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Properties of water as a novel stationary phase in capillary gas chromatography☆

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ABSTRACT

A novel method of separation that uses water as a stationary phase in capillary gas chromatography (GC) is presented. Through applying a water phase to the interior walls of a stainless steel capillary, good separations were obtained for a large variety of analytes in this format. It was found that carrier gas humidification and backpressure were key factors in promoting stable operation over time at various temperatures. For example, with these measures in place, the retention time of an acetone test analyte was found to reduce by only 44 s after 100 min of operation at a column temperature of 100 °C. In terms of efficiency, under optimum conditions the method produced about 20,000 plates for an acetone test analyte on a 250 μm i.d. × 30 m column. Overall, retention on the stationary phase generally increased with analyte water solubility and polarity, but was relatively little correlated with analyte volatility. Conversely, non-polar analytes were essentially unretained in the system. These features were applied to the direct analysis of different polar analytes in both aqueous and organic samples. Results suggest that this approach could provide an interesting alternative tool in capillary GC separations.

1. Introduction

Water is a relatively inexpensive, non-toxic, and widely available substance which is commonly utilized in chromatography as a polar mobile phase component. For example, in high pressure liquid chromatography (HPLC) it is often combined with organic solvents and/or additives for this purpose [1–5]. Water has also been previously utilized to humidify the mobile phase and affect peak shape in both gas chromatography (GC) [6–10] and supercritical fluid chromatography (SFC), where it was effectively used to deactivate particle surfaces [11–13]. More recently and further afield, a pure water mobile phase has also been used in subcritical water chromatography (SWC) [14,15], which offers advantages of compatibility with the universal flame ionization detector (FID) [16–18] and the ability to alter mobile phase polarity through temperature control [18–20].

Comparatively, however, examples of using water as a stationary phase are far less common. For example, in HPLC a very interesting stationary phase made of pure ice has previously been reported and shown to yield analyte separations determined, in part, by interactions with exposed surface sites such as hydroxyl groups [21]. This phase was also subsequently adapted and modified to perform chiral separations [22,23]. Alternately, in packed column GC, a few reports have also demonstrated that humidified carrier gases were observed to cause a water layer to adhere to the surface of stationary phase particles, where separations subsequently occurred [24–26]. Of particular interest, these reports clearly showed that water could uniquely alter analyte retention in such packed column GC systems, when using both pure or higher ionic strength coatings on the stationary phase particles. However, the primary challenges of this approach appeared to include relatively low column efficiencies and inconsistent analyte retention due to stationary phase evaporation [27]. Perhaps not surprisingly, related explorations in capillary column GC have not been reported, most likely due to the fused silica degradation that readily occurs in water and steam at elevated temperatures [28,29].

Considering the inherently longer columns and better efficiency associated with capillary column GC, it would be very interesting to explore if using a water stationary phase in this operating mode is possible in the absence of packed particles, and examine its characteristics if so. For instance, while several common polar phases such as cyano-propyl [30] or polyethylene glycol [31] based substrates exist for use, the development of novel stationary phases for capillary column GC continues to be of interest. Of note, recent work has shown that certain metal-organic frameworks can form unique polar GC stationary phases on fused silica capillaries [32].

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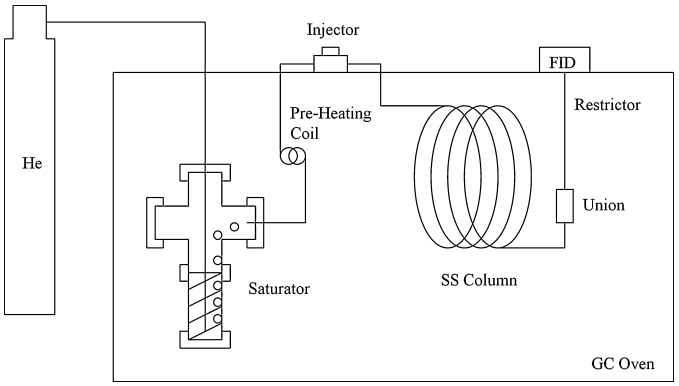

Fig. 1. Schematic diagram of the capillary GC water stationary phase instrument.

Therefore continued advances in this area can be beneficial and further expand the field.

Recently, we reported a capillary SFC method that utilizes pure water as a stationary phase [33]. In essence, the method creates a stationary layer of water on the interior surface of a stainless steel capillary, which is used in conjunction with a supercritical CO_2 mobile phase to provide analyte separations. In general, this method creates a simple and inexpensive polar stationary phase that can be readily replenished as required. As well, it produces normal phase separations for analytes of widely varying polarity with a unique selectivity over non-polar analytes. Additionally, it also provides good sample capacity, retention time reproducibility, and peak symmetry.

Considering these findings from a relatively high pressure capillary SFC system, it would be interesting and useful to see if such an approach would also be possible in capillary GC and, if it were, what properties it might possess. This paper describes a novel capillary GC system comprised of a water stationary phase within stainless steel tubing. The primary separation characteristics and operating parameters of the system are presented and discussed. As well, comparisons are made with conventional capillary GC columns and some applications of the system are demonstrated.

2. Experimental

2.1. Instrumentation

A standard HP 5890-Series 2 GC instrument equipped with an FID (Hewlett-Packard, Palo Alto, CA, USA) was adapted and used for the capillary GC water stationary phase experiments. A schematic diagram of the instrument is depicted in Fig. 1. To improve the stability of the water stationary phase, the helium carrier gas (Praxair, Calgary, AB, CAN) was saturated with HPLC grade water vapor (Burdick & Jaskson, Muskegan, MI, USA) prior to reaching the injector. To achieve this, a saturator was assembled from a 1/4″ Swagelok stainless steel (SS) cross union (Calgary Valve and Fitting, Calgary, AB, CAN) connected to a 5 cm length of SS tubing (4.6 mm I.D.; Chromatographic Specialties, Brockville, ON, CAN) that was sealed at the other end with a Swagelok cap. Prior to separations, this tubing was filled with HPLC grade water. The SS helium line was led through the saturator body via the opposite port and terminated 1 mm from the capped end, allowing carrier gas to flow through the water to the outlet. After leaving the saturator, the helium entered a SS pre-heating coil (1/16″ O.D. × 250 μm I.D. × 168 cm; Chromatographic Specialties). The remaining union port was capped. This saturator unit and pre-heating coil were kept inside the oven during operation.

The helium carrier gas was then led into the injector. Although attempts were made to use the original injection assembly, it was found that the quartz liner suffered from high temperature water erosion and the interior surface area of this injector was large enough that it required extra humidification, which ultimately disrupted operation. To circumvent this problem, a simplified injector was constructed from a 1/16″ SS Swagelok tee union (Calgary Valve and Fitting) that was fitted to the original heating block. Carrier gas entered and exited this union at opposing ends, while sample was injected perpendicular to this through a septum fitted into the remaining port. This injector was normally kept at 220 °C (but lower temperatures were also possible depending on the analyte) and was found to operate more stably. A SS injection liner designed for the original injector is being developed for exploration in future experiments.

A length of 316 SS tubing (1/16″ O.D. × 250 μm I.D. × 30 m; Chromatographic Specialties) was used as the separation column, since fused silica readily erodes at high temperature in the presence of water. For example, in our experience, only around 80–100 °C is required to completely deteriorate a humidified fused silica capillary in a short period of time. The SS column led from the outlet of the injector and was connected to a 50 μm I.D. × 11 cm long fused silica capillary restrictor (Polymicro Technologies, Phoenix, AZ, USA) via a zero dead volume union (Vici-Valco, Houston, TX, USA). The end of this restrictor was placed at the base of the flame in the FID jet to deposit column effluent directly into the detector. This fused silica restrictor was replaced about every 10–12 operational hours after deterioration due to hot water exposure was noted. The FID was set to a temperature of 300 °C and the typical gas flows used were 88 mL/min of hydrogen (Praxair) and 740 mL/min of medical grade air (Praxair). The hydrogen flow rate was occasionally increased to aid in flame stability if required.

2.2. Water stationary phase formation

To establish the water stationary phase, the 316 SS column was connected to a water reservoir fashioned from a large Swagelok union with interior dimensions of 4.5 mm I.D. × 6.7 cm long (Calgary Valve and Fitting). This was filled with 1.5 mL of HPLC grade water, connected to the empty column and then sealed. Next, 30 psi of nitrogen (Praxair) was applied to the reservoir for 30 min which steadily displaced the water through the column. After this time, water flow through the column stopped and it was removed from the reservoir and placed inside the GC instrument for use.

2.3. Conventional GC columns

During this study, some comparisons were made with two commercially available GC columns. The first column had a non-polar 95% methyl/5% phenyl polysiloxane stationary phase (1 μm thick × 0.53 mm I.D. × 30 m long; model EC-5; Alltech, Deerfield, IL, USA). The other had a polar polyethylene glycol stationary phase (1 μm thick × 0.53 mm I.D. × 30 m long; model Stabilwax Crossbond Carbowax; Chromatographic Specialties). A standard HP 5890 Series 2 GC-FID instrument was used for these comparative column separations.

2.4. Reagents and supplies

The reagents used in this study were obtained as follows: 1-propanol, 2-propanol, acetone, benzene, chloroform and dichloromethane (EMD, Gibbstown, NJ, USA); aniline, dioxane and glycerol (BDH, Poole, UK); formaldehyde, pyridine and toluene (EM, Darmstadt, GER); octanol, cyclohexanol and methanol (Baker, Philipsburg, NJ, USA); cyclohexadiol (K & K Labs, Plainview, NY, USA); propanal (Methson, Coleman & Bell, Norwood, OH, USA); 3-butyn-1-ol (Columbia Organic Chemicals, Columbia, SC, USA). All other reagents were purchased from Sigma-Aldrich (Oakville, ON,