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Capillary microextraction on sol–gel dendrimer coatings

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Abstract

Sol–gel capillary microextraction (CME) is a new direction in the solventless sample preparation for the preconcentration of trace analytes, and presents significant interest in environmental, pharmaceutical, petrochemical, biomedical, agricultural, food, flavor, and a host of other important areas. It utilizes advanced material properties of organic–inorganic hybrid sol–gel polymers to perform efficient extraction and preconcentration of target compounds from a wide variety of matrices. In the present work, a novel benzyl-terminated dendron-based sol–gel coating was developed for CME. A detailed investigation was conducted to evaluate the performance of the newly developed sol–gel dendrimer coatings to perform solventless extraction of a wide range of polar and nonpolar analytes. The characteristic branched architecture of dendrons makes them structurally superior extraction media compared with their traditional linear polymeric counterparts. Sol–gel chemistry was used to chemically immobilize dendritic macromolecules on fused silica capillary inner surface. Due to the strong chemical bonding with the capillary inner walls, sol–gel dendron coatings showed excellent thermal and solvent stability in capillary microextraction in hyphenation with chromatographic analysis. Efficient extraction of a wide range of analytes from their aqueous solutions was accomplished using sol–gel dendron coated fused silica capillaries. Low parts per trillion level detection limits were achieved in CME–GC for both polar and nonpolar analytes including polyaromatic hydrocarbons (PAHs), aldehydes, ketones, phenols, and alcohols.

Keywords: Capillary microextraction; Sol–gel dendrimer coating; Sol–gel; Solid-phase microextraction; Aldehydes; Ketones; Phenols; Alcohols; Polynuclear aromatic hydrocarbons

1. Introduction

Solid-phase microextraction (SPME) [1] is now considered to be a fairly mature sample preparation technique with a wide variety of applications ranging from environmental to biomedical to agricultural, and a host of other samples of scientific and industrial importance. It successfully overcomes the inherent shortcomings of conventional sample preparation methods by completely eliminating the use of organic solvents and by integrating a number of sample handling operations such as extraction, preconcentration, and sample introduction for instrumental analysis that follows the sample preparation step. In addition, SPME is a simple, inexpensive, easy-to-automate, portable, and time-efficient sample preparation technique. Due to these positive attributes, SPME has experienced an explosive growth since its inception a little over a decade ago.

SPME is based on the distribution of analytes between the sample matrix and the extracting phase coated either on the outer surface of a solid fiber (fiber-based SPME) or on the inner surface of a capillary (in-tube SPME or capillary microextraction (CME) [2]). Various SPME coatings have been successfully used to accomplish solventless extraction of analytes from different matrices. These include polydimethylsiloxane (PDMS) [1], polyacrylate [3], carbopack [4], polyimide [5], polypyrrole [6], molecularly imprinted materials [7,8], carbowax/divinylbenzene (CW/DVB) [9], polydimethylsiloxane/divinylbenzene (PDMS/DVB) [10], polydimethylsiloxane/carboxane (PDMS/Carboxane) [11], carbowax/templated resin (CW/TPR) [11], sol–gel PDMS [12,13], sol–gel PEG [2,14], sol–gel crown ether [15,16]. The extraction affinity is determined by various types of intermolecular and steric interactions between the analyte species and the extracting phase coating. Thus, selective extraction of analytes can be achieved based on their po-

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larity, hydrophobicity, chemical composition, shape/size, etc. To this end, selective extraction by SPME has often been performed based on solute polarity. However, such an approach is not very effective for samples where both polar and nonpolar contaminants are present, and both need to be analyzed. For such samples, it is very important to have a coating that can extract both polar and nonpolar compounds simultaneously with high extraction sensitivity.

Most of the SPME coatings that have been used so far are based on linear organic polymers. Linear polymers have some inherent shortcomings for their use as SPME coatings in that they possess a wide range of molecular weight distribution responsible for wide variations in their physical properties [17]; their wide dispersity makes it difficult to achieve batch-to-batch reproducibility; and moreover, they are highly viscous and poorly soluble in common organic solvents, putting limitations in their effective use as SPME coatings.

Dendrimers [18,19] are highly branched macromolecules that can easily overcome many of the inherent shortcomings of linear polymers. Dendrimers are created in a step-wise fashion using simple branched monomeric units, the nature and functionality of which can be easily controlled and varied. The supramolecular properties of dendrimers can be effectively tailored by the introduction of desired functional groups at either the core [20], the peripheral surface [21], the branching unit [22], or at multiple sites within the dendrimer [23]. Dendritic macromolecules possess physical properties that, in many cases, greatly differ from their linear analogs. For example, monodisperse structure of a dendrimer is built in generations (layer by layer) around a core moiety [24]. In organic solvents, they exhibit high solubility and low viscosity compared with their linear analogs [25]. These discrepancies in physical properties are reflections of the fundamental differences in the molecular architectures of these two types of macromolecules providing drastically different numbers of terminal functional groups [26].

Dendrimers possess open and vacuous structures characterized by channels and pockets which is especially true for higher generations [27]. Unlike first and second generations, the higher generation dendrimers have greater internal surface area compared with the external surface area [28]. Therefore, third and higher generation dendrimers should be well suited for applications where high surface area (both internal and external) is a prerequisite. Because of their tree-like branched architecture, functionalized dendrons are potential candidates for novel sorbents to be used in analytical sample enrichment and separations. This opens new possibilities in achieving enhanced selectivity, sensitivity, and performance in chromatographic separations and sample preparations.

To date, in the area of analytical separations, dendrimers have been used as: (a) pseudo-stationary phases in electrokinetic chromatography [29–31], (b) bonded stationary phases in capillary electrochromatography [32], (c) chiral stationary phases in HPLC [33], and (d) GC stationary phases [34].

Effective immobilization of the polymeric coating on fused silica fiber or capillary inner surface is a prerequisite for the maximum utilization of its analytical potential. However, it is often difficult to achieve acceptable degree of immobilization of thick SPME coatings through conventional approaches [35]. As has been pointed out by Chong et al. [12], the absence of chemical bonds between the polymeric coating and the fused silica fiber surface is responsible for low thermal and solvent stability of conventionally coated SPME fibers. Low thermal stability of thick coatings leads to incomplete sample desorption and sample carryover problems. On the other hand, low solvent stability of coatings presents a significant obstacle to the hyphenation of in-tube SPME (capillary microextraction (CME)) with liquid-phase separation techniques since organic or organo–aqueous liquids are employed for the desorption of analytes from the SPME coating used for extraction [36,37].

Most of the difficulties associated with the creation and immobilization of thick stationary phase coatings on the fused silica surface can be effectively addressed by using sol–gel coating technology [2,12,38,39]. In the context of SPME, sol–gel technology provides a number of significant advantages including single step fiber/capillary manufacturing process, material homogeneity at the molecular level, possibility to create hybrid sorbents by effectively combining material properties of organic and inorganic constituents, chemical bonding between the sorbent and the fused silica surface, high thermal and solvent stability of the created sorbent, and porous structure of the hybrid material. In a previous paper [34], we introduced sol–gel dendrimer stationary phase in gas chromatography. To date, we are not aware of any report on the use of sol–gel dendrimer coatings in analytical microextraction. In this paper, we describe a sol–gel approach to in situ creation of dendritic coating on the inner walls of fused silica capillaries, and application of such capillaries to solventless extraction of both polar and nonpolar trace analytes from aqueous samples.

2. Experimental

2.1. Equipment

Sol–gel dendrimer CME–GC experiments were carried out on a Shimadzu model 17A gas chromatograph (Shimadzu Corporation, Kyoto, Japan) equipped with a flame ionization detector (FID) and a programmed temperature vaporizer (PTV). An in-house built gravity-fed sample dispenser was used to flow the aqueous samples through the sol–gel dendrimer-coated capillary during CME experiments. A Fisher Model G-560 Ginie 2 vortex (Fisher Scientific, Pittsburgh, PA) was employed for proper mixing of different solutions. A Microcentaur model APO 5760 microcentrifuge (Accurate Chemical and Scientific Corporation, Westbury, NY) was used (at 13,000 rpm, $15{,}682 \times g$) to separate particulates from the sol solutions used for coating

the microextraction capillaries as well as the GC columns. A homemade, gas pressure-operated filling/purging device [40] was used to fill the fused silica capillary with the sol solution to purge it with helium at various stages of coating and extraction procedures. A Barnsted Model 04741 Nanopure deionized water system (Barnsted/Thermodyne, Dubuque, IA) was used to obtain 17.2 MΩ. deionized water. A JEOL model JSM-35 scanning electron microscope was used to obtain SEM images of the sol–gel dendrimer-coated capillary surfaces. On-line data collection and processing were done using ChromPerfect software (Version 3.5) for Windows (Justice Laboratory Software, Denville, NJ).

2.2. Chemicals and materials

Fused-silica capillary (250 μm i.d.) with an external protective polyimide coating and two-way fused silica press-fit connectors were purchased from Polymicro Technologies Inc. (Phoenix, AZ). Triethoxysilyl-terminated dendron was synthesized in one of our laboratories following a procedure described elsewhere [34]. Hydroxy-terminated PDMS was purchased from United Chemical Technologies, Inc. (Bristol, PA). Trimethoxysilyl-derivatized poly(ethylene glycol) (M-SIL-5000 and SIL-3400) were obtained from Shearwater Polymers (Huntsville, AL). Acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, nonyl aldehyde, *m*-tolualdehyde, undecylic aldehyde, butyrophenone, valerophenone, hexanophenone, heptanophenone, benzophenone, 2-chlorophenol, 3,4-dichlorophenol, 3,5-dimethylphenol, 2,4,6-trichlorophenol were purchased from Aldrich Chemical Co. (Milwaukee, WI) and *n*-decyl aldehyde was purchased from Sigma Chemical Co. (St. Louis, MO). Methanol (HPLC grade) and all borosilicate glass vials were purchased from Fisher Scientific (Pittsburgh, PA).

2.3. Preparation of sol–gel dendrimer-coated extraction capillaries

Sol–gel dendrimer microextraction capillaries were prepared by using a modified version of a previously described procedures for the preparation of sol–gel dendrimer-coated open tubular GC columns [34]. Briefly, a hydrothermally treated fused silica capillary (3 m × 250 μm i.d.) was filled with a specially designed sol solution using a gas pressure-operated filling/purging device [40]. The sol solution was prepared by dissolving methyltrimethoxysilane (MTMOS; sol–gel precursor, 5 μl), phenyl-terminated dendrimer with a triethoxysilyl containing root (sol–gel-active organic ligand, 50 mg), hexamethlyldisilazane (surface deactivation reagent, 10 μl), polymethylhydrosiloxane (PMHS; surface deactivation reagent, 25 μl), and trifluoroacetic acid (TFA; sol–gel catalyst, 50 μl) in methylene chloride (solvent, 900 μl). After filling, the sol solution was kept inside the capillary for 30 min to facilitate the formation of a surface-bonded sol–gel dendrimer coating. The free unbonded portion of the sol solution was then expelled from the capillary under helium pressure (50 psi) and the coated capillary was purged with helium for an hour. The sol–gel coated capillary was further conditioned in a GC oven using temperature-programmed heating from 40 to 300 °C at 1 °C/min, and holding the capillary at the final temperature for 5 h under helium purge. Before using for extraction, the coated capillary was rinsed sequentially with methylene chloride and methanol followed by drying in a stream of helium under the same temperature-programmed conditions, except that the capillary was held at the final temperature for 30 min. The capillary was further cooled down to ambient temperature and cut into 13 cm long pieces that were further used to perform microextraction.

2.4. Preparation of sol–gel PDMS- and Sol–gel PEG-coated capillary GC columns

Sol–gel PDMS- and sol–gel PEG-coated capillary GC columns were prepared according to procedures described elsewhere [38,39].

2.5. Gravity-fed sample dispenser for capillary microextraction

A gravity-fed sample dispenser was used for capillary microextraction (Fig. 1).

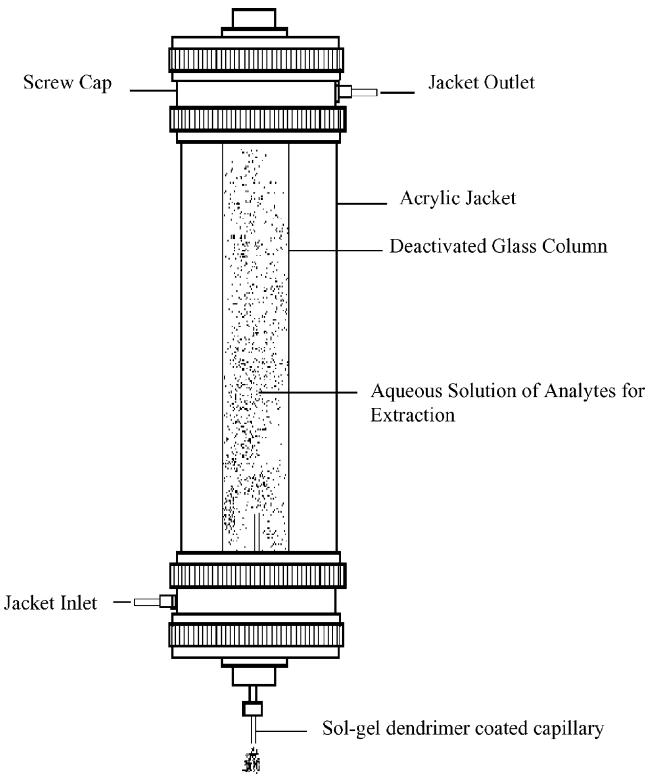


Fig. 1. Schematic of a gravity-fed sample dispensing unit used in sol–gel dendrimer capillary microextraction.

It was constructed by modifying a Chromaflex AQ column (Kontes Glass Co., Vineland, NJ) consisting of a thick-walled Pyrex glass cylinder concentrically placed in an acrylic jacket. Deactivation of the inner surface of the glass cylinder was accomplished by treating with HMDS solution (5% (v/v) solution in methylene chloride) followed by heating at 250 °C for 1 h in an inert gas environment. The cylinder was then cooled to ambient temperature, thoroughly rinsed with methanol and deionized water, and dried in a flow of helium. The system was then reassembled and was ready for use as a sample delivery device in capillary microextraction.

2.6. Deactivation of glassware

All glassware used in this study was cleaned using Sparkleen detergent, thoroughly rinsed with deionized water followed by drying at 150 °C for 2 h. The inner surface of the dried glassware was then treated with a 5% (v/v) solution of HMDS in methylene chloride followed by heating in an oven at 250 °C for 8 h under helium flow. The glassware was then rinsed sequentially with methylene chloride and methanol and dried in the oven at 100 °C for 1 h. Before use, all glassware was thoroughly rinsed with deionized water and dried at room temperature in a continuous flow of helium.

2.7. Preparation of standard sample solutions for sol–gel dendrimer CME

All stock solutions were prepared by dissolving 50 mg of each analyte in 5 ml of methanol in a 10 ml deactivated amber glass vial to obtain a concentration of 10 mg/ml. The solution was further diluted to 0.1 mg/ml in methanol. The final aqueous sample was prepared by further diluting this solution in water to achieve μg/ml to ng/ml level concentrations depending on the compound class.

2.8. Extraction of analytes on sol–gel dendrimer-coated capillaries

A 13 cm long piece of the sol–gel dendrimer-coated capillary (250 μm i.d.) was conditioned in a GC oven using a temperature program (from 40 to 300 °C at 10 °C/min, held at the final temperature for 30 min) carried out by simultaneously purging the capillary with helium. The conditioned capillary was vertically connected to the lower end of the gravity-fed sample dispenser using a plastic nut and a ferrule (Fig. 1). A 50 ml volume of the aqueous sample containing trace concentrations of the target analytes was added to the inner glass cylinder of the sample dispenser through the inlet located at the top. A small helium gas pressure (5 psi) was maintained in the system to assist the sample flow. The solution was allowed to pass through the capillary for 30 min. During this time, the analyte molecules were extracted by the sol–gel dendrimer coating as the sample passed through the capillary, and the system moved towards an extraction equilibrium. The capillary was further purged with helium for 1 min to remove residual water from the capillary walls.

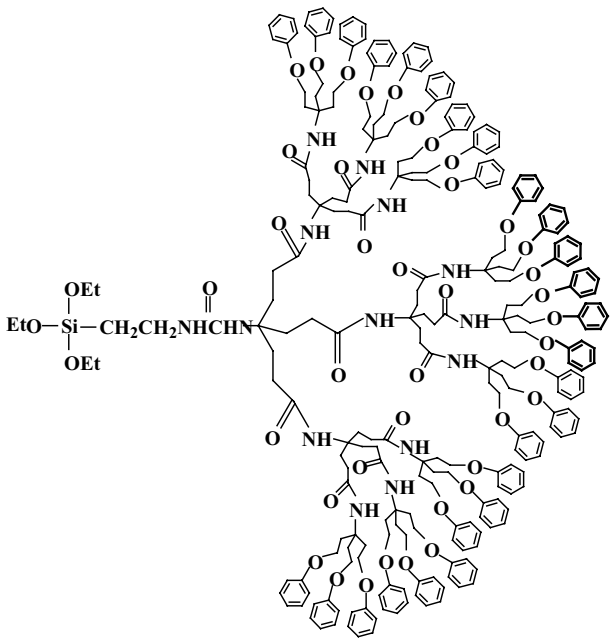
2.9. Thermal desorption and GC analysis of the extracted analytes

Thermal desorption of the extracted analytes from the sol–gel dendrimer-coated microextraction capillary was preceded by its installation in the GC injection port and its secured interfacing with the GC capillary column. To facilitate the installation, both the GC injection port and the oven were first cooled to 30 °C, and the quartz wool was removed from the injection port glass liner. The capillary was then introduced into the GC injection port from the bottom end of the port so that ∼8 cm of the capillary remained inside the injection port. A graphite ferrule was used to make an air-tight connection between the capillary and the injection port. The lower end of the capillary (residing inside the GC oven) was connected to the GC capillary column with a deactivated press-fit quartz connector. The temperature of the PTV injection port was then rapidly raised from 30 to 300 °C at 100 °C/min to desorb the analytes from the extraction capillary into the carrier gas flow, keeping the GC oven temperature at 30 °C during the whole desorption process (5 min). Under these conditions, the desorbed analytes were efficiently carried over by helium flow. As soon as the desorbed analytes reached the cooler CME capillary–GC column coupling zone residing inside the GC oven (30 °C), the analytes were focused into a narrow band. To facilitate transport of the focused zone through the GC column and its separation into individual components, the GC oven temperature was further programmed as follows: from 30 to 300 °C at 15 °C/min with a 10 min hold at the final temperature.

3. Results and discussion

The branched architecture of dendrimers makes them promising candidates for use as extraction sorbents with distinct advantages over linear polymers used for the same purpose. The main objective of the present work was to investigate the possibility of using benzyl-terminated dendrimers as a novel extraction medium for solid-phase microextraction. This was accomplished by creating immobilized dendrimer coatings on the fused silica capillary inner surface using principles of sol–gel column chemistry.

Sol–gel column technology [38] provides an elegant single-step procedure for creating organic–inorganic hybrid stationary phase coatings (both thick and thin) inside a fused silica capillary that can be further used to perform capillary microextraction [2] or high-resolution gas chromatographic separations [38,39]. Sol–gel technology also allows the creation of hybrid coatings on the outer surface of a solid fiber [12] that can be used in conventional fiber-based SPME analysis. In both instances, the coating is chemically bonded



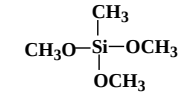
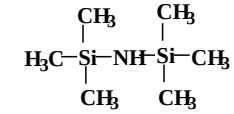
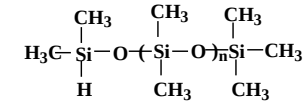
Scheme 1. Phenyl-terminated dendrimer with a triethoxysilyl root.

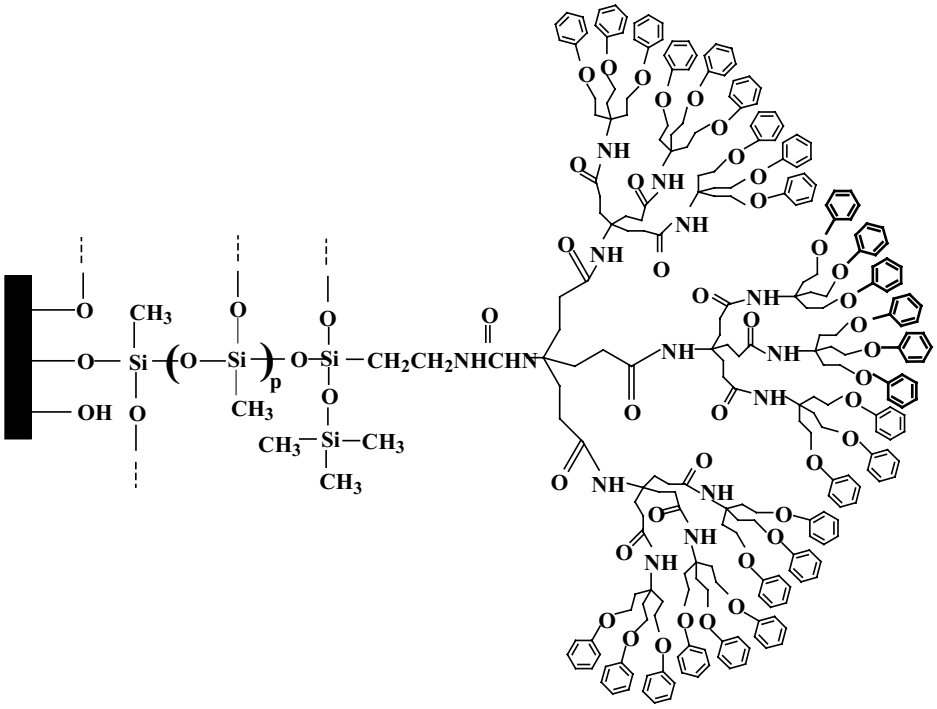
to the substrate, and provides high thermal stability required for SPME–GC analysis. Thanks to chemical bonding to the substrate, sol–gel coatings also possess high solvent stability required for hyphenating SPME with liquid-phase separation techniques (e.g., HPLC, MEKC, CEC, etc.) that use organo–aqueous mobile phases.

If an organic polymer or ligand is to undergo sol–gel reaction, it has to be sol–gel-active. The dendrimer used in this study contains ethoxysilyl groups (Scheme 1) in its root, making the dendrimer molecules sol–gel-active. Details of the synthesis of sol–gel-active dendrimers can be found elsewhere [34].

The chemical ingredients used to create the sol–gel dendrimer coating is presented in Table 1. As can be seen in Table 1, methyltrimethoxysilane is the second sol–gel precursor (sol–gel-active dendrimer being the first precursor) used in the coating solution. Under the experimental conditions used, both MTMOS and the triethoxysilyl moieties in the benzyl-terminated dendron (Scheme 1) can get hydrolyzed in the presence of the sol–gel catalyst, trifluoroacetic acid (TFA). The hydrolyzed precursors can then undergo polycondensations in a variety of ways to create a sol–gel network. The growing chain of the sol–gel polymer can also undergo polycondensation with hydrolyzed triethoxysilyl root of the dendron to form an organic–inorganic hybrid polymer network with the chemically incorporated dendrimers as an organic constituent. The condensation can also take place with the participation of the silanol groups on the inner surface of the fused silica capillary. The sol–gel dendritic network developed in the vicinity of the fused silica capillary inner surface get chemically anchored to the column walls forming a surface-bonded stationary phase film, and remain as such when the sol–gel solution is expelled after 30 min of residence inside the capillary. Both polymethylhydrosiloxane and hexamethyldisilazane (HMDS) used in the sol solution as surface deactivation reagents lack sol–gel-active sites. Therefore, it can be assumed that they rather get physically incorporated in the sol–gel network, and subsequently react with the silanol groups during the thermal conditioning step that follows the coating process. This provides a mechanism for a three-dimensional deactivation process taking place throughout the entire thickness of the sol–gel coating [38] as opposed to traditional two-dimensional deactivation process which is confined only to the capillary surface. Thus the sol–gel technology used for the coating process elegantly combines column deactivation, coating and stationary film immobilization in a simple and effective manner. A simplified scheme of the surface-bonded sol–gel dendrimer network on the fused-silica capillary inner walls is presented in Scheme 2.

Table 1
Names, functions and chemical structures of sol–gel dendrimer coating solution ingredients

Name	Function	Structure
Methyltrimethoxysilane	Sol–gel precursor	
Phenyl-terminated dendrimer with a triethoxysilyl root	Sol–gel precursor containing a dendritic ligand	Presented in Scheme 1
Trifluoroaceticacid/water 95:5 (v/v)	Catalyst	CF_3COOH
Methylene chloride	Solvent	CH_2Cl_2
Hexamethyldisilazane (HMDS)	Deactivating reagent	
Polymethylhydrosiloxane (PMHS)	Deactivating reagent	



Scheme 2. Surface-bonded sol–gel dendrimer coating.

Fig. 2 represents two scanning electron micrographs (SEM) of the inner surface of the sol–gel dendrimer-coated capillary. Remarkable uniformity in coating thickness is evident from these SEM images. The coating thickness was estimated at 0.5 μm. (Fig. 2a). Moreover, sol–gel dendrimer coating possesses a roughened, porous texture (Fig. 2b) with enhanced surface area which is favorable for extraction.

Fig. 3 illustrates the CME kinetic profile of a nonpolar analyte (phenanthrene) and a polar analyte (2,4,6-trichlorophenol) extracted on a sol–gel benzyl-terminated dendrimer-coated capillary. Extractions were carried out using aqueous samples containing 1 ppm concentration of each analyte. Both for the polar and nonpolar analytes, extraction equilibria were attained within 30 min (Fig. 3).

Based on these kinetic data, a 30 min extraction time was further used for all samples to ensure attainment of the extraction equilibrium during the extraction process.

Sol–gel dendrimer-coated capillaries were used to extract a wide variety of analytes having different polarity ranges (from nonpolar to highly polar) and of environmental, biomedical and ecological importance. Test analytes included polycyclic aromatic hydrocarbons (PAHs), aldehydes, ketones, alcohols, and phenols. The extracted compounds were further analyzed by GC. The CME–GC analysis data acquired for PAHs, aldehydes, and ketones are presented in Table 2 and those for alcohols and phenols are presented in Table 3.

Polycyclic aromatic hydrocarbons are among the most common environmental pollutants found in air, water, and soil in the USA and other industrialized countries where petroleum products are heavily used. Toxicity, mutagenicity, and carcinogenicity of these compounds in animals [41] has prompted the US Environmental Protection Agency (EPA) to place 16 unsubstituted PAHs in its list of 129 priority pollutants [42]. Fig. 4 represents a gas chromatogram of five unsubstituted polyaromatic hydrocarbons (PAHs) from EPA priority pollutants list. They were extracted from an aqueous sample (each PAH at 10 ppb) using a sol–gel dendrimer-coated microextraction capillary.

As can be seen from the data presented in Table 2, the detection limits obtained for PAHs in CME–GC–FID range between 2.1 and 3.6 ppt. These values are comparable to or better than the detection limits reported in the literature for conventionally coated SPME fibers. For instance, Doong et al. [42] reported a detection limit of 0.25 ng/ml (250 ppt) for fluoranthene obtained by SPME–GC–FID on a commercial 100 μm PDMS coated fiber, which is more than two order of magnitude higher than the value 0.002 ng/ml (2 ppt) obtained in the present work using sol–gel dendrimer CME–GC–FID.

The sol–gel dendrimer-coated CME capillaries were further used to extract trace levels of aldehydes and ketones (carbonyl compounds) in aqueous samples. Carbonyl compounds play an important role in aquatic oxidation processes. In natural waters, these compounds can be produced by the photodegradation of dissolved natural organic matter [43] as well as products of microbiological processes [44]. In recent years, carbonyl compounds are receiving increased attention since they are formed as by-products in the drinking water disinfection processes. Many of these by-products have been shown to be carcinogens or carcinogen suspects [45–47]. The polar nature and enhanced reactivity of carbonyl com-

Table 2
Run-to-run and capillary-to-capillary repeatability (peak area and retention time), and detection limit data for nonpolar and moderately polar analytes in five replicate measurements by CME–GC using sol–gel dendrimer-coated microextraction capillaries

Chemical class of the analyte	Name of the analyte	Peak area repeatability ($n = 5$)				Retention time (t_R) repeatability ($n = 10$)		Detection limits, S/N = 3 (ppt)
		Capillary-to-capillary		Run-to-run				
		Mean peak area (arbitrary unit)	R.S.D. (%)	Mean peak area (arbitrary unit)	R.S.D. (%)	Mean t_R (min)	R.S.D. (%)	
Polyaromatic hydrocarbons	Acenaphthene	20001	2.08	32748	5.27	14.90	0.05	3.6
	Fluorene	42705	2.58	50171	4.27	15.77	0.03	2.3
	Phenanthrene	48103	2.04	58985	2.33	17.41	0.02	2.1
	Fluoranthene	65389	3.46	63814	1.46	19.42	0.04	2.2
	Pyrene	82694	5.72	64783	2.56	19.80	0.02	2.3
Aldehydes	Nonyl aldehyde	32479	9.20	32389	7.36	10.87	0.05	19.4
	m-Tolualdehyde	96287	6.79	95077	2.90	12.00	0.03	5.6
	n-Decyl aldehyde	174085	8.97	170101	4.09	13.02	0.04	3.3
	Undecylic aldehyde	197249	7.60	213576	6.19	13.97	0.03	3.5
Ketones	Butyrophenone	31512	3.70	36832	1.37	12.58	0.04	44.3
	Valerophenone	60909	3.12	63127	2.52	13.58	0.04	11.7
	Hexanophenone	97759	3.81	80996	2.33	14.53	0.05	3.7
	Heptanophenone	92476	6.45	96529	2.31	15.41	0.06	1.9
	Benzophenone	68130	2.08	63168	3.39	16.12	0.04	15.2

pounds in water matrices often impose the need for their derivatization prior to extraction and/or detection by chromatographic techniques [48,49]. However, derivatization of these analytes, especially when present in trace concentrations, may complicate the analytical process, leading to poor accuracy and reproducibility. Fig. 5 is a gas chromatogram representing a mixture of underivatized aldehydes that were extracted from an aqueous solution containing 100 ppb of each analyte. The data presented in Table 2 indicates that the detection limits obtained for underivatized aldehydes in CME–GC–FID using a sol–gel dendrimer-coated microextraction capillary range between 3.5 and 19.4 ppt. These values are fairly comparable to the values reported in the literature, which were achieved through derivatization process using commercial SPME fibers. For instance, Cancho et al. [48] reported a detection limit of 0.02 ng/ml (200 ppt) for decanal obtained by SPME–GC–ECD on a commercial SPME fiber having 65 μm thick DVB-PDMS coating. This detection limit is significantly higher than the value 0.003 ng/ml (3 ppt) obtained on sol–gel dendrimer CME–GC–FID. The same trend was also observed for other aldehydes. It is worth mentioning that ECD often provides higher sensitivity than FID for organic compounds containing highly electronegative atoms like halogens and oxygen.

Fig. 6 represents a gas chromatogram of a mixture of five underivatized ketones extracted from an aqueous solution containing 100 ppb of each analyte.

Table 3
Run-to-run and capillary-to-capillary repeatability (peak area and retention time), and detection limit data for polar analytes in five replicate measurements by CME–GC using sol–gel dendrimer-coated microextraction capillaries

Chemical class of the analyte	Name of the analyte	Peak area repeatability ($n = 5$)				Retaintion time (t_R) repeatability ($n = 10$)		Detection limits, S/N = 3 (ppt)
		Capillary-to-capillary		Run-to-run				
		Mean peak area (arbitrary unit)	R.S.D. (%)	Mean peak area (arbitrary unit)	R.S.D. (%)	Mean t_R (min)	R.S.D. %	
Phenols	2-Chlorophenol	12870	7.59	16145	5.29	12.23	0.07	840
	2,5-Dimethylphenol	27643	5.58	28686	1.26	13.95	0.08	320
	3,4-Dichlorophenol	18879	2.53	19409	5.06	14.65	0.10	160
	2,4,6-Trichlorophenol	145939	3.87	155662	2.15	15.34	0.14	220
	4-Chloro, 3-methylphenol	64775	7.37	63808	0.49	16.03	0.14	260
Alcohols	1-Octanol	135305	5.58	137300	6.60	9.88	0.08	11.2
	1-Nonanol	132542	2.50	135503	6.14	10.53	0.07	2.3
	1-Decanol	110100	4.27	113715	2.50	11.14	0.08	1.0
	1-Undecanol	91432	6.18	97545	3.20	10.72	0.11	1.0
	1-Dodecanol	143432	4.36	146321	3.97	12.33	0.08	1.8

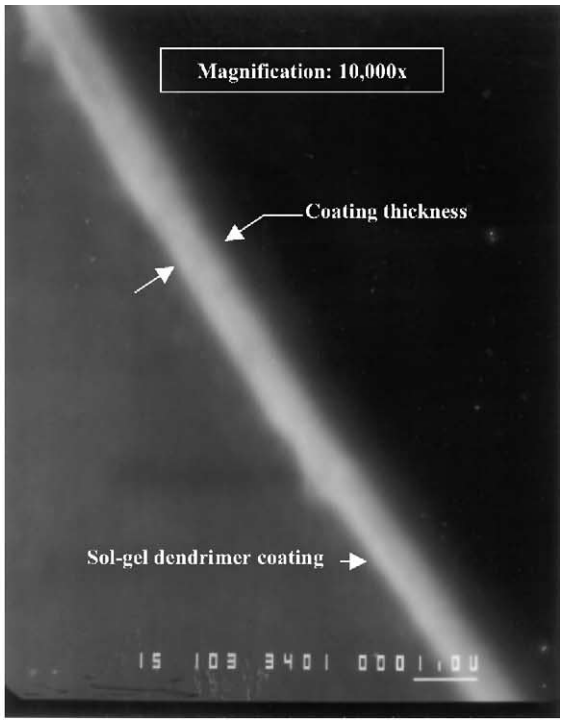


Fig. 2. Scanning electron microscopic images of a 250 μm i.d. sol–gel dendrimer-coated microextraction capillary. (a) Illustrating the coating thickness. Magnification: 10,000×. (b) Illustrating the typical roughened surface obtained by sol–gel coating process. Magnification: 10,000×.

The next class of compounds that were extracted using sol–gel dendrimer-coated capillaries was phenols. The presence of phenolic compounds in the environment is of great concern because of their role in drinking water pollution [50], their toxicity [51], and widespread use in the industry [52,53]. Due to their toxicity and persistence in the environment, 11 phenolic compounds have been included in EPA priority pollutant list [54]. Since phenolic compounds are highly polar, it is quite difficult to extract them directly

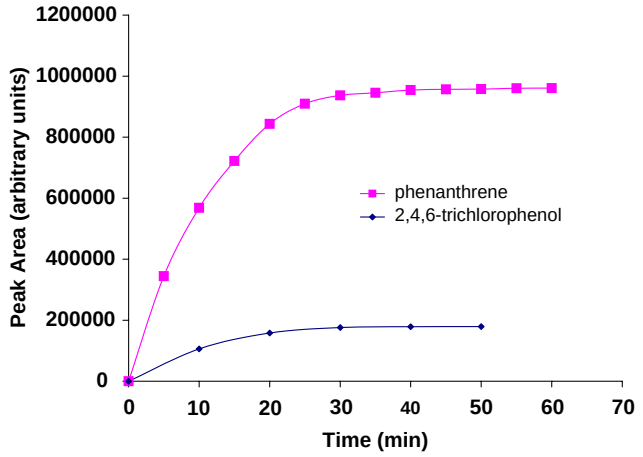


Fig. 3. Illustration of the extraction kinetics of a nonpolar compound (phenanthrene) and a polar compound (2,4,6-trichlorophenol) obtained on a 13 cm × 250 μm i.d. sol–gel dendrimer-coated microextraction capillary using 100 ppb aqueous solution. Extraction conditions: 13 cm × 0.25 mm i.d. microextraction capillary; extraction time, 10–50 min. GC analysis conditions: 10 m × 0.25 mm i.d. sol–gel PDMS column; splitless injection; injector temperature, initial 30 °C, final 300 °C; GC oven temperature programmed from 30 °C (hold for 5 min) to 300 °C at a rate of 15 °C/min; helium carrier gas; FID temperature 350 °C.

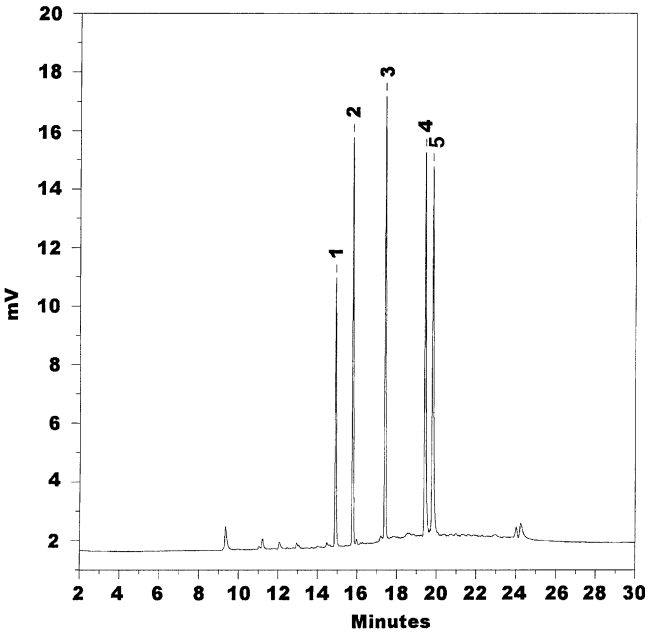


Fig. 4. CME–GC analysis of PAHs at 10 ppb concentration using sol–gel dendrimer-coated microextraction capillary. Extraction conditions: 13 cm × 0.25 mm i.d. microextraction capillary; extraction time, 30 min. GC analysis conditions: 10 m × 0.25 mm i.d. sol–gel PDMS column; splitless injection; injector temperature, initial 30 °C, program rate 100 °C/min, final 300 °C; GC oven temperature programmed from 30 °C (hold for 5 min) to 300 °C at a rate of 15 °C/min; helium carrier gas; FID temperature 350 °C. Peak identification: (1) acenaphthene, (2) fluorene, (3) phenanthrene, (4) fluoranthene, and (5) pyrene.

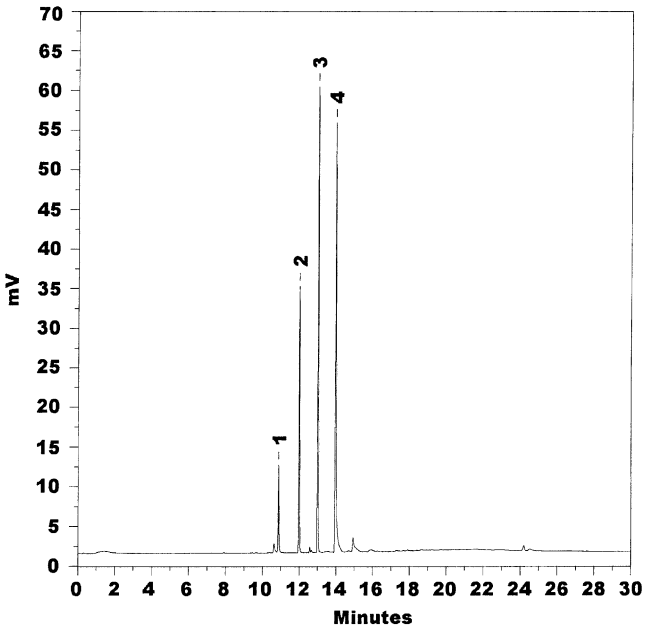


Fig. 5. Capillary microextraction–GC analysis of Aldehydes at 100 ppb concentration using sol–gel dendrimer-coated microextraction capillary. Extraction conditions: 13 cm × 0.25 mm i.d. microextraction capillary; extraction time, 30 min. GC analysis conditions: 10 m × 0.25 mm i.d. sol–gel PDMS column; splitless injection; injector temperature, initial 30 °C, program rate 100 °C/min, final 300 °C; GC oven temperature programmed from 30 °C (hold for 5 min) to 300 °C at a rate of 15 °C/min; helium carrier gas; FID temperature 350 °C. Peak identification: (1) nonylaldehyde, (2) *m*-tolualdehyde, (3) *n*-decylaldehyde, and (4) undecylic aldehyde.

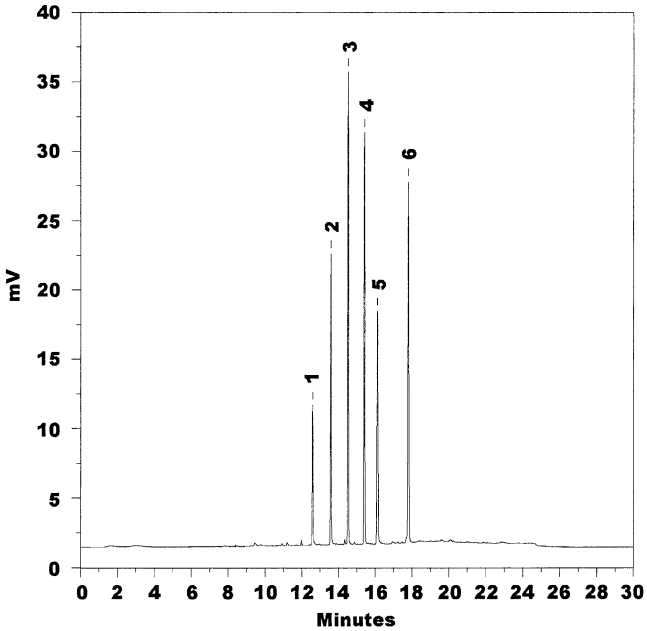


Fig. 6. Capillary microextraction–GC analysis of ketones at 100 ppb concentration using sol–gel dendrimer-coated microextraction capillary. Extraction conditions: 13 cm × 0.25 mm i.d. microextraction capillary; extraction time, 30 min. GC analysis conditions: 10 m × 0.25 mm i.d. sol–gel PDMS column; splitless injection; injector temperature, initial 30 °C, program rate 100 °C/min, final 300 °C; GC oven temperature programmed from 30 °C (hold for 5 min) to 300 °C at a rate of 15 °C/min; helium carrier gas; FID temperature 350 °C. Peak identification: (1) butyrophenone, (2) valerophenone, (3) hexanophenone, (4) heptanophenone, and (5) benzophenone.

from aqueous media. Derivatization, pH adjustment, and/or salting-out are often used to facilitate the extraction [3,55]. To avoid the analytical complexity due to derivatization, HPLC is frequently used for the analysis of phenolic compounds [56,57], even though it may compromise detection sensitivity. It should be pointed out that the UV detector frequently used in HPLC analysis possesses significantly lower sensitivity than the flame ionization detector commonly used in GC.

In the present study, the extracted phenols were analyzed by GC. No solute derivatization, pH adjustment or salting out of the aqueous sample was used to extract phenolic compounds from the aqueous medium. Still, sol–gel dendrimer-coated microextraction capillaries allowed to achieve lower detection limits compared to other reports in the literature. For example, in this study we achieved a detection limit of 0.26 ppb for 4-chloro, 3-methylphenol which is lower than the value (1.4 ppb) reported by Buchholz and Pawliszyn [3] obtained on an SPME fiber with 95 μm thick polyacrylate coating. Same trend was also observed for other phenolic compounds. Fig. 7 represents a gas chromatogram of five phenolic compounds obtained in a CME–GC–FID experiment using a sol–gel dendrimer microextraction capillary.

Fig. 8 represents a gas chromatogram of a mixture of alcohols (10 ppb concentration of each). Extraction of these polar compounds was conducted from aqueous samples without any derivatization, pH adjustment or salting-out effects. The presented data shows excellent affinity of the sol–gel dendrimer coating for these highly polar analytes that are often difficult to extract from aqueous media in the underivatized form using commercial coatings. Excellent symmetrical peak shapes and high detection sensitivity (Table 3) are indicative of outstanding performance and deactivation characteristics of sol–gel PEG column used for the GC analysis of the extracted alcohols.

As is revealed from the data presented in Tables 2 and 3, run-to-run and capillary-to-capillary repeatability data for peak area obtained in CME–GC–FID experiments are quite satisfactory. For most solutes, these R.S.D. values were under 5%. For the polar analytes, the R.S.D. values were higher than those for nonpolar analytes. Retention time repeatability data for PAHs, aldehydes, ketones, phenols, and alcohols were characterized by R.S.D. values of less than 0.14%.

Unique molecular architecture of dendrimers and the ability of sol–gel dendrimer coatings to provide efficient and reproducible extraction for both polar and nonpolar compounds with high detection sensitivity make these dendrimer-based materials very promising in analytical extraction technology.

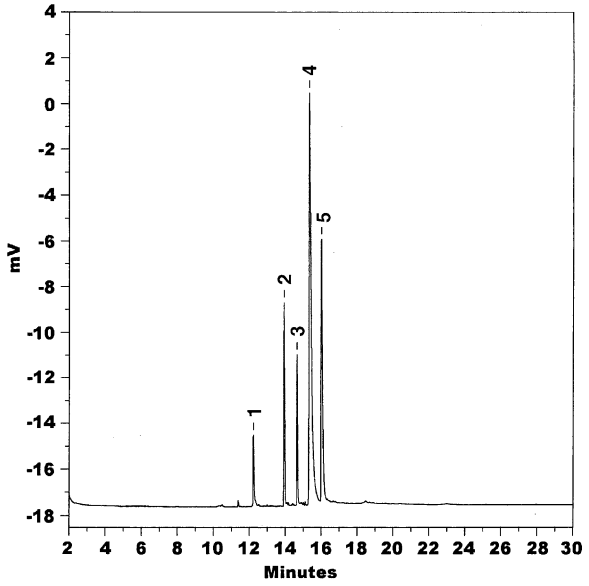


Fig. 7. Capillary microextraction–GC analysis of Phenols at 10 ppb concentration using sol–gel dendrimer-coated microextraction capillary. Extraction conditions: 13 cm × 0.25 mm i.d. microextraction capillary; extraction time, 30 min. GC analysis conditions: 10 m × 0.25 mm i.d. sol–gel PDMS column; splitless injection; injector temperature, initial 30 °C, program rate 100 °C/min, final 300 °C; GC oven temperature programmed from 30 °C (hold for 5 min) to 300 °C at a rate of 15 °C/min; helium carrier gas; FID temperature 350 °C. Peak identification: (1) 2-chlorophenol, (2) 2,5-dimethylphenol, (3) 3,4-dichlorophenol, (4) 2,4,6-trichlorophenol, and (5) 4-chloro, 3-methylphenol.

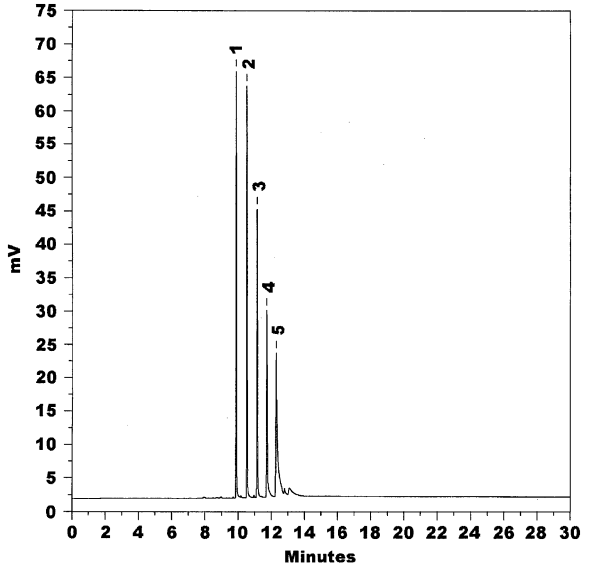


Fig. 8. Capillary microextraction–GC analysis of alcohols at ppb level concentrations using sol–gel dendrimer-coated microextraction capillary. Extraction conditions: 13 cm × 0.25 mm i.d. microextraction capillary; extraction time, 30 min. GC analysis conditions: 10 m × 0.25 mm i.d. sol–gel PEG column; splitless injection; injector temperature, initial 30 °C, program rate 100 °C/min, final 300 °C; GC oven temperature programmed from 30 °C (hold for 5 min) to 300 °C at a rate of 15 °C/min; helium carrier gas; FID temperature 350 °C. Peak identification: (1) 1-octanol (500 ppb), (2) 1-nonanol (100 ppb), (3) 1-decanol (30 ppb), (4) 1-undecanol (20 ppb), and (5) 1-dodecanol (50 ppb).

4. Conclusions

For the first time, sol–gel dendrimer-coated capillaries were used for solventless microextraction and preconcentration in chemical analysis. Both polar and nonpolar analytes were efficiently extracted from aqueous samples on the same sol–gel dendrimer capillary and provided excellent detection sensitivity. Parts per trillion level detection limits were achieved in CME–GC–FID using sol–gel dendrimer-coated extraction capillaries. It should be possible to further enhance the extraction sensitivity by using capillaries with (1) larger inner diameters (e.g., 320 and 520 μm), (2) greater lengths, (3) thicker CME coatings, and (4) sol–gel monolithic extraction beds, or any combination of these factors. Since sol–gel dendrimer extraction phase shows excellent thermal and solvent stability, sol–gel dendrimer-coated microextraction capillaries are suitable for coupling with both GC and HPLC.

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