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New liquid nitrogen cryogenic modulator for comprehensive two-dimensional gas chromatography

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Abstract

A new liquid nitrogen (LN_2) jet-based thermal modulator for performing comprehensive two-dimensional (2D) gas chromatographic (GC × GC) separations has been designed and constructed. Temperature measurements of the trapping zone, a segment of uncoated fused silica capillary, show that it can be cooled to −196 °C in about 300 ms. A film of liquid nitrogen develops on the outside of the trapping capillary even when the oven temperature is in excess of 200 °C. Compounds as volatile as propane can be trapped by the modulator and held for periods of at least 1 min without breakthrough. The peak widths for *n*-alkanes are on the order of 80 ms at half height after passing through an 80 cm second dimension column. Repeated analysis of gasoline demonstrated excellent run-to-run reproducibility of the system.

Keywords: Gas chromatography, comprehensive two-dimensional; Cryogenic modulators; Modulators

1. Introduction

Comprehensive two-dimensional (2D) gas chromatography (GC × GC) relies on coupling two columns of different selectivities by means of a special GC × GC interface (modulator). The interface collects or samples the effluent from the primary column and injects it periodically onto the second dimension column. The interfaces used to perform GC × GC separations can be broadly classified into two main categories: thermal- and valve-based. Traditional thermal modulators use either a segment of a thick-film capillary column, or a cryogenically generated cold spot, to trap the material eluting from the primary column. In the interfaces utilizing thick-film stationary phases, material is injected into the second dimension column through the application of a moving heat gradient, for example in the form of a rotating mechanical heater [1] or sequentially heated segments of metal tubing [2]. The other form of thermal modulation relies on using a cryogen (typically liquid CO_2, but occasionally cold N_2 gas) to cool a segment of a GC column and thereby trap the analytes in a local cold spot, either through partitioning or through freezing. When the cryogen is periodically removed, either by moving the cold spot to a different position on the capillary [3,4] or by interrupting its delivery [5], the trap is brought back to the oven temperature and the analytes are injected into the second column. One of the advantages of

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thermal-based modulators is that the entire sample is passed from one column to the next, resulting in peak amplitude enhancement. This is a very attractive feature for trace analytical work. The main drawback of thermal modulators, especially those that use CO_2 as the cryogen, is that most of them have difficulties in trapping very volatile analytes (C1–C6). However, with a cryogenic modulator that uses liquid nitrogen (LN_2) as the cryogen, this is not expected to be a problem.

In a typical valve-based modulator, the sample passes from the primary column to a multi-port valve and is vented to the atmosphere through a sample loop, while an auxiliary gas supply is provided to the second dimension column. By periodically actuating the valve, any material that is located within the sample loop is directed to the second dimension column [6]. This technique has the advantage that breakthrough does not occur even for highly volatile analytes. However, due to the fact that a large portion of the original sample does not pass to the secondary column, there is little to no peak amplitude enhancement, making this method less attractive for trace analysis. Additionally, there can be problems with sorption of higher-boiling analytes to the valve or off-gassing of the material from the valve itself. Thus, there is still an ongoing search for a thermal modulator that would perform well for compounds whose volatilities range from very high to very low.

Such a modulator is a crucial step in the development of stop-flow GC × GC that we are developing in our laboratory. In this technique, the flow in the primary column is stopped periodically so that the second dimension separation may proceed for a longer time than the modulation period would allow in conventional GC × GC [7]. In this way, the sampling period can be made shorter than the second dimension separation time. Experiments have demonstrated that the technique yields the greatest benefits for volatile analytes (<C6), whose primary dimension peak widths are small almost independently of the GC oven temperature programming rate [8] (unless the separation is started at subambient temperature). In conventional systems, this makes it nearly impossible to sample these peaks three or more times (which is necessary to maintain the comprehensive character of the separation) without compromising the separating power of the second dimension column or producing wrap-around peaks.

The need for an efficient modulator for very volatile species has also been demonstrated in atmospheric chemistry. GC × GC studies of urban air revealed the presence of previously unaccounted for low-molecular weight oxygenated organic compounds [9]. These compounds are very volatile, and as such cannot be easily modulated by thermal means. Since their concentrations may be very low, the peak amplitude enhancement available through thermal modulation would be of a great advantage.

2. Experimental

Experiments were performed using a model 6890 gas chromatograph (Agilent Technologies, Mississauga, ON) equipped with a split/splitless injector and an FID. The GC was controlled and data was collected using Agilent's MSD Chemstation software, and the interface was controlled by means of in-house written software. For the generation of two-dimensional chromatograms, the original raw data was exported as a text file and then converted using an in-house written software package. Temperature measurements of the capillaries in the interface were made using a 50 μm chromel/alumel thermocouple (Type K) (Omega, Laval, PQ) that was threaded through a segment of 0.25 mm capillary. The signal from the thermocouple was amplified using a custom-built high-speed thermocouple amplifier (100× gain) and recorded with a PM 3365A 100 MHz digital oscilloscope (Phillips, Toronto, ON). The time constant for a 25 μm thermocouple in still air is given as 3 ms; for the 50 μm thermocouple, it can be estimated at about 15 ms [10]. In contact with the walls of the capillary, the time constant of the thermocouple is likely faster than this. To allow for observation of the interface behavior while the system was operating, the oven door of the GC was removed and replaced with a window made of heat-resistant glass attached to a piece of sheet metal. The door interlock was defeated with a small magnet.

The custom-built cryogen system used high-pressure nitrogen gas cooled with liquid nitrogen. A pair of cryogenic valves (Asco Valve Canada, Brantford, ON) connected by a metal T-piece were used to con-

trol the flow of liquid nitrogen out of the cooling jet, connected to the third port of the T. The details of the interface are described in the Section 3. The primary column was a 30 m × 0.25 mm × 1.0 μm ZB-1 column (Phenomenex, Torrance, CA), and the secondary column was an 80 cm × 0.25 mm × 0.25 μm Innowax column (Agilent Technologies, Mississauga, ON). The modulator capillaries were 10 cm × 0.1 mm deactivated fused silica tubing (Polymicro Technologies, Phoenix, AZ). One was held in place by being threaded through a pair of Graphpack connectors (Gerstel Inc., Baltimore, MD) using only one ferrule and nut per connector. These were mounted on the plate with custom-built clips. The other capillary was threaded through the holes that exist in the connectors when only one ferrule is used. The loop between the trapping capillaries was a 1.2 m × 0.25 mm segment of deactivated fused silica tubing (Restek, Bellefonte, PA). The modulator capillary diameter was 0.1 mm to improve trapping performance. The delay loop had an internal diameter of 0.25 mm to avoid the high-pressure drop from the long length of 0.1 mm capillary that would be required to provide an adequate delay. All column connections were performed by means of glass press-fit connectors (Chromatographic Specialties, Brockville, ON).

For propane modulation tests, propane from a disposable cylinder was used (2 μl injection, split 100:1). A linear alkane test mix consisting of *n*-pentane through *n*-tridecane in CS_2 was prepared for testing of the interface with programmed oven conditions. Pentane was obtained from Sigma–Aldrich (Oakville, ON). Hexane and CS_2 were obtained from Fisher Scientific (Toronto, ON), and the remaining linear alkanes were obtained from PolyScience Corporation (Niles, IL). Regular unleaded gasoline was obtained from a local gas station.

For the analysis of the alkane test mix, the oven was programmed from 40 to 190 °C at 4 °C/min, with an initial hold time of 2 min. For gasoline, the final temperature of the oven program was changed to 220 °C, and the final hold time to 10 min. For all analyses, the inlet was maintained at 250 °C and operated in the split mode (1 μl split 100:1 for the alkane test mixture and 0.5 μl split 200:1 for gasoline). The FID detector was operated at 230 °C and 100 Hz. Helium carrier gas was used at a constant average flow rate of 40 cm/s through the entire column set.

3. Results and discussion

3.1. Development of the cryojet

When deciding what type of modulator to construct, we elected a single-jet cryogenic interface with a delay loop. This type of interface, introduced by Ledford et al. at Pittcon 2002 [11], allows for two-stage cryogenic modulation with a single jet of cryogen, greatly simplifying the design of the modulator compared to a dual-jet system. Liquid nitrogen was selected as the cryogen to enable trapping in uncoated fused silica capillaries, thus eliminating the potential problems occurring when coated capillaries are used for trapping. These problems include selective desorption and/or changes in trapping capabilities when the stationary phase is cooled below its glass transition temperature.

The biggest challenge when developing an LN_2-based interface is the fact that the entire system must be kept at a very low temperature. This is not the case with CO_2, which can be kept in the liquid form at room temperature under sufficient pressure. In addition, early experiments indicated that very volatile compounds (propane, CS_2) could not be trapped efficiently when gaseous nitrogen cooled to low temperature with LN_2 was used as the cryogen. To achieve this goal, the trapping capillaries had to be cooled with a jet of liquid nitrogen. On the other hand, rapid and reproducible desorption of the trapped compounds requires that the trapping capillaries are heated very quickly, which is best achieved by stopping the delivery of LN_2 instantaneously. Thus, the challenge was to develop a system that would deliver liquid nitrogen to the jet reliably and that could be turned on and off very quickly. Another design goal was minimization of the LN_2 consumption.

In the system developed (Fig. 1A), high-pressure nitrogen from an in-house supply line (50 psi) was directed through a heat exchanger (1) to a cooling coil (3) made of 1/4 in. copper tubing. All lines were thermally insulated. The coil was immersed in liquid nitrogen kept in a 50 l Dewar (2). Because of the low temperature and the elevated pressure in the lines, the nitrogen inside the coil condensed. The near-boiling liquid nitrogen was then directed to a phase separator (4) made of a 3/8 in. Swagelok tee. In the separator, the gas phase moved preferentially upwards, while the liquid phase flew down, driven by gravity. This

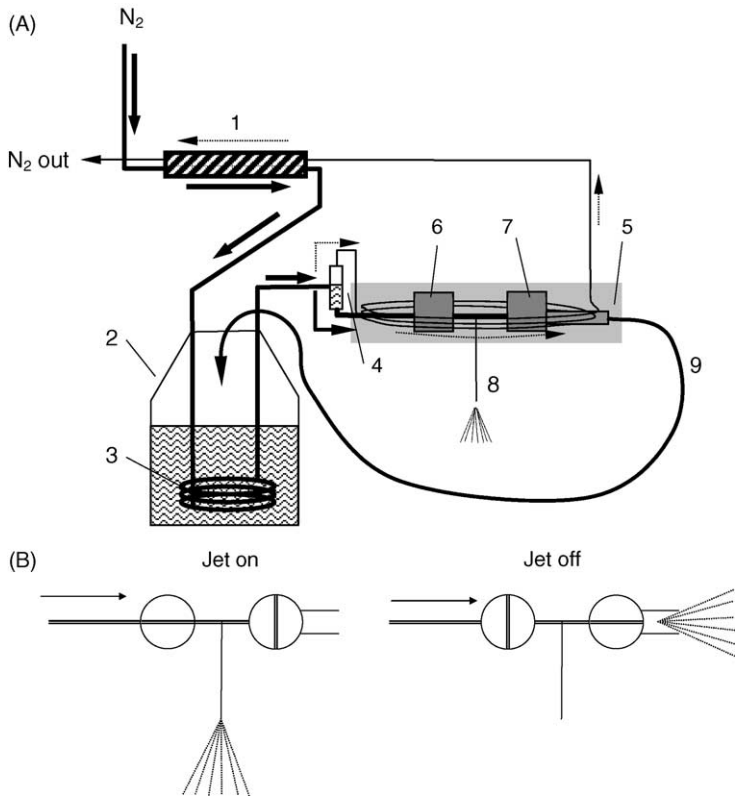

Fig. 1. (A) The cryogen supply system. Bold solid arrows denote the primary flow path of nitrogen from the high-pressure supply to the cryojet nozzle and back to the LN_2 Dewar. Dashed arrows denote the secondary flow path of cold gaseous nitrogen and excess liquid nitrogen from the phase separator through the cooling coils around the valves to the heat exchanger and finally to the atmosphere. (1) Heat exchanger; (2) Dewar with liquid nitrogen; (3) cooling coils; (4) phase separator; (5) modulator; (6) upstream solenoid valve; (7) downstream solenoid valve; (8) cryojet nozzle; (9) cryojet vent with liquid nitrogen return to the LN_2 Dewar. (B) The use of two on/off solenoid valves to control the flow of liquid nitrogen through the cryojet. The arrow denotes the direction of liquid nitrogen flow from the phase separator.

assured the supply of only liquid nitrogen to the cryojet. In the initial configuration, the liquid nitrogen entered the interface (5) through an LN_2-rated two-way solenoid valve (6) and was expelled through the cryojet (8) made of a bundle of 0.53 mm ID fused silica capillaries. The mixture of cold gaseous nitrogen and excess liquid nitrogen from the phase separator (4) was directed through 1/8 in. copper tubing wrapped tightly around the solenoid valves and connectors in the interface. In this way, the entire interface was continuously cooled, and excess heat produced by the valves was carried away from the main LN_2 delivery path. The cold gas was then directed to the heat exchanger (1), where it pre-cooled the high-pressure nitrogen supplied to the system. At the outlet of the system, the nitrogen was at room temperature, indicating efficient operation of the exchanger.

The configuration described above was capable of delivering liquid nitrogen to the cryojet efficiently. However, the flow of LN_2 did not stop immediately after valve (6) was closed. In fact, it took anywhere from 1 to 2 s for the flow to stop, depending on the supply pressure. This was caused by the relatively large dead volume inside the valve. Attempts to reduce this volume by a variety of inserts were only partly successful. To overcome this problem, a second solenoid valve (7) was added downstream of the cryojet. The two valves were connected through a custom-made low-volume tee, with the cryojet connected to the third port of the tee. Valve (7) had a large diameter outlet

(3/8 in.), which minimized flow restriction. The two valves operated alternately, as shown in Fig. 1B. The LN_2 supply to the jet was turned on by opening the upstream valve and closing the downstream valve. When the valves were switched, the supply of LN_2 through the upstream valve was cut off, and the downstream valve was opened, allowing the liquid nitrogen collected inside the valves and in the connectors to flow freely out of the interface. This resulted in immediate cessation of the LN_2 flow from the jet. The liquid nitrogen vented through the downstream valve (7, Fig. 1A) was recycled back to the Dewar (2) through a thermally insulated line (9) to reduce the consumption of the cooling agent.

There are several reasons why this approach to generating a jet of liquid nitrogen was chosen. Using the Dewar of liquid nitrogen at atmospheric pressure and cooling room temperature nitrogen allows excess liquid nitrogen from the T between the two cryogenic valves to be easily recycled, aiding in lowering the nitrogen consumption. This would not be possible if a high-pressure Dewar of liquid nitrogen was used as the supply. Besides, an atmospheric pressure Dewar is significantly less expensive than a high-pressure one, which helped reduce the costs of the interface.

The design of the interface is presented in Fig. 2. The effluent from the primary column (B) enters the first of the two trapping capillaries (G) where the analyte bands are cryogenically trapped at a cold spot created by LN_2 delivered by the cryojet (F). Turning the cold jet off and the warm jets on causes the cold spot to quickly warm up to the oven temperature and launches the analyte band into the delay loop (C). After a short, predetermined time, the warm jets

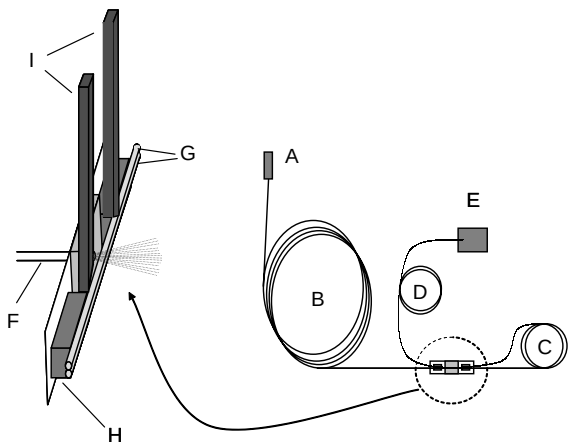

Fig. 2. Schematic of the interface setup. (A) Injector; (B) primary column; (C) modulator delay loop; (D) secondary column; (E) detector; (F) cryojet nozzle; (G) trapping capillaries; (H) capillary and cryojet mounting block; and (I) warm air jets.

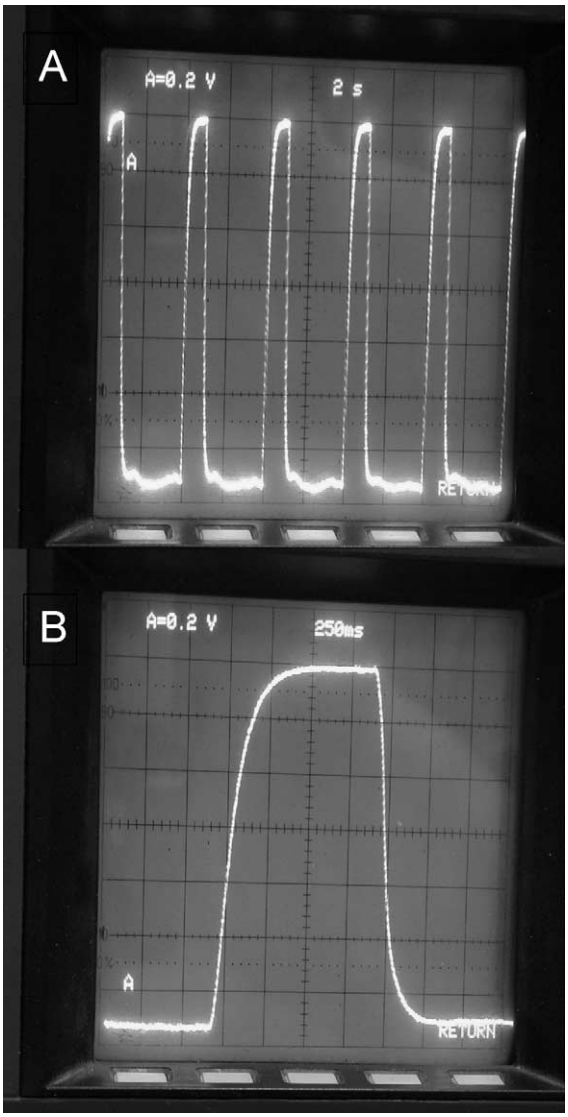

Fig. 3. Temperature profile of the cryotrap during modulation; oven at 200 °C, thermocouple amplifier gain of 100. Modulation period 4 s (cryojet on for 3 s, off for 1 s). (A) A series of modulation cycles; 0.2 V/div vertical scale, 2 s/div horizontal scale; (B) A single heating/cooling cycle; 0.2 V/div vertical scale, 250 ms/div horizontal scale.

are turned off and simultaneously the cryojet is turned back on, so that the material from the primary column begins to be trapped again. A second cold spot in the other trapping capillary is already cold by the time the material passing through the loop reaches it. Switching the cold jet off and the warm jets on again injects the material from the first trap to the loop and from the second trap to the second dimension column (D). The capillary and cryojet mounting block (H) is a custom-built piece mounted on the GC oven wall. It has two brackets (approximately 2.5 cm apart) for attaching the Graphpack connectors and a brass block with a hole in the center for the cryojet capillaries, mounted on an aluminum plate. The brass block can be moved vertically to allow proper alignment of the cryojet with the trapping capillaries. The brass plate and cryojet are approximately 0.5 cm from the trapping capillaries.

During temperature studies of the interface, we discovered that although the capillaries would heat up quickly in the oven air, the timing of the heating was not reproducible. Close observation revealed that droplets of liquid nitrogen would sometimes stick to the trapping capillaries. The heating of the traps could not commence until all of the liquid nitrogen had evaporated. The rate of this process depended on the size and number of the droplets, and was irreproducible. To eliminate this problem, two nozzles constructed

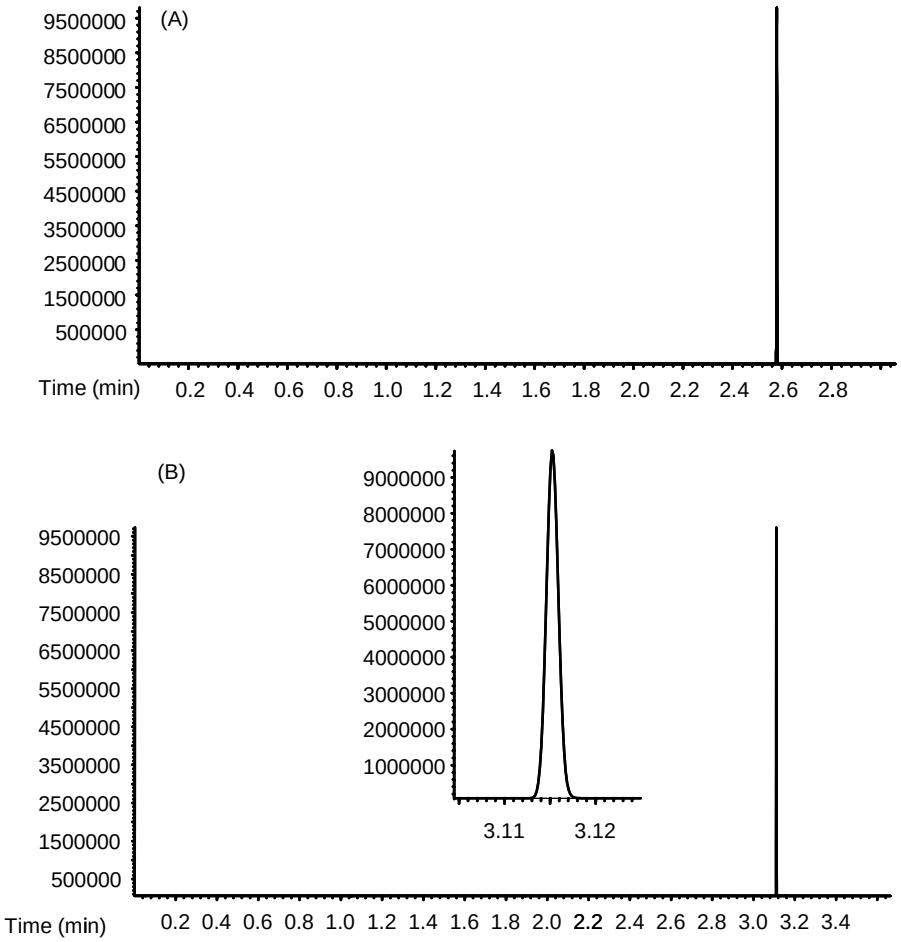

Fig. 4. (A) Trapping of propane in the first trapping capillary. The cryojet was turned on at 0.5 min and off at 2.5 min. (B) Propane peak from the second trapping capillary. The cryojet was turned on at 0.5 min, off at 2.5 min, on at 2.52 min and off again at 3.0 min. The inset shows a magnified propane peak from the second trapping capillary.

from 1/8 in. copper tubing (I) were mounted approximately 5 mm above the trapping capillaries to blow compressed air at oven temperature from the sides of the capillaries towards their centers. The warm air flow was controlled so that the flow would turn on when the cryojet turned off, and then turn off for trapping again. Dual nozzles were chosen rather than a single nozzle blowing compressed air directly onto the cold spots because it was observed that a single nozzle occasionally caused the droplets of liquid nitrogen to be forced along the capillaries, away from the center and towards the capillary mounts. This would create additional cold spots on the capillaries in areas with little flow of compressed air, causing irreproducible desorption from multiple random places. With the dual nozzles, all LN_2 droplets sticking to the capillaries were immediately blown away. To prevent the liquid nitrogen from the cryojet from affecting the oven temperature, a 1/2 in. brass tube bent at a 90° angle was mounted in the oven floor opposite the cryojet outlet. The tube collected all of the LN_2 spray and directed it out of the oven through the floor.

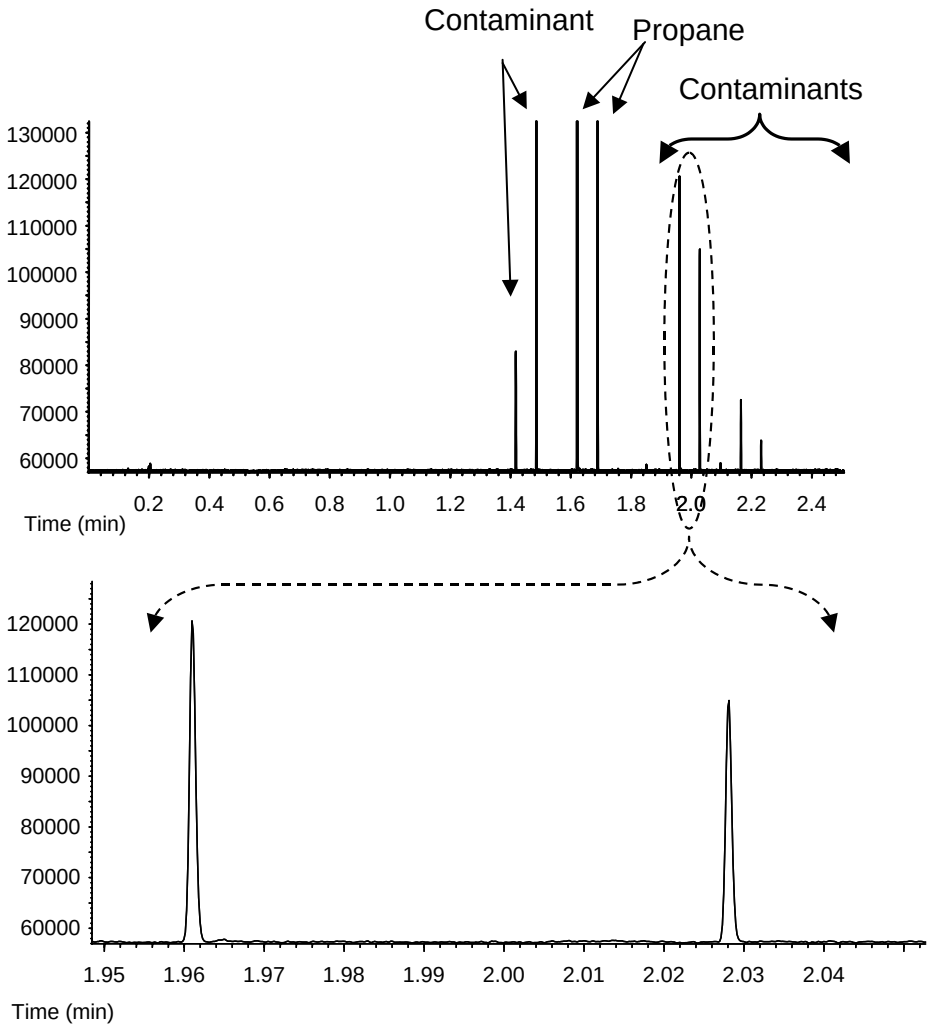

Fig. 5. GC × GC analysis of a propane sample with a 4 s modulation period. Peaks at 1.63 and 1.69 min are the major propane peaks. A close-up view of two of the minor contaminant peaks is shown at the bottom of the figure.

3.2. Thermal characteristics of the interface

When the interface was operating, a film of liquid nitrogen could be seen on the trapping capillaries independently of the oven temperature. This indicated that the temperature of the cold spot was approximately −196 °C, even when the oven temperature was in excess of 200 °C. A more accurate measure of the thermal characteristics of the interface was determined by placing a fine thermocouple inside a segment of a 0.25 mm ID fused silica capillary and locating the thermocouple junction in front of the cryojet (see Section 2). The response of the thermocouple was recorded with a digital oscilloscope. Fig. 3 presents the temperature profiles inside the trapping capillary during modulation. Both the heating and the cooling of the trapping capillary were very reproducible (see Fig. 3A). When desorption was initiated, the capillary reached 90% of the oven temperature in about 250 ms. Cooling from the oven temperature to the trapping temperature was even faster, with 90% of the final temperature reached in about 200 ms (see Fig. 3B). The trapping temperature was cold enough to freeze any analytes except some permanent gases.

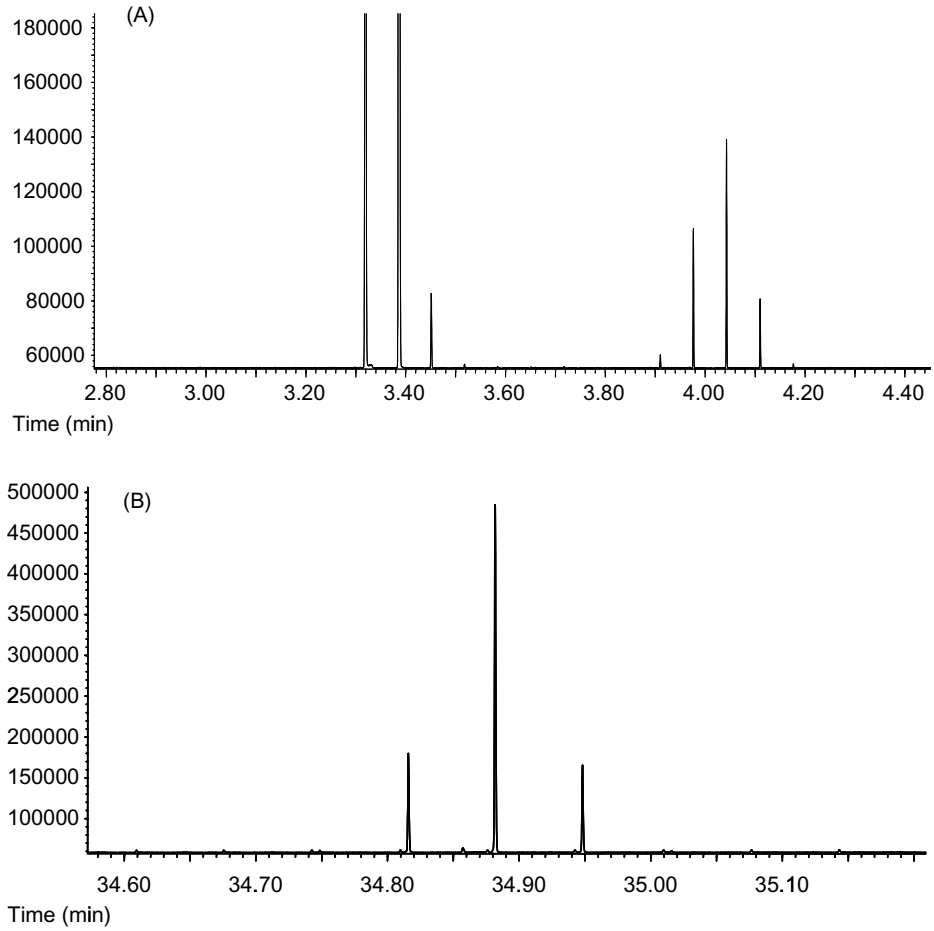

Fig. 6. Analysis of an alkane mixture (*n*-C5 to *n*-C13 in CS_2) with a 4 s modulation period. (A) Close-up view of the CS_2 and pentane peaks showing no breakthrough. (B) Close-up view of the tridecane peak.

3.3. Testing of the interface

Initial testing of the interface was performed with methane from an in-house supply, which could be modulated successfully most of the time. However, there were occasional breakthrough problems for methane, so further testing was performed using propane. The oven was kept at a constant temperature of 40 °C. When injected without modulation, propane had a retention time of 1.6 min. To test trapping in the first stage of the trap, the cryojet was turned on 0.5 min after the propane injection. After 2.5 min, the cryojet was turned off and the warm air nozzles were simultaneously turned on. Thus, the propane was trapped in the first trap, held in place for about 1 min and released to the second dimension column. Fig. 4A presents the results of this experiment. A single, perfectly shaped peak of propane was observed even though the trapping time was very long. No breakthrough was evident.

To evaluate the performance of the delay loop, the experiment was repeated with the cryojet turned off at 2.5 min, turned back on at 2.52 min and off at 3 min. In this way, the material trapped in the first capillary was first desorbed into the delay loop and re-trapped in the second trap. The focused band was injected at 3 min to the second dimension column. The results of this experiment are illustrated in Fig. 4B. Again, a single peak of propane was observed, with a perfectly Gaussian shape (inset Fig. 4B). The peak width at half height was ~80 ms, which is acceptable. It should be pointed out that this number does not represent the injection band width, as the band traveled through an 80 cm long second dimension column before reaching the detector.

A GC × GC separation of the propane was then performed with a 4 s modulation period. The results (in the linear form) are illustrated in Fig. 5. Propane was modulated without any difficulty (peaks at 1.63 and 1.69 min). This was also true for the minor

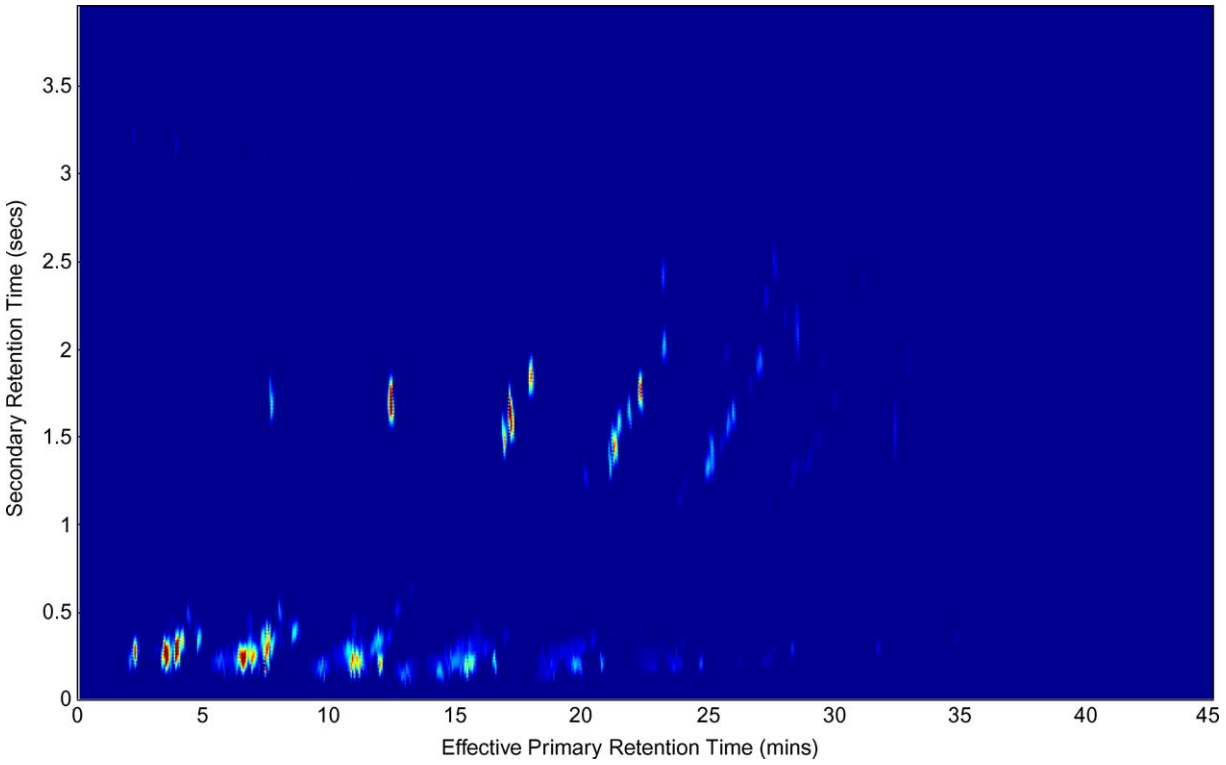

Fig. 7. 2D representation of the GC × GC analysis of gasoline with a 4 s modulation period. Note the lack of breakthrough peaks even for the large early eluting peaks.

components present in propane. No breakthrough was observed, and the peak shapes were very good, as seen in the magnification of the minor components in Fig. 5. The minor components could not be seen in the first two experiments (Fig. 4) because they were collected together with propane as a single band during cryotrapping and could not be separated from it in the short second dimension column.

To test the interface with a broader range of compounds, a mixture of C-5–C-13 *n*-alkanes in CS_2 was analyzed in the GC × GC mode with a modulation period of 4 s. Each analyte peak was sampled at least three times under the conditions of the experiment. Fig. 6A shows a magnification of the peaks for the solvent (CS_2) and *n*-pentane. No breakthrough was observed for either of the two. The small perturbation visible on the baseline after the first CS_2 peak was in fact a peak of an impurity. This result is particularly impressive considering that the amount of CS_2 in the injection was orders of magnitude higher than the amount of any of the analytes. To the best of our knowledge, very few GC × GC interfaces in use today are capable of trapping volatile injection solvents equally efficiently. Fig. 6B shows a magnification of the *n*-tridecane peak.

The final test of the interface was performed by analyzing regular unleaded gasoline. A 2D representation of the chromatogram obtained is presented in Fig. 7. An important feature of this chromatogram is the lack of tailing or breakthrough for any peaks, especially those that elute at the beginning of the run. Fig. 8 shows a close-up view of a region of the

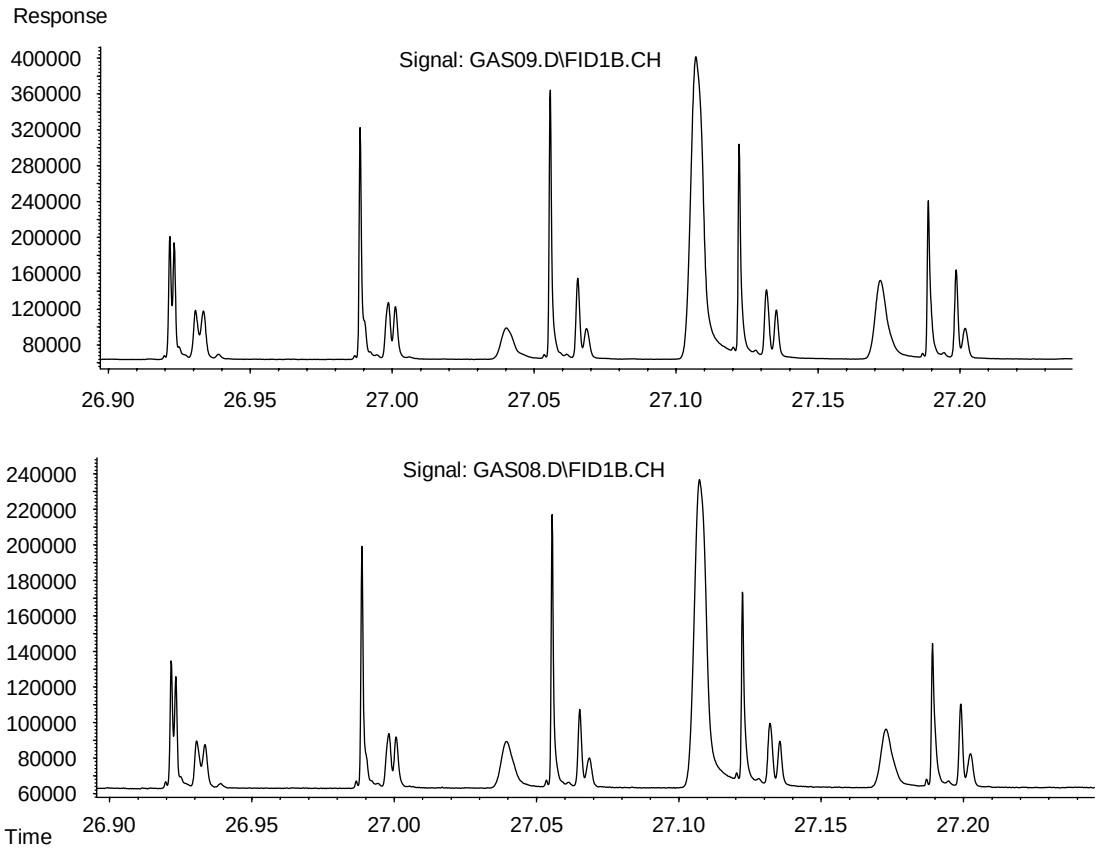

Fig. 8. Comparison of the same region of the original raw GC × GC signal from two separate analyses of gasoline carried on two different days, with two different injection volumes.

original linear data from two runs of the gasoline sample performed on two different days and with two different injection volumes. The run-to-run repeatability of the system was excellent, with no shifts in retention times or peak profiles.

Liquid nitrogen consumption for this interface is currently estimated at about 2 l per hour of operation. This can likely be improved with the use of better thermal insulation on the transfer lines and on the modulator valve control assembly.

4. Conclusions

The new interface presented here allows for easy modulation of even the most volatile analytes and provides extremely reproducible run-to-run results. The ability to cool the capillaries of the trap to liquid nitrogen temperature even when the oven temperature is in excess of 200 °C means that analytes can be trapped by the interface and held for arbitrary periods of time (at least 1 min) without breakthrough. The use of uncoated fused silica capillaries for the trapping eliminates problems commonly occurring when trapping is performed in a segment of a GC column (poor performance below the glass transition temperature of the stationary phase, selective desorption of the analytes). The interface should be of interest to any user requiring good quality GC × GC separation of very volatile compounds. This includes atmospheric chemists, who currently most often resort to valve-based interfaces with all the compromises involved in this approach. The main application of the interface will be stop-flow GC × GC. A paper describing this technique is forthcoming.

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