

# Rapid column heating method for subcritical water chromatography

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## Abstract

A novel resistive heating method is presented for subcritical water chromatography (SWC) that provides higher column heating rates than those conventionally obtained from temperature-programmed gas chromatography (GC) convection ovens. Since the polarity of water reduces dramatically with increasing temperature, SWC employs column heating to achieve gradient elution. As such, the rate at which the mobile phase is heated directly impacts the magnitude of such gradients applied in SWC. Data from the current study demonstrate that the maximum column heating rate attainable in a typical SWC apparatus (i.e. using a GC convection oven) is around 10 °C/min, even at instrument oven settings of over three times this value. Conversely, by wrapping the separation column with ceramic insulation and a resistively heated wire, the column heating rates are increased five-fold. As a result, elution times can be greatly decreased in SWC employing gradients. Separations of standard alcohol test mixtures demonstrate that the retention time of the latest eluting component decreases by 35 to 50% using the prototype method. Additionally, solute retention times in this mode deviate by less than 1% RSD over several trials, which compares very well to those obtained using a conventional GC convection oven. Results suggest that the developed method can be a useful alternative heating technique in SWC.

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## 1. Introduction

In recent years subcritical water chromatography (SWC) has been reported as a useful alternative to gradient elution reversed-phase liquid chromatography (LC) [1–16]. When water is heated above its boiling point and pressurized enough to maintain it in the liquid phase (i.e. the subcritical state), its polarity significantly lowers [17]. As a chromatographic mobile phase in SWC, this property of water is readily manipulated through controlling the temperature of the separation column. Therefore, temperature programming in SWC can be analogous to some mobile phase solvent gradients in conventional LC. Benefits of this approach include the relatively low cost, high purity and environmental compatibility of water relative to typical organic solvents. As well, water is compatible with the universal flame ionization detection (FID) method, which cannot be operated with organic mobile phases [2–5,9–11,13,15,18–21].

A factor that directly impacts the steepness of the gradient employed in SWC, and hence analysis time, is the rate at which

the column temperature can be raised. To date, this parameter has predominantly been controlled using gas chromatography (GC) convection ovens [2–15], which typically provide maximum instrumental heating rate settings of 30 to 50 °C/min [22]. However, an alternative method employing a machined column heater equipped with a coolant flow capability has also been introduced [16]. Recently, while performing gradient separations in SWC, we observed analyte retention times to converge at increasingly higher temperature programming rate settings when using a conventional GC oven for column heating. The inability of the system to further increase analyte peak velocities on the column suggested that the actual mobile phase heating rates had also converged at larger settings. Thus, a more effective column heating method that could provide better control over mobile phase temperature would, in turn, be useful in providing better control of analyte retention in SWC analyses.

This paper quantitatively describes the observed delay in attaining thermal equilibration between the separation column and a conventional GC convection oven used to control temperature in a typical SWC system. To overcome this obstacle, a novel means of controlling column temperature in SWC is presented, which is based on resistive heating [22–25]. The

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proposed method uses a resistively heated wire, wound in close contact with the SWC column, to reproducibly raise the column temperature significantly more rapidly than by regular means. Comparisons between the current heating approach and that used in a conventional SWC system will be presented and discussed.

## 2. Experimental

### 2.1. SWC-FID system

Fig. 1 shows a schematic diagram of the SWC-FID system used in these experiments, which is similar to previous reports [2]. A Shimadzu model GC-8A gas chromatograph (Shimadzu, Kyoto, Japan) provided the necessary FID system and convection oven. Mobile phase was delivered to the system by a Waters model M-6000 dual-piston reciprocating pump (Waters, Milford, MA, USA). A 1/16 in. Swagelok polyether ether ketone (PEEK) union (Alltech, Deerfield, IL, USA), acting as an electrically insulating shunt to protect the pump, was installed in the 1 m piece of stainless steel tubing (1/16 in. O.D.  $\times$  0.25 mm I.D.) connecting the pump to a Rheodyne model 7520 injector (Alltech). The proper function of this shunt requires the use of high purity (i.e. high resistivity) water. The injector was equipped with a 0.5  $\mu$ L sample loop. A 10 cm length of stainless steel tubing (1/16 in. O.D.  $\times$  0.25 mm I.D.) led from the injector, through the GC oven wall, and into the column inlet. Separations were performed using a 150 mm  $\times$  2 mm I.D. PRP-1 column containing a polystyrene-divinylbenzene stationary phase (5  $\mu$ m particles; Hamilton, Reno, NV, USA). A 2 cm length of stainless steel tubing (1/16 in. O.D.  $\times$  0.25 mm I.D.) led from the column outlet to a Valco 1/16 in. zero dead volume stainless steel tee (Alltech). One outlet of the tee was connected to the FID system via a 30 cm length of fused silica tubing (50  $\mu$ m I.D.; Alltech) while the other was connected to a waste container by an identical restrictor. This arrangement provided the necessary backpressure to maintain the mobile phase as a liquid at an optimal column flow rate of 200  $\mu$ L/min, while also redirecting a constant portion of the effluent to the FID system without overloading the detector flame. The 1:1 split ratio assembly used here is similar to that used previously in SWC [19].

The optimal FID air flow rate was 350 mL/min while that for hydrogen was normally 100 mL/min, although the latter was occasionally increased to maintain flame stability. The restrictor outlet was placed right at the base of the FID jet within the detector housing, where it provided the best performance in terms of flame stability and response.

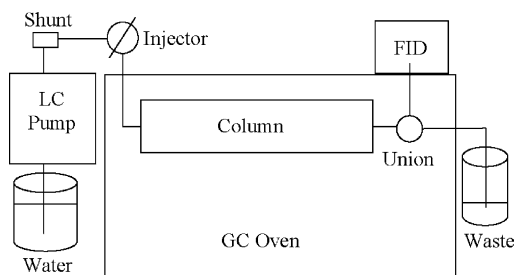


Fig. 1. Schematic diagram of the SWC-FID system.

### 2.2. Resistive heating

The column was initially wrapped once with a thin ceramic tape (0.14 mm thick  $\times$  2.5 cm wide) to electrically insulate it from the heating coils. A nickel-chromium wire (0.25 mm O.D.) was coiled around the insulated column by hand leaving approximately 1 mm between each wind. About 5 cm of the wire was left protruding from each end of the column to allow for attachment of the power leads. Next, to prevent heat loss, another two layers of insulating ceramic tape (2 mm thick  $\times$  7.6 cm wide) were wrapped around the coils followed by two layers of woven fibreglass tape insulation (2 mm thick  $\times$  5 cm wide). The insulation layers were held in place by short lengths of crimped wire.

Power was supplied to the coils through a standard laboratory variable transformer (120 V supply, 10 A max; model 3PN 1010, Staco, Dayton, OH, USA). Power lines led from the transformer and through the GC oven wall where they were connected by alligator clips (further insulated by encasement in a woven fibreglass sleeve) to the coil leads exposed on the column ends. The restrictor transfer lines extending from the column outlet were also resistively heated in order to maintain mobile phase conditions en-route to the detector. To do this, a second identical transformer was used to heat a length of the same nickel-chromium wire wrapped directly around the restrictor tubing. Note that a small length of ceramic tape was used to insulate the stainless steel tee fitting from the electrical wires. The restrictor tubing was normally kept at the highest temperature achieved in the column during a separation.

### 2.3. Reagents and solvents

Nitrogen-purged HPLC-grade water (2 M $\Omega$ /cm, Fischer, Hampton, NH, USA) was used as a mobile phase for all separations. Analyte solutions were prepared in water and were composed of alcohol standards of purity greater than 99% (Aldrich, Oakville, Canada). Ethanol and methanol concentrations were typically 100 mg/mL while others were normally around 50 mg/mL. All other variations are outlined in the text.

#### 2.3.1. Caution

Please note that while the above system assembly is inherently safe, extra precaution and careful attention to certain details is strongly advised. For example, it is imperative that high purity water (i.e. with an inherently high resistivity) be used. As well, all electrical connections should always be fully insulated and power should be disconnected while connecting them. Also, the column must be carefully insulated as described above. Finally, all instrumentation should be well grounded.

## 3. Results and discussion

### 3.1. Conventional convection oven heating

Initial SWC experiments were run using a conventional GC convection oven for heating. Various temperature programs were investigated in the elution of a standard test analyte mixture of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-

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