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Evaluation of injection methods for fast, high peak capacity separations with low thermal mass gas chromatography

Brian D. Fitz, Brandyn C. Mannion, Khang To, Trinh Hoac, Robert E. Synovec*

Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195-1700, USA

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ABSTRACT

Low thermal mass gas chromatography (LTM-GC) was evaluated for rapid, high peak capacity separations with three injection methods: liquid, headspace solid phase micro-extraction (HS-SPME), and direct vapor. An Agilent LTM equipped with a short microbore capillary column was operated at a column heating rate of 250 °C/min to produce a 60 s separation. Two sets of experiments were conducted in parallel to characterize the instrumental platform. First, the three injection methods were performed in conjunction with in-house built high-speed cryo-focusing injection (HSCFI) to cryogenically trap and re-inject the analytes onto the LTM-GC column in a narrower band. Next, the three injection methods were performed natively with LTM-GC. Using HSCFI, the peak capacity of a separation of 50 nl of a 73 component liquid test mixture was 270, which was 23% higher than without HSCFI. Similar peak capacity gains were obtained when using the HSCFI with HS-SPME (25%), and even greater with vapor injection (56%). For the 100 μl vapor sample injected without HSCFI, the preconcentration factor, defined as the ratio of the maximum concentration of the detected analyte peak relative to the analyte concentration injected with the syringe, was determined to be 11 for the earliest eluting peak (most volatile analyte). In contrast, the preconcentration factor for the earliest eluting peak using HSCFI was 103. Therefore, LTM-GC is demonstrated to natively provide in situ analyte trapping, although not to as great an extent as with HSCFI. We also report the use of LTM-GC applied with time-of-flight mass spectrometry (TOFMS) detection for rapid, high peak capacity separations from SPME sampled banana peel headspace.

1. Introduction

Gas chromatography (GC) is a powerful analytical tool used in the separation and identification of analytes in complex mixtures. Typical GC separations utilize 20–40 m columns with internal diameters ranging from 100 μm to 320 μm and are commonly temperature programmed at rates ranging from 5 °C/min to 20 °C/min. The temperature programming range for volatile and semi-volatile GC analysis is typically from ~50 °C to ~300 °C however specific applications exist which require cryogenic or extremely high operating temperatures [1–5]. Typical peak widths at base (4σ) associated with these typical conditions range from 3 s (20 peaks/min) to 6 s (10 peaks/min), with corresponding separation run times of 15 min to 1 h. Corresponding peak capacities, n_c, at unit resolution therefore range from ~300 to ~600 peaks for these commonly applied conditions [6].

Fast GC has been an active area of study for reducing analysis time and increasing sample throughput [7–17]. A recent review by Tranchida and Mondello [18] discusses the use of microbore capillary columns for fast GC, and another recent review by Wang et al. [19] outlines the use of resistive heating for fast GC. Other techniques for rapid column heating, such as thermal gradient chromatography [20–23] have shown promise as novel technologies in the fast GC field. The results we present herein, as well as the results presented in previous references have important implications for two-dimensional gas chromatography (GC × GC or GC–GC) [24–26]. Consideration of separation times, peak widths, flow rates, heating rates, and other instrumental parameters must be implemented in a way that adequately preserves the two-dimensionality of the data that make GC × GC and GC–GC such powerful techniques.

A fast GC separation should maintain an equivalent (or greater) amount of chemical information compared to a traditional GC analysis but should provide the information in a shorter amount of time. Chemical information, which is inferred from figures-of-merit such as peak capacity, peak capacity production, resolution between analytes of interest, supply of satisfactory elution profiles,

* Corresponding author. Tel.: +1 206 685 2328; fax: +1 206 685 8665.
E-mail address: synovec@chem.washington.edu (R.E. Synovec).

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sufficiently pure mass spectra, separation efficiency, and quantifiable peak signal, should be competitive with traditional GC. Fast GC is typically defined as GC separations taking between 1 min and 10 min. A typical separation temperature program from ~50 °C to 300 °C (i.e., a range of 250 °C) would require temperature programming rates of between 25 °C/min and 250 °C/min to complete the separations in 10–1 min, respectively. In order to maintain a similar peak capacity compared to traditional GC, the peak capacity production for fast GC would have to be increased by an order of magnitude, from 10 to 20 peaks/min, to 100 to 200 peaks/min, in order to compensate for the reduced separation run time. Indeed, a peak capacity production of 100 peaks/min has been achieved using GC–TOFMS by minimizing band broadening due to injection and by reducing on-column band broadening processes by operating at optimal experimental conditions, as dictated by chromatographic modeling [6].

Using in-house GC modeling software based on reports by Snijders et al. [27], and Wilson et al. [6], we predict that a separation using a 5 m × 100 μm inner diameter (i.d.) column should, in principle, provide a peak capacity of 250–300 in a 60 s separation, thereby affording a peak capacity production of 250–300 peaks/min. Also, peak widths at base (4σ) predicted by theory should be between 30 ms and 300 ms. To achieve the peak capacity goal of ~300 in 60 s, two instrumental challenges must be addressed: sample introduction must provide a narrow injected pulse to the GC column so as to obtain the theoretically possible peak capacity provided by the column, and rapid column heating must be provided to obtain a typical temperature program range of 250 °C in 60 s.

To address one of these challenges, a recently developed in-house thermal injection device was applied to provide a narrow sample injection pulse [11,28]. Referred to as high-speed cryo-focusing injection (HSCFI), a stream of cryogenically chilled nitrogen gas is applied to trap and preconcentrate analytes in a narrow band (700 nl volume) within a metal capillary column. A capacitive discharge device is then activated to resistively heat the metal capillary at rates approaching 6,000 °C/s to desorb preconcentrated analytes in 5–10 ms. Analyte peaks produced by the HSCFI approach 10 ms (width at base) which aids in substantially increasing the peak capacity ultimately achieved in the separation.

To address the other challenge of rapidly heating the separation column, we utilized a Generation I LTM (low thermal mass) GC instrument from Agilent to perform the rapid temperature program [29]. The LTM-GC was originally developed by RVM scientific [30,31]. Recently, Luong et al. [32] published an insightful overview covering LTM-GC fundamentals. Conventional air bath GC is generally limited to a maximum heating rate of ~50 °C/min (with 5–20 °C/min commonly applied). The LTM design bundles the analytical column, resistive heating wires, and thermocouples together in a small toroid configuration which significantly reduces the thermal mass of the device allowing for faster heating rates and reduced cool down times compared to conventional GC. The LTM column module is held outside of the GC in a case attached to the door. Fans are located under the column assembly that rapidly cools the LTM-GC in less than 1 min, which aids in increasing sample throughput. The LTM-GC is rated to heat at rates up to 1800 °C/min which, in theory, could accomplish a typical temperature separation range of 250 °C in just under 10 s. However, we opted to evaluate the LTM-GC at of 250 °C/min to span a typical temperature program range 250 °C (50–300 °C) in 60 s. Based on the theoretical capabilities for separation efficiency, we expect that using HSCFI in conjunction with LTM-GC should produce peak capacities of 250–300 in a 60 s separation.

Herein, we describe recent studies in which we have explored the use of a commercially available fast GC platform, namely the Generation I LTM from Agilent, for fast, high peak capacity separations. A 73 component mixture was created as a test sample to evaluate the platform. The mixture contained primarily hydrocarbons and substituted hydrocarbons with boiling points spanning a traditional temperature program, i.e., from 50 °C to 300 °C. The 73 component sample mixture was introduced to the LTM platform in three different modes: neat liquid, headspace solid phase microextraction (HS-SPME), and direct vapor headspace. The goal was to test the performance and robustness of the platform with different injection techniques commonly used in GC. The sampling methods were analyzed in two sets of experiments, each with a flame ionization detector (LTM-GC-FID). First, the three sampling methods were evaluated in conjunction with HSCFI. Second, the three sampling methods were evaluated without using HSCFI in order to assess the native on-column focusing ability of the LTM platform alone. A third experiment was performed to demonstrate a suitable range of retention indices that the LTM-GC platform can analyze. Finally, in a fourth experiment the LTM-GC was coupled to a time-of-flight mass spectrometer (TOFMS). The LTM-GC–TOFMS was applied to the fast separation of volatile analytes from the headspace of banana peels.

2. Experimental

2.1. Samples and injection conditions

All chemicals for the 73 component mixture were reagent grade or higher (unless otherwise noted), as listed in Table 1. For the direct liquid injection of the 73 component mixture onto the LTM-GC-FID, an auto-injector equipped with a 500 nl (0.5 μl) micro-syringe (Hamilton, Reno, NV) injected 50 nl into the inlet, operated in split-less mode. A calibration curve for the syringe was prepared with volumes ranging from 40 nl to 300 nl and was determined to be linear with an $R^2 = 0.9983$. For the HS-SPME analysis of the 73 component mixture, 50 μl of the mixture was placed into a 4 ml vial and heated to 50 °C. A 65 μm DVB-PDMS (divinylbenzene/polydimethysiloxane) SPME fiber was used (Supelco, St. Louis, MO, USA). Prior to use, the fiber was conditioned at 250 °C for 30 min. The fiber was exposed to the mixture headspace for 1 min then transferred to the inlet and exposed in the inlet for 15 s at 250 °C. It was determined that 15 s was sufficient to desorb all analytes from the fiber during sample injection; when removing the fiber after a single injection and performing another injection using the same fiber, no signal was observed in the subsequent injection. For the direct vapor headspace analysis of the 73 component mixture, 50 μl of the mixture was placed into a 4 ml vial and heated to 50 °C for 5 min. One hundred microliters of the headspace was extracted using a 100 μl gas tight syringe and injected manually into the GC inlet, operated in split-less mode.

For the LTM-GC–TOFMS demonstration with HS-SPME sampling, banana peel vapor was analyzed. Bananas were purchased from a local grocery store. To prepare the banana peels for SPME analysis, 30 g from three separate banana peels (90 g total) were homogenized with 150 ml of water and placed in a 250 ml Erlenmeyer flask. A 65 μm DVB-PDMS (divinylbenzene/polydimethysiloxane) fiber was conditioned for 30 min at 250 °C prior to use. The SPME fiber was then exposed to the headspace of the magnetically stirred banana peel solution for 5 min at room temperature. The SPME fiber was desorbed in the inlet for 7 s for injection.

2.2. Chromatographic conditions and instrumentation

2.2.1. LTM-GC-FID

The modified LTM-GC-FID instrumental platform is presented in Fig. 1, utilizing an Agilent 6890 GC with a Series I LTM module (Agilent Technologies, Palo Alto, CA, USA). The column module was a standard 7 inch cartridge, attached to a modified Agilent GC door,