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Review article

Supercritical water-treated fused silica capillaries in analytical separations: Status review

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ABSTRACT

Near- and supercritical water (SCW) has recently been shown to provide an unusual but effective tool to roughen the inner surface or manipulate the internal diameter of fused silica capillaries for analytical separation methods. In this review, the to-date existing variants of instrumental arrangement for etching the fused silica capillaries with SCW are described, the currently accessible morphologies of SCW-etched capillaries are outlined, and both existing and prospective applications of the SCW-etched capillaries in analytical separations are briefly discussed. Relative merits of SCW and other agents to treat the inner surfaces of fused silica capillaries are also mentioned.

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1. Introduction

The necessity to treat and/or modify the surface of separation space has been omnipresent in capillary analytical separations by both electromigration and chromatographic methods. In electromigration methods, the main reasons for surface modification come from the needs to reduce the analyte–wall interactions and to control the electroosmotic flow [1–3]. In column chromatographic methods, the motivation for surface modification may involve the improvement of adhesion of the stationary phase to the column wall, the suppression of spurious adsorption of analytes, or the pre-treatment of the wall prior to *in-situ* synthesis of a monolithic

column. Currently, most analytical separations in capillary format make use of fused silica capillaries [4] of internal diameter ranging within 10–700 μm . Depending on the intended purpose, the most important reagents used to treat the inner surface of fused silica capillaries included, e.g., ammonium bifluoride [5,6], aqueous acids and aqueous bases [7], long-term aging in water [8], formation of microcrystalline layer of NaCl to improve wettability of the capillary inner wall [9] or compounds such as 2-chloro-1,1,2-trifluoroethyl methyl ether [10–12] decomposing at elevated temperature to produce species capable to react with silica. While the aqueous acids and bases have often been used for milder pre-treatment of the capillary surface (e.g., before the synthesis of silica-based monolithic column in the capillary), the treatment with hydrogen fluoride-containing mixtures leads to real etching with some resultant surface unevenness. After application, all these

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agents may leave the surface polluted with heteroatoms (that is, with atoms other than Si, O, and H).

In the role of agent for treatment of fused silica capillaries, the near- and supercritical water (SCW) was introduced a few years ago [13] although it had been used before to wet micro- and nanofluidic fused-silica devices [14]. Because of significant variations in the solvent properties of SCW with operating temperature and pressure, SCW makes a tunable solvent. Furthermore, SCW contains no heteroatoms to pollute the treated surface that may be difficult to remove or undesirable in the subsequent application of the capillary. Besides, as an etching agent, SCW is certainly greener than the mixtures containing hydrogen fluoride. Before discussing the pros and cons of SCW, however, a brief overview of most important etching and surface modification agents in current use will be given.

2. Commonly used agents for etching and surface modification of fused silica capillaries

Within the short extent of this review, it would be impossible to provide a complete account of all the agents ever used to etch or modify the inner surfaces of fused silica capillaries. To fix ideas, it should be noted that etching has mostly been used to facilitate the subsequent chemical modification of the surface, and that the chemical modification can involve either covalent bonding or physical adsorption. Etching also increases the inner surface area of the capillary and, therefore, the loading capacity of the inner surface for subsequent chemical modification. Although traditional agents used to etch glass or silica surfaces contain hydrofluoric acid, an important agent to etch fused silica capillaries has been ammonium bifluoride (NH_4HF_2), usually applied in the form of methanolic solution. Methanol is subsequently driven off by a flow of dry nitrogen, the capillary is sealed and heated for several hours to a temperature of 300–400 °C. Different combinations of heating time and temperature result in different surface morphologies [5,15]. Occasionally, the etching with NH_4HF_2 has been carried out in the presence of additional inorganic salt, with specific effects in open tubular capillary electrochromatography of heterocyclic aromatic amines [16] and enkephalins [17]. After etching, chemical modification of the inner surface via covalent bonding has often involved silanization with triethoxysilane to convert the accessible silanol groups to a hydride layer on the surface [18]. Subsequently, the desired chemical functionality may be attached via hydrosilation with suitably substituted olefin; this procedure involves forming stable silicon–carbon bonds and avoiding the Si–O–Si linkages in the attachments. The selection of moieties attached by hydrosilation has involved, e.g., C18 chains [5,19–23], 1,2-octanediol [19], butylphenyl [24], bonded liquid crystals containing cholesterol-10-undecenoate [21–26] and 4-cyano-4'-pentoxybiphenyl [25], as well as chiral selectors [27]. The modified capillaries have mostly been employed to separate the target analytes by open tubular capillary electrochromatography. For these applications, the silanization/hydrosilation route of chemical modification has been shown to be preferable [28] to the organosilanization path that makes use of chlorosilane agents and results in coupling the desired moiety to the surface via a Si–O–Si linkage.

In capillary electrophoresis (CE), an important strategy to control the surface chemistry for the above mentioned purposes has been to coat the inner wall with a layer of suitable agent. The selection of agents used to create physically adsorbed layers included neutral polymers (e.g., poly(ethylene oxide) [29,30], poly(vinyl alcohol) [31], hydroxyethyl cellulose [32]), charged polymers (e.g., 1,5-dimethyl-1,5-diazaundecamethylene polymethobromide (polybrene) [33], polyarginine [34], polyethyleneimine [35]), small-molecule agents (e.g., cetyltrimethylammonium bromide

[36], didodecyltrimethylammonium bromide [37], triethylenetetramine [38], 1,2-dioleoyl-3-trimethylammoniumpropane [39] or *N*-dodecyl-*N,N*-dimethyl-(1,2-propanediol) ammonium chloride [40]), or other cationic polyelectrolyte coatings [41]. In general, physically adsorbed coatings are easy to prepare but their usable lifetimes are limited. These features have prompted the development of more stable, covalently bonded coatings including, e.g., polyacrylamide [1,42–45], polyvinylpyrrolidone [46], vinylpyrrolidone–vinylimidazole copolymers [47], poly(ethylene glycol) [48], photografted zwitterionic monomer *N,N*-dimethyl-*N*-methacryloxyethyl-*N*-(3-sulfopropyl)ammonium betaine [49], hydroxylated polyacrylamides and polyacrylates [50], quaternary ammonium cations [51], surface-bound dextran layer crosslinked with diepoxypolyethylene glycol [52], surface-bound fibrinogen protein layer [53] or tentacle-like oligourethanes [54]. More recent examples of covalent coatings include, e.g., multilayer coatings [55,56], polyaniline–polydopamine–graphene oxide coating [57], quaternized cellulose-supported gold nanoparticle coating [58], pH-responsive poly(2-dimethylaminoethylmethacrylate)-*block*-poly(acrylic acid)-based coating [59], or dendritic glycopolymer coatings [60]. Most of the covalent coatings mentioned above have been applied in CE of proteins, and they have proven to be instrumental in the control of electroosmotic flow. Reviews covering the progress in CE coatings are also available [61–65].

3. Supercritical water: properties, applications and interactions with silica

Considered alone, the critical properties of water ($T_c = 647.096 \text{ K} = 373.946 \text{ °C}$ and $P_c = 22.064 \text{ MPa}$) [66] certainly make SCW an uncommon supercritical fluid to be applied in analytical separation methods, unlike carbon dioxide with its much more “friendly” critical properties. Yet there is an essential difference between water and CO_2 , suggesting that application of SCW in analytical chemistry may ultimately pay off despite the somewhat dramatic critical properties of water. The difference derives from the fact that, unlike CO_2 , water is a polar and protic solvent. Therefore, the solvent characteristics of water vary widely with the operating temperature and pressure. To illustrate, Table 1 shows several relevant properties of pure water at selected temperature and pressure settings. Consequently, the solvent properties of water may be tuned by proper selection of operating temperature and pressure, giving rise to diverse applications ranging from pressurized hot water extraction [70,71] through the use of SCW as a reaction medium [72–74] to hydrothermal conversion of biomass to fuels [75] and supercritical water oxidation [76]. However, applicability of SCW is not limited to organic compounds, and the attempts to use SCW for treatment of silica surfaces have partly been inspired by the important role of SiO_2 –water interactions in geochemistry as regards the transport, crystallization and deposition of quartz and siliceous minerals from hydrothermal solutions. There have been numerous reports of experimental determination [77–80] and modeling [81–85] of the aqueous solubility of silicon dioxide at elevated temperature and pressure. Naturally, most of these efforts have focused on quartz as the most common crystalline form of SiO_2 , with amorphous silica receiving less attention. It turns out that, at a temperature and pressure somewhat above the respective critical properties of water, the aqueous solubility of amorphous silica may reach several grams per 1 kg of water, certainly an interesting value from the viewpoint of using SCW to treat or etch fused silica surfaces.

The solubility studies mentioned above concerned the binary SiO_2 –water systems. However, real hydrothermal fluids of geochemical relevance are hardly ever pure water. In the geochemical

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