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Supercritical water as an agent to treat fused silica capillaries for analytical separations

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ABSTRACT

In analytical separation methods, both chromatographic and electromigration, the separation frequently occurs in a fused silica capillary with the internal diameter ranging from about 0.01 to 0.7 mm. Fused silica capillaries are produced by high-temperature drawing from larger diameter silica tubes, and so the inner wall of the produced capillary is perfectly smooth. Prior to application for a separation, it is often useful to make the inner surface rough; this is usually accomplished by etching the capillary surface with hydrogen fluoride provided either in the form of hydrofluoric acid or produced in situ by thermal decomposition of other compounds such as 2-chloro-1,1,2-trifluoroethyl methyl ether or ammonium bifluoride. The etching processes employing hydrogen fluoride are sometimes difficult to control. At temperatures and pressures near its vapor–liquid critical point, water can dissolve appreciable amounts of fused silica. Therefore, supercritical water (SCW) makes a powerful, tunable agent to manipulate the internal diameter and adjust the inner surface roughness of fused silica capillaries, and we have used SCW in these roles for a few years. The purpose of this contribution is to outline the current options and applications of SCW to pretreat fused silica capillaries for analytical separations. Different evolution stages of the etching apparatus will be mentioned, originally enabling the treated capillary to be only heated along its full length, and, in a subsequent version, enabling a continuous movement of the capillary through a heated zone of variable length (from a few mm to about 10 cm). In either case, water in the capillary can either be stagnant or it can flow through the capillary at a selected rate in either direction, thus providing multiple options to morph the inner surface or change the internal diameter of the capillary. A brief review of up-to-date applications of the SCW-etched capillaries will follow.

INTRODUCTION

Currently, a large part of analytical-scale separations by both chromatographic and electromigration methods have been performed in fused silica capillaries with internal diameter ranging from about 0.01 to 0.7 mm. Owing to the production by high-temperature drawing from larger-diameter silica tube, the inner wall of a ready-made fused silica capillary is perfectly smooth. Before application for a separation, it is often very useful to make the inner surface rough (e.g., to facilitate the *in-situ* preparation of a silica monolithic column). This is most often accomplished by etching the capillary surface with hydrogen fluoride provided either in the form of hydrofluoric acid or produced in situ by thermal decomposition of other compounds such as 2-chloro-1,1,2-trifluoroethyl methyl ether [1] or ammonium bifluoride [2]. However, the etching processes employing hydrogen fluoride are sometimes difficult to control, and they may leave the surface polluted with heteroatoms (that is, atoms other than Si, O or H). Therefore, we have sought for an alternative technique to etch the fused silica surface that would not be prone to surface contamination with heteroatoms.

MOTIVATION FROM GEOCHEMISTRY

Near- and supercritical water (SCW) has been known to dissolve appreciable amounts of quartz [3,4] and fused (amorphous) silica [5,6], and several approaches have been described to model the aqueous solubilities of quartz [7–9] and fused silica [10,11]. 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.

VARIANTS OF ETCHING APPARATUS

The original design of the etching apparatus was constructed for static or dynamic in-cell treatment of glass tubes or glass chips [12]. To treat fused silica capillaries, the extraction cell has been complemented with a massive thermostated bloc to heat a capillary of any length (> 25 cm) to a uniform temperature along the whole effective length of the capillary [13]. This arrangement will be referred to as whole-length etching, and the schematic diagram of the apparatus is shown in Fig. 1.

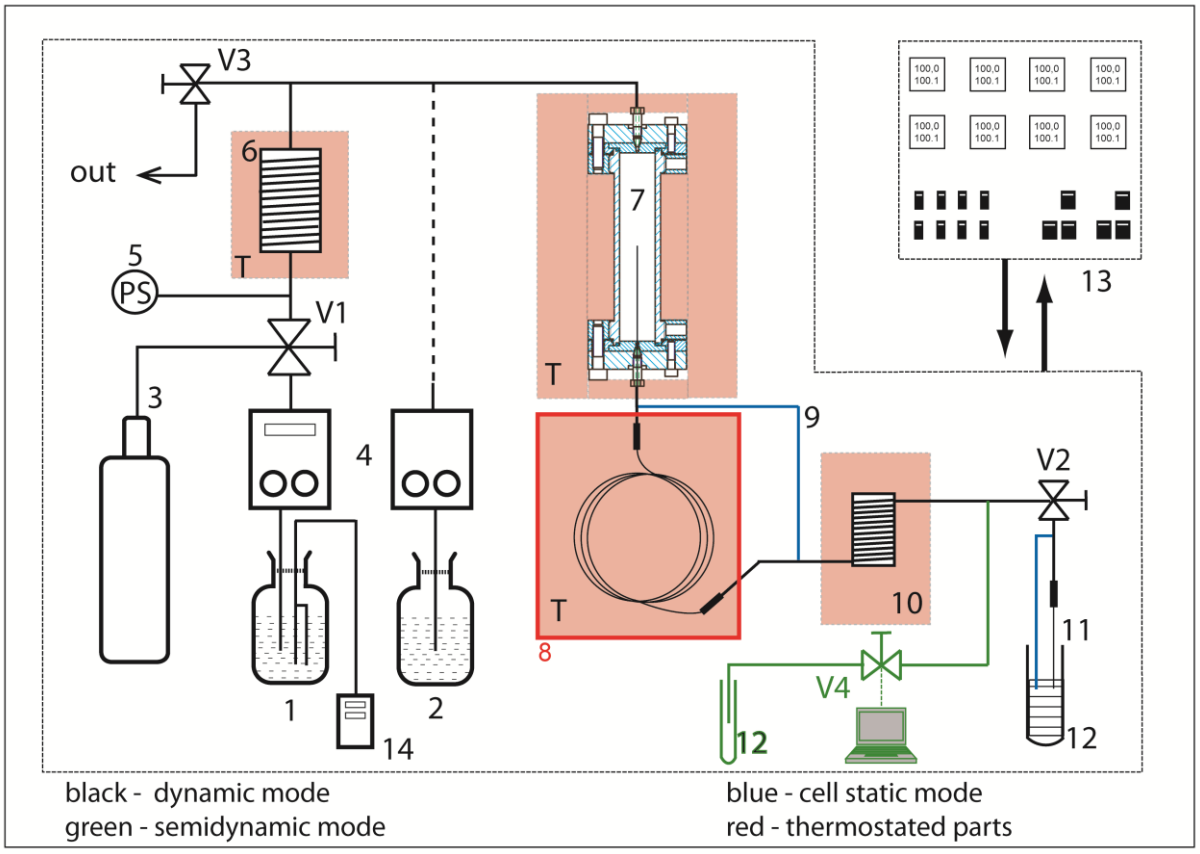

Figure 1. Schematic diagram of the apparatus for whole-length etching of fused silica capillaries with SCW. (1) water reservoir, (2) modifier/organic reservoir (if needed), (3) helium tank, (4) high pressure pumps, (5) pressure sensor, (6) preheater coil, (7) extraction cell housing, (8) fused-silica capillary, (9) in-cell etching output (if needed), (10) liquid cooling system, (11) fused-silica restrictor, (12) sample/waste collection vial, (13) PC control units and pressure indication, (V1) main control valve, (V2) output control valve, (V3) discharge valve (dynamic mode), (V4) PC-controlled quick valve (semi-dynamic mode). Reprinted with permission from [13]. Copyright (2013) American Chemical Society.

Initial experiments involved filling the capillary with water and bringing the stagnant water to supercritical conditions (a static mode of etching). A single-step operation of this kind did not produce any significant effect on the inner surface, possibly because of rapid saturation of the

small amount of water in the capillary with the dissolved silica. A repeated filling-and-heating operation with flash replacements of water in the capillary (semi-dynamic mode), however, resulted in uniform etching along a part of the capillary, producing a crest-and-gorge-like inner surface suitable for synthesis of silica-based monolithic columns. A dynamic arrangement of etching, that is, a continuous flow of water through fused silica capillary heated to a temperature above the critical of water, produced significant changes in the internal diameter of the capillary. The diameter changes generally involved both an increase and a decrease with respect to the original diameter, with the decreased diameter always resulting from deposition of silica on the capillary wall from the upstream-generated aqueous solution. The dynamic mode of etching turned out to be useful in producing tapered capillaries with a continuous change in the internal diameter along the capillary length.

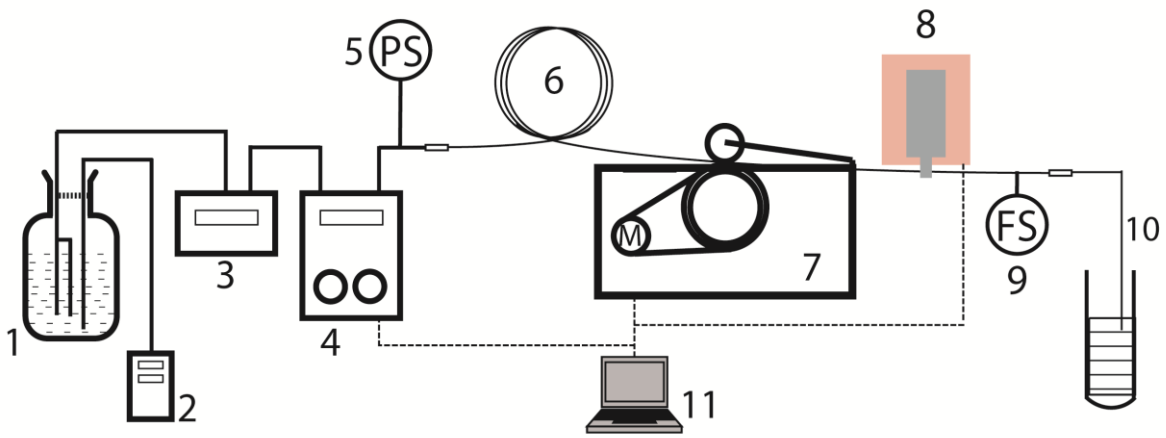

Figure 2. Schematic diagram of the apparatus for local etching of fused silica capillaries with SCW. (1) water reservoir, (2) oxymeter, (3) degasser, (4) pump, (5) pressure sensor, (6) fused silica capillary, (7) programmable moving device, (8) heater, (9) flowrate sensor, (10) restrictor, (11) PC control unit. Reprinted with permission from [14]. Copyright (2017) Wiley-VCH.

It follows from the above description that whole-length etching was not very flexible as regards the diversity of the effects produced. To overcome this limitation, a new arrangement of the etching apparatus has been designed and constructed, with the schematic diagram shown in Fig. 2 [14]. The principal feature of the new arrangement involves heating of just a short section of the treated capillary (adjustable from 2 to 10 mm). This arrangement will be referred to as local etching. The treated capillary can move through the heated zone at a selected speed controlled by a programmable drive, and water can flow through the capillary at an adjustable flow rate in the same or the opposite direction to the capillary movement. These features of the new apparatus combine to provide a large variety of attainable surface structures in the treated capillaries. An essential point to note is that, at any moment, only a short segment of the capillary is exposed to SCW because the flowing water cools down rapidly after leaving the heated zone.

During the manufacturing process, the outer surface of fused silica capillary is coated with a thin layer of polyimide to provide a mechanical protection of the capillary. In our experience, the outer polyimide coating does not present any problems during treatment of the inner surface with SCW as the polyimide coating is thermally stable enough to withstand the operating temperatures at least up to 420 °C. The coating neither degrades nor becomes

detached from the silica surface. Further, although the SCW-etched capillaries are less flexible as compared with the original fused silica tubing, they can still be handled comfortably without risk of breaking.

CURRENTLY ACCESSIBLE CAPILLARY MORPHOLOGIES

Whole-length etching apparatus (Fig. 1) has been used to produce two different morphologies of the capillary. First, repeated static etching (several tens of repetitions) produced a uniform, crest-and-gorge-like inner surface while preserving an essentially constant internal diameter, at least in a part of the capillary.

Such capillaries can potentially be useful for *in-situ* preparation of monolithic silica columns. Second, dynamic etching with a continuous flow of water can be used to produce tapered capillaries, that is, capillaries with a continuous change of the internal diameter along the capillary.

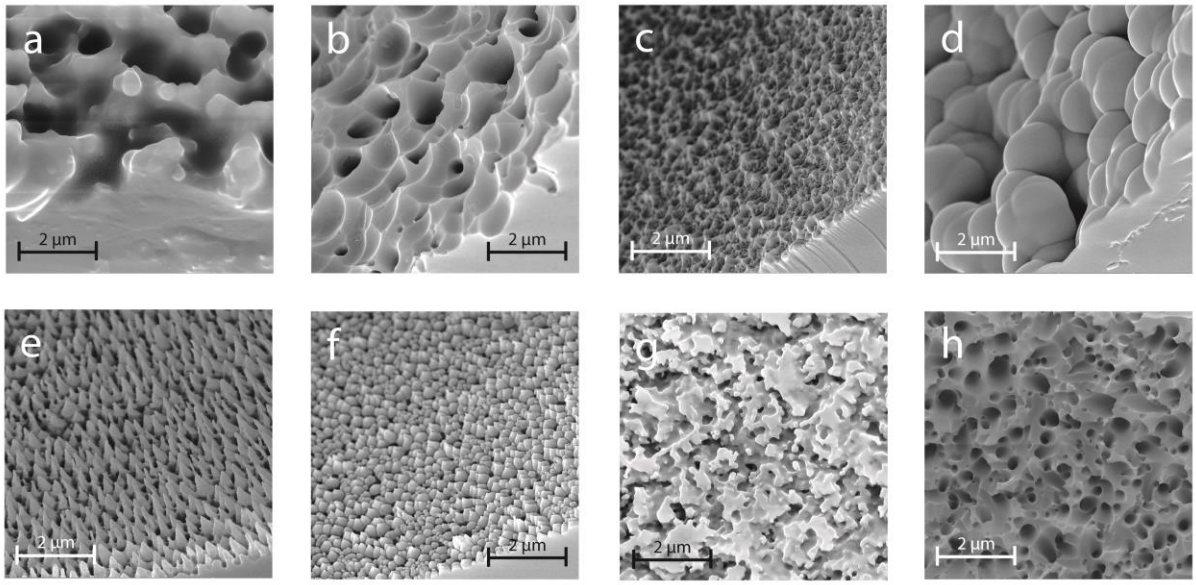

Figure 3. SEM micrographs of capillary inner surfaces obtained by local etching with SCW under various operating conditions. Magnification 25,000× throughout. In frames (d) and (e) water flew in the opposite direction to the capillary movement, in the other frames the directions of flow and movement were the same. (a) Capillary ID = 50 µm, temperature T = 380 °C, pressure P = 40 MPa, water flow rate F = 10.8 mg/min, capillary movement velocity v = 7.1 mm/min; (b) ID = 50 µm, T = 340 °C, P = 20 MPa, F = 5.0 mg/min, v = 7.1 mm/min; (c) ID = 50 µm, T = 360 °C, P = 20 MPa, F = 5.0 mg/min, v = 1.7 mm/min; (d) ID = 50 µm, T = 360 °C, P = 20.5 MPa, F = 5.0 mg/min, v = 7.9 mm/min; (e) ID = 50 µm, T = 360 °C, P = 20.5 MPa, F = 5.0 mg/min, v = 19.6 mm/min; (f) ID = 100 µm, T = 340 °C, P = 50 MPa, F = 19.2 mg/min, v = 3.5 mm/min; (g) ID = 100 µm, T = 460 °C, P = 30 MPa, F = 19.6 mg/min, v = 1.7 mm/min; (h) ID = 100 µm, T = 320 °C, P = 40 MPa, F = 75 mg/min, v = 1.7 mm/min.

Unlike the whole-length etching, the local etching (Fig. 2) has been able to produce a wide portfolio of capillary morphologies as regards both the inner surface quality and the internal diameter. Figure 3 shows some examples of the inner surfaces obtained by the local etching under various operating conditions. Moreover, in principle, the local etching makes it possible to produce single-piece capillaries featuring several consecutive segments of different morphologies. To date, the basic types of capillaries that have been produced by local etching include a constant-diameter capillary with uniform surface roughness [15], a constant-diameter capillary with surface roughness gradient [16], and a capillary with two sections differing in the internal diameter and in the inner surface roughness (two-ID capillary) [14].

Figure 4 presents a summary of the currently accessible morphologies of SCW-treated capillaries, with the tapered capillaries being produced by the whole-length etching and the remaining morphologies by the local etching.

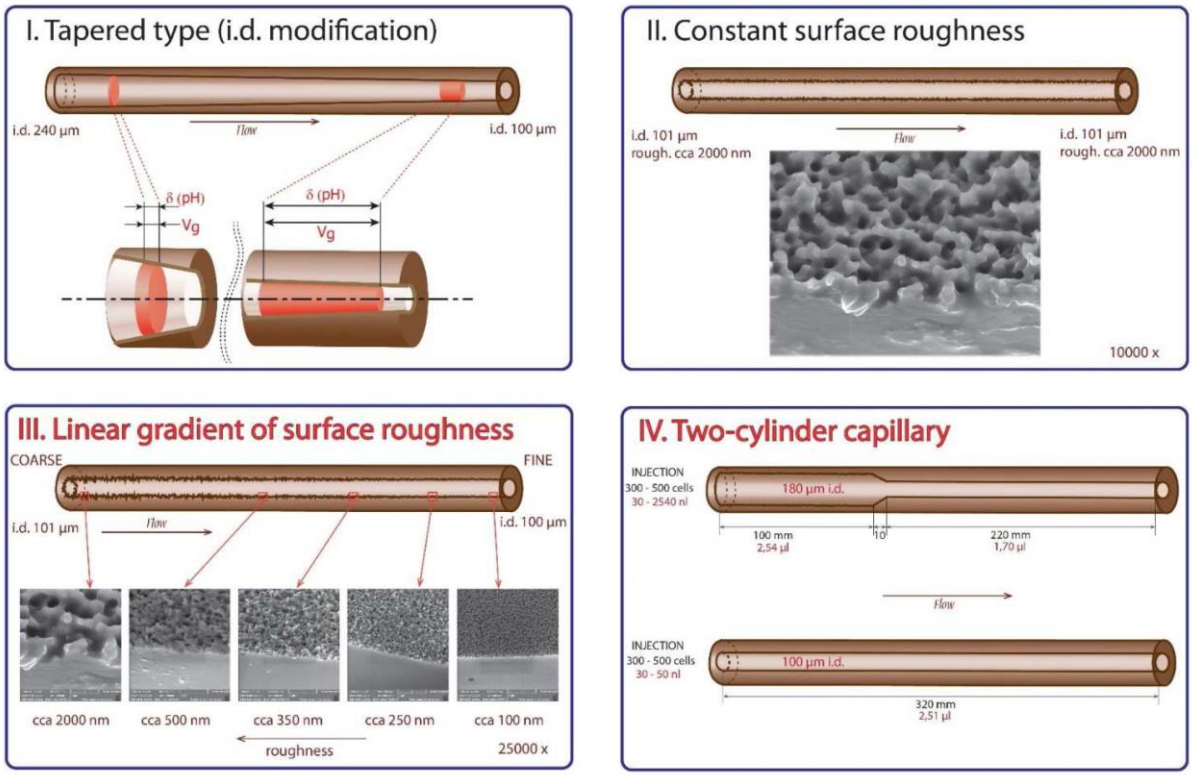

Figure 4. Currently accessible morphologies of SCW-treated capillaries

APPLICATIONS OF SCW-TREATED CAPILLARIES

Up to now, the SCW-etched capillaries have been applied in electromigration separations either by capillary isoelectric focusing (CIEF) or by capillary electrophoresis (CE). Overall, the tapered capillaries produced by whole-length etching [13] have so far been applied in CIEF [17–19] whereas the capillaries treated by local etching [14] have been used in CE [14–16,20,21]. Following earlier theoretical predictions, resolution of a model mixture of isoelectric point markers and proteins by isoelectric focusing in a tapered capillary with electroosmotic displacement was found to be superior to that in a conventional cylindrical capillary [17] under comparable applied voltage and analysis time. Later on, isoelectric focusing in tapered capillaries has been employed to separate important microorganisms including probiotic, lactic acid bacteria (*Lactobacillus* sp.) [19] and phytopathogenic bacteria of the *Dickeya* genus [18]. With microorganisms, again, the application of tapered capillaries improved the species resolution over that attained in constant-diameter, cylindrical capillaries as shown in Fig. 5. Uniform diameter, constant surface roughness (~2 µm) capillaries have been employed for rapid separation of methicillin-resistant *Staphylococcus aureus* (MRSA) bacteria from methicillin-susceptible *Staphylococcus aureus* (MSSA) [15,20]. This result may be of interest in clinical microbiologic screening as MRSA is a prevalent bacterial pathogen responsible for both hospital and community-associated infections. The surface roughness gradient capillaries have been shown [16] to provide a significant narrowing of analyte zones in CZE as compared with conventional smooth capillaries when tested with albumin and antifungal agent amphotericin B as analytes. Finally, the two-ID capillaries have been successfully used in separations of proteins [14] and microorganisms [21]. In the larger-

diameter inlet section of the capillary, the analytes were online pre-concentrated using transient isotachophoretic stacking.

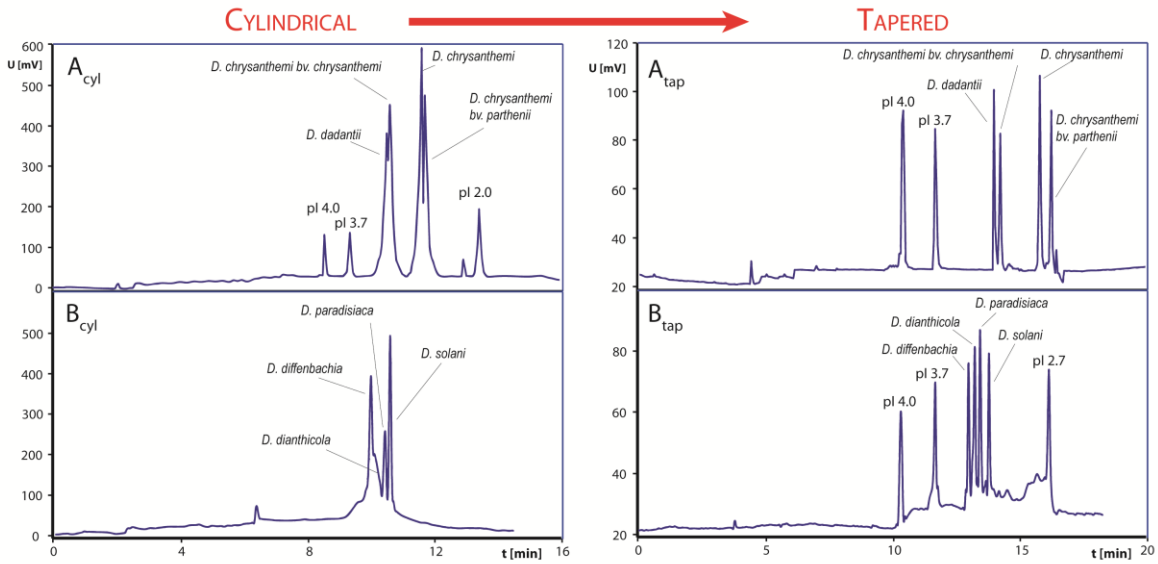

Figure 5. Resolution of two different samples (A and B) of several Dickeya bacterium species with similar isoelectric points by CIEF in 2.0–4.0 pH gradient employing uniform-diameter (left) and tapered (right) capillary. Reprinted with permission from [18]. Copyright (2013) American Chemical Society.

To-date applications of SCW-treated capillaries in electromigration methods have recently been reviewed [22].

CONCLUSION

Supercritical water can serve not only to roughen the inner surface but also to induce significant changes in the internal diameter of the capillary. In principle, the diameter changes can occur in both directions [13]: increase in the I.D. because of dissolution of fused silica from the capillary wall, and reduction in the I.D. because of downstream deposition of silica on the capillary wall from the upstream-generated aqueous solution although the capillaries with the deposited layer have not been tested in separation applications. Isoelectric focusing in tapered capillaries provides improved separation efficiency over that in uniform-diameter capillaries.

An important virtue of SCW as an etching agent is that, unlike other agents used for the purpose, pure water cannot introduce undesirable residual heteroatoms to the treated surface. Besides, owing to significant effects of operating temperature and pressure on the density and solvent power of near-critical water, it is also possible to tune the etching effects of SCW by careful adjustments of the operating conditions. Further, in the latter variant of the apparatus described above, the effects of etching can be localized fairly precisely. This feature makes it possible to combine several segments with different effects of etching within a single capillary. On the contrary, it should be admitted that, with decreasing internal diameter of the treated capillary, it becomes more difficult to control the water flow rate through the capillary.

To date, the SCW-treated fused silica capillaries have only been applied in electromigration separations. However, the surface-roughened capillaries can also be useful in capillary chromatography, notably in the synthesis of silica-based or hybrid organic–silica monolithic columns. Compared with the smooth surface, the roughened surface provides larger surface area and the ensuing possibility to form more monolith-to-wall chemical bonds. Besides, the

roughened surface also helps to stabilize the monolithic core against movement in the axial direction, making the column more robust with respect to high pressure and/or pressure surges. Further, the treatment with SCW can also be expected to help in curbing the danger of bypass channel formation when preparing silica-based monolithic columns in larger-bore capillaries (> 100 µm I.D.).

In our view, the only shortcomings of SCW as an etching agent are the initial investment into high-pressure equipment and, unfortunately, a limited compatibility of SCW with most analytical chemistry laboratories as the lab personnel have not been trained to work with high-compressibility, high-temperature, and high-pressure media. Therefore, it should be stressed that safety measures against an accidental release of hot steam have to be strictly observed at all times. However, because of versatility and tunable etching power of SCW, the applications of SCW to treat silica surfaces for analytical separations are certainly worth exploring.

ACKNOWLEDGEMENTS

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