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Development of a new consumable-free thermal modulator for comprehensive two-dimensional gas chromatography

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ABSTRACT

A simple and cost-effective GC × GC modulator requiring no moving parts or consumables, hence suitable for field analysis and monitoring, was developed. The modulator was constructed from a specially designed Silcosteel® trapping capillary, installed outside the GC oven, and coated inside with polydimethylsiloxane (PDMS) stationary phase. Dual-stage modulation was accomplished by resistively heating alternate segments of the trap with a custom-designed capacitive discharge power supply. The performance of the proposed modulator was comparable to many GC × GC systems currently in use, with the injection band widths as low as 60 ms at half height. With proper selection of the stationary phase in the trap, the modulator can be used for the analysis of complex mixtures with volatility range spanning from *n*-C5 to *n*-C40.

1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) significantly increases peak capacity and resolution, improves mass sensitivity and generates structured three-dimensional chromatograms. This is accomplished by subjecting the sample to separation in two columns, or dimensions, coated with stationary phases differing in their selectivity. The two columns are coupled through a special interface, or modulator, which ensures that all sample components are subject to separation in both dimensions, and that separation accomplished in the first dimension is preserved in the second dimension. Regardless of the interface type or design, the modulator traps or samples compounds eluting from the first dimension column and periodically injects them as narrow pulses into the second dimension column for further chromatographic analysis. GC × GC has been successfully used in applications ranging from petrochemical analysis and forensics to environmental, health and food analysis. Readers interested in GC × GC instrumentation are directed to review papers, e.g. [1–3].

All existing GC × GC interfaces can be broadly categorized as thermal or valve-based. Heater-based and cryogenically operated modulators are considered subclasses of thermal interfaces. While valve-based interfaces are gaining in popularity and can be a good choice for portable and cost-effective GC × GC instrumentation, description of their operation is beyond the scope of this paper, and details can be found in the literature, e.g. [4–7].

The first GC × GC modulator was reported in 1991 by Liu and Phillips. It was of the heater-based type [8]. This simple interface consisted of a segment of a thick-film fused silica capillary, with the outer surface coated with gold paint. Modulation of analytes was accomplished by periodical resistive heating of the gold-painted trap. While this interface provided a proof-of-concept, it was far from ideal, as the injection bands onto the second column were broad and irregular. Later, Phillips and co-workers developed and commercialized the rotating thermal modulator [9,10]. Similarly to his original model, trapping and focusing of analytes exiting the first dimension was accomplished with a thick-film capillary; however, instead of using direct resistive heating to remobilize and inject the analytes into the second dimension column, a rotating thermal heater was implemented. While this modulator produced better results and was generally more robust, it suffered from drawbacks associated with the moving parts. Later, an interface consisting of resistively heated Silcosteel® trapping capillaries packed with a microsorbent bed was developed in our laboratory [11]. Burger et al. also developed a thermal heater-based interface that consisted of a thick-film capillary column encased by a steel jacket, allowing for multi-stage trapping that mimicked the rotating thermal modulator [12]. However, the inability of heater-based modulators to effectively trap volatile compounds and to quickly release

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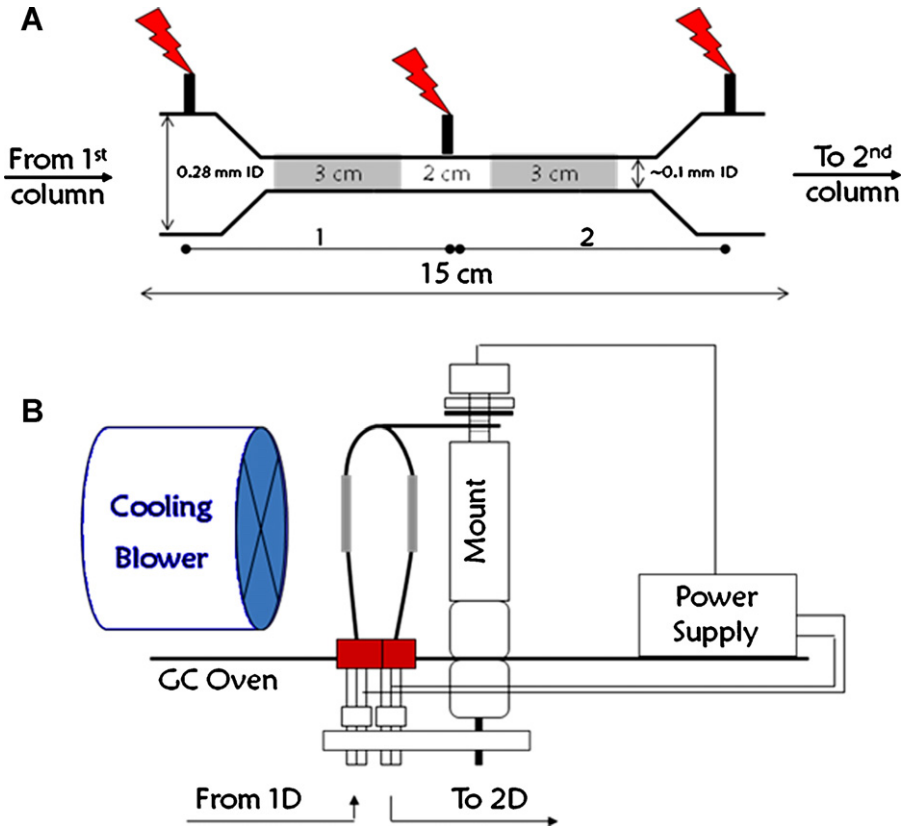

Fig. 1. Schematic diagrams of the modulator: (A) The flattened trapping capillary with two trapping zones (areas with intact stationary phase, shown in gray). Electrical contacts at 3 points ensure dual-stage modulation via alternative resistive heating. (B) The trap installed atop the GC oven and secured in place with two GC septa. The cooling blower was in close vicinity of the trapping capillary (~1–3 cm) and was continuously operated during the analysis. Two electrical contacts were located at the stainless steel unions inside the oven, while the middle contact was supported by the middle mount.

semi-volatile compounds at the allowed desorption temperatures led to their discontinued use. Presently, all commercially available GC × GC systems are either cryogenic or valve-based.

Around the time that Phillips reported the development of the rotating thermal modulator ("sweeper"), Kinghorn and Marriot constructed the first cryogenic modulator, the longitudinally modulated cryogenic system (LMCS) [13]. In cryogenically operated GC × GC instrumentation, analyte trapping is achieved by cooling a short segment of a column with a cryogenic agent (liquid CO_2 or N_2, or gas cooled with LN_2), and remobilization of the band is accomplished by rapidly heating the trap with a hot jet or by removing the source of cold temperature to allow the trap to quickly reach the oven temperature.

Even though the LMCS proved to be reliable over time, the use of moving parts was considered a drawback. Complementary research efforts were aimed at interfaces with no moving parts and colder cryogenic consumables. For example, interfaces utilizing LCO_2 [14] and liquid nitrogen (LN_2) [11] with no moving parts enabled the analysis of the most volatile analytes. Following this, various cryogenic interfaces were developed and commercialized [15–17].

Although cryogenic modulators are considered the most effective and have in fact contributed to the majority of applications to date, the commercial GC × GC systems are not universal in nature; indeed, every modulator has distinct advantages and limitations. Cryogenically operated GC × GC interfaces require a constant supply of LCO_2 or LN_2, which make them costly to operate and impractical for field analysis. It is likely therefore that the transition of GC × GC instrumentation from the research sector to routine laboratories or into the field will depend on the development of systems that are simple, robust, cost-effective, devoid of cryogenic consumables, and field transportable. Satisfying such criteria requires further research efforts focused on the development and engineering of interface technology. A consumable-free cryogenic system was introduced relatively recently by LECO based on the work of Libardoni et al. [18], but it is not suitable for the analysis of the most volatile fractions. Agilent introduced a differential flow modulator based on the work of Seeley et al. [19], but it works effectively only for short modulation periods, hence offers limited separation space in the second dimension. In addition, it cannot be easily coupled to a mass spectrometer because of the high carrier gas flow required in the second dimension (~20 mL/min). The goal of this research was to develop a cryogen-free modulator with no moving parts which could be used for a thermal desorption comprehensive two-dimensional gas chromatography system for in situ measurements of the semi-volatile fraction of organic aerosols (so-called 2D-TAG) [20]. While that contribution introduced only the basic principle of operation of the modulator, this paper focuses on its detailed characterization.

2. Experimental

The design of the modulator is depicted in Fig. 1. The interface consists of a flattened Silcosteel® trapping capillary, a cooling blower, and a custom-designed capacitive discharge power supply. Dual-stage modulation is carried out in the following manner: analytes eluting from the 1D column enter the trapping capillary, whose lower temperature promotes their partitioning into the non-polar stationary phase. This accomplishes analyte trapping and

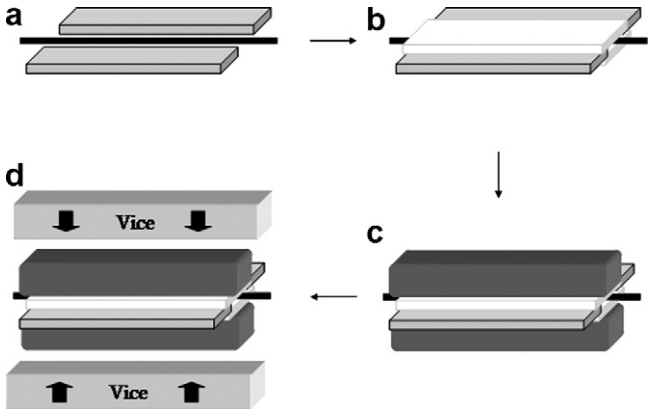

Fig. 2. Mechanical flattening of the trapping capillaries: (a) The tubing (black) was placed between two shims (gray) and was (b) secured in place with masking tape (white). (c) Two parallels were placed on both sides and (d) inserted into a vice. The force applied by the vice ensured uniform and precise flattening of the trap along its entire length.

focusing. Re-mobilization of the analytes in the first segment of the trap (segment 1 in Fig. 1A) is achieved by briefly passing electric current from the power supply through segment 1 of the Silcosteel® capillary. Upon reaching a cooler portion of the trap in segment 2, the desorbed analytes are re-trapped and focused once again. Simultaneously, the first segment of the trapping capillary cools down to prevent analyte breakthrough, while resistive heating of the second segment (segment 2 in Fig. 1B) injects a narrow band of the refocused analytes onto the second column. This process is repeated throughout the entire GC × GC analysis.

The interface and all required supplies were constructed in-house from commercially available materials. The trapping capillaries were developed from MXT-1 15 cm × 0.28 mm × 3 μm and 1 μm Silcosteel® capillaries, as well as from 15 cm × 0.28 mm deactivated Silcosteel® guard tubing (Restek, Bellefonte, PA). The length of the traps was arbitrarily chosen to be 15 cm. All traps were mechanically flattened to an inner distance of ca. 0.1 mm from wall to wall with a custom-designed flattening device, described in detail in Fig. 2. Fracturing of the trapping capillary prevented us from flattening the traps to a greater degree than indicated above. The ends of the capillaries, however, were not flattened in order to facilitate standard ferrule-based connection of the modulator to the column train.

The method for flattening the trapping capillaries (Fig. 2) is based on two parallels and shims. The 3/8″ × 3/4″ × 6″ parallels were purchase locally (KBC Tools, Kitchener, Ontario, Canada) and their edges were smoothened with a stone grinder. Two 0.005″ stainless steel shims were cut into strips representative of the length of the flattened trapping capillary (ca. 15 cm × 1 cm). The tubing was placed between two thin stainless steel sheets (0.005″ shims), each 15 cm in length. Masking tape was used to hold the capillary in place. Two 15 cm steel blocks, or parallels, with smoothened edges were placed on both sides of the trap, shims and tape, and were then inserted in this configuration into a vice (Fig. 2d). The force applied by turning the vice handle by ∼90° flattened the tubing to the desired wall-to-wall distance, consistently ensured by the shims. The smoothened edges of the parallels prevented cracking of the tubing at the transition between the flattened and the non-flattened sections of the trap. This procedure guaranteed inner diameter uniformity throughout the entire trapping capillary and provided reproducibility between individual modulators. The latter was chromatographically confirmed as the second dimension retention times between any two trapping capillaries did not differ by more than 15 ms.

The dimensions of the flattened trap were determined by measuring the tubing thickness with a metric micrometer (Mitutoyo, Japan). A short piece (ca. 1–2 cm) of flattened Silcosteel® capillary (Restek, Bellefonte, PA) was spot-welded perpendicular to the trapping capillary at the midpoint and served as the middle contact. The remaining two contacts were made by connecting alligator clips to the stainless steel connector nuts. The middle mount shown in Fig. 1B was constructed in house from ceramic stand-offs, a banana jack, and a machineable ceramic plate (ca. 1 cm × 3 cm). It was used to support the trap and connect the trap's middle electrical contact to the power supply via a banana jack.

The interface assembly was installed on the roof of the GC. Inside the GC oven, a ceramic plate separated the electrical contacts on the two ends of the trap from each other and simultaneously relieved pressure from the middle contact. This was achieved by resting the stainless steel unions connecting the trap to the 1D and 2D columns on the ceramic plate, with the columns going through grooves machined in the plate.

Resistive heating of the trapping capillaries was carried out with a dual-channel capacitive discharge power supply that was custom-designed and constructed in house. The power supply was equipped with variable, user-controlled discharge voltage and modulation period functions. Calibration of the capacitive discharge power supply was carried out by recording the temperature generated across designated lengths of trapping capillary at various discharge voltages. Measurements were carried out using a 50 μm chromel/alumel K-type thermocouple (Omega, Laval, PQ) made by spot-welding the thermocouple wires one on top of the other onto the capillary. The signal was acquired with a PM 3365A 100 MHz digital oscilloscope (Phillips, Toronto, ON). Depending on the volatility of the compounds analyzed, the capacitive discharge power supply was operated to generate desorption temperatures between 275 °C and 325 °C. The internal clock of the FID electrometer was utilized for timing desorption events during the GC × GC analysis, thereby eliminating the need for timestamps.

The power supply was also used to selectively remove the stationary phase along segments of the trapping capillary (see Section 3). This was achieved by subjecting selected segments of the trap to frequent high-power discharge events (4 s apart) causing the tubing to glow red, with a constant flow of air through the capillary. At these temperatures, most of the stationary phase was assumed to be destroyed. A series of experiments were carried out to determine the number of discharge events required to ensure removal of the stationary phase in the trap that would produce results comparable to an interface constructed from uncoated deactivated Silcosteel® capillaries. It was determined that this was achieved when the number of consecutive discharge events was at least 30.

Forced cooling of the trapping capillary was carried out with two types of commercially available blowers. Initially, a locally purchased hairdryer (Conair 1625 W) was used for the analysis of semi-volatile mixtures. Later, the analysis of volatile mixtures was conducted with a dual nozzle adjustable spot cooler, also known as a Vortex tube (Exair Corporation, Cincinnati, OH). In both setups, the blower temperature was monitored during GC × GC analyses with a K-type thermocouple and model 8529-00 digital thermocouple thermometer (Cole-Parmer Instrument Company, Chicago, IL). The thermocouple junction was positioned ca. 1–2 mm from the nozzle of the blower.

All experiments were performed on a model 6890 gas chromatograph (Agilent Technologies, Mississauga, ON), equipped with a split/splitless (S/SL) injector and operated with hydrogen as the carrier gas, set at a constant flow of 1.2 mL/min. Data was acquired with FID at 100 Hz (Agilent). The 1st dimension column was a VF-5ms 30 m × 0.25 mm × 1 μm/0.5 μm (Varian, Canada), and the 2nd dimension column was a SolGel WAX

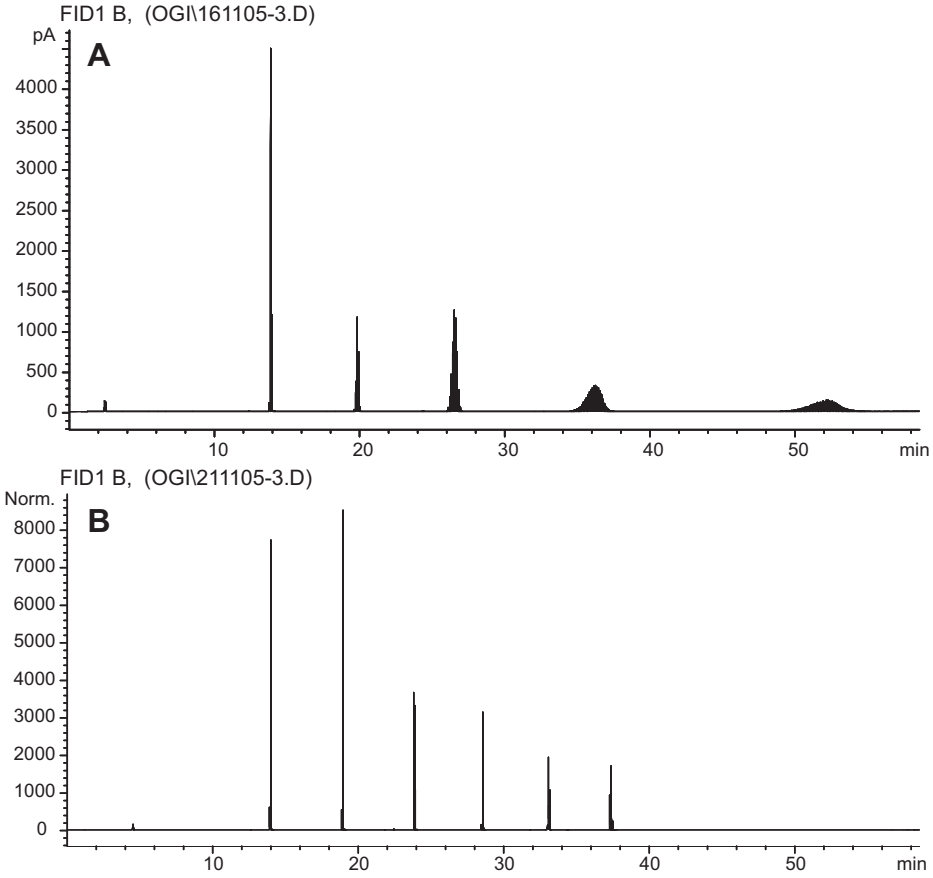

Fig. 3. The effect of cold spots on GC × GC separation of an *n*-alkane standard (C_8–C_{13}). (A) Raw GC × GC chromatogram obtained with a flattened trapping capillary equipped with an alligator clip as the middle electrical contact. Band broadening worsened with increasing boiling point of the *n*-alkanes. (B) Application of hot air from a hairdryer during modulation of the same *n*-alkane sample eliminated the cold spot and the associated band broadening. The differences in retention times between the two chromatograms were due to extra retention at cold spots.

1.4 m/2.5 m × 0.25 mm × 0.25 μm (SGE Inc., Austin, TX). For testing of the injection band width, the second column was replaced with a 0.9 m × 0.25 mm uncoated fused silica capillary (Chromatographic Specialties, Brockville, ON). Manual injections of the samples and standards (1 μL) were carried out using hot needle technique. Chromatographic parameters and data collection were controlled with Agilent's Chemstation software. Generation of GC × GC chromatograms required exporting the linear FID signals as comma delimited files (.csv) and processing them with software written in-house in Matlab (Mathworks, Natick, MA).

Evaluation of the interface was conducted with standard solutions containing normal alkanes from *n*-hexane to *n*-decane (Sigma–Aldrich, St. Louis, MO) in CS_2 (EMD Chemicals Inc., Gibbstown, NJ) and *n*-octane to *n*-tridecane (Sigma–Aldrich, St. Louis, MO) in CS_2 (EMD Chemicals Inc., Gibbstown, NJ). The working volatility range of the interface was determined by analyzing a linear alkane standard consisting of *n*-octane to *n*-tetracontane in chloroform (AccuStandard Inc., New Haven, CT), diluted 100 times. The system's suitability for analyzing complex samples was evaluated with petrochemical mixtures. Unleaded 87 octane gasoline and diesel fuel were obtained from a local gas station. Kerosene was purchased from a local hardware store. Polychlorinated biphenyls (PCBs) were analyzed as a 1:1 mixture of Arochlor 1260/1254, and Arochlor 1260 in transformer oil (Supelco, Bellefonte, PA). Undiluted essential oil of neroli (*Citrus aurantium*) was purchased at a health food store. With the exception of gasoline, all of the above were analyzed with the 1 μm trap, desorption temperature of 325 °C and a modulation period of 6 s. Gasoline was modulated with trapping capillaries coated with 3 μm PDMS.

3. Results and discussion

3.1. Trapping capillary

Successful operation of resistively heated thermal modulators requires thin-walled, electrically conductive trapping capillaries that are internally coated with stationary phase of appropriate choice. Previous experiments in our laboratory indicated that 0.53 mm ID Silcosteel® tubing coated with films thicker than 3 μm required long cooling times, rendering modulation periods of 3–6 s practically unattainable. Consequently, 0.28 mm ID Silcosteel® capillaries coated with 3 μm of polydimethylsiloxane (PDMS) stationary phase, supplemented with forced cooling throughout the analysis, were selected as the interface prototype.

The two unique developments that distinguish this interface from Phillips' original modulator [8] and our previous resistively heated interface models [11] are the flattening of the trapping capillary to an inner distance of ca. 0.1 mm from wall to wall, and the selective removal of the stationary phase within the capillary, creating two trapping zones, each 3 cm in length. The two inventions are illustrated in Fig. 1, and the rationale for them is explained below.

Modulation efficiency was evaluated based on the peak widths at half-height of *n*-alkanes in the second dimension. Our experiments indicated that flattening of the capillary was the most important factor contributing to the decrease in 2D peak widths. The flattening led to the reduction of the trap's internal volume without unduly increasing the pneumatic resistance offered by the trap (as would be the case if smaller diameter tubing was used). This, in turn, reduced the amount of gas expanding inside

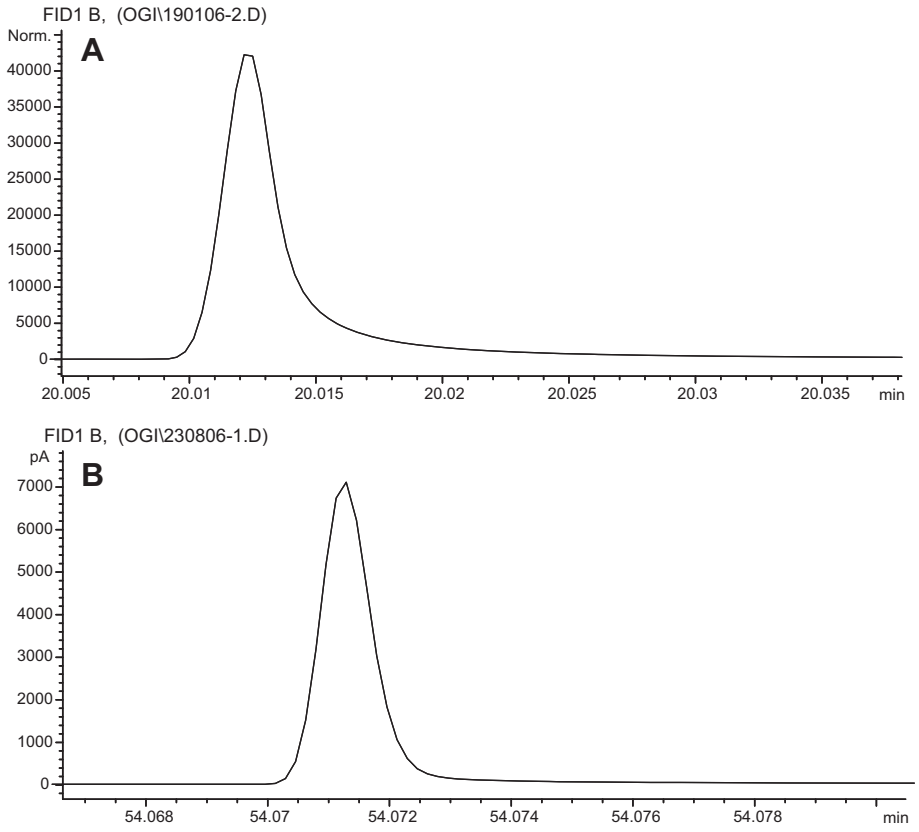

Fig. 4. The effect of the efficiency of stationary phase removal on the injection band width and shape. (A) Raw GC × GC chromatogram illustrating one slice of an *n*-C_{11} peak generated with a flattened trapping capillary subject to removal of the stationary phase with 13 consecutive discharge events. Tailing is evident and the peak width at half height is approximately 140 ms. (B) A slice of octadecane (*n*-C_{18}) peak when the selective removal of the stationary phase in the trap was achieved with 30 consecutive discharge events. The peak was ~60 ms wide at half height.

the trap during the rapid heating at the desorption stage. The rapidly expanding gas carried analyte molecules both downstream and upstream of the trap, which significantly contributed to band broadening in tubular traps. In addition, flattening reduced the distance analyte molecules had to travel before colliding with the wall, which resulted in increased trapping efficiency. The flattened traps produced injection bands onto the 2D column that were as narrow as 60 ms, and generated second dimension peak widths on the order of 120 ms at half height. This was a significant achievement considering that conventional, non-flattened trapping capillaries constructed in our laboratory generated 2D peak widths similar to those previously reported by Phillips and Liu [8] and Lee et al. [21], approximately 350 ms at half-height. Other geometrical modifications of the trap were explored; for example, the overall length the trapping capillary was decreased to 7.5 cm, and in independent experiments, the trapping zone lengths were decreased to 1.5 cm each. While this was conducted in an effort to further reduce the amount of gas available for expansion during desorption events, these designs provided no significant improvements when compared to the original prototype.

One of the drawbacks of resistively heated multi-stage thermal modulators is the presence of at least three electrical contacts to accomplish dual- or multi-stage modulation. Such contacts represent extraneous masses in contact with the trapping capillary and act as thermal sinks during analyte desorption. The cold spots that they create are detrimental to the GC × GC separation of semi-volatile compounds because they lead to inefficient desorption at the lower temperature of the cold spot, which subsequently causes peak broadening in the first dimension and tailing peaks in the second dimension. Fig. 3A illustrates that modulation of an *n*-alkane standard (C_8–C_{13}) with a flattened trapping capillary coated with the stationary phase along its entire length led to first dimension peak broadening becoming pronounced for C_{10} and increasing with decreasing volatility of the analytes. In addition, the first dimension retention times of the less volatile analytes were significantly increased due to the increased retention at the cold spots. Fig. 3B shows a raw 2D chromatogram obtained when the alligator clip serving as the middle contact was heated with a stream of hot air from a hair dryer during the analysis. In the absence of the cold spot, the associated band broadening was completely eliminated, and the 1st dimension retention times of the analytes became comparable to their retention times in conventional 1D separation under the same conditions.

While heating of the middle contact produced expected results, it was not considered a practical solution for field applications. In a first attempt to remediate the problem, the alligator clip was replaced with a short segment of the same Silcosteel tubing spot welded to the trapping capillary, which was then connected to the power supply. The significant reduction of the thermal mass of the middle contact led to an improvement in the chromatograms, but band broadening was not completely eliminated for the least volatile analytes (results not shown). An effective method to minimize the detrimental effects of the cold spots proved to be selective destruction of the stationary phase around all potential thermal sinks. This generated two areas with intact stationary phase, which are denoted in gray in Fig. 1.

The efficiency of removing the stationary phase in the trapping capillary had a profound effect on peaks observed in the second dimension. For trap prototypes in which the removal of the stationary phase around the electrical contacts was incomplete, 2D tailing was evident. This is illustrated in the raw GC × GC chromatogram in Fig. 4A, showing a single modulation "slice" of an *n*-C_{11} peak

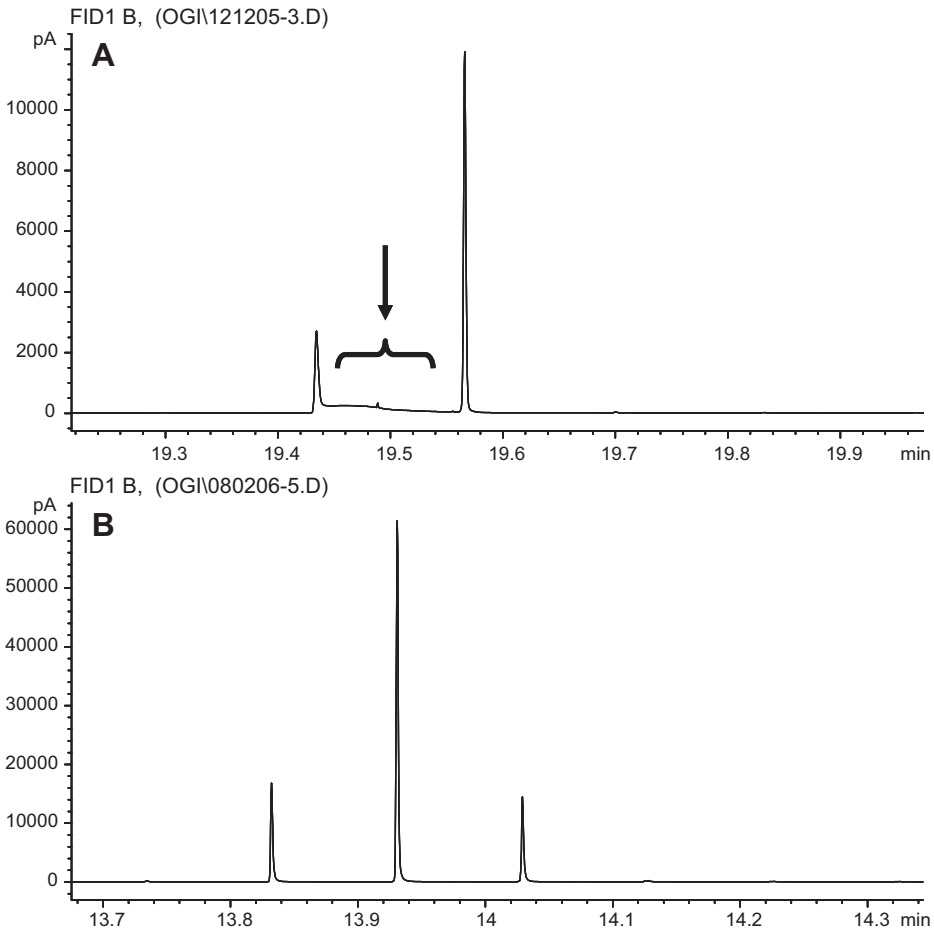

Fig. 5. The effect of forced cooling on modulation efficiency. (A) Part of a raw GC × GC chromatogram illustrating unsuccessful modulation of *n*-undecane with a modulation period of 9 s in the absence of forced cooling. Analyte breakthrough (arrow) was observed between the injection bands; (B) A chromatogram of the same standard obtained with forced cooling (using compressed air) with a modulation period of 6 s.

generated with a flattened trapping capillary subject to removal of the stationary phase with 13 consecutive discharge events. With this capillary, peak widths at half height for *n*-C_8 to *n*-C_{13} were approximately 140 ms, while analytes with boiling points higher than *n*-C_{16} produced peak widths too large for proper GC × GC analysis. In contrast, tailing was eliminated when the selective removal of the stationary phase in the trapping capillary was considered complete, and the peak width at half height was reduced to as little as ~60 ms for *n*-C_{18} (Fig. 4B) and ~100 ms for *n*-C_{40} (not shown).

The choice of the stationary phase thickness within the trapping capillary played an important role in the performance of the modulator. As a general rule, the thicker was the PDMS coating inside the trapping capillary, the better suited the interface was for the analysis of volatile components, and vice versa. Trapping capillaries with 3 μm and 1 μm PDMS stationary phase, as well as traps constructed from deactivated Silcosteel® tubing were tested. The latter were found to be particularly well suited for the analysis of semi-volatile compounds (see below), which were targeted by the 2D-TAG system [20]. The modulator made with deactivated tubing was also easier to construct, as it did not require the removal of the stationary phase around the electrical contacts.

3.2. Capacitive discharge power supply and cooling blower

Desorption of analytes from the trapping capillary requires rapid and reproducible discharge events from the power supply. Calibration of the power supply determined the discharge voltages required to heat segments of the trapping capillary with a wall thickness of 0.13 mm to the desired temperatures. Desorption temperatures above 325 °C (discharge voltage of 39.4 V) were considered a significant risk factor for thermal destruction and bleed of the intact PDMS phase within the trapping capillary. Hence, this upper limit was never exceeded. On the other hand, we found that desorption temperatures below ~275 °C (discharge voltage of ca. 36.6 V) generated broad and non-symmetrical injection bands onto the 2D column. In such experiments, the second dimension peaks widths were on the order of 250 ms at half height, and the peaks exhibited tailing. In addition, analytes with volatilities similar to and higher than *n*-C_{13} could not be efficiently desorbed from the trap, which led to band broadening in the first dimension. Therefore, the optimum desorption temperature range was determined to be between 275 and 325 °C.

Efficient modulation with heater-based interfaces depends on rapid heating and cooling of the trapping capillary [2,8]. While the capacitive discharge power supply ensured prompt and reproducible heating of the interface, the cooling times were excessively long. For example, when heated to 275 and 325 °C, the trapping capillary required 10 and 13.5 s to cool, respectively. Since modulation periods exceeding 13 s are impractical, forced cooling was applied to the interface. In initial experiments it was demonstrated that the use of a stream of compressed air to cool the trapping capillary reduced their cooling times to below 5 s in both cases.

The importance of forced cooling and its effect on modulation quality are depicted in Fig. 5. Without forced cooling, efficient modulation of the *n*-alkane standard could not be accomplished when alternately heating the two segments of the trapping capillary to

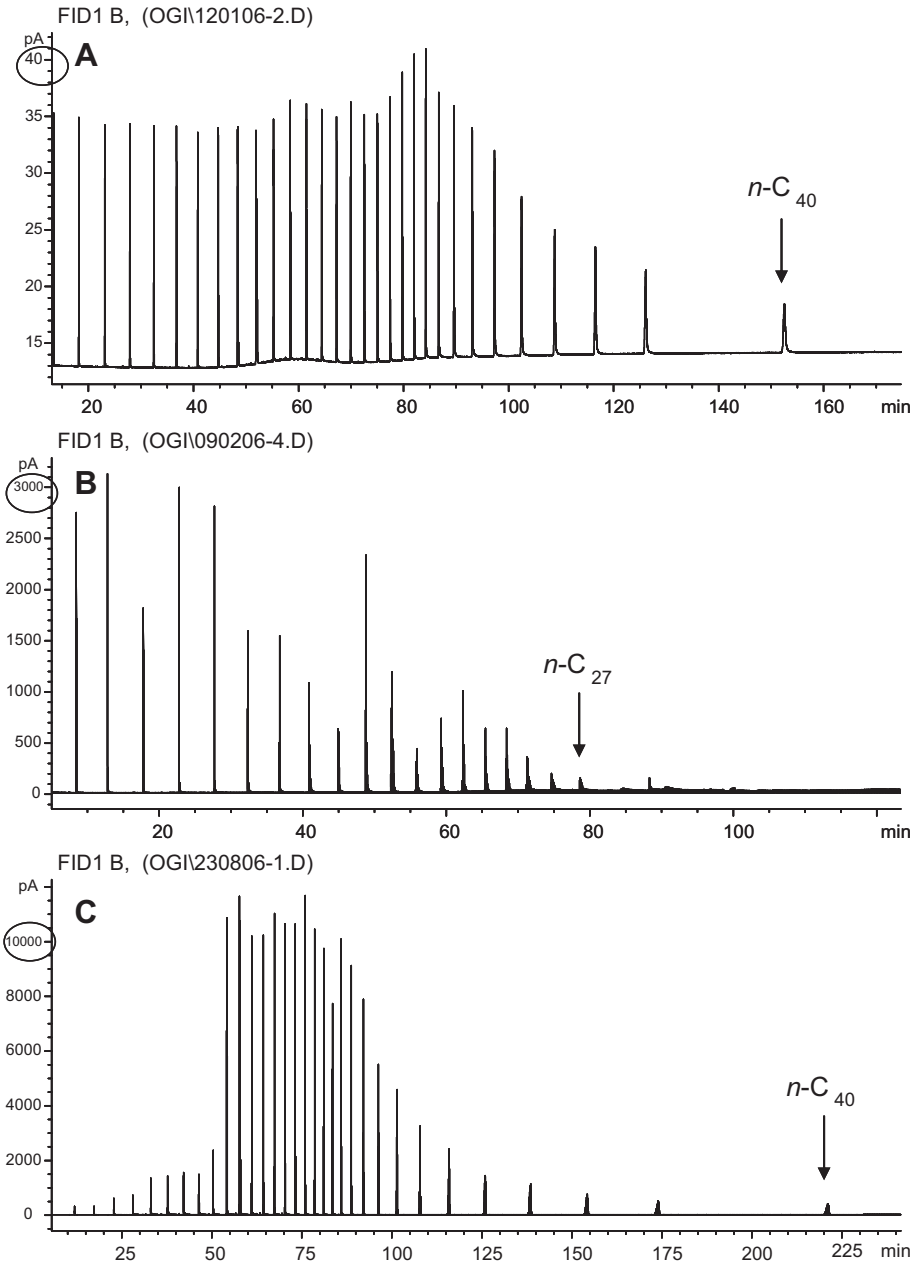

Fig. 6. Analysis of *n*-alkane standard (*n*-C_8 to *n*-C_{40} in chloroform; 35 °C (3 min) to 280 °C at 3 °C/min) to define the range of volatilities that can be modulated. (A) 1D-GC analysis (split ratio 10:1); (B) GC × GC analysis with a 3 μm PDMS film trap, the blower at the cool setting, and a split ratio of 5:1; (C) GC × GC analysis with a flattened deactivated guard Silcosteel® trapping capillary, the blower operated at the hot setting, and a split ratio of 2:1. Gains in sensitivity with the GC × GC method are circled.

275 °C. Even at a modulation period of 9 s, analyte breakthrough was observed in the form of a raised baseline between two slices in the unprocessed GC × GC chromatogram (Fig. 5A). When air from the laboratory compressed air line was used to cool the trapping capillary during modulation of the same *n*-alkane standard, analyte breakthrough was completely eliminated, as illustrated in Fig. 5B for a modulation period of 6 s. The incorporation of forced cooling therefore eliminated analyte breakthrough and simultaneously permitted the use of shorter modulation periods.

In field applications, the use of compressed air for cooling of the modulator might be cumbersome. Consequently, the use of blowers was considered as an alternative solution. Two types of blowers were tested, a standard hairdryer and a rotary blower. The former was found to be well suited for the analysis of the least volatile analytes (from ~*n*-C_{16} to *n*-C_{40}) when set on the hot air setting (110 °C); the latter was more efficient when working with more volatile analytes (see below).

Cooling of the modulator to room temperature proved insufficient when analyzing the most volatile compounds (from *n*-C_6 to ~*n*-C_8). This problem was overcome by using a vortex cooler, which was capable of generating cool air in the range from −20 °C to +20 °C when supplied with room temperature compressed air. In fact, the vortex cooler was capable of trapping analytes previously only modulated with cryogenic interfaces, a prime example of which is the separation of gasoline (see below).

3.3. Evaluation of the interface

Interface performance was evaluated by measuring injection band widths and 2D peak widths for the *n*-alkane standard mixtures. When uncoated deactivated fused silica tubing was used in

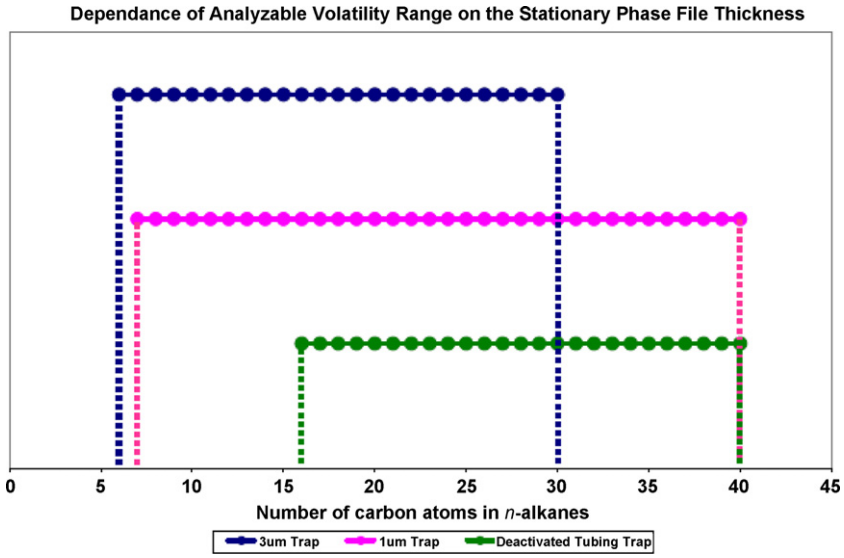

Fig. 7. Volatility ranges of the interface prototypes as a function of stationary phase film thickness. For each trapping capillary, compounds from the most volatile range were trapped by employing the vortex cooler, while the least volatile fraction was modulated with the hairdryer set on hot.

place of the second dimension column, injection bands as narrow as 60 ms at half height were obtained. Following the installation of an actual 2D column, the peak widths increased to 120 ms, largely due to peak broadening in the second dimension. Considering that Lee et al. previously reported peak widths in excess of 350 ms for interfaces utilizing resistively heated stainless steel capillaries [21], the result obtained in this study was very good. Furthermore, the results suggest comparable performance to some cryogenic modulators, since the LMCS system by Marriott et al. generated 2D peak widths on the order of 100 ms at half height [22,23].

The range of volatilities that can be efficiently modulated with the new interface was determined with a standard consisting of *n*-alkanes ranging from C_8 to C_{40}. The two parameters that were adjusted to permit flexibility with respect to the volatility range of analyzable compounds were the PDMS film thickness and the blower temperature (Fig. 6). The chromatogram in Fig. 6B indicates that trapping capillaries coated with 3 μm of stationary phase were not suitable for modulating compounds with volatilities below that of C_{27} *n*-alkane (marked), and earlier eluting compounds displayed detrimental peak broadening in the first dimension indicative of excessive retention in the interface. Consequently, trapping capillaries coated with thinner films were used for the analysis of less volatile mixtures. Interface models with 1 μm film thickness allowed the modulation of *n*-alkanes up to C_{38}. The chromatogram in Fig. 6C illustrates that simple trapping capillaries made of deactivated Silcosteel® tubing could efficiently modulate the analytes all the way up to *n*-C_{40}. It should be noted that the least volatile compounds were modulated while operating the blower on the hot setting.

Fig. 7 summarizes the trapping potential of each interface developed in our laboratory as a function of the stationary phase film thickness. For each modulator prototype, results generated with the cold and hot blower were combined – volatile fractions were analyzed with the vortex cooler, while the mid-volatiles and semi-volatiles with the blower on cool and hot air setting, respectively. The trapping capillary coated with a 1 μm thick stationary phase could be classified as a universal trap, as it was capable of modulating compounds with the widest volatility range.

Changes in cooling air temperature required to cover the full volatility range of the analytes were accomplished in the experiments described in this paper by changing the cooling air source, which was clearly impractical. However, this inconvenience was overcome in later research through the introduction of a simple heat exchanger for the supply air of the vortex cooler, which allowed temperature-programming of the cooling air synchronous with the GC oven temperature program. The details of this research will be described in an upcoming contribution [24].

The new modulator proved to be quite robust. Under laboratory conditions (~8 h a day), it could typically be used for up to 3 months without a significant drop in performance. The most typical failure mode involved detachment of the spot-welded middle contact after prolonged usage, caused by the strong electrodynamic forces occurring during the discharge.

3.4. Selected applications

Performance of the modulator was examined through the analysis of real-world complex mixtures. Fig. 8A presents the GC × GC separation of a mixture of PCBs, while Fig. 8B presents the chromatogram of a sample of transformer oil spiked with the same congeners. Even in the absence of MS detection, PCBs could be identified in transformer oil based on first and second dimension retention times and the overall pattern. Fig. 8C presents a GC × GC-FID separation of neroli essential oil, representative of other essential oils analyzed in our laboratory.

GC × GC analysis of petrochemical fractions is a convincing aid in illustrating the advantages of comprehensive two-dimensional gas chromatography over conventional 1D-GC methods. The interface developed in this study was successfully used for the modulation of gasoline, kerosene and diesel fuel (Fig. 9). While the analysis of diesel fuel has been illustrated with nearly all modulator types (see e.g. [2]), the separation of more volatile fractions, however, has traditionally been carried out with GC × GC instruments equipped with cryogenic modulators only. Even in this category, only those utilizing liquid N_2 were deemed suitable for the separation of gasoline [25,16]. In the analyses carried out with liquid CO_2-based interfaces, successful modulation of compounds with boiling points below that of *n*-octane has not been reported to the best of our knowledge [15,22,23]. In comparison, the modulator developed in this study was capable of efficient modulation of analytes with volatilities similar to or lower than *n*-hexane without any cryogens, which is a significant achievement in heater-based modulator design.

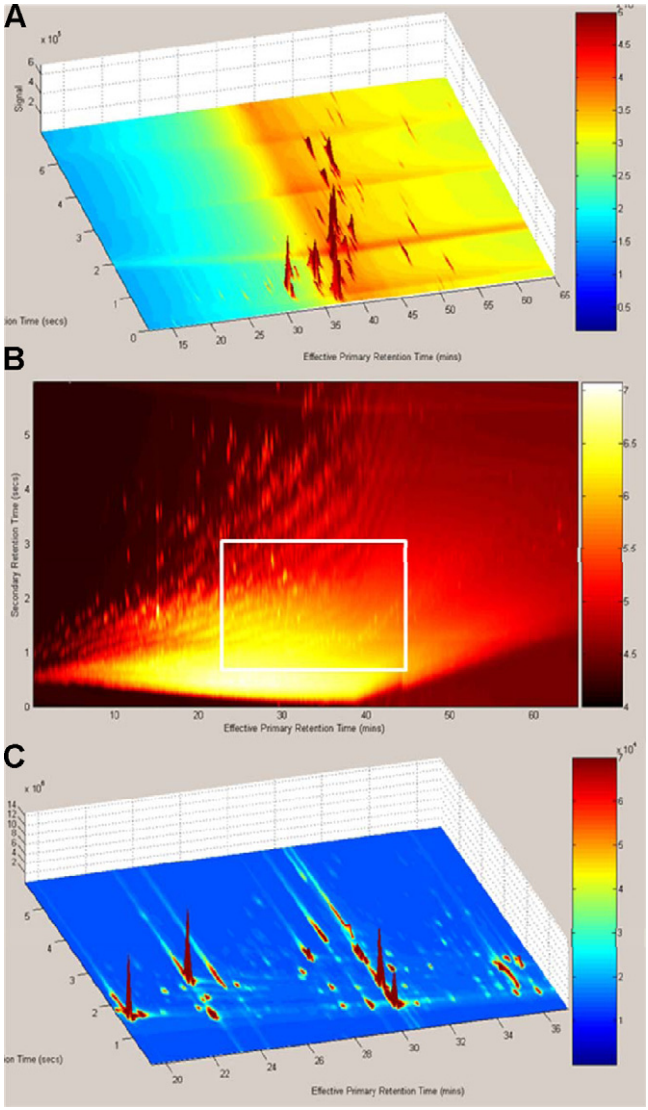

Fig. 8. GC × GC-FID analysis in splitless mode of (a) PCBs as a 1:1 mixture of Arochlor 1245/1260 (125–260° (45 min) to 270° (35 min) to 280° at 3 °C/min); (b) transformer oil spiked with a technical mixture of Arochlor 1245 (115–270° (25 min) to 280° at 3 °C/min). The area containing suspected congeners is marked with the white box; (c) 100% undiluted essential oil of neroli (70° (3 min) to 260° (40 min) to 280° (10 min) at 3 °C/min).

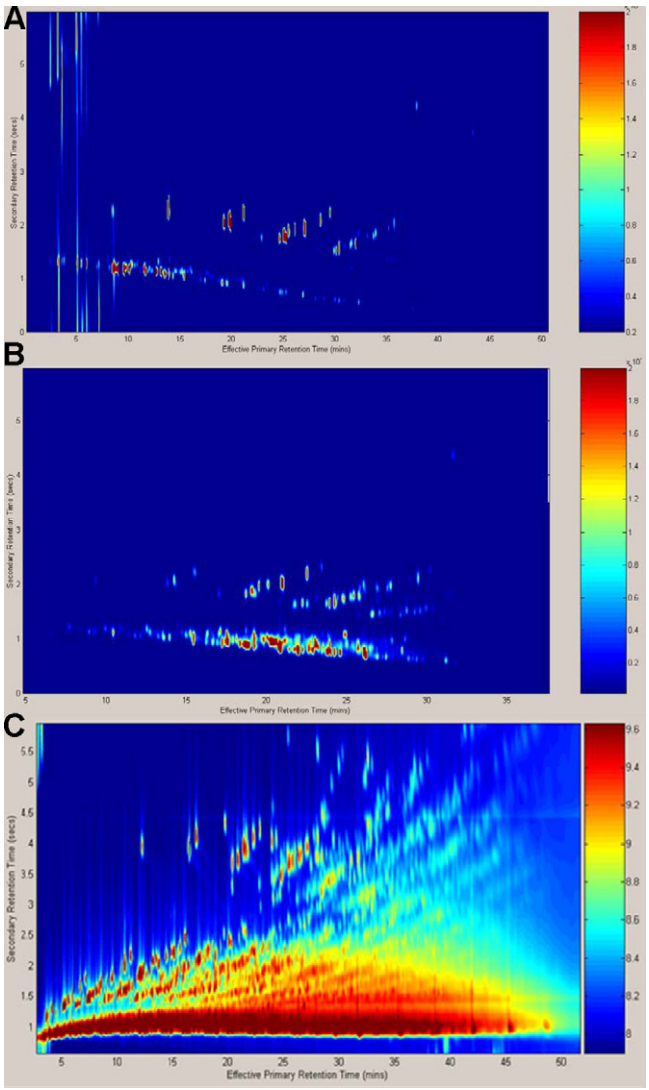

Fig. 9. GC × GC-FID separation of (a) gasoline (35° (3 min) to 260° at 3 °C/min); (b) kerosene (35° (3 min) to 260° at 3 °C/min); and (c) diesel fuel (70–260° (3 min) at 3 °C/min).

The most significant application of the interface has been the recently reported on-site monitoring of semi-volatile organics in air particulate matter in Berkeley, CA ($PM_{2.5}$) [20]. Briefly, the developed interface was integrated into an instrument designed for field analysis of semi-volatile organic compounds found in urban air particulate matter ($PM_{2.5}$), so-called 2D-TAG. Automated GC × GC analysis was carried out on ambient air samples every 2 h for a period exceeding 12 h. The study represented the first ever application of GC × GC instrumentation for the monitoring of organic aerosols in the field.

4. Conclusions

In spite of the general criticism of heater-based modulators, the interface presented in this paper has a great potential to once again play an active role in GC × GC separations. The two unique inventions presented in this paper, flattening of the trap and selective removal of the stationary phase, successfully eliminated the traditional drawbacks of resistively heated modulators. The narrow injection bands and the ability to efficiently modulate volatile mixtures suggest on-par performance with at least some cryogenic interfaces. A prime example of this was the analysis of gasoline in the absence of cryogenic agents. On top of that, the interface developed was suitable for the separation of analytes with very low volatilities (comparable to that of n-C_{40}), a task not achievable with all types of cryogenic modulators.

The simple and cost-effective operation of the interface, devoid of moving parts or cryogenic consumables, is an advantage that makes the modulator suitable for both laboratory and field analysis. The operational costs of the interface equipped with the vortex cooler are significantly lower than those of existing cryogenic systems.

Recently the design of the modulator has been further simplified through elimination of one heating stage (i.e. single-stage operation). The results of this research will be presented in an upcoming contribution [24].

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