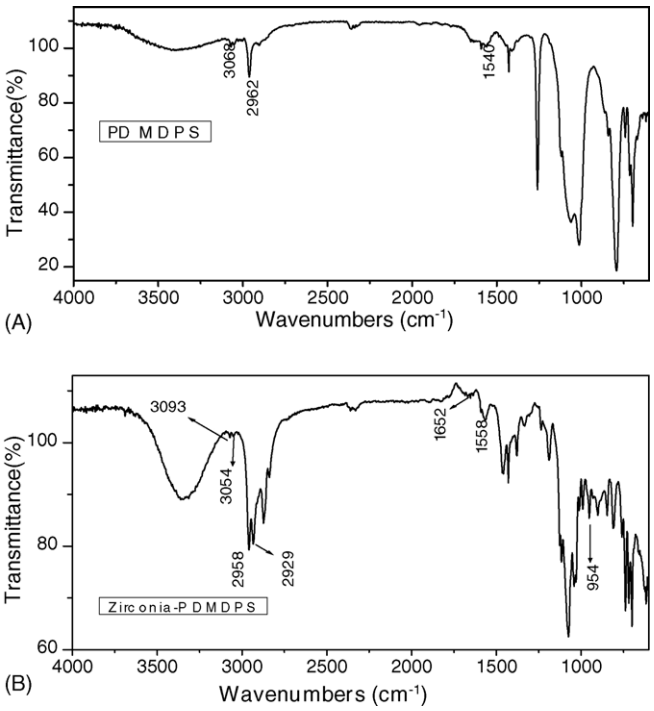


Fig. 2. IR spectra representing: (A) pure silanol-terminated PDMDPS copolymer with 2–3% diphenyl-containing component; and (B) sol–gel zirconia-PDMDPS material prepared using PDMDPS copolymer with 14–18% diphenyl-containing component.

This advantageous chemical incorporation of an organic component into the sol–gel network is responsible for the formation of an organic–inorganic hybrid material system that can be conveniently used for in situ creation of surface coating on a substrate like the inner walls of a fused silica capillary. Besides, the organic groups help to reduce the shrinkage and cracking of the sol–gel coating [64,65]. Furthermore, sol–gel process can be used to control the porosity and thickness of the coating and to improve its mechanical properties [66]. Poly (methylhydrosiloxane) and 1,1,1,3,3,3-hexamethyldisilazane that were used in the sol solution, served as deactivation reagents to perform chemical derivatization of the strongly adsorptive residual hydroxyl groups on the resulting sol–gel material. The purpose of these reactions was to minimize the strong adsorptive interactions between polar solutes and the sol–gel sorbent that may lead to sample loss, peak tailing, sample carry-over and other deleterious effects. In the presented method for the preparation of the sol–gel zirconia coated microextraction capillary, the deactivation reactions were designed to take place mainly during thermal conditioning of the capillary following the sol–gel coating procedure.

Hydrolytic polycondensation reactions for sol–gel-active reagents are well established in sol–gel chemistry [67–70], and constitute the fundamental mechanism in sol–gel synthesis. The condensation between sol–gel-active zirconia and silicon compounds is also well documented [71–73]. According to published literature data, [74,75] the characteristic IR band for Zr–O–Si bonds is located in the vicinity of 945–980 cm^{-1}. Fig. 2B shows an IR spectrum of sol–gel zirconia PDMDPS material prepared by using a PDMDPS polymer containing

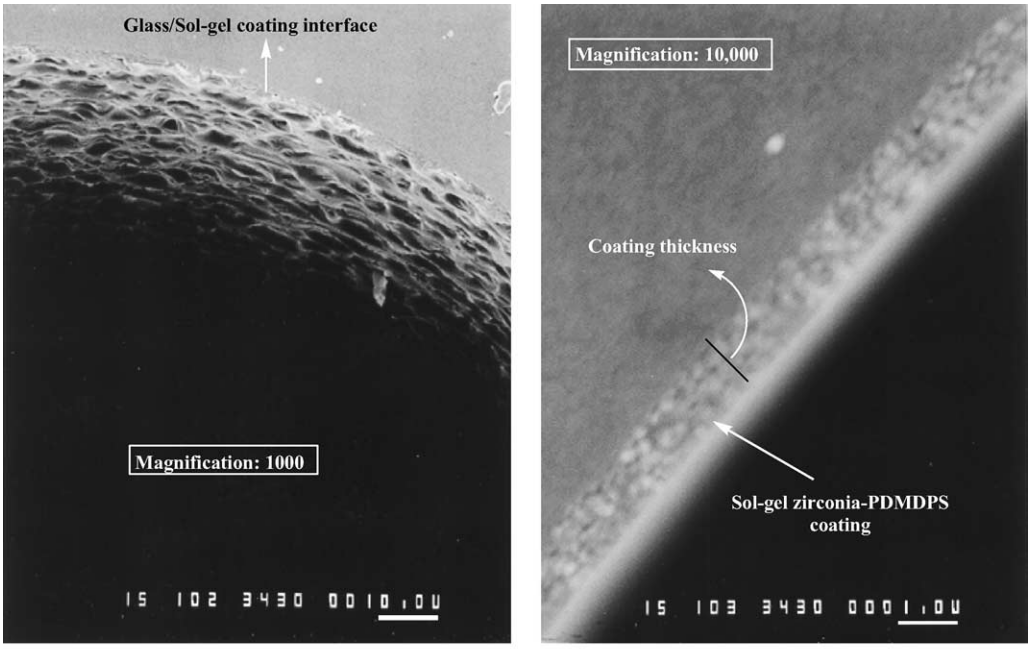


Fig. 3. Scanning electron microscopic images of a 0.32 mm i.d. Sol–gel zirconia-PDMDPS coated microextraction capillary. (A) Illustrates cross-sectional view (1000×) of roughened surface obtained by sol–gel coating process. (B) Illustrates the coating thickness (10,000×).

approximately eight time higher amounts of the phenyl group than that presented in Fig. 2A. The presence of the stretching at 954 cm^{-1} indicates to the presence of Zr–O–Si bonds in the prepared sol–gel material [74].

Metal-bound hydroxyl groups on the created sol–gel coating represent strong adsorptive sites for polar solutes. In the context of analytical microextraxtion or separation, presence of such groups is undesirable, and may lead to a number of deleterious effects including sample loss, reproducibility problems, sample carryover problems, and peak distortion and tailing. Therefore, appropriate measures need to be taken to deactivate these adsorptive sites. This may be accomplished by chemically reacting the hydroxyl groups with suitable derivatization reagents. Like silica-based sol–gel coatings, the surface hydroxyl groups of sol–gel zirconia coating can be derivatized using reactive silicon hydride compounds such as alkyl hydrosilanes [76,77] and hexamethyldisilazane [78]. In this work, we used a mixture of polymethylhydrosiloxane and hexamethyldisilazane for this purpose: the underlying chemical reactions are

Table 2
Peak area and retention time repeatability data for PAHs, aldehydes, and ketones extracted from aqueous samples using four replicate measurements by CME-GC using sol–gel zirconia-PDMDPS

Analyte		Peak area repeatability ($n = 4$)		t_R Repeatability ($n = 4$)		Detection limit (ng/mL)
Chemical class	Name	Mean peak area (aribitary unit)	R.S.D. (%)	Mean t_R (min)	R.S.D. (%)	
PAHs	Naphthalene	11692.42	7.25	15.32	0.11	0.57
	Acenaphthene	23560.38	4.58	17.12	0.05	0.16
	Fluorene	30970.30	2.45	17.73	0.12	0.09
	Phenanthrene	09010.92	3.46	18.76	0.10	0.06
	Pyrene	55005.40	2.78	20.22	0.22	0.03
	Naphthacene	22378.12	5.42	21.44	0.14	0.05
Aldehyde	1-Nonanal	15910.25	1.29	15.27	0.03	0.33
	1-Decanal	22908.98	5.45	15.94	0.16	0.08
	Undecanal	30413.15	5.08	16.61	0.10	0.10
	Dodecanal	32182.70	3.72	17.22	0.11	0.05
Ketones	Valerophenone	03712.88	3.10	16.79	0.06	0.92
	Hexanophenone	13780.88	1.24	17.40	0.07	0.33
	Heptanophenone	47398.87	1.24	18.19	0.27	0.08
	Decanophenone	83156.67	2.20	19.44	0.11	0.02
	Trans-chalcone	06546.25	5.57	19.82	0.03	0.57

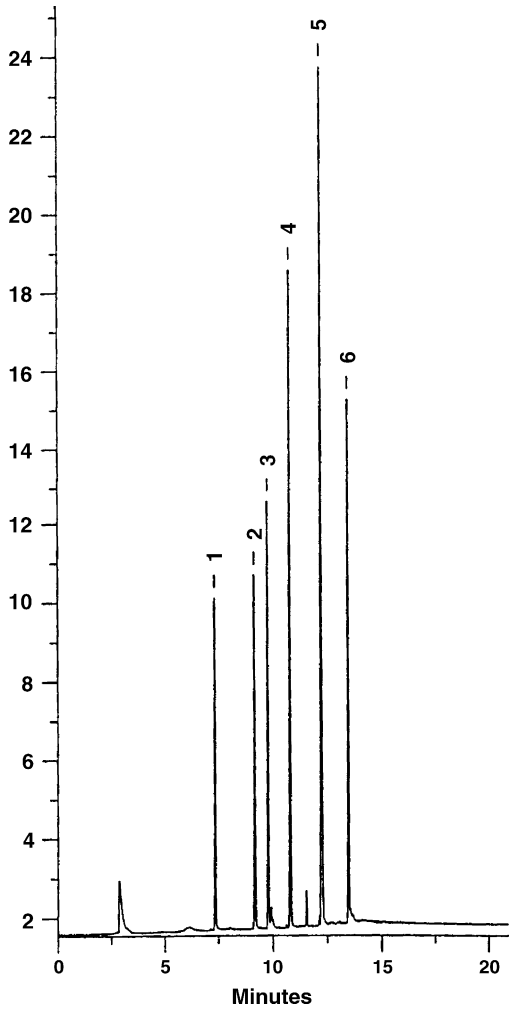


Fig. 4. CME-GC analysis of PAHs using a sol–gel zirconia-PDMDPS coated extraction capillary. Extraction parameters: 10 cm × 0.32 mm i.d. microextraction capillary; extraction time, 30 min (gravity fed at room temperature). Other conditions: 10 m × 0.25 mm i.d. Sol–gel PDMS GC column; splitless desorption; injector temperature rose from 30 to 300 °C: column temperature program from 30 to 300 °C at rate of 20 °C/min; helium carrier gas: FID 350 °C. Peaks: (1) naphthalene; (2) acenaphthene; (3) fluorene; (4) phenanthrene; (5) pyrene; and (6) naphthacene.

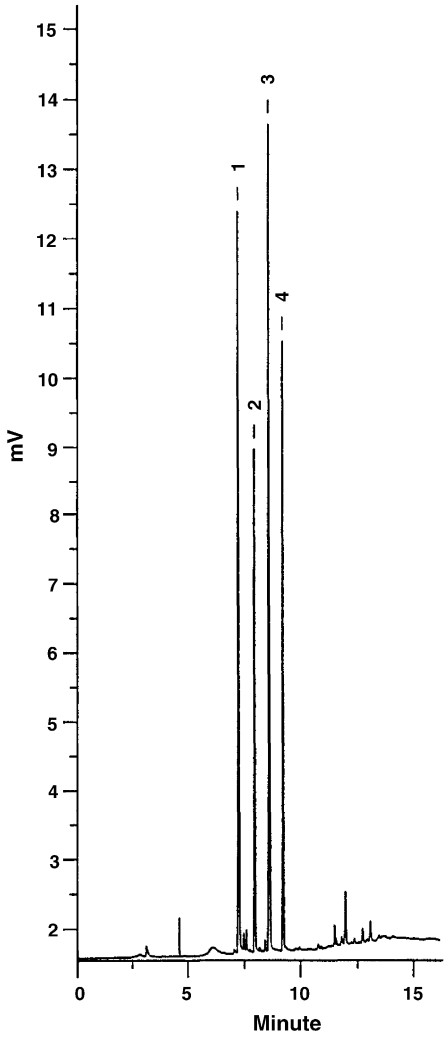


Fig. 5. CME-GC analysis of aldehydes using a sol–gel zirconia-PDMDPS coated extraction capillary. Extraction parameters: 10 cm × 0.32 mm i.d. microextraction capillary; extraction time, 40 min (gravity fed at room temperature). Other conditions: 10 m × 0.25 mm i.d. Sol–gel GC PDMS column; splitless desorption; injector temperature rose from 30 to 300 °C: column temperature program from 30 to 300 °C at rate of 20 °C/min; helium carrier gas: FID 350 °C. Peaks: (1) nonylaldehyde; (2) *n*-decylaldehyde; (3) undecylic aldehyde; and (4) dodecanal.

schematically represented in Scheme 2 (A and B illustrate the chemical structure of the sol–gel zirconia surface coating before and after deactivation respectively).

One of the most important undertakings in CME is the creation of a stable, surface-bonded sorbent coating on the inner walls of a fused silica capillary. Fig. 3 represents scanning electron microscopic images of a sol–gel Zirconia-PDMDPS coated fused silica capillary prepared in the present work. The SEM images A and B were obtained at a magnification

Table 3
Capillary-to-capillary and run-to-run peak area repeatability for mixture of PAHs, aldehydes, and ketones in four replicate measurements by CME-GC using sol–gel zirconia-PDMDPS coated extraction capillaries

Name of the analyte	Peak area repeatability ($n = 4$)			
	Capillary-to-capillary		Run-to-run	
	Mean peak area (aribitary unit)	R.S.D. (%)	Mean peak area (aribitary unit)	R.S.D. (%)
Undecanal	47940.9	4.60	60364.2	4.03
Hexanophenone	27538.4	1.61	25055.5	2.13
Fluorene	53250.7	5.40	59485.7	2.14
Phenanthrene	51399.9	4.91	54867.9	2.84

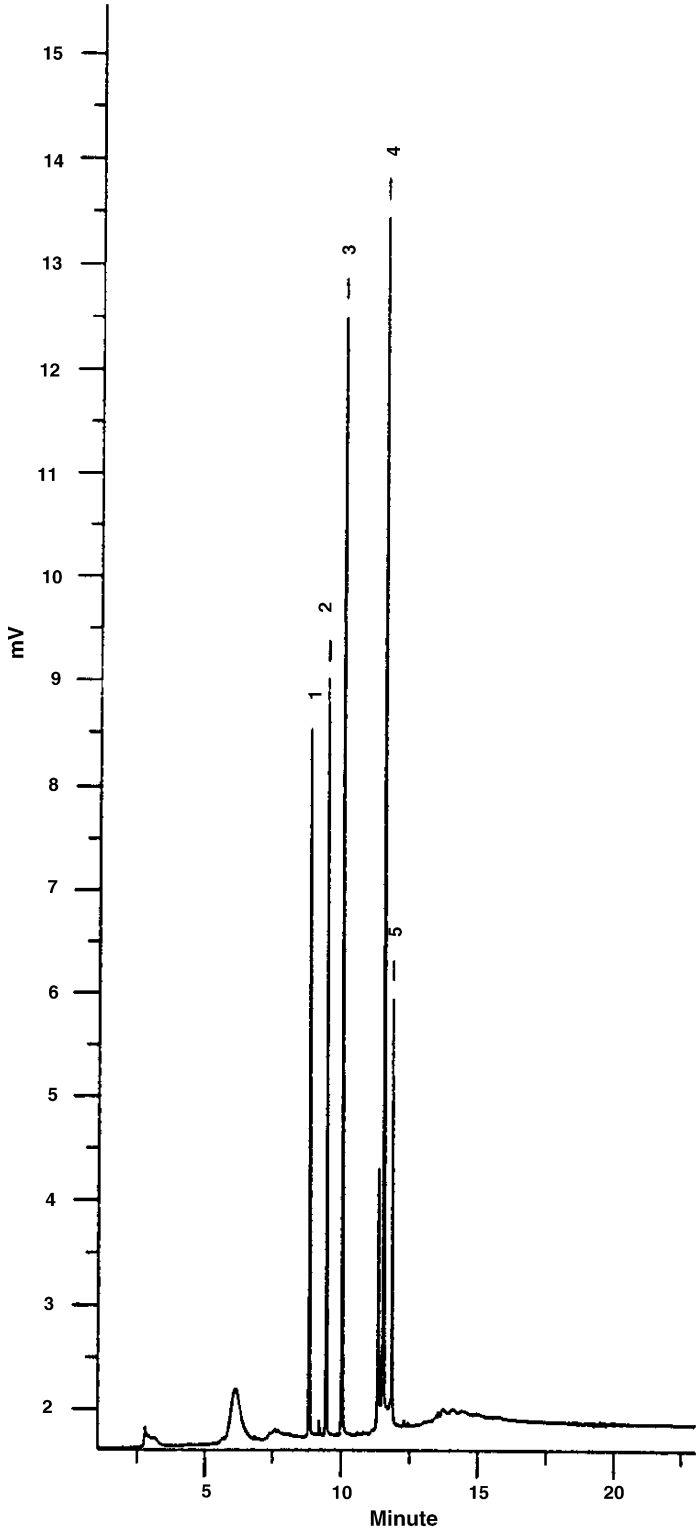


Fig. 6. CME-GC analysis of ketones using a sol–gel zirconia-PDMDPS coated extraction capillary. Extraction parameters: 10 cm × 0.32 mm i.d. microextraction capillary; extraction time, 40 min (gravity fed at room temperature). Other conditions: 10 m × 0.25 mm i.d. Sol–gel PDMS GC column; splitless desorption; injector temperature rose from 30 to 300 °C: column temperature program from 30 to 300 °C at rate of 20 °C/min; helium carrier gas: FID 350 °C. Peaks: (1) valerophenone; (2) hexanophenone; (3) heptanophenone; (4) decanophenone; and (5) trans-chalcone.

of 1000 and 10,000×, respectively. The microstructural details revealed in these images clearly show that the created sol–gel zirconia coating possesses a porous make-up which substantially differs from that obtained by us for sol–gel titania coating [79].

Sol–gel zirconia-PDMDPS-coated capillaries allowed the extraction of analytes belonging to various chemical classes. Experimental data highlighting CME-GC analysis of polycyclic aromatic hydrocarbons using a sol–gel zirconia-PDMDPS coated capillary is shown in Fig. 4.

CME-GC experiments were performed on an aqueous sample with low ppb level analyte concentrations. Experimental data presented in Table 2 shows that CME-GC with a sol–gel zirconia-PDMDPS coating provides excellent run-to-run repeatability in solute peak areas (3–7%) and the used sol–gel GC column provided excellent repeatability in retention times (less than 0.2%). It should be pointed out that the column used for GC analyses was also prepared in-house using a sol–gel method described by us in a previous publication [22].

The reproducibility of the newly developed method for the preparation of sol–gel hybrid organic–inorganic zirconia coated capillaries was evaluated by preparing three sol–gel zirconia PDMDPS-coated capillaries in accordance with the new procedure and following their performance in CME-GC analysis of different classes of analytes extracted from aqueous samples. The GC peak area obtained for an extracted analyte was used as the criterion for capillary-to-capillary reproducibility which ultimately characterizes the capillary preparation method reproducibility. The results are presented in Table 3 For each analyte, four replicate extractions were made on each capillary and the mean of the four measured peak areas was used in Table 3 for the purpose of capillary-to-capillary reproducibility. The presented data show that the capillary-to-capillary reproducibility is characterized by an RSD value of less than 5.5% for all three classes of compounds used for this evaluation. For a sample preparation method, a less than 5.5% R.S.D. is indicative of excellent reproducibility.

Fig. 5 illustrates a gas chromatogram of several free aldehydes extracted from an aqueous sample using a sol–gel zirconia-PDMDPS coated capillary. Here, the concentrations of the used aldehydes were in 80–500 ppb range. The extraction was carried out on a 10 cm × 0.32 mm i.d. Sol–gel zirconia-PDMDPS coated microextraction capillary for 30–40 min. The extraction of the analytes was performed at room temperature. Aldehydes are known to have toxic and carcinogenic properties, and therefore, their presence in the environment is of great concern because of their adverse effects on public health and vegetation [80]. Aldehydes are major disinfection by products formed as a result of chemical reaction between disinfectant (ozone or chlorine) and organic compounds in drinking water [81]. Therefore, accurate analysis of trace-level contents of aldehyde in the environment and in drinking water is important [82]. Aldehydes are polar compounds that are often derivatized [83] for GC analysis to avoid undesirable adsorption that causes peak tailing. Sol–gel zirconia-PDMDPS coated capillary provided highly efficient extraction of the aldehydes, and the used sol–gel GC column provided excellent peak shapes which is also indicative of high quality of deactivation in the used sol–gel GC column. This also demonstrates effective focusing of the analytes at the column inlet after their thermal desorption from the microextraction capillary. For the aldehydes, sol–gel CME-GC with the zirconia-PDMDPS coated capillary provided excellent repeatability in peak area (R.S.D. < 5%) and retention time (R.S.D. < 0.16%).

Fig. 6 shows a gas chromatogram illustrating CME-GC analysis of several ketones extracted from an aqueous sam-

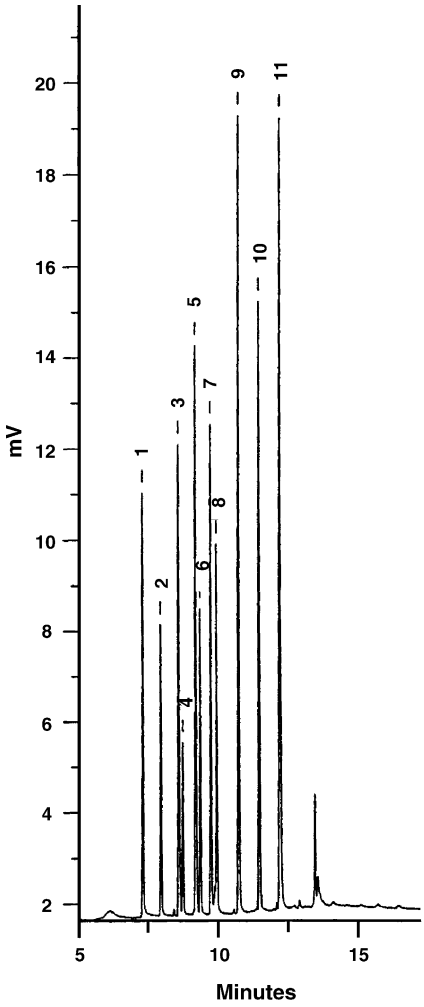


Fig. 7. CME-GC analysis of mixture of PAHs, aldehydes and ketones using a sol–gel zirconia-PDMDPS coated extraction capillary. Extraction parameters: 10 cm × 0.32 mm i.d. microextraction capillary; extraction time, 40 min (gravity fed at room temperature). Other conditions: 10 m × 0.25 mm i.d. Sol–gel PDMS GC column; splitless desorption; injector temperature rose from 30 to 300 °C: column temperature program from 30 to 300 °C at rate of 20 °C/min; helium carrier gas: FID 350 °C. Peaks: (1) napnthalene; (2) *n*-decylaldehyde; (3) undecylic aldehyde; (4) valerophenone; (5) dodecanal; (6) hexanophenone; (7) fluorene; (8) heptanophenone; (9) phenanthrene; (10) pyrene; and (11) naphthacene.

ple. Like aldehydes, there was no need for derivatization of the ketones, either during extraction or GC analysis. Sharp and symmetrical GC peaks, evident from the chromatogram, show the effectiveness of the used CME-GC system, as well as the practical utility of the mini-union metal connector providing leak free connection between the extraction capillary and the GC column. Excellent reproducibility was achieved in CME-GC of ketones using sol–gel zirconia-PDMDPS coated capillary as shown in Table 2. The peak area RSD% values for ketones were less than 5.6% and their retention time repeatability on used sol–gel PDMS column was characterized by R.S.D. values of less than 0.27%.

Fig. 7 shows a gas chromatogram illustrating CME-GC analysis of an aqueous sample containing different classes of compounds including PAHs, aldehydes and ketones, and shows that the sol–gel zirconia-PDMDPS extraction capillary can provide simultaneous extraction of polar and non-polar compounds present in the aqueous sample, and demonstrates the advantage over conventional SPME coatings that often do not allow such effective extraction of both polar and non-polar analyte from the same sample.

In capillary microextraction technique, the amount of analyte extracted into the sorbent coating depends not only on the polarity and thickness of the coated phase, but also on the extraction time. Fig. 8 illustrates the kinetic profile for the extraction of fluorene (a non-polar analyte), heptanophenone and undecylic aldehyde (both are moderately polar analytes) on a sol–gel zirconia-PDMDPS-coated microextraction capillary. The CME experiments were carried out using aqueous samples of individual test analytes. The extraction equilibrium for fluorene reached in 10 min, which is much shorter than extraction equilibrium time for heptanophenone and undecylic aldehyde (both approximately 30 min). This is because fluorene exhibits hydrophobic behavior that has higher affinity toward the non-polar PDMDPS-based sol–gel zirconia coating than toward water. On the other hand, heptanophenone and undecylic aldehyde, being more polar and hydrophilic than fluorene showed a slower extraction by the coated non-polar sol–gel zirconia-PDMDPS sorbent.

Sol–gel zirconia-PDMDPS coating showed high pH stability, and retained excellent performance after rinsing with 0.1 M NaOH (pH 13) for 24 h. Chromatograms in Fig. 9a and b show CME-GC analysis of four PAHs before (Fig. 9a) and after (Fig. 9b) zirconia-PDMDPS extraction capillary was rinsed with 0.1 M NaOH solution.

As is evident from Fig. 9, the extraction performance of the sol–gel zirconia-PDMDPS capillary remained practically unchanged after rinsing with NaOH as it can be seen in Table 4.

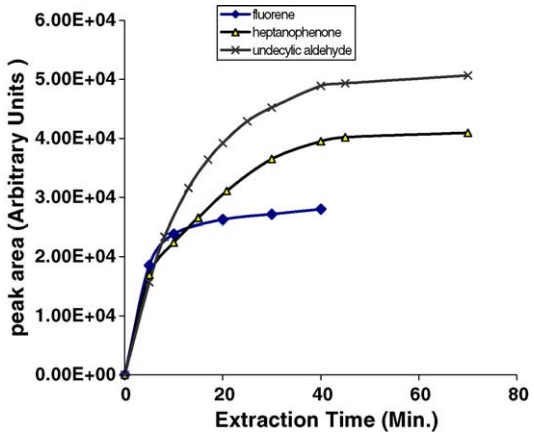


Fig. 8. Extraction kinetics of aqueous undecylic aldehyde, heptanophenone, and fluorene on a sol–gel zirconia-PDMDPS microextraction coated capillary. Extraction parameters: 10 cm × 0.32 mm i.d. microextraction capillary; Other conditions: 10 m × 0.25 mm i.d. Sol–gel GC PDMS column; splitless desorption; injector temperature from 30 to 300 °C: column temperature program from 30 to 300 °C at rate of 20 °C/min; helium carrier gas: FID 350 °C.

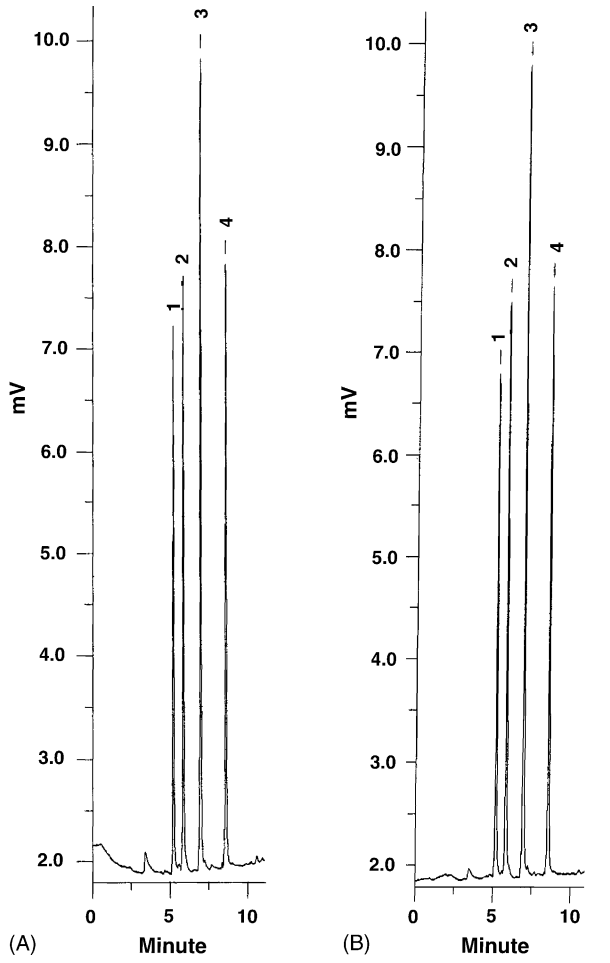


Fig. 9. CME-GC analysis of PAHs using a sol–gel zirconia-PDMDPS coated microextraction capillary: before (a) and after (b) rinsing the microextraction capillary with 0.1 M NaOH solution for 24 h. Extraction parameters: 10 cm × 0.25 mm i.d. microextraction capillary; coating thickness 0.3 mm, extraction time, 30 min (gravity fed at room temperature). Other conditions: 10 m × 0.25 mm i.d. Sol–gel GC PDMS column; splitless desorption; injector temperature rose from 30 to 300 °C: column temperature program from 30 to 280 °C at rate of 20 °C/min then from 280 to 300 °C at rate of 2 °C/min; helium carrier gas: FID 350 °C. Peaks: (1) acenaphthene; (2) fluorene; (3) phenanthrene; and (4) pyrene.

Table 4
Peak area repeatability data for ppb level concentrations of PAHs before and after extraction capillary treated with 0.1 M NaOH

Name of the analyte	Peak area repeatability before rinsing with 0.1 M NaOH Mean peak area A_1 (aribitary unit)	Peak area repeatability after rinsing with 0.1 M NaOH Mean peak area A_2 (aribitary unit)	Relative change in peak area $\lvert(A_2–A_1)/A_1\rvert \times 100$ (%)
Acenaphthene	30380.91	29432.76	3.12
Fluorene	35425.63	33428.86	5.64
Phenanthrene	47547.31	46525.33	2.15
Pyrene	33884.61	35636.56	5.17

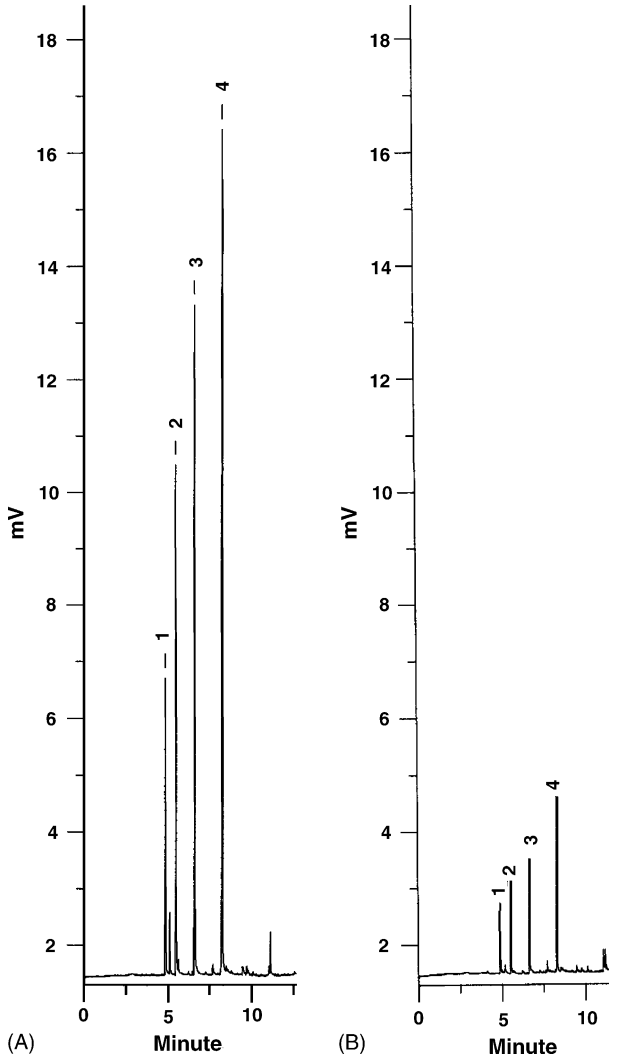


Fig. 10. CME-GC analysis of PAHs using a commercial coated capillary with 0.25 mm coating thickness: before (a) and after (b) rinsing the microextraction capillary with 0.1 M NaOH solution for 24 h. Extraction parameters: 10 cm × 0.25 mm i.d. microextraction capillary; extraction time, 30 min (gravity fed at room temperature). Other conditions: 10 m × 0.25 mm i.d. Sol–gel GC PDMS column; splitless desorption; injector temperature rose from 30 to 300 °C: column temperature program from 30 to 280 °C at rate of 20 °C/min then from 280 to 300 °C at rate of 2 °C/min; helium carrier gas: FID 350 °C. Peaks: (1) acenaphthene; (2) fluorene; (3) phenanthrene; and (4) pyrene.

For comparison, the same experiment was conducted using a 10 cm piece of a conventionally coated commercial PDMDPS-based GC column as the microextraction capillary. The results are shown in Fig. 10. A drastic loss in extraction sensitivity after rinsing the conventionally coated silica-based microextraction capillary with 0.1 M NaOH solution is obvious (Fig. 10).

These data suggest that the created hybrid sol–gel zirconia-based coatings have significant pH stability advantage over conventional silica-based coatings, and that such coatings have the potential to extend the applicability of capillary microextraction and related techniques to highly basic samples, or analytes that require highly basic condition for the extraction and/or analysis.

4. Conclusion

Sol–gel zirconia-based hybrid organic–inorganic sorbent coating was developed for use in microextraction. Principles of sol–gel chemistry was employed to chemically bind a hydroxy-terminated silicone polymer (polydimethyldiphenylsiloxane) to a sol–gel zirconia network in the course of its evolution from highly reactive alkoxide precursor (zirconium tetrabutoxide) undergoing controlled hydrolytic polycondensation reactions. For the first time, sol–gel zirconia-PDMDPS coating was employed in capillary microextraction. The newly developed sol–gel zirconia-PDMDPS coating demonstrated exceptional pH stability: its extraction characteristics remained practically unchanged after rinsing with a 0.1 M solution of NaOH (pH 13) for 24 h. Solventless extraction of analytes was carried out simply by passing the aqueous sample through the sol–gel extraction capillary for approximately 30 min. The extracted analytes were efficiently transferred to a GC column via thermal desorption, and the desorbed analytes were separated by temperature programmed GC. Efficient CME-GC analyses of diverse range of solutes was achieved using sol–gel zirconia-PDMDPS capillaries. Parts per trillion (ppt) level detection limits were achieved for polar and non-polar analytes in CME-GC-FID experiments. Sol–gel zirconia-PDMDPS coated microextraction capillaries showed remarkable run-to-run repeatability (R.S.D. < 0.27%) and produced peak area R.S.D. values in the range of 1.24–7.25%.

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