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Softening of fused-silica capillaries during particle packing

When a semipreparative capillary electrochromatography (CEC) capillary is packed with silica particles and exposed to solvent, its mechanical strength is markedly reduced. In our studies, a fused-silica capillary (internal diameter > 200 μm and wall thickness < 150 μm) was packed under pressure (approximately 200 psi) with spherical silica particles (1.5–5 μm) suspended in water or various common organic solvents. After one hour of exposure, the capillary can be readily deformed, and it keeps its deformed shape upon release of the force causing deformation. It is suggested that capillary softening is promoted through the propagation of internal microcracks that have been caused by action of the particles during packing in the presence of solvent. Application of a protective coating to the inside of the capillary is found to reduce or eliminate capillary softening.

Keywords: Capillary electrochromatography / Capillary softening EL 3807

CEC is a rapidly developing analytical separation technique [1]. In this procedure, fused-silica capillaries are typically packed with uncoated or modified spherical silica particles suspended in various solvents. Large-bore capillaries (internal diameter > 200 μm) that are commercially available have a wall thickness less than 150 μm. Among these capillaries, we have observed a dramatic loss of wall strength under certain conditions that we describe here. The rigidity of the structure is markedly reduced in approximately 1 h after the start of particle packing. For capillaries with smaller internal diameters and larger wall thicknesses the effect is not apparent, although some modification may be occurring. The loss of wall strength may present a serious problem in the fabrication of micro high performance liquid chromatography (micro-HPLC) columns and semipreparative CEC columns. Most of the micro-LC columns are covered with stainless steel tubings to increase the column strength. For CEC columns, pretreatment of the inside of the capillary wall by various polymeric materials to form a protective coating appears to overcome capillary softening. In the following we describe our packing procedure, present examples of capillary softening, suggest a mechanism for softening, and offer one method for reducing or eliminating softening by the application of a protective coating.

The fused-silica capillaries used in this study were purchased from Polymicro Technologies (Phoenix, AZ). The 1.5 μm spherical octadecyl silica (ODS) particles were provided by Micra Scientific (Lafayette, IN). The 3 μm and 5 μm ODS particles were purchased from YMC (Wilmington, DE). Methanol, ethanol, and acetonitrile (HPLC-grade), [3-(methacryloxy)propyl]trimethoxysilane (Bind-Silane) and tetraethylorthosilicate (TEOS) were pur-

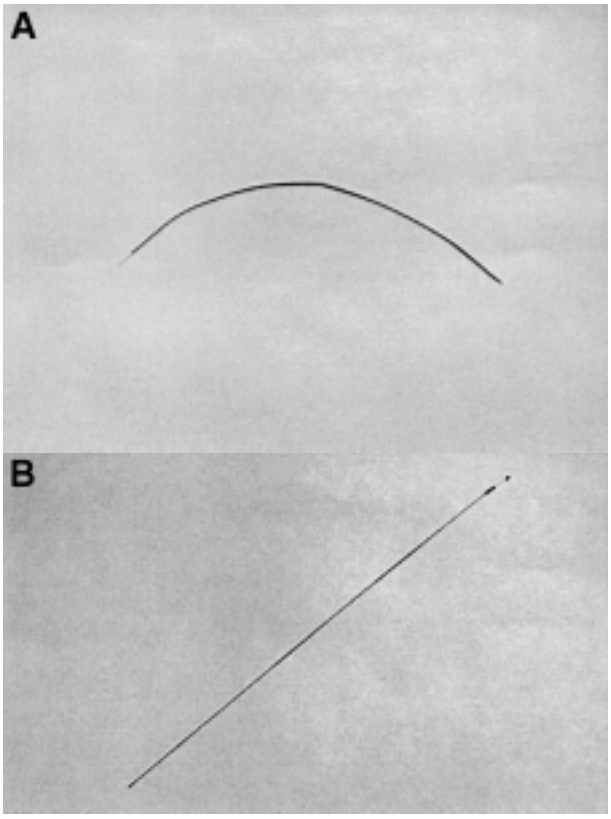

Figure 1. Photographs of (A) a softened capillary and (B) a pretreated capillary after packing procedure. Both capillaries are 250 μm ID × 360 μm OD and are approximately 10 cm in length.

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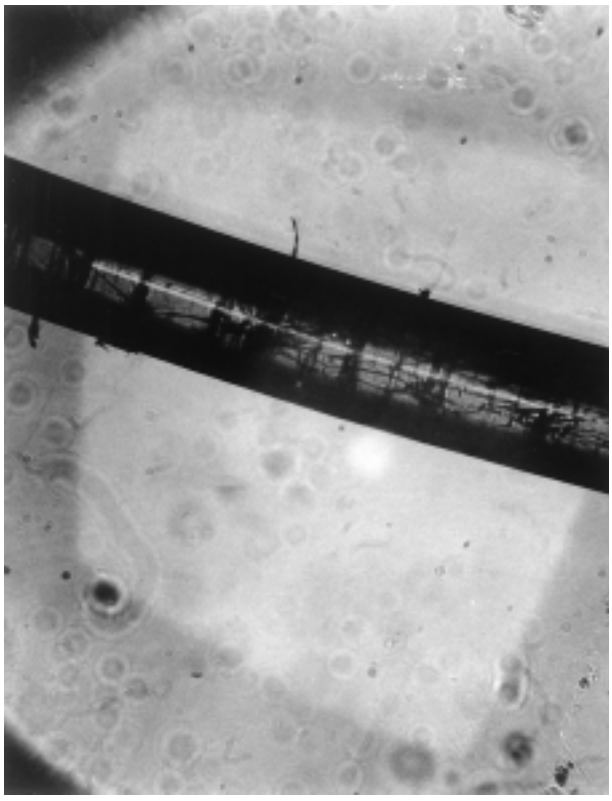

Figure 2. A magnified (40×) image of a longitudinal section of a 530 μm ID × 640 μm OD softened capillary in which cracks are visible.

chased from Aldrich (Milwaukee, WI). Water was purified with an Ultra-Pure water system from Millipore (Milford, MA). Capillaries that have an internal diameter (ID) of 75 μm, 250 μm, and 530 μm and an outside diameter (OD) of 365 μm, 360 μm, and 640 μm, respectively, were slurry-packed in a standard manner [1]. A syringe pump was used in place of a high-pressure pump. For control purposes, capillaries were also treated the same way but with no particles present. Figure 1 compares a capillary that (A) has undergone softening with one that (B) has had its inside coated with a polymeric material, consisting of 50:50 v/v [3-(methacryloxy)propyl]trimethoxysilane (Bind-Silane) in acetone [2], prior to packing. The softened capillary is easily bent whereas the pretreated capillary maintains its wall strength. The pretreated capillary was observed to retain its rigidity for the length of our examination (three days of continuous operation). We also found that a similar pretreatment using TEOS sol gel solution [3] was able to protect the capillary wall against softening. Figure 2 presents a magnified (40×) image of a 530 μm ID, 640 μm OD softened capillary in which cracks are readily seen. Capillaries with larger wall thicknesses do not appear to show internal cracking. No softening is found in any of the capillaries that are not exposed to particles.

These results suggest that the particles in the slurry may scratch the surface of the capillary wall while being packed into the column, therefore causing internal microcracks to form in the presence of a solvent [4–10]. The coating appears to prevent softening by protecting the inner capillary walls from particle abrasion. Once abrasion occurs, crack propagation proceeds by stress corrosion that is promoted by the solvent. Studies were also made as a function of packing rate. Thin-wall capillary columns that were packed more rapidly showed increased softening. This observation is again consistent with the stress-corrosion mechanism for capillary softening. It appears that crack propagation is promoted by methanol and ethanol just as well as by water.

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