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Parts per quadrillion level ultra-trace determination of polar and nonpolar compounds via solvent-free capillary microextraction on surface-bonded sol–gel polytetrahydrofuran coating and gas chromatography–flame ionization detection

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Abstract

Sol–gel polytetrahydrofuran (poly-THF) coating was developed for high-sensitivity sample preconcentration by capillary microextraction (CME). Parts per quadrillion (ppq) level detection limits were achieved for both polar and nonpolar analytes through sample preconcentration on sol–gel poly-THF coated microextraction capillaries followed by gas chromatography (GC) analysis of the extracted compounds using a flame ionization detector (FID). The sol–gel coating was in situ created on the inner walls of a fused silica capillary using a sol solution containing poly-THF as an organic component, methyltrimethoxysilane (MTMOS) as a sol–gel precursor, trifluoroacetic acid (TFA, 5% water) as a sol–gel catalyst, and hexamethyldisilazane (HMDS) as a deactivating reagent. The sol solution was introduced into a hydrothermally-treated fused silica capillary and the sol–gel reactions were allowed to take place inside the capillary for 60 min. A wall-bonded coating was formed due to the condensation of silanol groups residing on the capillary inner surface with those on the sol–gel network fragments evolving in close vicinity of the capillary walls. Poly-THF is a medium polarity polymer, and was found to be effective in carrying out simultaneous extraction of both polar and nonpolar analytes. Efficient extraction of a wide range of trace analytes from aqueous samples was accomplished using sol–gel poly-THF coated fused silica capillaries for further analysis by GC. The test analytes included polycyclic aromatic hydrocarbons (PAHs), aldehydes, ketones, chlorophenols, and alcohols. To our knowledge, this is the first report on the use of a poly-THF based sol–gel material in analytical microextraction. Sol–gel poly-THF coated CME capillaries showed excellent solvent and thermal stability (>320 °C).

Keywords: Sol–gel; Capillary microextraction; In-tube solid-phase microextraction; Polytetrahydrofuran; Polynuclear aromatic hydrocarbons; Aldehydes; Ketones; Chlorophenols; Alcohols

1. Introduction

Solid-phase microextraction (SPME) [1] is an excellent solventless alternative to the traditional sample preparation techniques like liquid–liquid extraction (LLE), Soxhlet extraction, solid-phase extraction (SPE), etc. It is a simple, sensitive, time-efficient, cost-effective, reliable, easy-to-automate, and portable sample preparation technique. In SPME, analyte enrichment is accomplished by using a sorbent coating in two different formats: (a) conventional fiber-based format [1] and; (b) the more recently developed "in-tube" format [2]. In its conventional format, SPME uses a sorbent coating on the external surface of a fused silica fiber (typically 100–200 μm in diameter) covering a short segment at one of the ends. In the in-tube format, the sorbent coating is applied to the inner surface of a capillary. SPME completely eliminates of the use of organic solvents in sample preparation, and effectively integrates a number of critically important analytical steps such as sampling, extraction,

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preconcentration, and sample introduction for instrumental analysis. Thanks to these positive attributes, SPME has experienced an explosive growth over the last decade.

Despite rapid advancements in the area of SPME applications, a number of important problems still remain to be solved. First, existing SPME coatings are designed to extract either polar or nonpolar analytes from a given matrix. For example, being a nonpolar stationary phase, polydimethylsiloxane (PDMS) shows excellent selectivity towards nonpolar analytes. The polar polyacrylate coating, on the other hand, demonstrates excellent selectivity towards polar compounds. Such an approach is not very convenient for samples where both polar and nonpolar contaminants are present and both need to be analyzed. For such applications, it is important to have a sorbent that can extract both polar and nonpolar compounds with high extraction sensitivity needed for trace analysis. Second, in conventional SPME only a short length of the fiber is coated with sorbent. The short length of the coated segment on the SPME fiber translates into low sorbent loading which in turn leads to low sample capacity. This imposes a significant limitation on the sensitivity of the classical fiber-based SPME. Improving sensitivity is still a major challenge in SPME research. This is particularly important for analyzing ultra-trace contaminants that are present in the environment. One possible way of improving extraction sensitivity in SPME is by increasing the coating thickness [3,4]. However, equilibration time rapidly increases with the increase in coating thickness because of the dynamic diffusion-controlled nature of the extraction process [3]. As a consequence, both extraction and subsequent desorption processes become slower, resulting in longer total analysis time. Moreover, immobilization of thicker coating on fused silica surface is difficult to achieve by conventional approaches [5] indicating to the necessity of an alternative approach to effective immobilization of thick coatings. Third, low thermal and solvent stability of SPME coatings represents a major drawback of conventional SPME technology, and is a direct consequence of the poor quality of sorbent immobilization. With a very few exceptions, SPME fibers have been coated by mere physical deposition of the stationary phase. The absence of chemical bonding of the sorbent coating to the fused silica surface is considered to be the main reason for low thermal and solvent stability of SPME fibers [6]. Low thermal stability of thick coatings forces one to use low desorption temperatures to preserve coating integrity, which in turn, leads to incomplete sample desorption and sample carryover problems. Besides, low solvent stability of the coating poses a significant obstacle to reliable hyphenation of in-tube SPME with liquid-phase separation techniques (e.g. high-performance liquid chromatography (HPLC)) that employ organic or organo-aqueous mobile phases [3]. It is evident that future advancements in SPME would greatly depend on new developments in the areas of sorbent chemistry and coating technology that will allow preparation of chemically immobilized coatings from advanced material systems providing desired selectivity and performance in SPME.

One possible approach to address most of the problems described above is to use sol–gel technology to create sorbent coatings [6–9]. Sol–gel chemistry provides a simple and convenient pathway leading to the synthesis of advanced material systems that can be used to prepare surface coatings [10,11]. In the context of fused silica fiber/capillary-based SPME, major advantages offered by sol–gel technology are as follows: (1) it combines surface treatment, deactivation, coating, and stationary phase immobilization into a single-step procedure making the whole SPME fiber/capillary manufacturing process very efficient and cost-effective; (2) it creates chemical bonds between the fused silica surface and the created sorbent coating; (3) it provides surface-coatings with high operational stability ensuring reproducible performance of the sorbent coating under operation conditions involving high temperature and/or organic solvents, and thereby it expands the SPME application range towards both higher-boiling as well as thermally labile analytes; (4) it provides the possibility to combine organic and inorganic material properties in extraction sorbents providing tunable selectivity; (5) it offers the opportunity to create sorbent coatings with a porous structure which significantly increases the surface area of the extracting phase and provides acceptable stationary phase loading and sample capacity using thinner coatings.

A number of shortcomings inherent in conventional SPME originate from the design and physical construction of the fiber and the syringe-like SPME device. These include susceptibility of fiber to breakage during coating or operation, mechanical damage of the coating due to scraping, and operational uncertainties due to needle bending. In-tube SPME [2], also termed capillary microextraction [7], is practically free from these inherent format-related shortcomings of conventional SPME. It uses a fused silica capillary (generally a small piece of GC column) with a stationary phase coating on the inner surface to perform extraction. The protective polyimide coating outside the capillary remains intact and provides reliable protection against breakage. Moreover, this format provides a simple, easy, and convenient way to couple SPME to high-performance liquid chromatography.

Despite numerous advantageous features, in-tube SPME still has several inherent shortcomings that originate mainly from the deficiency of the coating technique used to prepare the extraction capillary. Conventional static coating technique, commonly employed to prepare GC capillary columns (short segments of which are used for in-tube SPME), is not suitable for generating thick coatings necessary for enhanced extraction sensitivity in SPME. Besides, in general, a conventionally prepared coating is not chemically bonded to the fused silica capillary surface. As a consequence, such coatings exhibit low thermal and solvent stability. Recently, sol–gel capillary microextraction (CME) has been proposed [7] to address the above mentioned problems through in situ creation of surface-bonded coatings via sol–gel technology, which is suitable for creating both thick and thin coatings on the capillary inner walls.

In both conventional SPME and CME, the sorbent coating plays a critically important role in the extraction process. To date, several types of sorbent coatings have been developed and used for extraction. These coatings can be broadly divided into two major types: (1) single-phase and (2) composite coatings. Single-phase SPME coatings include polydimethylsiloxane (PDMS) [12], polyacrylate [3], carbopack [13], polyimide [14], polypyrrole [15], and molecularly imprinted materials [16,17]. Among the composite coatings are carbowax/divinylbenzene (CW/DVB) [18], polydimethylsiloxane/divinylbenzene (PDMS/DVB) [19], polydimethylsiloxane/carboxane (PDMS/carboxane) [20], and carbowax/templated resin (CW/TPR) [20].

In recent years, sol–gel SPME coatings [6,7,21–27] have drawn wide attention due to their inherent advantageous features and performance superiority over traditional coatings (both non-bonded and cross-linked types). Sol–gel PDMS [6,7,22,28] coatings possess significantly higher thermal stability (>360 °C) than their conventional counterparts for which the upper temperature limit generally remains within 200–270 °C [29]. High thermal and solvent stability have been demonstrated for other sol–gel stationary phases: sol–gel PEG [23] (320 °C), sol–gel crown ethers [25] (340 °C), sol–gel hydroxyfullerene [27] (360 °C), sol–gel polymethylphenylvinylsiloxane [26](350 °C).

Sol–gel PEG coating [23] has been recommended for polar analytes. Sol–gel crown ether [24,25] demonstrated higher extraction efficiencies for aromatic amines compared to CW/DVB fiber. Gbatu et al. [21] described the preparation of sol–gel octyl coatings for SPME-HPLC analysis of organometalic compounds from aqueous solutions. Compared with the commercial SPME coatings, a hydroxyfullerene-based sol–gel coating [27] showed higher sensitivity, faster mass transfer rate for aromatic compounds and possessed molecular planarity recognition capability for polychlorinated biphenyls (PCBs). Yang et al. [26] prepared sol–gel poly (methylphenylvinylsiloxane) (PMPVS) coating using sol–gel technology that provided very high extraction efficiency for aromatic compounds.

Poly-THF (also called polytetramethylene oxide, PTMO) is a hydroxy-terminated polar material that has been used as an organic component to synthesize organic–inorganic hybrid materials [30–35]. Sol–gel poly-THF has been used as bioactive bone repairing material [36], and as a proton conducting solid polymer electrolyte that might allow the operation of high temperature fuel cells [37]. Little work has been devoted to explore the potential of the sol–gel poly-THF material for use as an extraction medium in analytical chemistry. In the present work, we describe a sol–gel chemistry-based approach to in situ creating poly-THF based hybrid organic–inorganic stationary phase coatings on the inner walls of fused silica capillaries and demonstrate the possibility of using such coatings to extract parts per trillion (ppt) and parts per quadrillion (ppq) level concentrations of both polar and nonpolar analytes from aqueous sample matrices.

2. Experimental

2.1. Equipments

Capillary microextraction–gas chromatography (CME–GC) experiments with sol–gel poly-THF coated capillaries were carried out on a Shimadzu model 17A GC system (Shimadzu Corporation, Kyoto, Japan) equipped with a programmed temperature vaporizer (PTV injector) and a flame ionization detector (FID). An in-house designed liquid sample dispenser (Fig. 1) was used to perform CME via gravity-fed flow of the aqueous samples through the sol–gel poly-THF coated capillary. A Fisher Model G-560 Genie 2 Vortex (Fisher Scientific, Pittsburgh, PA) was used for thorough mixing of sol solution ingredients. A Microcentaur model APO 5760 microcentrifuge (Accurate Chemical and Scientific Corporation, Westbury, NY) was used for centrifugation (at 13,000 rpm, 15,682 × g) of sol solutions made for coating the microextraction capillaries. An Avatar model 320 FTIR System (Nicolet Analytical Instruments, Madison, WI) was used to obtain the IR spectra of poly-THF, sol solution having all ingredients except poly-THF and sol–gel poly-THF sorbent. A JEOL model JSM-35 scanning electron microscope (SEM) was used for the investigation of the coated capillary surface. A homebuilt, gas pressure-operated filling/purging device [38] was used to fill the ex-

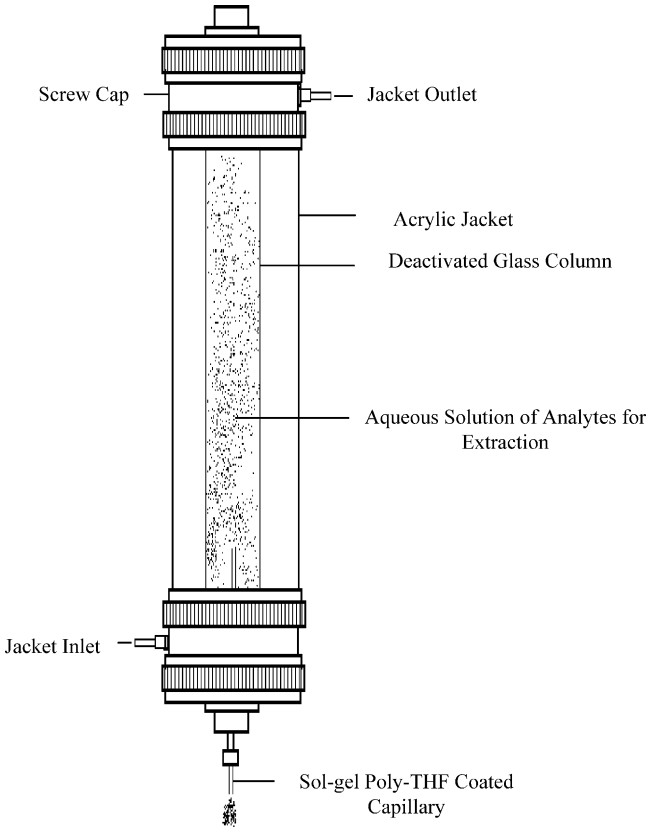


Fig. 1. Schematic of a gravity-fed sample dispensing unit used in capillary microextraction with a sol–gel poly-THF coated capillary.

traction capillary with the sol solution, to expel the solution from the capillary after predetermined period of in-capillary residence, as well as to purge the microextraction capillary with helium. Ultra pure (17.2 MQ) water was obtained from a Barnsted Model 04741 Nanopure deionized water system (Barnsted/Thermodyne, Dubuque, IA). ChromPerfect (Version 3.5 for Windows) computer software (Justice Laboratory Software, Denville, NJ) was used for on-line collection, integration, and processing of the experimental data.

2.2. Chemicals and materials

Fused silica capillary (250 μm i.d.) with a protective polyimide coating on the external surface was purchased from Polymicro Technologies Inc. (Phoenix, AZ). Poly-THF 250 was a gift from BASF Corporation (Parsippany, NJ). Acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, *n*-nonanal, undecanal, dodecanal, tridecanal, valerophenone, hexanophenone, heptanophenone, decanophenone, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 4-chloro, 3-methyl phenol, and pentachlorophenol were purchased from Aldrich (Milwaukee, WI); *n*-decyl aldehyde, 1-nonanol, 1-decanol, 1-undecanol, and 1-tridecanol were purchased from Acros Organics (Pittsburgh, PA). Lauryl alcohol was purchased from Sigma (St. Louis, MO). HPLC-grade methanol and methylene chloride and all borosilicate glass vials were purchased from Fisher Scientific (Pittsburgh, PA).

2.3. Preparation of sol–gel poly-THF coated microextraction capillaries

Sol–gel poly-THF coated microextraction capillaries were prepared by using a modified version of a previously described procedure [8]. Briefly, a sol solution was prepared by dissolving 250 mg of poly-THF 250, 250 μL of methyltrimethoxysilane (sol–gel precursor), 20 μL of 1,1,1,3,3,3-hexamethlyldisilazane (surface deactivation reagent), and 100 μL of trifluoroacetic acid (5% H_2O) (sol–gel catalyst) in 400 μL of methylene chloride. The mixture was then vortexed (3 min), centrifuged (5 min) and the clear supernatant of the sol solution was transferred to another clean vial. Following this, a piece of cleaned and hydrothermally treated fused silica capillary (5 m) was filled with the sol solution using a helium pressure-operated filling/purging device [38]. The sol solution was kept inside the capillary for 60 min to facilitate the formation of a surface-bonded sol–gel coating. On completion of the in-capillary residence time, the unbonded portion of the sol solution was expelled from the capillary under helium pressure (50 psi) and the coated capillary was purged with helium for an hour. The sol–gel poly-THF coated capillary was further conditioned in a GC oven using temperature-programmed heating (from 40 to 320 °C at 1 °C/min, held at 320 °C for 5 h under helium purge). Before using for extraction, the sol–gel poly-THF coated capillary was rinsed sequentially with methylene chloride and methanol followed by drying in a stream of helium under the same temperature-programmed conditions as above, except that the capillary was held at the final temperature for 30 min. The sol–gel poly-THF coated capillary was then cut into 12.5 cm long pieces that were further used to perform microextraction.

2.4. Preparation of sol–gel PDMS and sol–gel PEG columns for GC analysis

The GC capillary columns used to analyze the extracted compounds were also prepared in-house by sol–gel technique. For nonpolar and moderately polar analytes, a sol–gel PDMS column was used. For polar analytes, a sol–gel PEG capillary column was employed. The sol–gel PDMS and sol–gel PEG columns were prepared by procedures described by Wang et al. [8] and Shende et al. [39], respectively.

2.5. Cleaning and deactivation of glassware

To avoid any contamination of the standard solutions from the glassware, all glassware used in the current study was thoroughly cleaned with Sparkleen detergent followed by rinsing with copious amount of deionized water and drying at 150 °C for 2 h. To silanize the inner surface of the dried glassware, they were 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 purge. The silanized glassware was then rinsed sequentially with methylene chloride and methanol and dried in an oven at 100 °C for 1 h. Prior to use, all glassware were rinsed with generous amounts of deionized water and dried at room temperature in a flow of helium.

2.6. Preparation of standard solutions for CME on sol–gel poly-THF coated capillaries

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

2.7. Gravity-fed sample dispenser for capillary microextraction

A gravity-fed sample dispenser was used for capillary microextraction (Fig. 1). It was built by modifying a Chromaflex AQ column (Kontes Glass Co., Vineland, NJ), which consists of a thick-walled Pyrex glass cylinder concentrically placed in an acrylic jacket. Since glass surfaces tend to adsorb polar analytes, the inner surface of the glass cylinder was deactivated by treating with HMDS solution as described before. The cylinder was then cooled down to ambient temperature, thoroughly rinsed with methanol and deionized water, and

dried in a helium gas flow. The system was then reassembled.

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

A 12.5 cm long segment of the sol–gel poly-THF coated capillary (250 μm i.d.) was conditioned under helium purge in a GC oven using a temperature program (from 40 to 320 °C at 10 °C/min, held at the final temperature for 30 min). The conditioned capillary was then vertically connected to the lower end of the gravity-fed sample dispenser (Fig. 1) using a plastic connector. A 50 mL volume of the aqueous sample containing trace concentrations of the target analytes was added to the inner glass cylinder through the sample inlet located at the top of the dispenser. The solution was passed through the capillary for 30 min to facilitate the extraction equilibrium to be established. The capillary was then detached from the dispenser and purged with helium for 1 min to remove residual water from the capillary walls.

2.9. Thermal desorption of extracted analytes and CME–GC analysis

For GC analysis, the sol–gel poly-THF coated capillary containing the extracted analytes was installed in the GC injection port and interfaced with the GC capillary column. Before carrying out the installation, both the injection port and the GC oven were cooled down to 30 °C and the glass wool was removed from the injection port liner. One end of the capillary was then introduced into the glass liner from the bottom end of the injection port so that 8 cm of the capillary remained inside the injection port. A graphite ferrule was used to secure an airtight connection between the capillary and the injection port. Interfacing of the extraction capillary with the GC column was accomplished by using a deactivated two-way press-fit quartz connector. Installation and interfacing of the extraction capillary with the GC column were followed by thermal desorption of extracted analytes from the installed sol–gel poly-THF coated microextraction capillary. For this, the temperature of the PTV injection port was rapidly raised to 300 °C @ 100 °C/min while keeping the GC oven temperature at 30 °C (5 min). Under these temperature program conditions, the extracted analytes were effectively desorbed from the sol–gel poly-THF coating and were transported to the cooler coupling zone consisting of the lower end segment of the microextraction capillary and/or to the front end of the GC column both located inside the GC oven and maintained at 30 °C. As the desorbed analytes reached the cooler interface zone (30 °C), they were focused into a narrow band. On completion of the 5 min desorption and focusing period, the analytes in this narrow band were analyzed by GC using temperature-programmed operation as follows: from 30 to 300 °C at 20 °C/min with a 10 min hold time at the final temperature.

3. Results and discussion

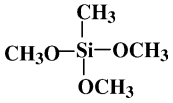
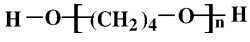
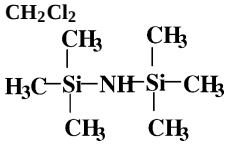
Sol–gel chemistry is an elegant synthetic pathway to advanced materials [8,39–41] that can be effectively utilized to create surface-bonded organic–inorganic hybrid coatings on the outer surface of conventional SPME fibers [6] as well as on the inner walls of a capillary for use in CME [7] (in-tube SPME). Additionally, sol–gel technology can be used for creating both thin [21] and thick [24] coatings employing a wide variety of sol–gel active organic ligands [21,23–27].

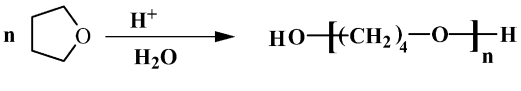
Polytetrahydrofuran (poly-THF) [42] is a medium polarity polymer with terminal hydroxyl groups that can be utilized to bind this polymer to a sol–gel network via polycondensation reaction. It consists of tetramethylene oxide repeating units, and is synthesized through cationic ring opening polymerization of tetrahydrofuran using various initiators [43].

Table 1 lists the chemical ingredients used in this work to prepare the sol solution for creating a sol–gel poly-THF coated capillary.

The in situ creation of a highly stable, deactivated sol–gel coating involved the following processes: (1) catalytic hydrolysis of the alkoxide precursors; (2) polycondensation of

Table 1
Names, functions and chemical structures of sol–gel poly-THF coating solution ingredients

Name	Function	Structure
Methyltrimethoxysilane (MTMOS)	Sol–gel precursor	
Polytetrahydrofuran	Organic ligand	
Trifluoroacetic acid/water 95:5 (v/v)	Catalyst	CF_3COOH
Methylene chloride	Solvent	CH_2Cl_2
Hexamethyldisilazane	Deactivating reagent	

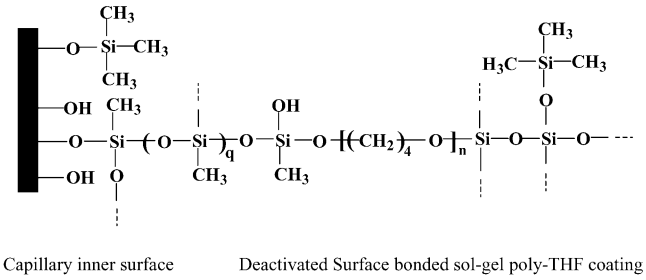


Scheme 1. Cationic ring opening polymerization of tetrahydrofuran.

the hydrolyzed precursor with other sol–gel-active components of the sol solution; (3) chemical bonding of poly-THF to the evolving sol–gel network; (4) chemical anchoring of the evolving hybrid organic–inorganic polymer to the inner walls of the capillary; and (5) derivatization of residual silanol groups on the coating by HMDS.

In order to create the sol–gel poly-THF coating in situ, the sol solution was kept inside the capillary for 60 min to allow for the hydrolytic polycondensation reactions to take place in the sol solution located inside the capillary. In presence of the sol–gel catalyst (TFA), the sol–gel precursor (MTMOS) undergoes hydrolysis reaction. The hydrolysis products can then take part in polycondensation reactions in a variety of ways to create a three-dimensional sol–gel network (Scheme 1).

During this polycondensation process, the growing sol–gel network can chemically incorporate the poly-THF molecules resulting an organic–inorganic hybrid network



Scheme 2. Surface-bonded sol–gel poly-THF network on the fused-silica capillary inner walls.

structure. Fragments of this network located in close vicinity of the fused silica capillary walls have the opportunity to become chemically bonded to the capillary inner surface as a result of condensation reaction with the silanol groups on the capillary walls. This leads to the formation of a surface-bonded sol–gel coating on the inner walls of the capillary. HMDS, used in the coating solution, deactivates the residual silanol groups on the sorbent coating during the post-coating thermal conditioning of the capillary.

A simplified scheme of the surface-bonded sol–gel poly-THF network on the fused-silica capillary inner walls is presented in Scheme 2.

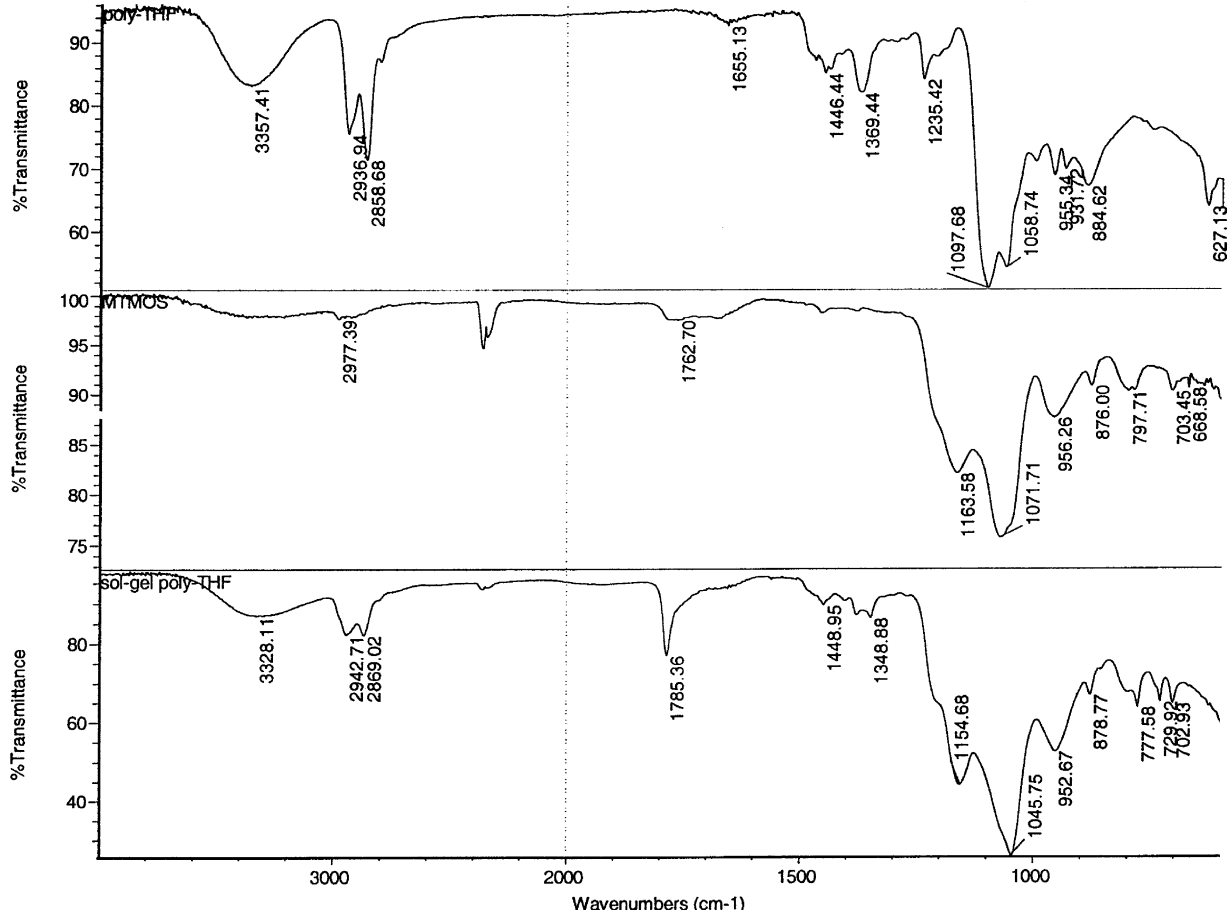


Fig. 2. IR spectra of pure polytetrahydrofuran (top), sol solution having all ingredients except polytetrahydrofuran (middle), sol–gel polytetrahydrofuran coating (bottom).

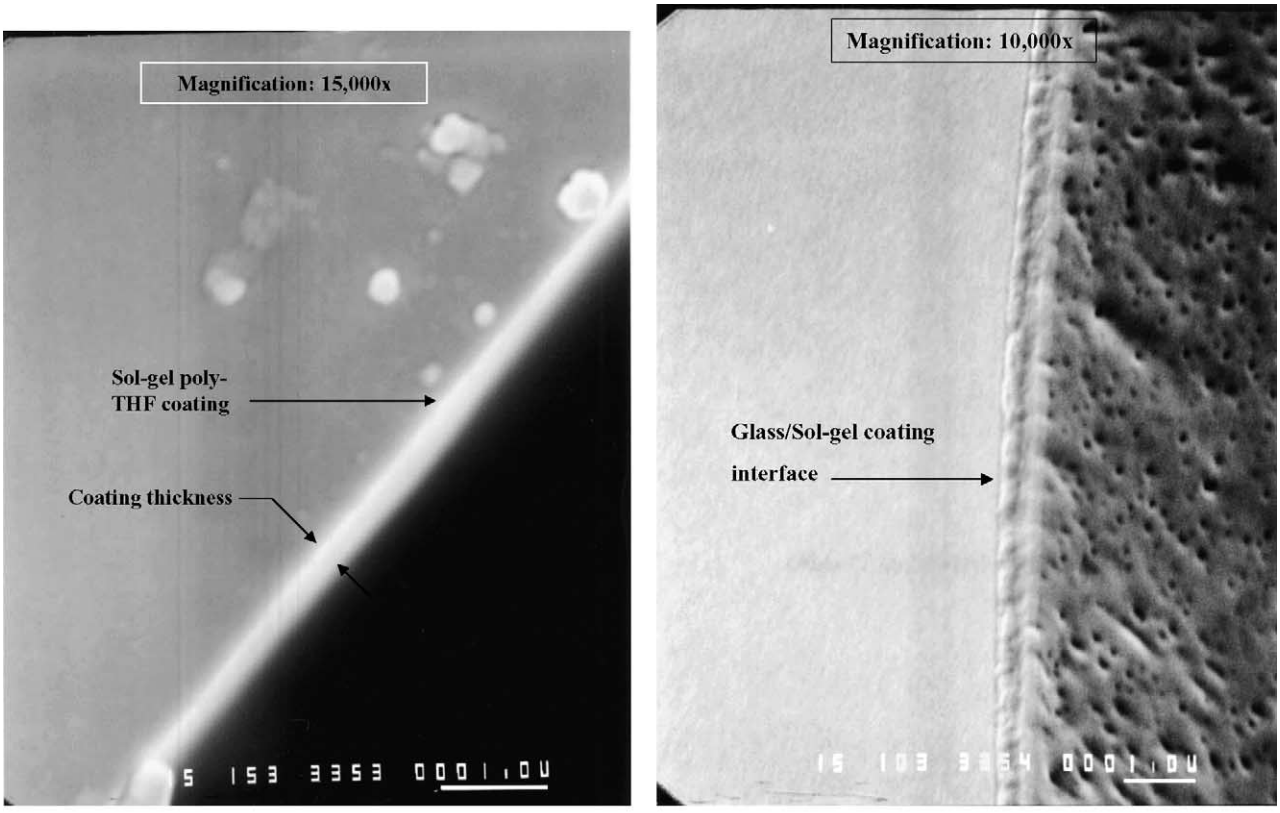


Fig. 3. Scanning electron microscopic image of a 320 μm i.d. sol–gel poly-THF coated fused silica capillary used in capillary microextraction. (a) Illustrating uniform coating thickness on the inner surface of the fused silica capillary, magnification: 15,000×. (b) Illustrating porous network of the poly-THF coating obtained by sol–gel coating technology, magnification: 10,000×.

Fig. 2 represents three FTIR spectra representing pure poly-THF (top), sol solution having all ingredients except poly-THF (middle), sol–gel poly-THF sorbent (bottom). The bottom spectrum contains an IR band at 1045 cm^{-1}, which is characteristics of Si–O–C bonds and is indicative of the successful chemical incorporation of polytetrahydrofuran in the silica-based sol–gel network [35].

Fig. 3 represents scanning electron micrographs of a sol–gel poly-THF coated capillary at two different orientations using two different magnifications: 15,000× (3a) and 10,000× (3b)

From Fig. 3a, the coating thickness was estimated at 0.5 μm. As can be seen from the image, sol–gel poly-THF coating is remarkably uniform in thickness. Fig. 3b represents the surface view of the coating obtained at a magnification of 10,000×. It reveals the underlying porous structure of the sol–gel poly-THF coating. Due to the porous nature, the sol–gel poly-THF extraction media possesses enhanced surface area, an advantageous feature to achieve enhanced sample capacity. The porous structure also facilitates efficient mass transfer through the coating, which in turn, translates into reduced equilibrium time during extraction.

CME is a non-exhaustive extraction technique. Quantitation by CME is based on solute extraction equilibrium established between the sample solution and the coating. Therefore, the time required to reach the equilibrium is particularly important. Fig. 4 illustrates the CME kinetic profiles of two nonpolar analytes (fluoranthene and pyrene), two moderately polar analytes (heptanophenone and dodecanal) and a highly polar analyte (pentachlorophenol) extracted on a sol–gel poly-THF coated capillary. Extractions were carried out using aqueous solutions of fluoranthene (10 ppb), pyrene (10 ppb), dodecanal (20 ppb), heptanophenone (20 ppb), and pentachlorophenol (50 ppb). As can be seen, both nonpolar, moderately polar, and highly polar compounds reached respective equilibria within 30 min. This is indicative of the fast diffusion in the sol–gel poly-THF coating. Based on these experimental results, further experiments in this work were carried out using a 30 min extraction time.

Sol–gel poly-THF coated capillaries were used to extract analytes of environmental, biomedical, and ecological importance, including polycyclic aromatic hydrocarbons (PAHs), aldehydes, ketones, alcohols, and phenols. The extracted compounds were further analyzed by GC. The CME–GC analysis data for PAHs, aldehydes, and ketones are presented in Table 2, and those for alcohols and phenols are provided in Table 3.

PAHs are ubiquitous environmental pollutants that present potential health hazards because of their toxic, mutagenic, and carcinogenic properties [44,45]. Because of this,

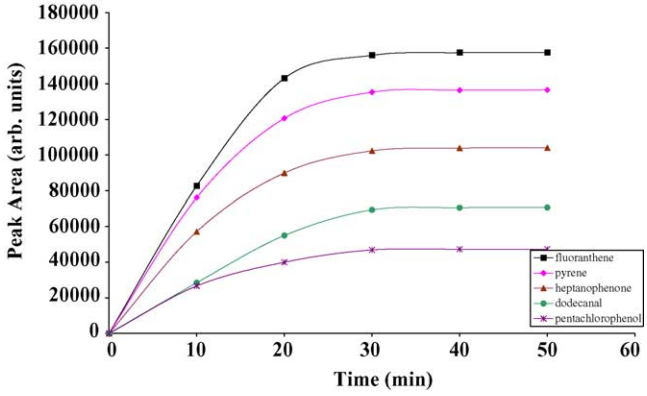


Fig. 4. Illustration of the extraction kinetics of nonpolar (fluoranthene and phenanthrene) and moderately polar (heptanophenone and dodecanal) compounds extracted on a 12.5 cm × 320 μm i.d. sol–gel poly-THF coated capillary using 10 ppb aqueous solution of each analyte in a mixture. Extraction kinetic of highly polar compound pentachlorophenol was obtained separately on a 12.5 cm × 320 μm i.d. sol–gel poly-THF coated capillary using 50 ppb aqueous solution. Extraction conditions: extraction time, 10–50 min. GC analysis conditions: 10 m × 250 μm i.d. sol–gel PDMS column; splitless injection; injector temperature, initial 30 °C, final 300 °C, at a rate of 100 °C/min; GC oven temperature programmed from 30 (hold for 5 min) to 300 °C at a rate of 20 °C/min; helium carrier gas; FID temperature 350 °C.

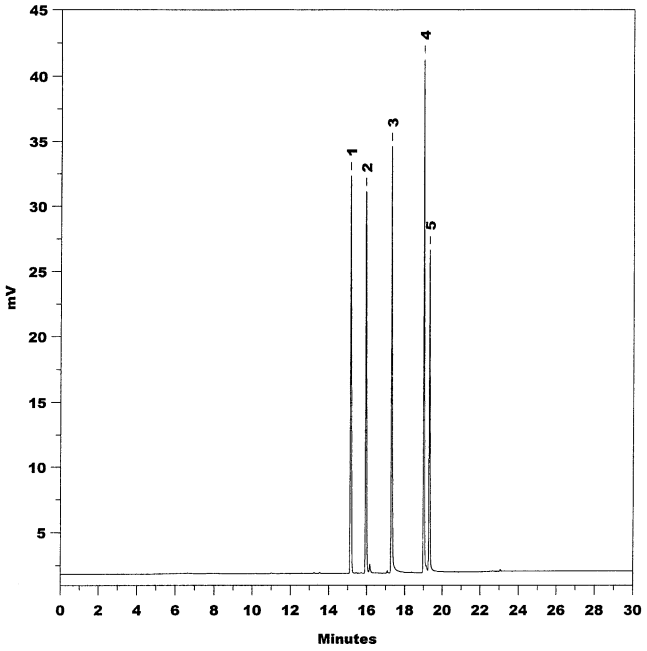


Fig. 5. Capillary microextraction–GC analysis of PAHs (20 ppb each) using sol–gel poly-THF coated capillary. Extraction time, 30 min. GC analysis conditions: 10 m × 320 μm i.d. sol–gel PDMS column; splitless injection; injector temperature, initial 30 °C, final 300 °C, at a rate of 100 °C/min; GC oven temperature programmed from 30 (hold for 5 min) to 300 °C at a rate of 15 °C/min; helium carrier gas; FID temperature 350 °C. Peaks: (1) acenaphthene; (2) fluorene; (3) phenanthrene; (4) fluoranthene; and (5) pyrene.

Table 2
Run-to-run and capillary-to-capillary peak area repeatability, retention time repeatability, and detection limit data for PAHs, aldehydes, and ketones in three replicate measurements by capillary microextraction–GC using sol–gel poly-THF coated extraction capillaries

Chemical class of the analyte	Name of the analyte	Peak area repeatability (n = 3)				Retention time (t_R) repeatability (n = 5)		Detection limits S/N = 3 (ppq)
		Capillary-to-capillary		Run-to-run		Mean t_R (min)	R.S.D. (%)	
		Mean peak area (arbitrary unit)	R.S.D. (%)	Mean peak area (arbitrary unit)	R.S.D (%)			
Polyaromatic Hydrocarbons	*Acenaphthene*	137139	2.13	125289	5.05	15.21	0.09	625
	Fluorene	118764	2.62	110767	3.01	16.01	0.10	460
	Phenanthrene	146853	4.49	139518	3.13	17.37	0.10	400
	Fluoranthene	144590	6.17	136260	2.92	19.08	0.08	260
	Pyrene	89573	6.45	94873	1.07	19.39	0.09	750
Aldehydes	*Nonanal*	80550	4.35	78583	2.19	10.98	0.09	1000
	Decanal	102377	4.01	98444	7.48	11.71	0.04	625
	Undecanal	76601	5.37	67730	5.38	12.41	0.07	750
	Dodecanal	61995	10.31	51594	6.77	13.05	0.06	940
Ketones	*Butyrophenone*	116887	3.48	110735	2.03	11.95	0.10	1000
	Valerophenone	121583	3.02	106301	3.09	12.66	0.10	460
	Hexanophenone	152281	3.43	120600	8.36	13.30	0.09	600
	Heptanophenone	158320	4.79	124831	5.10	13.92	0.10	340
	Decanophenone	113741	8.01	79475	5.75	15.55	0.09	1000

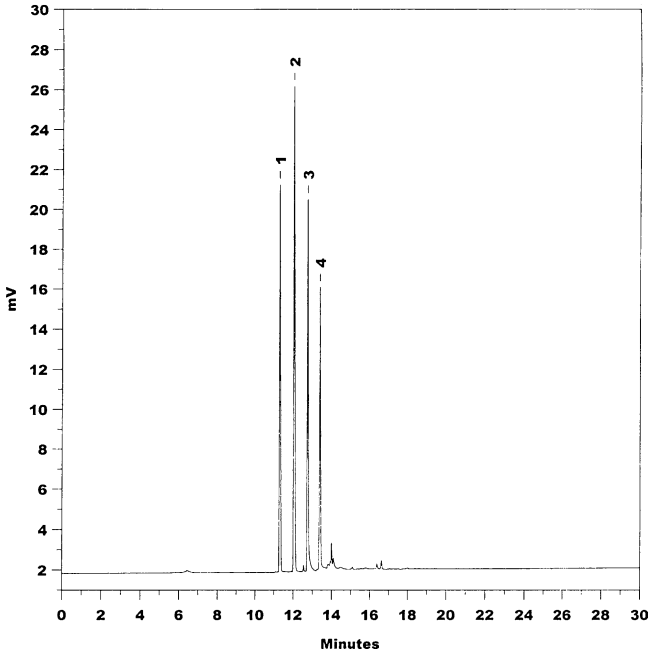


Fig. 6. Capillary microextraction–GC analysis of aldehydes at 20 ppb concentration using poly-THF coated capillary. Extraction time, 30 min. GC analysis conditions: 10 m × 320 μm i.d. sol–gel PDMS column; splitless injection; injector temperature, initial 30 °C, final 300 °C, at a rate of 100 °C/min; GC oven temperature programmed from 30 (hold for 5 min) to 300 °C at a rate of 20 °C/min; helium carrier gas; FID temperature 350 °C. Peaks: (1) *n*-nonanal; (2) decanal; (3) undecanal; and (4) dodecanal.

Environmental Protection Agency (EPA) has promulgated 16 unsubstituted PAHs in its list of 129 priority pollutants [46a]. Fig. 5 shows a gas chromatogram representing CME–GC analysis of 5 unsubstituted polyaromatic hydrocarbons from EPA priority list. They were extracted from an aqueous solution (each at 10 ppb) by capillary microextraction using a sol–gel poly-THF coated capillary. As can be seen from the data presented in Table 2, run-to-run and capillary-to-capillary repeatability in peak area obtained in CME–GC–FID experiments was quite satisfactory. For all PAHs, the relative standard deviation (R.S.D.) values were under 6%. Moreover, parts per quadrillion level detection limits were obtained for PAHs in the CME–GC–FID using by sol–gel poly-THF microextraction capillaries. These detection limits are significantly lower than those reported by others [46b] via SPME–GC–FID (e.g. 260 ppt for pyrene) using 100 μm thick PDMS coated commercial SPME fiber.

Aldehydes and ketones (carbonyl compounds) are of increasing concern due to their potential adverse health effects and environmental prevalence [47–49]. Aldehydes and ketones can form in water by the photodegradation of dissolved natural organic matter [50]. They may also form as disinfection by-products due to chemical reactions of chlorine and/or ozone (frequently used to disinfect water) with natural organic matter present in water [51]. Many of these by-products have been shown to be carcinogens or carcinogen suspects [52]. This is, in part, due to the high polarity and reactivity of carbonyl compounds in water matrices [51,53,54].

Table 3
Run-to-run and capillary-to-capillary peak area repeatability, retention time repeatability, and detection limit data for phenols and alcohols in three replicate measurements by capillary microextraction–GC using sol–gel poly-THF coated extraction capillaries

Chemical class of the analyte	Name of the analyte	Peak area repeatability (n = 3)				Retention time (t_R) repeatability (n = 6)		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*	4531	8.74	7278	7.32	10.02	0.10	150
	2, 4 – Dichlorophenol	8599	3.99	11297	5.63	11.37	0.10	85
	2, 4, 6 – Trichlorophenol	10272	7.02	13823	3.83	12.24	0.09	81
	4 – Chloro, 3 – methylphenol	13731	4.50	16933	2.21	12.52	0.09	30
	Pentachlorophenol	28379	3.72	32551	4.10	14.80	0.10	18
Alcohols	*Heptanol*	33644	11.75	40576	6.78	9.32	0.16	13
	Octanol	69227	2.62	81241	2.21	10.01	0.15	5
	Nonanol	84151	1.21	97397	2.56	10.67	0.19	0.75
	Decanol	119187	4.67	136046	2.85	11.30	0.18	0.61
	Undecanol	156758	4.71	167255	3.85	11.90	0.10	0.59
	Dodecanol	140261	6.74	143091	4.34	12.48	0.20	1.15
	Tridecanol	187638	6.91	216896	4.69	13.02	0.16	1.15

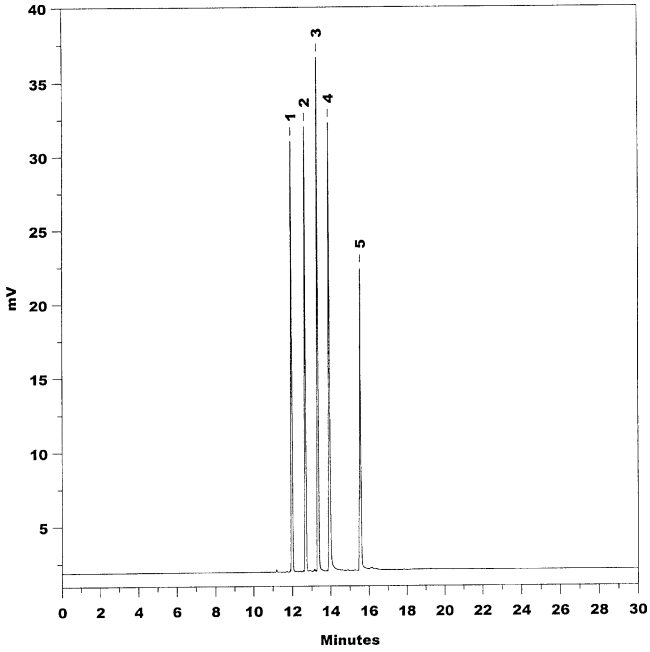


Fig. 7. Capillary microextraction–GC analysis of ketones at 20 ppb using poly-THF coated capillary. Extraction time, 30 min. GC analysis conditions: 10 m × 250 μm i.d. sol–gel PDMS column; splitless injection; injector temperature, initial 30 °C, final 300 °C, at a rate of 100 °C/min; GC oven temperature programmed from 30 (hold for 5 min) to 300 °C at a rate of 20 °C/min; helium carrier gas; FID temperature 350 °C. Peaks: (1) butyrophenone; (2) valerophenone; (3) hexanophenone; (4) heptanophenone; and (5) decanophenone.

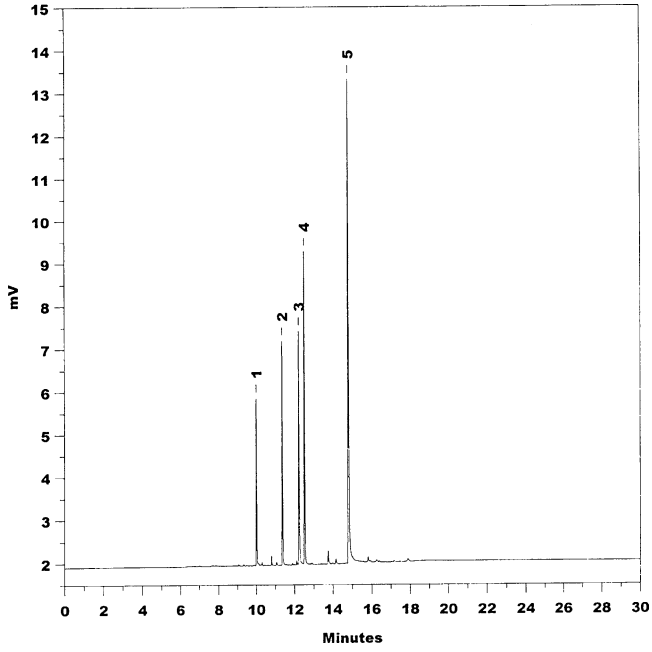


Fig. 8. Capillary microextraction–GC analysis of chlorophenols using poly-THF coated capillary. Extractions were carried out from a solution containing 2-chlorophenol (1 ppm); 2,4-dichlorophenol (50 ppb); 2,4,6-trichlorophenol (50 ppb); 4-chloro, 3-methylphenol (100 ppb); and pentachlorophenol (50 ppb). Extraction time, 30 min. GC analysis conditions: 10 m × 250 μm i.d. sol–gel PDMS column; splitless injection; injector temperature, initial 30 °C, final 300 °C at a rate of 100 °C/min; GC oven temperature programmed from 30 (hold for 5 min) to 300 °C at a rate of 20 °C/min; helium carrier gas; FID temperature 350 °C. Peaks: (1) 2-chlorophenol; (2) 2,4-dichlorophenol; (3) 2,4,6-trichlorophenol; (4) 4-chloro, 3-methylphenol; and (5) pentachlorophenol.

Fig. 6 represents a gas chromatogram of a mixture of underivatized aldehydes that were extracted from an aqueous solution containing 20 ppb of each analyte.

The data presented in Table 2 indicate that a sol–gel poly-THF coated capillary can extract free aldehydes from aqueous media to provide a limit of detection (LOD) which is comparable with, or lower than that achieved through derivatization [53]. For example, LOD for decanal has been reported as 200 ppt [53] (in SPME–GC–ECD) on a 65 μm DVB/PDMS coating after derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) whereas in the present work a significantly lower detection limit (625 ppq) was achieved for the same analyte using a sol–gel poly-THF coated capillary in hyphenation with GC–FID, even though ECD often provides higher sensitivity than FID for oxygenated compounds. The same trend has also been observed for other analytes. It should be pointed out that derivatization of these analytes, especially when they are present in trace concentration, may complicate the analytical process, thus compromising quantitative accuracy.

Fig. 7 represents a gas chromatogram of a mixture of five underivatized ketones (20 ppb each) extracted from an aqueous solution. Excellent peak shapes (Fig. 7) and run-to-run and capillary-to-capillary extraction reproducibility (Table 2) are indicative of preserved separation efficiency in CME–GC analysis and versatility of the sol–gel coating procedure used to prepare the extraction capillaries and the used GC column.

Chlorophenols (CPs) represent an important class of contaminants in environmental waters and soils due to their widespread use in industry, agriculture, and domestic purposes. Chlorophenols have been widely used as preservatives, pesticides, antiseptics, and disinfectants [55]. They are also used in producing dyes, plastics and pharmaceuticals. In the environment, chlorophenols may also form as a result of hydrolysis, oxidation and microbiological degradation of chlorinated pesticides. Chlorine-treated drinking water is another source of chlorophenols [56]. As a result, chlorophenols are often found in waters [57,58], soils [59], and sediments [59]. Chlorophenols are highly toxic, poorly biodegradable, carcinogenic and recalcitrant [60]. Owing to their carcinogenicity and considerable persistence, five of the chlorophenols (2-chlorophenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol; 4-chloro-3-methylphenol and pentachlorophenol) have been classified as priority pollutants by the US EPA [61]. Since chlorophenols are highly polar, it is quite difficult to extract them directly from polar aqueous media. Derivatization, pH adjustment, and/or salting-out are often used to facilitate the extraction [3]. To reduce the analytical complexity due to derivatization, HPLC is frequently used for the analysis of phenolic compounds [58]. Fig. 8 represents CME–GC analysis of five underivatized chlorophenols extracted from an aqueous medium using a sol–gel poly-THF coated capillary.

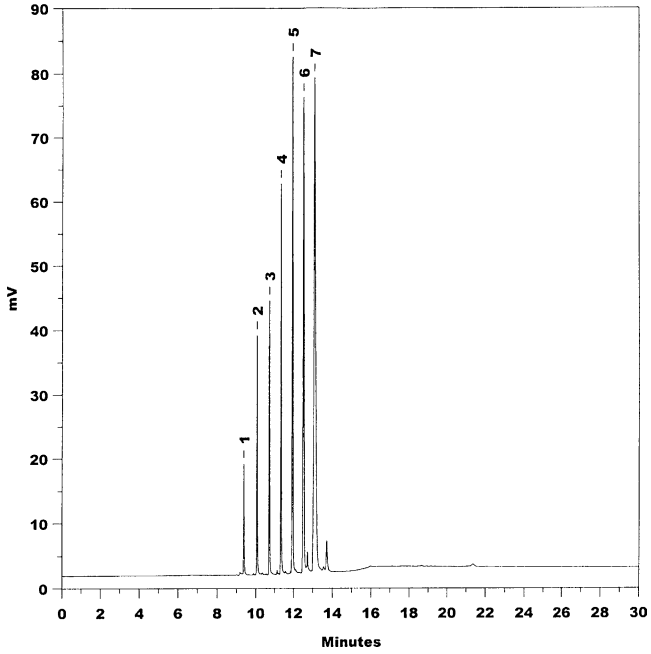


Fig. 9. Capillary microextraction–GC analysis of alcohols (100 ppb each) using poly-THF coated capillary. Extraction time, 30 min. GC analysis conditions: 10 m × 250 μm i.d. sol–gel PEG column; splitless injection; injector temperature, initial 30 °C, final 300 °C at a rate of 100 °C/min; GC oven temperature programmed from 30 (hold for 5 min) to 280 °C at a rate of 20 C/min; helium carrier gas; FID temperature 350 °C. Peaks: (1) 1-heptanol; (2) 1-octanol; (3) 1-nonanol; (4) 1-decanol; (5) 1-undecanol; (6) 1-dodecanol; and (7) 1-tridecanol.

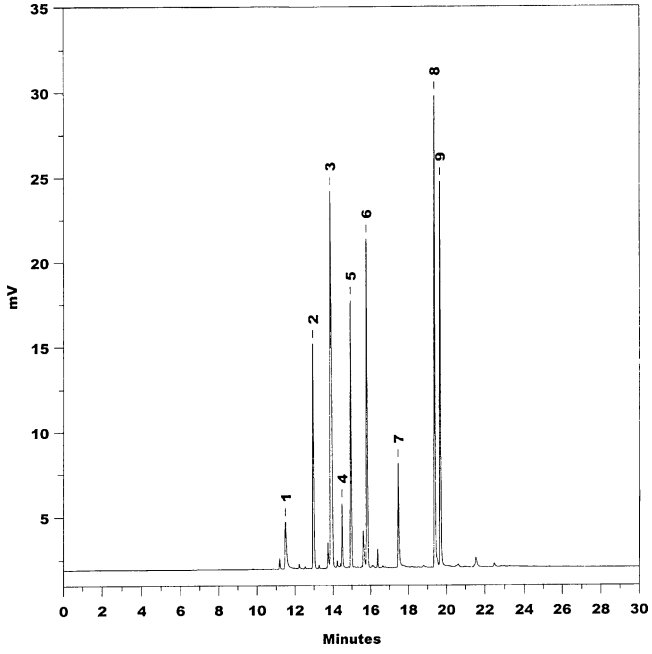


Fig. 10. Capillary microextraction–GC analysis of a mixture of nonpolar, moderately polar and polar compounds using poly-THF coated capillary. Extractions were carried out from a solution containing 2-chlorophenol (1 ppm); 2,4,6-trichlorophenol (50 ppb); pentachlorophenol (50 ppb); valerophenone (10 ppb); hexanophenone (10 ppb); nonanal (10 ppb); decanal (10 ppb); fluoranthene (10 ppb); pyrene (10 ppb). Extraction time, 30 min. GC analysis conditions: 10 m × 250 μm i.d. sol–gel PDMS column; split–splitless injection (desorption of analyte in splitless mode); injector temperature, initial 30 °C, final 300 °C at a rate of 100 °C/min; GC oven temperature programmed from 30 (hold for 5 min) to 300 °C at a rate of 15 °C/min; helium carrier gas; FID temperature 350 °C. Peaks: (1) 2-chlorophenol; (2) nonanal; (3) decanal; (4) 2,4,6-trichlorophenol; (5) valerophenone; (6) hexanophenone; (7) pentachlorophenol; (8) fluoranthene; and (9) pyrene.

We did not have to use derivatization, pH adjustment or salting out effect to extract chlorophenols from aqueous medium. Still, we have achieved a lower detection limit (e.g. 18 ppt for pentachlorophenol, by CME–GC–FID) compared to other reports in the literature (1.4 ppb for the same compound, by SPME–GC–FID) [3].

Fig. 9 represents a gas chromatogram for a mixture of alcohols. Being highly polar compounds, alcohols demonstrate higher affinity for water and are usually difficult to extract them from an aqueous matrix. In the present study, these highly polar analytes were extracted from aqueous samples using sol–gel poly-THF capillaries without exploiting any derivatization, pH adjustment or salting-out effects. The presented data indicate excellent affinity of the sol–gel poly-THF coating for these highly polar analytes that are often difficult to extract from aqueous media in underivatized form using commercial coatings. Moreover, high detection sensitivity (Table 3) and excellent symmetrical peak shapes also demonstrate outstanding performance of the sol–gel poly-THF coating and excellent deactivation characteristics of the sol–gel PEG column used for GC analysis, respectively.

Finally, a mixture containing analytes from different chemical classes representing a wide polarity range was extracted from an aqueous sample using a sol–gel poly-THF coated capillary. As is revealed from the chromatogram (Fig. 10), a sol–gel poly-THF coated capillary can simultaneously extract nonpolar, moderately polar, and highly polar compounds from an aqueous matrix. This may be explained by the existence of different polarity domains [62] (organic and inorganic) in the sol–gel poly-THF coating.

Run-to-run repeatability and capillary-to-capillary reproducibility are two important characteristics for CME as a microextraction technique and for the sol–gel coating method used for their preparation. These parameters were evaluated through peak area relative standard deviation values obtained from experimental data involving replicate measurements carried out on the same capillary under one set of conditions (run-to-run repeatability) and on a number of sol–gel coated capillaries prepared using the same protocol (capillary-to-capillary reproducibility). For nonpolar and moderately polar analytes (Table 2), these parameters had values in the range of 2.19–7.48 and 4.35–10.31%, respectively. In the case of polar analytes (Table 3), these values were less than 7.4 and 11.8%, respectively. For a sample preparation technique, such peak area R.S.D. values are quite acceptable and may be regarded as indicative of good consistency in microextraction process as well as satisfactory reproducibility of the sol–gel method used for the preparation of the microextraction capillaries. Additionally, the retention time (t_R) repeatability data for

sol–gel PDMS (0.04–0.10% R.S.D., Table 2) and sol–gel PEG (0.15–0.20% R.S.D., Table 3) GC columns show outstanding consistency in chromatographic performance of the in-house prepared GC columns used in this study.

In the present work, sol–gel CME–GC operation was performed manually which is not convenient from a practical point of view. For wide acceptance of the technique, the inconvenience associated with manual installation of the microextraction capillary in the GC system needs to be overcome. There are various possibilities to solve this problem, including the use of a robotic arm equipped with devices necessary for performing CME, desorbing the analytes, and transferring the desorbed analytes into the separation column.

In our opinion, sol–gel capillary microextraction technique described in the present manuscript has a great potential for automated operation in hyphenation with both gas- and liquid-phase separation techniques. Thanks to the capillary format of the extraction device combined with high thermal and solvent stability of the surface-bonded sol–gel extraction phase, sol–gel capillary microextraction can be expected to offer high degree of versatility in automated operation.

4. Conclusion

Novel sol–gel poly-THF coating was developed for high-performance capillary microextraction to facilitate ultra-trace analysis of polar and nonpolar organic compounds. Parts per quadrillion level detection limits were achieved using poly-THF coated microextraction capillaries in conjunction with GC–FID. To the best of our knowledge, this represents the first report on the use of sol–gel poly-THF sorbent in analytical microextraction. Sol–gel poly-THF coatings showed extraordinarily high sorption efficiency and proved to be highly effective in providing simultaneous extraction of nonpolar, moderately polar, and highly polar analytes from aqueous media. Sol–gel poly-THF coated microextraction capillaries showed excellent thermal and solvent stability, making them very suitable for hyphenation with both gas-phase and liquid-phase separation techniques, including GC, HPLC, and CEC. In CME-HPLC and CME-CEC hyphenations, sol–gel poly-THF coated microextraction capillaries have the potential to provide new levels of detection sensitivity in liquid-phase trace analysis, and to extend the analytical scope of CME to thermally labile-, high molecular weight-, and other types of compounds that are not amenable to GC. Further sensitivity enhancement should be possible through the use of monolithic microextraction capillaries. This could open up new possibilities in ultra-trace analysis of organic pollutants in aqueous media.

Acknowledgement

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