

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

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Abstract

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

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1. Introduction

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

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

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

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

Sol–gel organic–inorganic hybrid materials provide desirable sorptive properties that are difficult to achieve by using either purely organic or purely inorganic materials. Because of this unique opportunity to achieve enhanced selectivity, hybrid sol–gel materials have created a great deal of interest in the field of microcolumn separations and sample preparation. In the recent past, silica-based organic–inorganic hybrid stationary phases have been developed in the form of surface coatings [16–18] and monolithic beds [19]. In 1993, Dabrio and co-workers [20] developed a procedure for the preparation of a thin layer of silica gel with chemically bonded C₁₈ moieties on the inner walls of fused-silica capillaries for use as open tubular columns in reversed-phase high-performance liquid chromatography. Colon and Guo [21] used sol–gel technology to prepare stationary phase coatings for open-tubular liquid chromatography and electrochromatography. Malik and co-workers introduced sol–gel coated columns for capillary GC [22] and sol–gel coated fibers for solid-phase microextraction [13,23]. Subsequently, other groups also got involved in sol–gel research aiming at developing novel sorbents for solid-phase microextraction [24–28] and solid-phase extraction [29,30]. Compared with conventional fibers, sol–gel SPME fibers demonstrated superior performance by exhibiting high thermal stability (up to 380 °C) [24] and solvent stability [25]. This enhanced stability of sol–gel coated fibers is attributed to the chemical bonding between the sol–gel coating and the fiber surface. Compared with the conventionally prepared fibers, in many instances, sol–gel SPME fibers showed better selectivity and extraction sensitivity, [26] less extraction time, [27] and extended lifetime [26]. Recently, sol–gel capillary microextraction was

reported by Malik and co-workers [9]. In this format, also known to as in-tube SPME, sample extraction was accomplished using a sol–gel coating created on the inner surface of a fused silica capillary.

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

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

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

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

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