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Ultra-high-stability, pH-resistant sol–gel titania poly(tetrahydrofuran) coating for capillary microextraction on-line coupled to high-performance liquid chromatography

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ABSTRACT

A sol–gel titania poly(tetrahydrofuran) (poly-THF) coating was developed for capillary microextraction hyphenated on-line with high-performance liquid chromatography (HPLC). Poly-THF was covalently bonded to the sol–gel titania network which, in turn, became chemically anchored to the inner surface of a 0.25 mm I.D. fused silica capillary. For sample preconcentration, a 38-cm segment of the sol–gel titania poly-THF coated capillary was installed on an HPLC injection port as a sampling loop. Aqueous samples containing a variety of analytes were passed through the capillary and, during this process, the analytes were extracted by the sol–gel titania poly-THF coating on the inner surface of the capillary. Using isocratic and gradient elution with acetonitrile/water mobile phases, the extracted analytes were desorbed into the on-line coupled HPLC column for separation and UV detection. The sol–gel titania poly-THF coating was especially efficient in extracting polar analytes, such as underivatized phenols, alcohols, amines, and aromatic carboxylic acids. In addition, this coating was capable of extracting moderately polar and nonpolar analytes, such as ketones and polycyclic aromatic hydrocarbons. The sol–gel titania poly-THF coated capillary was also able to extract polypeptides at pH values near their respective isoelectric points. Extraction of these compounds can be important for environmental and biomedical applications. The observed extraction behavior can be attributed to the polar and nonpolar moieties in the poly-THF structure. This coating was found to be stable under extremely low and high pH conditions—even after 18 h of exposure to 1 M HCl (pH ≈0.0) and 1 M NaOH (pH ≈14.0).

1. Introduction

Solid-phase microextraction (SPME) is an important technique for solvent-free sample preparation [1]. In SPME, a sorbent coating created on the end segment (~1 cm) of a fused silica fiber is used for extraction [1]. Various sorbent coatings, including polysiloxanes with a diverse range of side chains [2–5], polyamide [6], polyvinyl chloride [7], inorganic polymers [8], and molecularly imprinted polymers (MIPs) [9,10] have been reported. To perform extraction, the coated fiber is submerged into a sample under mechanical agitation until analyte sorption–desorption equilibrium is reached between the fiber coating and the sample [1]. The extracted analytes are most commonly desorbed into the injection port of a gas chromatography (GC) system [1,11]. SPME has also been coupled with capillary electrophoresis (CE) [12,13], supercritical fluid chromatography (SFC) [14], and high-performance liquid chromatography (HPLC) [15,16], but in the latter cases it requires complicated desorption devices, often resulting in sample loss, sample dilution, and reduced extraction sensitivity [17].

Shortcomings of fiber SPME include low sample capacity due to small sorbent loading in the short coated segment of the fiber, bending of the needle on the syringe-like SPME device, frequently encountered mechanical damage to the coating during operation, and breaking of the delicate fiber. In-tube SPME [18] was developed to overcome these problems inherent in fiber SPME. In this format, SPME uses the sorbent coating on the inner surface of a fused silica capillary. Commonly, a piece of commercial GC column is used for this, and extraction is performed by permitting samples to pass through it until a sorption–desorption equilibrium of the analytes is reached between the sample and the sorbent coating. In-tube SPME uses a longer coated segment, which should increase the overall extraction sensitivity. However, conventional in-tube SPME coat-

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ings are thin (<1 μm in thickness), and despite using longer coated segments, the extraction sensitivity of this method is still low [19]. The creation of stable coatings of greater thickness is extremely difficult using conventional coating techniques [19]. Since conventional coatings are not chemically bonded to the capillary surface, such coatings are characterized by moderate thermal stability. This seriously limits the allowable desorption temperature (hence the maximum boiling point) of analytes amenable to in-tube SPME-GC analysis [20]. Finally, the absence of chemical anchorage to the inner surface of the capillary results in poor solvent stability of conventional coatings that are prone to getting stripped off the capillary by the mobile phase when coupled to HPLC.

Sol–gel coatings were developed to address these problems by chemically anchoring the coating to the surface of the fiber [20] or capillary [21]. Since their introduction in 1997 [20], a variety of coatings have been reported, including poly(dimethylsiloxane) (PDMS)- [20], hydroxy fullerene- [22], crown ether- [23], oligomer- [24], PDMS/poly(vinyl alcohol)- [25], and poly(ethylene glycol) (PEG)-based [26] sol–gels. Introduced in 2002, sol–gel coatings for capillary microextraction (CME) include sol–gel PDMS [21], sol–gel PEG [21,27], sol–gel dendrimer [28], sol–gel cyano-PDMS [29], electrically charged sol–gels [30,31], sol–gel zirconia poly(dimethyldiphenylsiloxane) [32], and sol–gel germania PDMS [33]. Sol–gel CME was successfully applied to GC [21,27–29,32,33], CE [30,31], and inductively coupled plasma mass spectrometry [34,35]. The solvent stability of sol–gel CME coatings allows for an effective on-line hyphenation of CME with HPLC [36–39]. Malik and co-workers [36] introduced the first on-line hyphenation of CME to HPLC in 2004. A silica-based sol–gel β-cyclodextrin coated capillary was developed and used in the HPLC analysis of non-steroidal anti-inflammatory drugs in urine samples [37]. Recently, we reported sol–gel methyl [38] and sol–gel poly(dimethyldiphenylsiloxane) (PDMDPS) [39] coated capillaries for on-line coupled CME–HPLC.

Our group introduced a sol–gel titania PDMS coated capillary [36] and successfully hyphenated CME on-line with HPLC. This PDMS coating was effective in extracting nonpolar analytes with superior pH stability to that of silica-based sol–gel coatings [36]. A sol–gel titania-hydroxy-terminated silicone oil fiber was coupled to GC in the analysis of phenols, amines, and polycyclic aromatic hydrocarbons (PAHs) [40]. Also, a titania-based sol–gel dimethyl-3,7-diaminobenzothiophene-5,5-dioxide-3,3,4,4,-diphenylsulfone tetracarboxylic dianhydride fiber was developed for the determination of benzene, toluene, ethylbenzene, xylene, and halocarbons using SPME-GC [41]. Zirconia- [32], alumina- [42], and germania-based [33] sol–gel coatings have also been used in microextraction and they were shown to possess good pH stability.

In a previous study [43], a silica-based sol–gel poly(tetrahydrofuran) coated capillary was found to be very effective in extracting polar and nonpolar analytes when coupled to GC analysis. Titania's superior pH stability [36] and poly-THF's excellent extracting capabilities [43] for polar and nonpolar analytes inspired us to develop a novel sol–gel coating possessing both of these desirable characteristics presented in this paper. To our knowledge, this is the first report on the creation of a sol–gel titania-based poly-THF coated capillary and its use in CME on-line coupled to HPLC.

2. Experimental

2.1. Equipment

A Micro-Tech Scientific (Vista, CA, USA) Ultra Plus HPLC system equipped with a Linear UVIS 200 variable-wavelength UV detector was used for on-line CME–HPLC analysis using a sol–gel titania poly-THF coated microextraction capillary. A Phenomenex (Torrence, CA, USA) reversed-phase Luna C_{18} column (15 cm × 4.6 mm I.D.) was used for HPLC separations. A Fisher model G-560 Vortex Genie 2 system (Fisher Scientific, Pittsburg, PA, USA) was employed for thorough mixing of the sol solution constituents. Nanopure water (15 MΩ) was obtained from a Barnstead model 04741 Nanopure deionized water system (Barnstead/Thermodyne, Dubuque, IA, USA). On-line collection and processing of the CME–HPLC data were carried out using Chrom Perfect (version 3.5 for Windows) computer software (Justice Laboratory Software, Denville, NJ, USA).

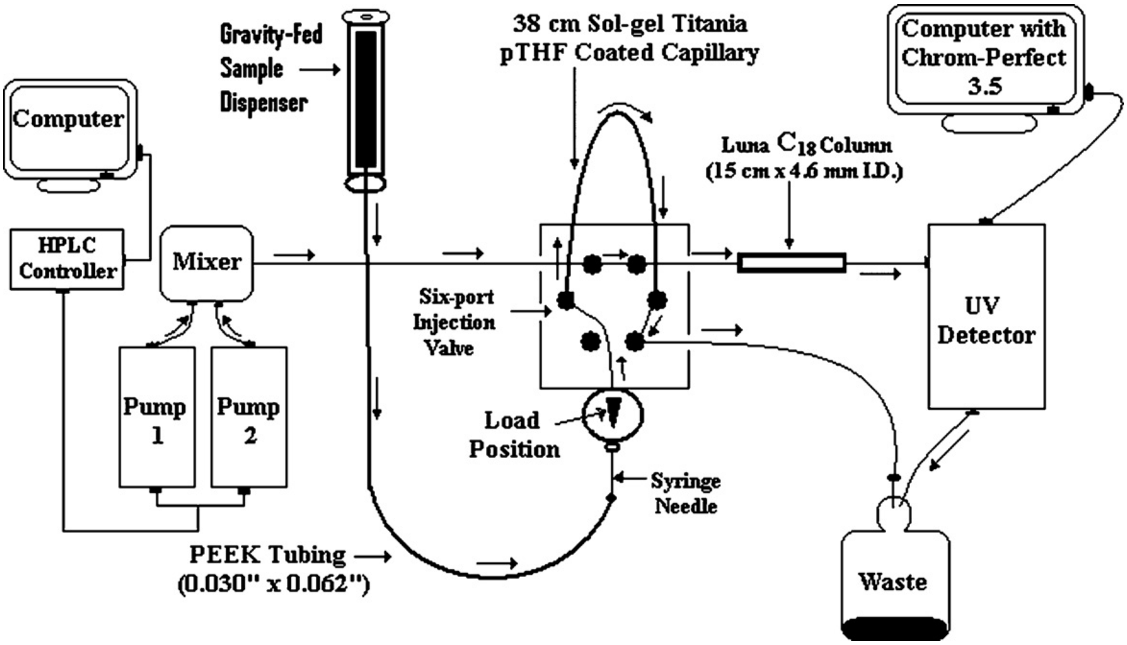

Fig. 1. Experimental setup used to carry out the CME–HPLC experiments using the sol–gel titania poly-THF coated capillary. To perform extraction, aqueous samples containing analytes flow from the gravity-fed sample dispenser through the sol–gel titania poly-THF coated capillary, and then into a waste container. To perform analysis, the HPLC injection valve is turned to the inject position. This allows the mobile phase to flow through the coated capillary, which desorbs the analytes and transfers them into the HPLC column for separation followed by subsequent UV detection.