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High-speed cryo-focusing injection for gas chromatography: Reduction of injection band broadening with concentration enrichment

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ABSTRACT

In order to maximize peak capacity and detection sensitivity of fast gas chromatography (GC) separations, it is necessary to minimize band broadening, and in particular due to injection since this is often a major contributor. A high-speed cryo-focusing injection (HSCFI) system was constructed to first cryogenically focus analyte compounds in a 6 cm long section of metal MXT column, and second, reinject the focused analytes by rapidly resistively heating the metal column via an in-house built electronic circuit. Since the cryogenically cooled section of column is small (~750 nl) and the direct resistive heating is fast (~6000 °C/s), HSCFI is demonstrated to produce an analyte peak with a 6.3 ms width at half height, $w_{1/2}$. This was achieved using a 1 m long column with a 180 μm inner diameter (i.d.) operated at an absolute head pressure of 55 psi and an oven temperature of 60 °C, with a 10 V pulse applied to the metal column for 50 ms. HSCFI was also used to demonstrate the head space sampling and fast GC analysis of an aqueous solution containing six test analytes (acetone, methanol, ethanol, toluene, chlorobenzene, pentanol). Using Henry's law constants for each of the analytes, injected mass limits of detection (LODs) were typically in the low pg levels (e.g., 1.2 pg for acetone) for the high speed separation. Finally, to demonstrate the use of HSCFI with a complex sample, a gasoline was separated using a 20 m × 100 μm i.d. column and the stock GC oven for temperature programming, which provided a separation time of 200 s and an average peak width at the base of 440 ms resulting in a total peak capacity of 460 peaks (at unit resolution).

1. Introduction

Gas chromatography (GC) is often used in repetitive, routine, time sensitive applications to analyze complex mixtures of volatile and semi-volatile analytes. For such applications, the reduction of analysis time is desired, from a traditional time scale of 10 min–60 min down to emerging applications in the minutes to seconds time frame, and is commonly achieved by using short (1 m–10 m), narrow (100 μm–180 μm inner diameter) columns at high linear flow velocities and either fast temperature program ramp rates or an isothermal oven. However, unless off-column sources of band broadening (due to injection, detection, electronics, etc.) are minimized, the peak widths obtained are not minimized, and the resulting chromatograms may lack the peak capacity and separation power of GC performed on a longer, more traditional time scale.

It has been supported from GC theoretical considerations [1], and demonstrated experimentally [2] with a state-of-the art injector, that an unretained peak, eluting from a long (40 m × 180 μm) column under optimal flow rate conditions and with no off-column band broadening, should and does have a width of only ~250 ms. Various commercial instruments for common practice, equipped with a standard auto-injector, often produce peaks typically ~2 s wide, even on 180 μm wide columns [2]. This gap between GC theory and state-of-the-art experimentation versus common practice (and the desire for faster analysis) has prompted researchers to devote a significant amount of attention to reducing off-column sources of broadening, particularly the injection pulse width. The resulting reports cover a wide variety of techniques for producing narrow injection bandwidths (fluid logic gates [3,4], split injection with high split ratios [5], microloop systems [6] and micro gas valve inlets [7], etc.). Recent reports from our group demonstrated that single high-speed diaphragm valves are extremely capable injection systems, producing peaks ~20 ms wide [8], and dual diaphragm synchronized-injection valve systems are capable of 0.5 ms wide peaks [9]. Unfortunately, for a valve-based injection system, a GC-like separation can inadvertently occur in the transfer capillary between the GC inlet and the valve when oven temperatures are low, as is typically the case at the beginning of a temperature programmed separation. Unless special attention is given to the

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transfer capillary leading from the inlet to the valve the separation suffers [2]. While valve-based injection provides an excellent platform for proof-of-principle, it also suffers from poor detection sensitivity because only a small portion of the sample initially injected onto the GC via the auto-injector, then to the valve, is transferred to the column head. Conversely, thermal modulation injection, including systems for both injection in one-dimensional (1D) GC instruments and modulation in comprehensive two-dimensional gas chromatography ($GC \times GC$) instruments, have been demonstrated to be capable of producing peaks 20 ms wide at the base (four standard deviation peak width), although commercial systems produce peaks minimally $\sim$50 ms wide [10,11] while transferring the entire sample to the separation column. The cryogenic focusing step of these thermal modulation techniques has the added benefit of enriching the sample concentration at the head of the separation column, leading to an improved concentration limit of detection (LOD).

Herein, we build upon previous reports on thermal injection techniques by applying resistive heating to a short section of cryogenically cooled, commercially available metal MXT column. It is shown that this simple and efficient injection system, referred to as high-speed cyro-focusing injection (HSCFI), will produce peak widths approaching the single digit ms time frame, while simultaneously providing sample concentration enrichment with minimum boiling point bias (basically, all analytes injected are trapped, focused, and thermally injected). The peak widths resulting from HSCFI are evaluated as a function of voltage applied to the metal MXT column and the various sources of band broadening in the instrument. Sample enrichment is demonstrated by sampling different headspace volumes of an aqueous test solution to determine the volume of vapor that can be cryofocused without break through. Using Henry's law constants, the concentration of analyte in the vapor phase and concentration and mass LODs are both determined before demonstrating the application of HSCFI to the temperature programmed separation of a complex sample (gasoline).

2. Experimental

2.1. Reagents and chemicals

All chemicals were reagent grade or higher: methanol, pentane (J.T. Baker, Phillipsburg, NJ, USA), toluene, pentanol, octane (Aldrich, Fairlawn, NJ, USA), chlorobenzene (Alfa Aesar, Ward Hill, MA, USA), acetone (EMD, Gibbstown, NJ, USA), and ethanol (Decon Labs, King of Prussia, PA, USA). For the peak width study a two component test mixture was made by mixing neat pentane and octane in a 1:3 ratio by volume. For the LOD study an aqueous solution was prepared by mixing the analytes listed in Table 1 with deionized water to form a six component test mixture. The identity and boiling point of each analyte, along with the concentration of that analyte in solution and in the head space (calculated using Henry's law constants [12]) is given in Table 1. The aqueous concentration of each analyte was chosen such that peak heights would be somewhat similar in the final chromatogram. The head space concentrations (and the mass injected) in Table 1 are related to the solubility of each analyte in water as expressed in the Henry's law constant, resulting in more water soluble analytes requiring larger solution phase concentrations. For preparation of the six component test mixture, an initial solution of toluene and chlorobenzene in water was made by diluting 10 mg of toluene and 50 mg of chlorobenzene to 100 ml in water giving 100 ng/μl of toluene and 500 ng/μl of chlorobenzene. 1 ml of this initial solution was then mixed with 5 mg of acetone, 25 mg of ethanol, 26 mg of methanol, and 50 mg of pentanol and again diluted to 100 ml of water to make the final aqueous solution with the concentrations given in Table 1. A 2.0 ml screw top vial was filled with 1.0 ml of the final aqueous solution, leaving 1.0 ml head space to be sampled by the auto-injector syringe at room temperature. Gasoline obtained from a local gas station was used to demonstrate the HSCFI sampling and injection with a temperature programmed separation of a complex sample.

Table 1
Boiling point, concentration (both solution phase and headspace vapor) and mass of analyte in 30 μl of head space for each analyte in the six component sample solution.

Analyte	Boiling point (°C)	Concentration in aqueous solution (ng/μl)	Concentration in head space vapor (pg/μl)[a]
Acetone	56	50	89
Methanol	65	260	76
Ethanol	78	250	86
Toluene	111	1	260
Chlorobenzene	131	5	930[b]
Pentanol	137	500	250

[a] Head space concentration calculations are based on aqueous concentration at room temperature with a 1 ml head space volume, using Henry's Law constants [12].
[b] Solution containing chlorobenzene was prepared near the solubility limit, so Henry's law calculation is not accurate and the actual headspace concentration is probably not as high as indicated.

2.2. Instrumentation

All chromatograms were obtained using an Agilent 6890 gas chromatograph with an auto-injector controlled by ChemStation software (Agilent Technologies, Palo Alto, CA, USA) modified for implementation and study of the HSCFI system as illustrated in Fig. 1(A), using flame ionization detection (FID). The Agilent FID electrometer was replaced with an in-house built electrometer board that provided a data acquisition rate of up to 20 kHz in order to avoid introducing off-column band broadening due to the FID [9]. This electrometer was interfaced to a National Instruments data acquisition board (National Instruments, Austin, TX, USA) and the resulting data was collected using a LabVIEW 2010 (National Instruments) program written in-house at a rate of 20 kHz for the peak width study, 10 kHz for the LOD study and 1 kHz for the gasoline separation. Post-run data processing (baseline correction, Savitzky–Golay filtering, etc.) was performed in Matlab R2010b (The Mathworks, Inc., Natick, MA, USA).

This Agilent 6890 gas chromatograph and modified electrometer served as a platform to study the performance of the HSCFI. The injection system is comprised of the stock auto-injector and inlet, the diaphragm valve (Valco Instruments Co., Inc., Houston, TX, USA), and the HSCFI working in concert. Initially the carrier gas flows from the inlet through the diaphragm valve, then to the HSCFI, and on to the column and detector. Sample is introduced to the injection system by a microsyringe (either via auto-injector, or manually for volumes larger than 5 μl), flash vaporized in the inlet, and transported via deactivated fused silica transfer capillary line (Restek, Bellefonte, PA, USA) at a low flow of carrier gas to the HSCFI, where it is cryofocused. The diaphragm valve then actuates, causing the inlet flow to be vented and the HSCFI to be connected to an auxiliary EPC with a higher flow of carrier gas. The time interval between the introduction of sample at the inlet and the actuation of the diaphragm valve is referred to as the load time. A short time after the diaphragm valve actuates, an electrical pulse is applied to the HSCFI, causing the sample to be revaporized onto the head of the separation column. The time

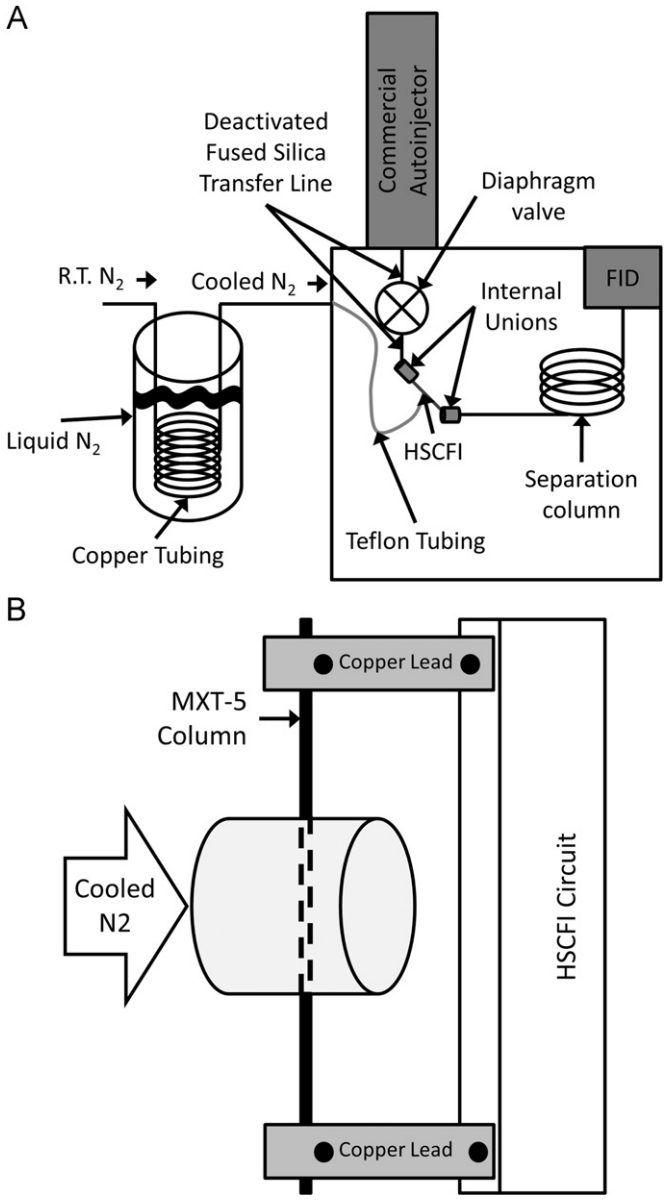

Fig. 1. Instrument schematic. (A) Diagram of the modified Agilent 6890 GC. Modifications include installing a flow switching diaphragm valve and the HSCFI inside the oven. A constant flow of cooled nitrogen is delivered from the liquid nitrogen heat exchanger to the HSCFI via copper and Teflon tubing. (B) Diagram illustrating the orientation of the Teflon tube, MXT column and the HSCFI circuit inside the oven. The circuit and MXT column lie in the same plane, with the Teflon tube perpendicular. Electrical contact between the circuit and MXT column is maintained by clamping the MXT column between a thin sheet of copper and a solid copper post.

interval between the introduction of the sample at the inlet and the initiation of the electrical pulse is referred to as the cryo-focusing time. For the LOD experiments and the temperature programmed gasoline separation, the diaphragm valve was removed and the inlet connected directly to the HSCFI, negating the need for a load time for those separations.

Fig. 1(B) schematically depicts the HSCFI, which consists of a short section of MXT column (Restek), ~6 cm long, passing through a perpendicular Teflon tube with a 1 mm inner diameter (i.d.). Analytes are cryo-focused in a short section of MXT column (~3 cm) that is cooled by a flow of nitrogen gas which was chilled in a liquid nitrogen heat exchanger. This flow of cooled N_2 was delivered to the HSCFI in the Teflon tube and was not interrupted during the resistive heating.

To reinject the focused analytes, the MXT column is resistively heated by delivering a pulse of variable voltage and duration via an in-house built circuit, DC power supply (TDK-Lambda, San Diego, CA, USA) and the labVIEW program described above. Appropriate electrical contact is achieved by clamping the MXT column between a thick copper lead and a thin flexible sheet of copper. For the peak width and LOD studies, the short copper electrical leads required the HSCFI circuit to be housed within the GC oven, limiting oven temperatures to 60 °C for the current proof-of-principle studies. For the gasoline separation the short copper leads were separated from the HSCFI circuit with copper wire, allowing the circuit to be placed outside the oven and removing the limitation on oven temperatures. Further development of HSCFI should include additional circuitry to measure the resistance of the MXT column during heating to facilitate determining the actual temperature and heating rate of the trap.

The i.d. of all tubing (both transfer capillary line and MXT) was matched to the i.d. of the column. Connections between the transfer lines and the HSCFI and the separation column were made using low dead volume unions of the appropriate inner bore (Agilent Ultimate Union for the peak width and LOD studies and Valco internal unions for the gasoline separations). For the peak width and LOD studies the MXT column in the HSCFI was coated with 5% phenyl/95% dimethyl polysiloxane stationary phase, while the HSCFI used for the gasoline separation comprised deactivated MXT column.

2.3. Chromatographic conditions

The separations used to study the peak width and LOD were performed on a 1 m Rtx-5 (5% phenyl/95% dimethyl polysiloxane) column (Restek) with a 180 μm i.d. and 0.4 μm film thickness with the inlet and FID set to 250 °C. The gasoline separation was performed on a 20 m Rtx-5 (5% phenyl/95% dimethyl polysiloxane) column (Restek) with a 100 μm i.d. and 0.4 μm film thickness with the inlet and FID set to 250 °C. For clarity, the absolute head pressure, injection volumes, column head pressures, oven temperature, and HSCFI conditions are given in the text and figure captions for each separation.

3. Results and discussion

To study the peak broadening produced by the HSCFI, which includes broadening resulting from the flow dynamics and heating of the HSCFI, in addition to broadening from the separation column and detection, 0.2 μl of a two component test mixture (pentane and octane) was introduced via the stock auto-injector and inlet to the transfer line at 18 psi absolute (psia) with a 300:1 split and a 60 °C oven temperature. Following a 10 s cryo-focusing step time, the chromatogram resulting from applying a 10 V, 50 ms electrical pulse is shown in Fig. 2. A cryo-focusing time of 10 s was chosen for initial runs because it was much larger than the time required for analyte to travel from the GC instrument inlet to the HSCFI, thereby ensuring complete focusing prior to reinjection. The absolute column head pressure was 55 psi and was applied to the HSCFI after a 9 s load time. The resulting baseline corrected chromatogram in Fig. 2 shows nearly baseline resolution between the two analytes, and the nearly unretained pentane peak is only 6.3 ms wide at half height, $w_{1/2}$, thus with a standard deviation σ_{peak} of 2.7 ms.

The dependence of the electrical power applied to the MXT column on resulting peak widths is shown in Fig. 3. Various voltages were applied to the HSCFI, at a constant current level of 1 A, while maintaining a load time of 9 s, a cryo-focusing time of 10 s and a pulse duration of 50 ms. As expected, increasing the

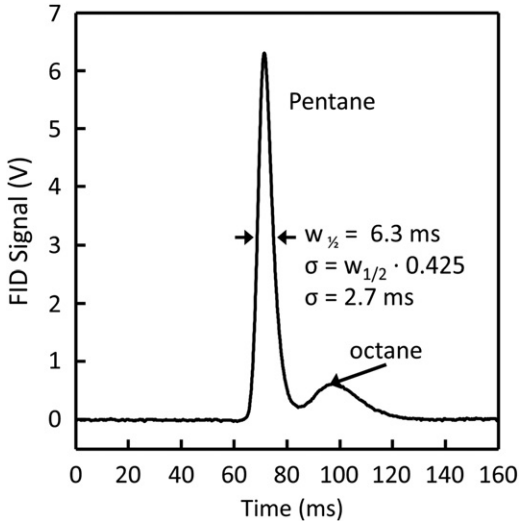

Fig. 2. Chromatogram of pentane (72 ms) and octane (97 ms). Sample was transferred from the inlet to the HSCFI at an absolute column head pressure of 18 psi and a split of 300:1. After 9 s of transfer, the flow rate was switched by the diaphragm valve to a column head pressure of 55 psi absolute. 1 s after the change in flow rate, a 10 V pulse was applied to the MXT column for 50 ms. The oven was held at 60 °C throughout.

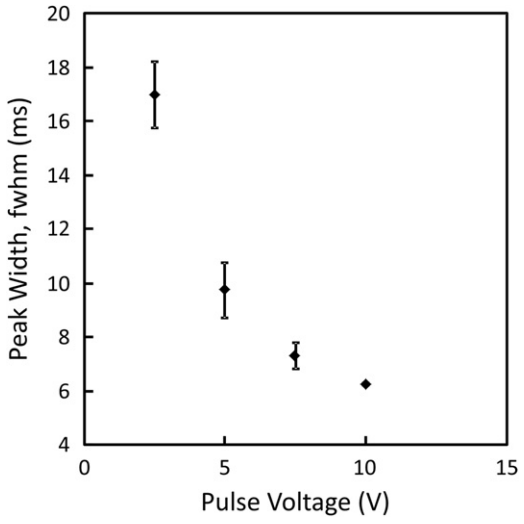

Fig. 3. Plot of peak width at half height as a function of HSCFI pulse voltage for pentane. All instrument parameters remained the same as in Fig. 2 except for the applied voltage. The error bars indicate +/− one standard deviation, and the error bars at 10 V are smaller than the symbol.

applied voltage increases the heating rate of the MXT column, increases the desorption rate of the analyte, and decreases the resulting peak width. At 12.5 V (chromatogram omitted for brevity), other large peaks appeared in the chromatogram potentially indicating degradation of either the MXT-5 stationary phase or analyte is occurring during HSCFI injection. No adverse effects were observed at or below 10.0 V. Considering the minor reduction in peak width between 7.5 V and 10 V, and the poor performance indicated in the chromatogram at 12.5 V (not shown for brevity), 10 V was selected as the operating voltage for the HSCFI.

Based on the novel design of the HSCFI circuit, the voltage rise time should be on the order of microseconds, meaning that very little band broadening would be introduced from the injection electronics. The band broadening from HSCFI injection is the result of the volume occupied by the cryo-focused analyte and the rate at which analyte is desorbed into the carrier gas stream. Assuming that broadening due to the FID is negligible [9,11] and that variances are statistically independent (as is commonly done for band broadening calculations), the variance of the peak as measured at the detector (σ^2_{peak}) can be written as

$$\sigma^2_{peak} = \sigma^2_{vol} + \sigma^2_{vap} + \sigma^2_{col} \quad (1)$$

where σ^2_{vol} is the variance due to the analyte cryo-focused volume, σ^2_{vap} is the variance due to the analyte vaporization time, and σ^2_{col} is variance due to the chromatographic separation process in the column. For the pentane peak measured above (Fig. 2), the standard deviation of σ_{peak} is 2.7 ms. Using in-house modeling of on-column peak broadening [13,14], that has been extended to high speed separations, indicates the pentane peak should have a width at the base of ~3.2 ms, thus a standard deviation for σ_{col} of ~0.8 ms. Due to conductive cooling around the junction between the Teflon tube and the MXT column, the maximum cryo-focusing length of MXT column is ~3 cm, resulting in a maximum internal volume of 750 nl, which at a column inlet flow rate of ~20 ml/min should produce a peak at most ~2.3 ms wide with a standard deviation for σ_{vol} of ~0.6 ms. Rearranging Eq. (1) and evaluating for σ_{vap} yields ~2.5 ms, which is approximately three times larger than σ_{col} and four times larger than σ_{vol}, meaning the vast majority of broadening for the pentane peak in Fig. 2 is due to the desorption rate and thus the most direct avenue to further reducing peak widths is to increase the heating rate of the MXT column. Due to the limited data set reported herein, further study of σ_{vap} for retained analytes is warranted for quantitatively probing (via the relationship between σ_{vap} and the enthalpy of vaporization for various analytes) the boiling point bias inherent in HSCFI, and also the effect of the presence of stationary phase in the trap portion of the device on the desorption rate.

To assess the LOD using HSCFI for gas phase sampling, an aqueous mixture of six analytes of varying concentrations (given in Table 1) was prepared. Fig. 4(A) shows the chromatogram resulting from a 1 μl headspace vapor of the sample solution, introduced via a gas tight syringe in the auto-injector and a splitless inlet with a column head pressure of 22 psia. A 10 V, 10 ms pulse was applied to the HSCFI after 5 s of cryo-focusing time, resulting in the 5 s chromatogram for a total analysis time of ~10 s. The oven was held at 40 °C throughout the separation. Baseline correction and a Savitzky–Golay filter (250 points, where each point is 0.05 ms) were both applied post separation run. The inset in Fig. 4(A) focuses on the first second of the separation and shows the elution order for the first 4 analytes. The inset also highlights the presence of an unknown contaminant peak overlapping with methanol, making peak width and area measurements inaccurate for methanol. The identity and source of this peak is unknown though it is reliably visible in small volume injections and did not increase in intensity with an increase in the vapor injection volume.

To explore the performance of HSCFI while preconcentrating a larger volume of sample (headspace vapor) during the focusing step, injections of increasing volume (ranging from 1 μl to 40 μl) were made under conditions identical to those given above for Fig. 4(A). Fig. 4(B) shows the chromatogram resulting from injection of 30 μl of head space vapor collected with the syringe from above the aqueous solution. The chromatogram demonstrates that as expected, increasing the volume of head space injected increases the peak height. The relationship between volume injected and peak height for acetone and pentanol (the other analytes were omitted for clarity) is quantified in Fig. 5. The slope, *y*-intercept, and coefficient of determination for each analyte are listed in Table 2 and demonstrate that the

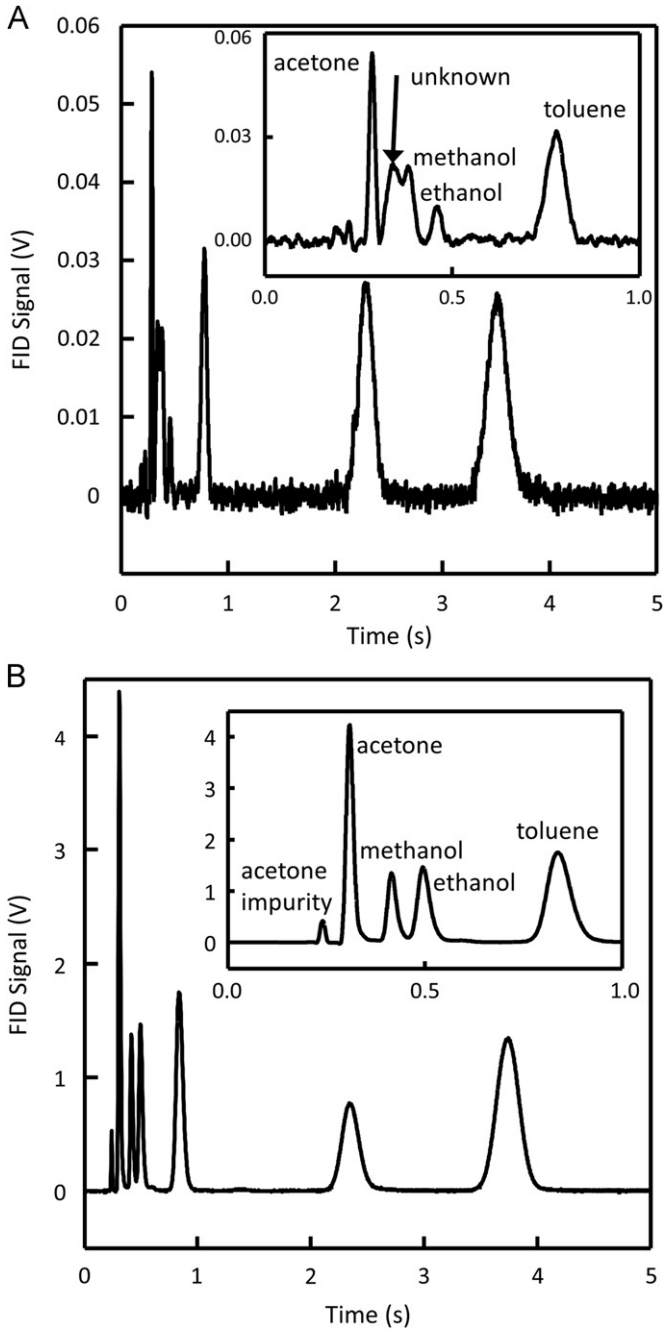

Fig. 4. Separation of head space injection of the vapor collected above a six component aqueous mixture (see Table 1) via HSCFI and a 1 m × 180 μm i.d. Rtx-5 column. Elution order: acetone, methanol, ethanol, toluene, chlorobenzene, pentanol. An absolute head pressure of 22 psi and an oven temperature of 40 °C were maintained throughout the run. A 10 V, 10 ms pulse was applied to the HSCFI after 5 s of cryo-focusing time. (A) 1 μl of head space vapor injected. (B) Separation in which 30 μl of head space vapor was injected.

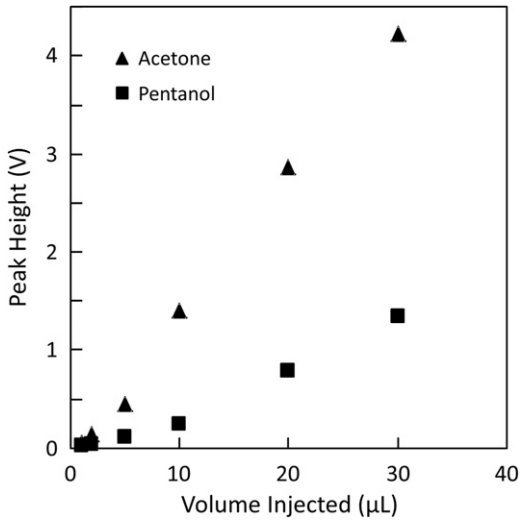

Fig. 5. Plot of peak height as a function of the volume of aqueous solution head space vapor being introduced to the inlet. For clarity, only two analytes (acetone and pentanol) were included. Separation and HSCFI conditions are identical to those in Fig. 4.

Table 2
For each of the six analytes in the aqueous mixture slope, *y*-intercept and coefficient of determination (R^2) were calculated for the volume injected versus peak height curves (see Fig. 5 for representative data curves and Fig. 4 caption for experimental conditions).

Analyte	Slope (V/μl)	*y*-intercept (V)	R^2
Acetone	0.15	−0.15	0.99
Methanol	0.049	−0.094	0.98
Ethanol	0.053	−0.11	0.99
Toluene	0.067	0.020	0.89
Chlorobenzene	0.025	−0.016	0.97
Pentanol	0.046	−0.091	0.98

Table 3
For each of the six analytes in the aqueous mixture, the peak height, sensitivity, concentration LOD and mass LOD resulting from a 30 μl injection of head space vapor and preconcentration via HSCFI (see Fig. 4(B) for chromatogram and experimental conditions) are reported. Minimum distinguishable signal used to calculate the concentration LOD is 3 times the standard deviation of the signal collected between 3.0 s and 3.2 s, and has a value of 1.8×10^{-3} V.

Analyte	Peak height at 30 μl (V)	Sensitivity (V μl/pg)	Concentration LOD (pg/μl)	Mass LOD (pg)
Acetone	4.2	0.047	0.039	1.2
Methanol	1.4	0.018	0.10	3.1
Ethanol	1.5	0.017	0.11	3.2
Toluene	1.8	0.0068	0.27	8.1
Chlorobenzene	0.77	0.00083	2.2	67
Pentanol	1.3	0.0053	0.35	10

preconcentration process is relatively linear, with coefficient of determination ranging from 0.89 to 0.99. Based on baseline noise (between 3 s and 3.2 s) in the chromatogram of Fig. 4(B), the peak height of each analyte, and the concentration of analyte injected (from Table 1), the concentration LODs were calculated and reported in Table 3. LODs ranging from 0.039 pg/μl to 2.2 pg/μl were achieved in the high speed separation, corresponding to mass LODs (calculated using 30 μl as the volume injected) that ranged from 1.2 pg to 67 pg, and sensitivities from 0.00083 V μl/pg to 0.047 V μl/pg. This improved detection sensitivity is highlighted in the inset of Fig. 4(B) with the first peak in the chromatogram, which is an unknown impurity introduced with the acetone and is not seen with the smaller injection volume in Fig. 4(A). The high LOD and consequent low sensitivity of chlorobenzene is due to the initial aqueous solution being prepared near its solubility limit in water, reducing the amount of analyte in both the aqueous solution and in the head space. Under the present trapping conditions, 30 μl was found to be the maximum vapor volume dependably analyzed. Break through was observed in the chromatogram of the 40 μl head space vapor injection (not shown for brevity), indicated by a broad peak of unresolved compounds. Further research is necessary to determine whether the observed break through is the result of the limited capacity of the

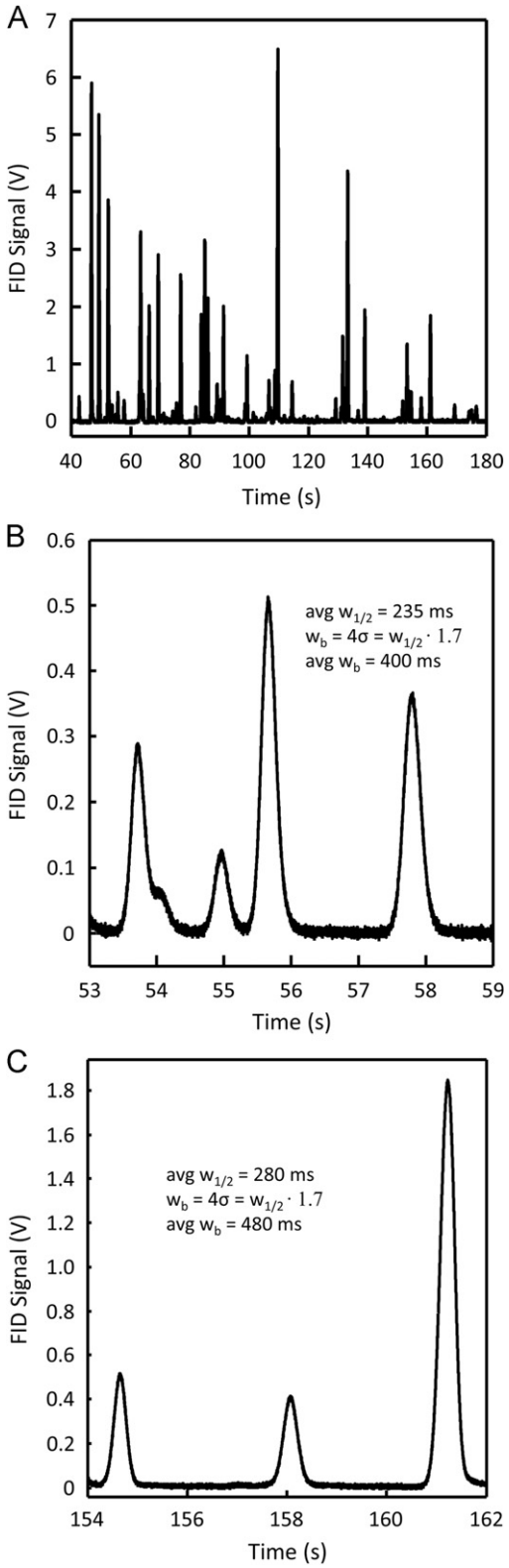

Fig. 6. (A) Rapid separation of a gasoline sample via a Rtx-5 column (20 m long, 100 μm i.d.), utilizing HSCFI and the stock oven for column temperature programming. A ~40 nl liquid injection was cryo-focused for 32 s and reinjected by applying a 50 ms, 10 V pulse to the HSCFI. The oven was held at 50 °C for 1 min, then increased at a rate of 50 °C/min to 150 °C where it was held for 3 min. The inlet pressure was initially held at 20 psia for 0.1 min then ramped at 150 psi/min to 75 psia, where it was held for 0.53 min. Then, the pressure was increased at 20 psi/min to 115 psia and held until the end of the temperature program. (B) Detail depicting peak width (average four standard deviation width at base of w_b=400 ms) of early eluting compounds. (C) Detail depicting peak widths (average w_b=480 ms) of late eluting compounds.

trap, or the limited efficiency of the trapping process at the flow rate and loading time given above.

To demonstrate the potential for application to complex samples, HSCFI was applied to the fast separation of a gasoline sample. A relatively long (20 m), narrow (100 μm i.d.) column was selected to minimize volumetric flow, while producing a separation time that would allow the stock GC oven to apply an effective temperature program to the separation column. To this end, the oven was held at 50 °C for 1 min, then ramped to 150 °C at 50 °C/min (the maximum rate over this temperature range), and held at 150 °C for 3 min, resulting in a 6 min temperature program. The inlet was programmed to hold at 20 psia for 0.1 min, then ramped to 75 psia at 150 psi/min where it was held for 0.53 min. This initial ramp occurred during the first minute of the temperature program and was meant to maximize the cryo-focusing efficiency while minimizing the resulting peak width by focusing at a low linear flow velocity but with HSCFI injection at a high linear flow velocity. The inlet pressure was then ramped from 75 psia to 115 psia at a rate of 20 psi/min, and then held until the end of the program in order to approximate a volumetric flow of 1 ml/min throughout the temperature program. The HSCFI applied a 10 V pulse for 50 ms, with 32 s of cryo-focusing time to ~40 nl of neat gasoline. The appearance of extra peaks in the peak width study chromatograms described above provided the impetus for using a deactivated section of MXT column in the HSCFI design in the gasoline separation. The resulting chromatogram is shown in Fig. 6(A), with a separation time of ~200 s. The early eluting peaks, as shown in Fig. 6(B) are 400 ms wide at the base (four standard deviation peak width at base definition), while the late eluting peaks (shown in Fig. 6(C)), are 480 ms wide at the base. Using an average peak width of 440 ms, the total peak capacity over the separation time is 460 peaks, with a peak capacity production of 140 peaks/min. For comparison sake, traditional GC separations, performed with an auto-injector and 200:1 split generally produce peaks ~2 s wide, resulting in a peak capacity production of ~30 peaks/min. HSCFI improves peak capacity production by a factor 4.7 when compared to traditional GC, an improvement similar to that seen with valve based injection [2], but with significantly improved detection sensitivity due to the preconcentrating effects detailed herein.

4. Conclusion

With the high speed cryo-focusing injection system developed herein, peaks as narrow as 6.3 ms width at half height ($w_{1/2}$) have been obtained (~10 ms w_b), while simultaneously providing mass LODs of less than 10 pg. Peak capacity production of 140 peaks/min has been demonstrated using HSCFI with the stock GC oven and a temperature programming rate of 50 °C/min. It is envisaged that coupling HSCFI to a separation column that is temperature programmed via direct resistive heating [15] may result in ~5 s separations with equivalent peak capacity and separation power as a 10 min separation performed under traditional GC parameters. Thus, HSCFI represents a significant step towards developing very fast separations that still maintain the high peak capacity and good sensitivity associated with traditional GC.

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