



Hybrid carbon nanoparticles modified core–shell silica: A high efficiency carbon-based phase for hydrophilic interaction liquid chromatography

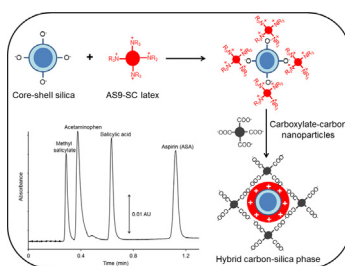
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HIGHLIGHTS

- High efficiency core–shell silica combined with selectivity of carbon for HILIC.
- Reduced plate height of 1.9 (95,000 plates m^{-1}) achieved.
- Hybrid phase has different selectivity than ten HILIC column chemistries.
- Mixed-mode HILIC/RPLC separations possible on the hybrid carbon–silica phase.
- Shape selectivity for positional isomers in HILIC.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrophilic interaction liquid chromatography (HILIC) is a fast growing separation technique for hydrophilic and polar analytes. In this work, we combine the unique selectivity of carbon surfaces with the high efficiency of core–shell silica. First, 5 μm core–shell silica is electrostatically coated with 105 nm cationic latex bearing quaternary ammonium groups. Then 50 nm anionic carbon nanoparticles are anchored onto the surface of the latex coated core–shell silica particles to produce a hybrid carbon–silica phase. The hybrid phase shows different selectivity than ten previously classified HILIC column chemistries and 36 stationary phases. The hybrid HILIC phase has shape selectivity for positional isomeric pairs (phthalic/isophthalic and 1-naphthoic/2-naphthoic acids). Fast and high efficiency HILIC separations of biologically important carboxylates, phenols and pharmaceuticals are reported with efficiencies up to 85,000 plates m^{-1} . Reduced plate height of 1.9 (95,000 plates m^{-1}) can be achieved. The hybrid phase is stable for at least 3 months of usage and storage under typical HILIC eluents.

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1. Introduction

Many biological compounds are hydrophilic molecules bearing amino, hydroxyl, or carboxylate functionalities. These polar

analytes may be weakly retained in reversed phase liquid chromatography (RPLC). In recent years, the usage of hydrophilic interaction liquid chromatography (HILIC) has increased dramatically [1–3], as HILIC can retain highly polar compounds [1]. Polar stationary phases and organic rich mobile phases are employed in HILIC [1,3] for the separation of hydrophilic analytes such as amino acids [4–6], nucleotides [4,6,7] and carbohydrates [8,9]. An additional attractive feature is that the organic rich mobile phases are

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mass spectrometry friendly [10]. The low viscosity of the organic rich eluents also enhances solute diffusivity which improves the mass transfer kinetics, leading to faster high efficiency separations in HILIC mode [11].

Under HILIC conditions, a water rich layer is said to form on the surface of the HILIC packing into which the analyte partitions [3,12]. The presence of this water layer has recently been confirmed by Dinh et al. using Karl Fischer titrations [13]. In addition to partitioning, other interactions have been shown to be involved in HILIC retention, including H-bonding [14,15], ion-exchange [16,17], adsorption [18] and dipole–dipole interactions [17].

Currently, the majority of commercial HILIC phases are silica based [19]. Silica-based HILIC stationary phases can be classified by their chemical nature as neutral (e.g., amide and diol), positively charged (e.g., amine and triazole) and negatively charged phases (e.g., polysuccinimide and bare silica) [19]. Alternately, silica phases may be classified morphologically as totally porous, superficially porous (often called core–shell) and monolithic silica. Core–shell silica particles consist of a solid core (2.2–5 μm) and an outer porous shell (0.2–0.6 μm) [20]. Until recently, fast and high efficiency separations in few minutes were offered by ultra-high performance liquid chromatography (UHPLC) employing high pressure pumps (>10,000 psi) and sub-2 micron particles. With their availability, core–shell silica particles offer the same high efficiency at much lower back pressures [11]. Thus, core–shell silica particles can be used on a conventional HPLC system to achieve the high efficiency of UHPLC. However, changing the particle morphology does not change the surface chemistry. Therefore the selectivity of core–shell silica particles remains similar to that of the totally porous silica particles [20].

Recently, we introduced a new class of carbon-based HILIC phases [4]. Porous graphitic carbon (PGC) is a very hydrophobic material, suitable for RPLC purposes [21,22]. We showed that porous graphitic carbon modified with benzene carboxylate groups (carboxylate-PGC) exhibits strong HILIC character with a different selectivity from that of either silica or polymer stationary phases [4]. The HILIC behavior of the carboxylate-PGC was illustrated by the separation of model hydrophilic analytes such as phenols, carboxylic acids, amino acids and nucleotides [4]. Unfortunately, PGC generally exhibits lower efficiencies than silica phases due to its slow mass transfer properties [23]. The attractive selectivity of carboxylate modified carbon gives an impetus to develop phases that carry the best properties of core–shell silica (high efficiency) and carbon (unique retention properties) phases.

Many hybrid stationary phases have been developed on inorganic oxides clad in monolayers of carbon such as carbon clad zirconia [24], carbon clad alumina [25] and carbon clad silica [26]. These hybrid phases were developed by a complex procedure of vapor deposition of carbon at high temperature. More recently, vapor deposition of carbon has been used to create a carbon clad core–shell silica (2.7 μm) phase [27].

In this work, we develop a hybrid HILIC phase consisting of core–shell silica particles onto which carbon nanoparticles have been anchored (Fig. 1). First, the core–shell silica particles are modified via attaching cationic latex nanoparticles to impart a positive charge to the silica surface. Carbon nanoparticles are made negatively charged by introduction of benzene carboxylate groups to their surface through diazonium chemistry as reported previously [4]. The anionic carbon nanoparticles are electrostatically adsorbed onto the positively charged latex silica particles. As will be demonstrated, such electrostatic interactions are very stable under HILIC conditions. The hybrid carbon-fused core silica phase exhibits high efficiency and distinct selectivities for the separation of carboxylates, phenols, and pharmaceuticals.

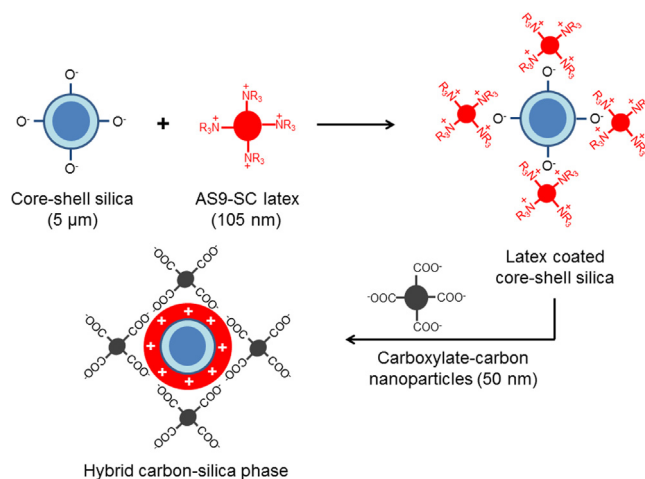


Fig. 1. Schematic for the preparation of the hybrid carbon–silica phase*. The latex and carbon nanoparticles are represented as monolayers for simplicity.

2. Experimental

2.1. Apparatus

The HPLC system consists of: a model 709 dual-piston pump (Metrohm, Herisau, Switzerland); a 6-port Rheodyne 8125 (Cotati, CA, USA) with a 2 μL loop; and a Lambda-Max Model 481 UV detector (Waters, Milford, MA, USA) at 240 or 254 nm. Connecting tubes were made of polyether ether ketone (PEEK). Data was collected at 20 Hz using a Dionex advanced computer interface with Dionex PeakNet 5.2 software. The eluent consists of ammonium acetate buffer, ACN and water. The pH was adjusted with either NaOH or HCl. The eluents were degassed by sonication in a VWR[®] sonicator (Radnor, PA, USA) for 10 min. The reported buffer strength is the final concentration in the eluent after mixing with ACN. The reported % ACN stands for the volume of the ACN relative to the total volume of the eluent. Column efficiencies were calculated using the half-peak width method (Eq. (1)) and corrected for extra-column band broadening [28]. The calculations are briefly described in the Supplementary material.

$$N = 5.54 \left(\frac{t_R}{w_h} \right)^2 \quad (1)$$

where t_R is the retention time of the peak of interest and w_h is the peak width at 50% of the peak height.

2.2. Materials

Carbon graphite nanopowder (99.5%, average particle size ~ 50 nm, Lot #1173992379-249) was purchased from American Elements (Los Angeles, CA, USA). Core–shell bare silica particles were a gift of Phenomenex (5 μm , Lot # Bulk.Beta.01, Torrance, CA, USA). AS9-SC latex nanoparticles with quaternary ammonium functionalities (105 nm in diameter, Lot #025-07-042), ultra-high molecular weight polyethylene (UHMWPE) frits, 2 μm Ti and stainless steel frits, Zitex membranes and empty PEEK columns (100 \times 4 mm i.d.) were gifts from Thermo Fisher Scientific (Sunnyvale, CA, USA). Deionized water was obtained from a Barnstead E-pure system (Barnstead, Dubuque, IA, USA). Sodium nitrite ReagentPlus[™], 4-aminobenzoic acid, 50% sodium hydroxide, uracil, cytosine, 1-naphthoic acid, acetylsalicylic acid (ASA, Aspirin), gentisic acid, α -hydroxyhippuric acid, hippuric acid, salicylic acid, benzoic acid, resorcinol and acetaminophen were from Sigma–Aldrich (St. Louis, MO, USA). Phthalic acid, isophthalic acid and 2-naphthoic acid were from Aldrich (Milwaukee, WI, USA).

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