Stacked Injection with Low Thermal Mass Gas Chromatography for PPB Level Detection of Oxygenated Compounds in Hydrocarbons

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Abstract

The presence of oxygenated compounds in light hydrocarbons can have a negative impact in manufacturing processes and on the quality of products produced. The development of an analytical technique termed "stacked injection" has been reported earlier. With this technique, sensitivity in the parts-per-billion (ppb) range for oxygenated compounds can be achieved, even with a flame ionization detector; however, there are drawbacks for this approach that limit its overall effectiveness. A new, improved analytical technique has been developed that not only addresses the shortcomings encountered, but offers markedly higher analytical performance. The new concept employs multidimensional gas chromatography (GC) with low thermal mass GC. With this new approach, throughput improvements of up to 5 times, range extension of solutes amenable for this analysis of up to nC_{16} alcohol, and ppb levels of detection for oxygenated compounds are achieved. Apart from alcohols, this technique is successfully employed for the ppb level analysis of other classes of oxygenated compounds, such as ethers, aldehydes, and aromatics.

Introduction

The presence of oxygenated compounds in light hydrocarbon products can have a negative impact on the quality of products produced, such as ethylene, as well as down-stream final products like polyethylene. Until recently, monitoring of oxygenated compounds at the sub parts-per-million (ppm) level has been difficult, if not impossible, for the following reasons: (*i*) complicated valving configurations are required to "heart-cut" and concentrate oxygenated compounds from the hydrocarbon matrix (1,2). (*ii*) The lack of a selective detector that has a high degree of sensitivity for oxygenated compounds. For example, an atomic emission detector's detection limit for oxygen at 777 nm is only approximately 5 to 10 ppm under optimum conditions, making it unsuitable for said application. The detection limit of an oxygen flame ionization detector is even worse, at the hundreds of ppm level (3–6). Mass selective detection in selective ion monitoring mode provides improved sensitivity for most compounds but is of limited effectiveness for primary alcohols because of the lack of mass fragmentation. (*iii*) Solvent venting exit and programmable temperature vaporization techniques have been found to be unreliable for very volatile polar compounds like methanol or acetaldehyde (7).

We had reported earlier on the development of an analytical technique termed "stacked injection", where the analysis is conducted by performing successive injections of the same sample on a highly selective column such as the CP-Lowox (Varian, Middelburg, the Netherlands) (8). Because of the selectivity of this column, light hydrocarbon matrices of the samples elute rapidly from the column, whereas oxygenated compounds, from the sum of all of the injections, are trapped when the oven is at a low temperature. The oxygenated compounds are then refocused and elute as one Gaussian peak upon temperature programming. Enhancement of the sensitivity is proportional to the number of injections made. Although this technique is very simple to practice, requires no additional hardware, and delivers the high sensitivity required, there are drawbacks for this approach that limit its overall effectiveness. The drawbacks include: (*i*) the coupling of trapping temperature to the oven initial temperature because the column itself is also used as the trapping medium; (*ii*) the trapping medium and the analytical column cannot be individualized, leading to compromises in chromatographic performance; (*iii*) the coupling of the rate of desorption to the rate of temperature programming; and (*iv*) the narrow range of oxygenated compounds this technique can engage because of the high degree of retention, yet low solute capacity for oxygenates of the column used for stacked injection.

The advent and commercialization of low thermal mass gas chromatography (LTMGC) offered new performance enhancements, which are ideal for use with fast GC (9). LTMGC technology has been described in great detail by Mustacich et al. (10–14).

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In addition, LTMGC offered novel analytical strategies for conducting chromatography (15). LTMGC can independently control up to four chromatographic modules in one single bench-top chromatograph such as the Agilent HP-6890 series with unprecedented heating rate and cool down time (10–17). These features make LTMGC an ideal platform to implement multidimensional gas chromatography (MDGC). The incorporation of MDGC would allow both the trapping and analytical columns to be individually optimized for the chromatography required, thereby, improving overall system analytical performance.

This paper summarizes the development of a new, stacked injection approach based on MDGC and LTMGC, chromatographic performance of the new method, and potential applications (18).

Experimental

An Agilent HP-6890A GC (Wilmington, DE), equipped with a split/splitless injector and a flame ionization detector (FID) (Agilent) was used. A RVM Scientific A-68 LTMGC system (Santa Barbara, CA) was also installed. This A-68 system was configured with two modules as follows: the first module, a 2-m × 0.53-mm i.d., Varian CP-Lowox, was connected directly in series to the second module, a 25-m × 0.32-mm i.d., 1.2 µm Varian CP-Sil 52CB.

The connection between the two modules was first made by press-fit connectors and later augmented by the employment of Valco ultra low mass unions (Houston, TX) to prevent leaks caused by multiple thermal cycles. Both modules were in the 5-in. wide tray format. Figure 1 shows a picture of the apparatus used, and the GC conditions used, unless otherwise stated in the individual chromatograms, were as follows: GC, Agilent HP-6890A GC. Column and temperature profile were: host oven temperature, 220°C; Module 1, 2-m × 0.53-mm i.d., CP-Lowox with a temperature profile of 90°C, 300 s, 600°C/min, 300°C, 120 s; and Module 2, 25-m × 0.32-mm i.d., 1.2 µm, CP-Sil 52CB with a temperature profile of 50°C, 300 s, 20°C/min, 180°C, 150 s. The injector conditions were: split/splitless injector, split mode, SGE focus liner; temperature, 250°C; split ratio, 5:1 with split flow at 50 mL/min; injection size, 1 µL; system, Transcendent pressurized liquid injection system (PLIS) (Transcendent Enterprise, Alberta, Canada). The carrier gas used was hydrogen at 20 psig, with an average flow velocity estimated at 135 cm/s. The flame ionization detector conditions were: temperature, 300°C; auxiliary gas, nitrogen at 25 mL/min; air, 400 mL/min; and hydrogen, 30 mL/min.

Figure 1. Picture of an Agilent HP-6890A used for stacked injection with LTMGC. Note the two modules mounted on the oven door. Module 1, 2-m × 0.53-mm i.d., CP-Lowox connected in series to Module 2, 25-m × 0.32-mm i.d., 1.2 µm CP-52CB.

Samples were introduced either manually with a Hamilton 701N syringe (Reno, NV) or via Transcendent Enterprise's unheated PLIS (19). Test standards and solvents were obtained from Aldrich, Supelco, VWR, and Fisher Scientific, and samples used for testing were obtained from the local hydrocarbon production facilities.

Results and Discussion

Principles of operation of stacked injection with LTMGC and MDGC

To determine ppb levels of oxygenated compounds in hydrocarbons using this approach, an analysis was conducted by: (*i*) performing successive injections of the same sample on the LTMGC's first chromatographic module, typically a very short, yet highly selective column, such as the CP-Lowox. In this first dimension of the MDGC system, the column acts as a trap for oxygenated compounds when kept at a low temperature. (*ii*) Once the hydrocarbon matrices have eluted, the first chromatographic module was heated rapidly to transfer the trapped solutes onto the second chromatographic module, which is in series with the first module. (*iii*) Separation of oxygenated compounds was carried out in the LTMGC's second chromatographic module (second dimension), a CP-Sil 52CB.

The flexibility of this analytical approach was clearly illustrated. Unlike the classical stacked injection approach, where the analytical column was also the trapping medium and compromises had to be made between effectiveness in trapping solutes of interest versus capability to elute heavier boiling point solutes, in this new approach, the most ideal trapping medium and analytical column can be individually selected to deliver the best chromatographic performance.

Retentive porous-layer open-tubular columns can be used to enhance trapping efficiency, and a wide variety of high-performance wall-coated open-tubular columns can be employed as analytical columns to obtain the best possible separations.

As an example, for the analysis of oxygenated compounds in light hydrocarbons with boiling points lower than *n*-hexane, a column set involving the use of a 2-m × 0.53-mm i.d. CP-Lowox was tested as a trapping medium (first dimension) and a 25-m × 0.32-mm i.d., 1.2 µm CP-Sil 52CB as an analytical column (second dimension). The CP-Lowox offers the highest degree of trapping efficiency for oxygenated compounds (6). Depending on separation requirements, the CP-Sil 52CB can be easily substituted with other commercially available analytical columns with

different polarities such as Varian's VF-1MS, VF-5MS, VF-35MS, or VF-17MS or Agilent's DB-XLB or DB-1701. As a result, the new analytical approach was highly tunable and adaptable to the applications encountered.

Analytical parameters optimization

The GC conditions employed for the separation of solutes of interest in the second dimension was analogous to the normal process used for the optimization of conventional GC (i.e., to achieve the best separation of critical pairs in the minimum amount of time).

In addition, successful implementation of this technique required careful optimization of the conditions used for the trapping medium (first dimension).

Column length used for trapping purposes

An adequate length should be chosen to provide sufficient solute capacity for the retention of analytes of interest. Too short of a length will result in overloading of the trap, causing distorted or split peaks, but too long of a length can cause severe peak broadening because of the slow mass transfer from the trap to the analytical column. Previous experiments showed that a 2-m × 0.53-mm i.d., Varian CP-Lowox was sufficient for the application described.

Initial trapping temperature and hold time

To obtain the best chromatography, careful optimization of trapping temperature was required. The temperature must satisfy the relatively rapid elution of the matrix, and it must retain the solutes of interest. For the configuration described for the analysis of oxygenated compounds in hydrocarbons, a temperature of no lower than 20°C lower than the boiling point of the matrix was recommended to keep the matrix from condensing on the surface of the trap. Figure 2 shows chromatograms of 1-octene at 50°C, 75°C, and 110°C. With the initial temperature at 50°C, 1-octene was condensed and retained on the surface of the Lowox, resulting in a severe baseline perturbation. When temperature programming was engaged (2 min into the analysis), the rise in temperature aided in establishing a linear isotherm. This results in 1-octene leaving the Lowox quickly, depicted as the sharper peak in the chromatogram. This effect was less severe but definitely noticeable at 75°C. When the temperature approaches that of the boiling point of 1-octene (boiling point 122°C) as shown in

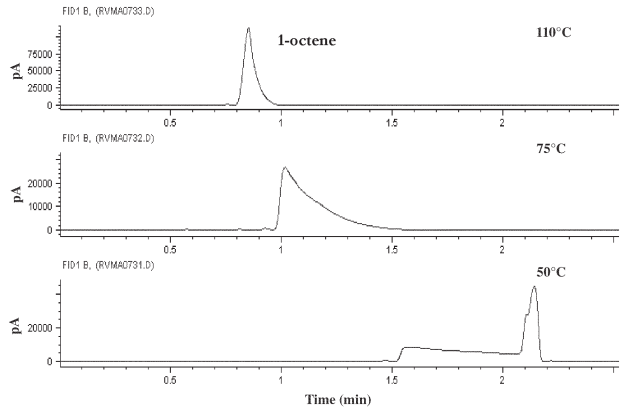

Figure 2. Analytical parameter optimization, the effect of initial trapping temperature with 1-octene. Unless otherwise stated, chromatographic conditions are listed in the text.

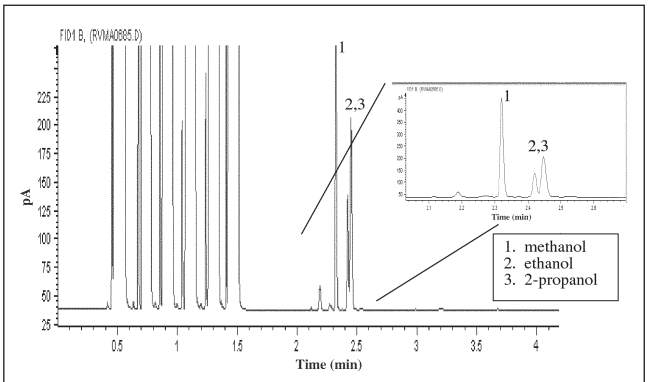

Figure 3. Analytical parameter optimization, the effect of trapping temperature (oxygenated compounds in *n*-hexane). A stack of six 1-µL injections, each containing 5 µL/L of methanol, ethanol, and 2-propanol. Note the excellent peak symmetry of hexane and the lack of band migration of alcohols. Unless otherwise stated, chromatographic conditions are listed in the text.

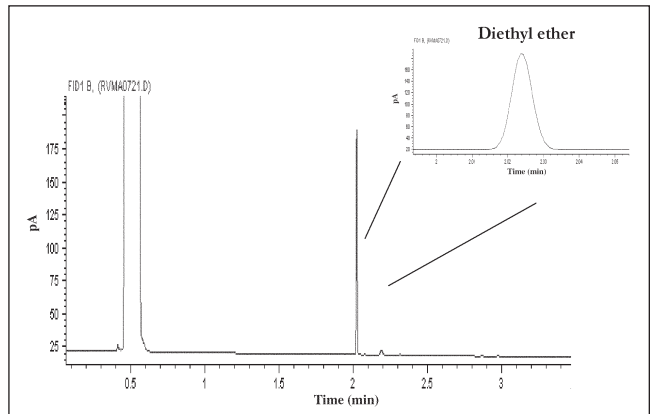

Figure 4. Analytical parameter optimization, the effect of initial trapping temperature on 100 µL/L diethyl ether in *n*-hexane at 75°C. Unless otherwise stated, chromatographic conditions are listed in the text.

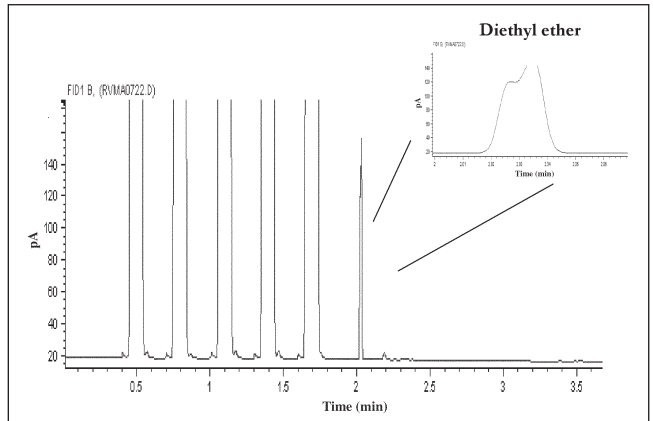

Figure 5. Analytical parameter optimization, the effect of initial trapping temperature on 100 µL/L diethyl ether in *n*-hexane at 70°C (stack of five injections). Note that band migration of diethyl ether resulted in split peak.

the case of 110°C, much better peak symmetry can be obtained as illustrated in Figure 2. For this reason, an initial temperature that causes condensation of the matrix to occur should be avoided.

In contrast, Figure 3 shows a stack of six injections of 5 µL/L each of methanol, ethanol, and 2-propanol in hexane (boiling point 69°C) using the same system with an initial temperature at 110°C, which was substantially higher than the boiling point of hexane. Note the excellent peak symmetry obtained for *n*-hexane and the absence of band migration of alcohols as indicated by the single Gaussian or symmetrical oxygenated peaks despite the high initial temperature.

The initial temperature hold time of the trapping column should be long enough to account for the number of stacked injections to be made, and the peak symmetry should be verified to ensure solute band migration has not occurred in the trap. Figure 4 shows a single injection of 100 µL/L of diethyl ether (boiling point 35°C) in *n*-hexane at a trap temperature of 75°C. Under the same conditions, Figure 5 shows a stack of five injections of the same sample. Notice that band migration of diethyl ether has occurred, resulting in a split peak. This situation can be mitigated easily by lowering the trapping temperature by 20°C as shown in Figure 6. Under this new condition, diethyl ether and other oxygenated compounds such as methanol, 2-propanol, and methyl octyl ether can be focused and held up to 4 min (240 s) as shown in Figure 7. For this length of time, a stack of 10 injections could be made.

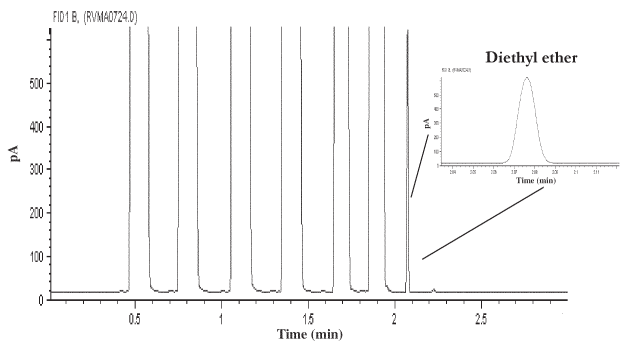

Figure 6. Analytical parameter optimization, the effect of initial trapping temperature on 100 µL/L diethyl ether in *n*-hexane at 50°C (stack of six injections). Note that band migration of diethyl ether has been eliminated by lowering the initial trapping temperature by 20°C.

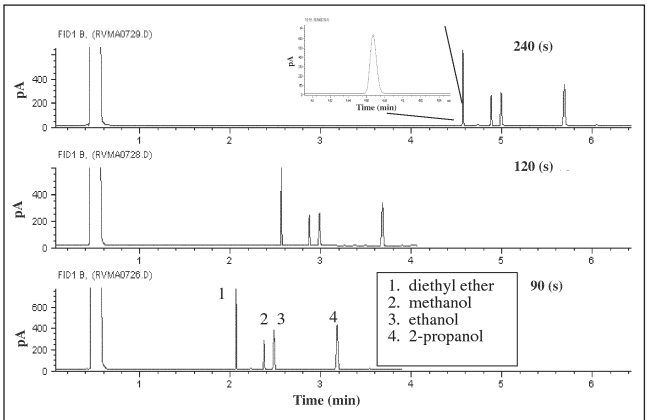

Figure 7. Analytical parameter optimization, the effect of initial hold time. Injection of 1 µL of 100 µL/L of diethyl ether, methanol, 2-propanol, and methyl octyl ether in *n*-hexane. Note that in up to 240 s of hold time, no band migration was observed, even for the fastest moving solute, diethyl ether (see inset).

Rate of desorption

A fast desorption rate was preferred to transfer the trapped solutes onto the analytical column rapidly. Although LTMGC can operate with a very fast heat up rate of up to 1800°C/min, it was not always necessary to operate under such extreme conditions. Under the configuration proposed, the CP-Lowox column has two functions: to act as a trap and as a separating medium, coarse as the separation might be because of the length of column used. In the second dimension, the CP-Sil 52CB performed as a classical

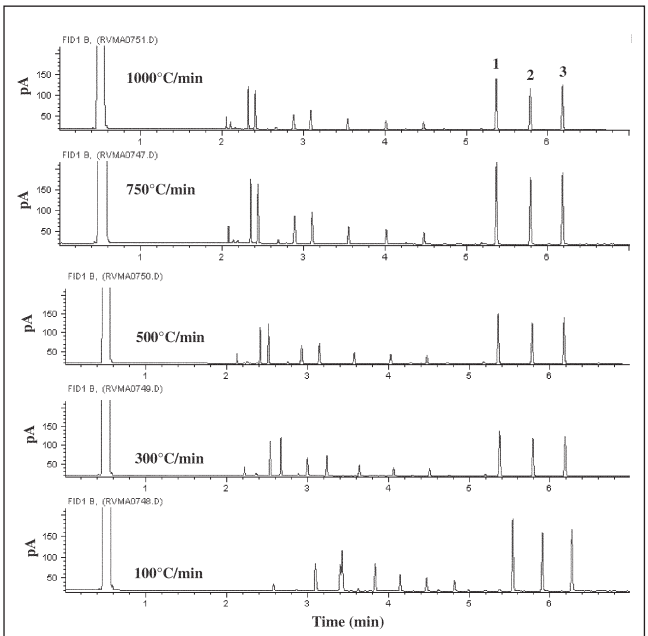

Figure 8. Analytical parameter optimization, rate of desorption of nC_9OH (peak 1), $nC_{10}OH$ peak 2, and $nC_{11}OH$ (peak 3). Unless otherwise stated, chromatographic conditions are listed in the text.

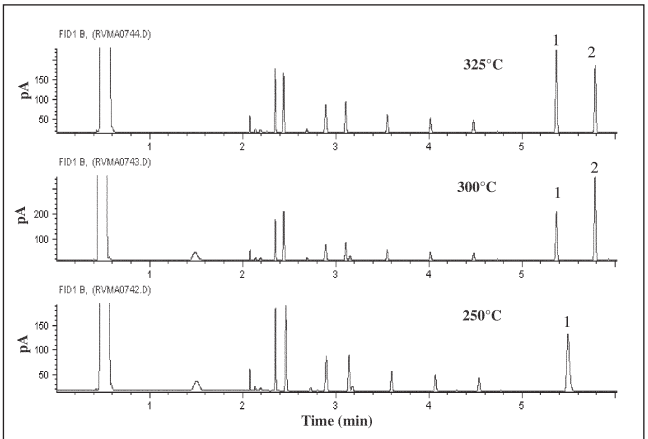

Figure 9. Analytical parameter optimization. Final trapping temperature of 250°C, 300°C, and 325°C for nC_9OH (peak 1) and $nC_{10}OH$ (peak 2). Unless otherwise stated, chromatographic conditions are listed in text.

analytical column. If the goal was to operate the CP-Lowox as a rapid injection device and trap, it was important to make sure the rate of desorption was fast enough to ensure good band transfer.

In Figure 8, the effect of Lowox as a separating medium is clearly illustrated as the rate of desorption was varied from 1000°C/min to 100°C/min. The retention time of the solutes, especially for the low retention time compounds, was higher at lower heating rates such as 100°C/min, 300°C/min, and 500°C/min. No noticeable retention time reduction for these solutes was observed once the heating rate exceeds 750°C/min. At 750°C/min and beyond, the influence of Lowox on the separation of the trapped solutes diminishes. Therefore, for fastest mass transfer under the flow rate used, 750°C/min was determined to be the optimum heating rate. If improved selectivity of the overall chromatographic system was required, a lower rate could be used at the expense of slower mass transfer.

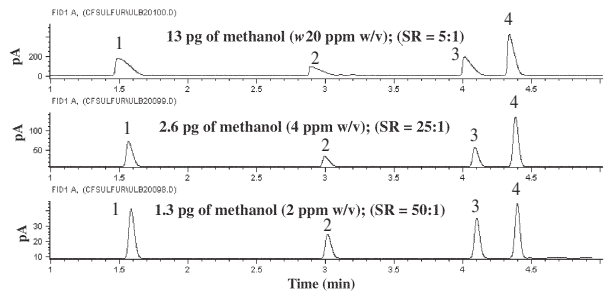

Figure 10. Analytical performance and applications, the various split ratios of methanol (peak 1), ethanol (peak 2), 2-propanol (peak 3), and acetone (peak 4) in hexane on 2-m × 0.53-mm i.d., CP-Lowox.

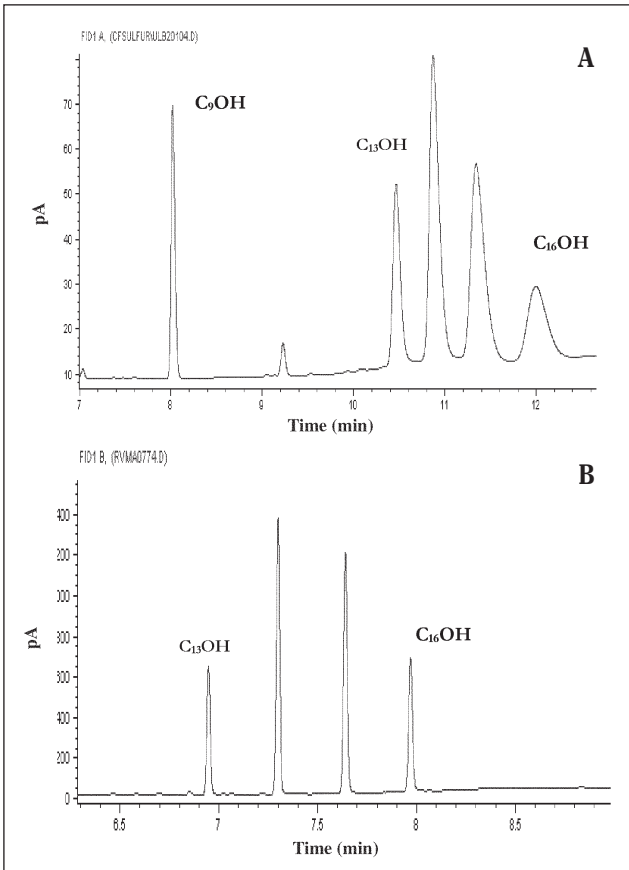

Figure 11. Analytical performance and applications, the classical stacked injection versus stacked LTMGC. Analysis of *n*-alcohols with classical stacked injection (single Lowox column) (A) and analysis of *n*-alcohols stacked injection with MDGC–LTMGC (nC_9OH not added) (B).

Final trapping temperature and hold time

The final temperature was optimized such that the last solute of

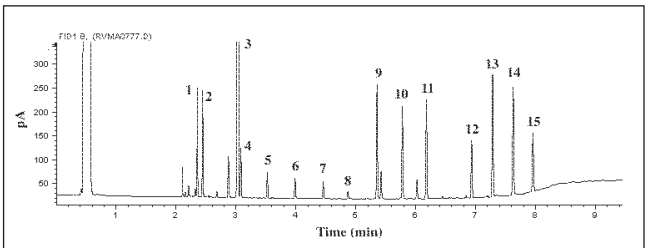

Figure 12. Analytical performance and applications, analysis up to nC_{16} alcohols. A single injection of methanol (peak 1), 2-propanol (peak 2), ethyl benzene (peak 3), butanol (peak 4), pentanol (peak 5), hexanol (peak 6), heptanol (peak 7), octanol (peak 8), nonanol (peak 9), decanol (peak 10), undecanol (peak 11), tridecanol (peak 12), tetradecanol (peak 13), pentadecanol (peak 14), and hexadecanol (peak 15) in hexane using the approach described. The range extension of solutes is clearly shown in this chromatogram.

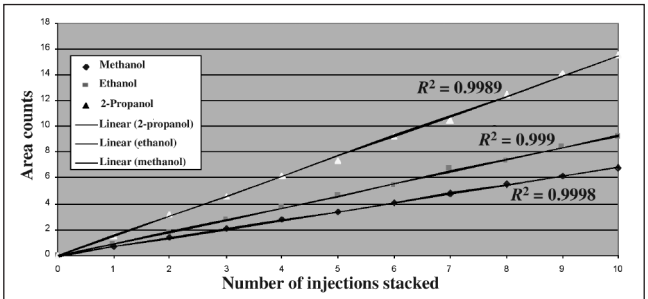

Figure 13. Staked injection by PLIS–LTMGC–FID. Various numbers of injections of 1 µL each verses area counts 5 ppm (w/v) each of methanol, ethanol, and 2-propanol in hexane.

Table I. Precision Data of PLIS–LTMGC–FID

Run	Methanol area	Ethanol area	2-Propanol area
1	0.71	0.90	1.52
2	0.69	0.91	1.51
3	0.70	0.89	1.50
4	0.71	0.89	1.53
5	0.72	0.90	1.52
6	0.70	0.90	1.51
7	0.72	0.92	1.51
8	0.71	0.90	1.50
9	0.69	0.87	1.52
10	0.72	0.92	1.48
Average	0.7073	0.9008	1.51
Std. Deviation	0.0117	0.014778	0.0141421
RSD* (95%)	3.64	3.61	2.06

* Relative standard deviation.

interest is desorbed and transferred. Either slightly higher temperature or longer duration ensured the trap was clean for the next analysis. Figure 9 shows chromatograms of a mixture of solutes ranging from diethyl ether to decanol, obtained using final temperatures of 250°C, 300°C, and 325°C. Partial desorption of solutes occurred at 250°C as shown by the broad peak of nonanol and the missing decanol peak. At 300°C and 325°C, all of the solutes of interest were removed. Note the excellent peak symmetry of nonanol and decanol at both 300°C and 325°C desorption temperatures.

Analytical performance and applications

In classical stacked injection (1), a 10-m × 0.53-mm i.d., CP-Lowox column was used as both the first and second dimension. Because of the nature of the stationary phase employed and as the name implied, the CP-Lowox has low solute capacity for oxygenated compounds. In addition, with the 10-m column, limitation of the range of solutes that can be analyzed was observed. For example, C_6 alcohols elute in 20 min at 290°C, and the chromatographic profiles obtained showed some degree of tailing as a result of poor mass transport and excessive retention (1).

The low capacity for oxygenated compounds was demonstrated in Figure 10 with a 2-m CP-Lowox column. In this example, the split ratios were varied to increase the solute loading for methanol, ethanol, and 2-propanol from 1.3 to 13 pg. At a mere 13 pg per solute, severe peak distortion for alcohols was observed. Despite this limitation, in the new stacked injection technique, a 2-m × 0.53-mm i.d., CP-Lowox column was used with the main purpose of trapping oxygenated compounds. Separation of solutes was performed by the CP-Sil 52CB column. The higher chromatographic performance offered by the CP-Sil 52CB allowed C_{16} alcohols to elute in approximately 8 min at 250°C. Lower eluting temperature was usually a desirable feature in GC.

Furthermore, individual dimensions of the chromatographic system can be optimized for improved chromatographic performance. Figure 11 shows the separation of C_9, C_{13}, C_{14}, C_{15}, and C_{16} alcohols on a classical stacked injection system employing only a 2-m × 0.53-mm i.d., Varian CP-Lowox column. Note the broad peak shape because of poor mass transfer. In contrast, excellent peak symmetry was obtained for the same solutes with MDGC–LTMGC. The improvement in peak symmetry, because of more effective mass transfer and column solute capacity, aided in the improvement of overall detection limit. As shown in Figure 12, using this configuration up to $nC_{16}OH$ can elute symmetrically.

The possibility of lowering the detection limit of the analytical system by making multiple injections of the same sample per method described is demonstrated in Figure 13. This figure shows the relationship between the numbers of stacked injections versus area counts. The data obtained was regressed linearly. A correlation coefficient of at least 0.999 or better for methanol,

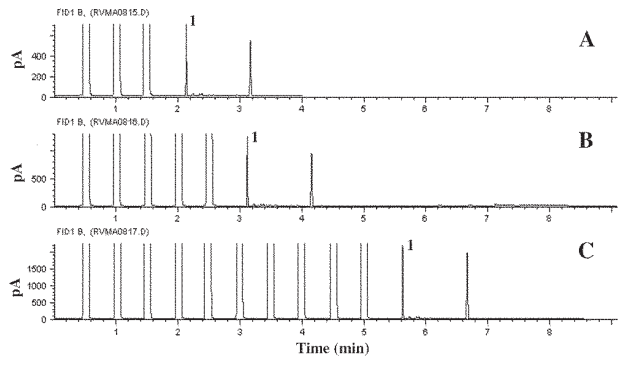

Figure 14. Analytical performance and applications, the analysis of methyl tertiary butyl ether (MTBE) (peak 1) in hexane, 3 injections (A), 5 injections (B), and 10 injections (C). GC conditions listed in text

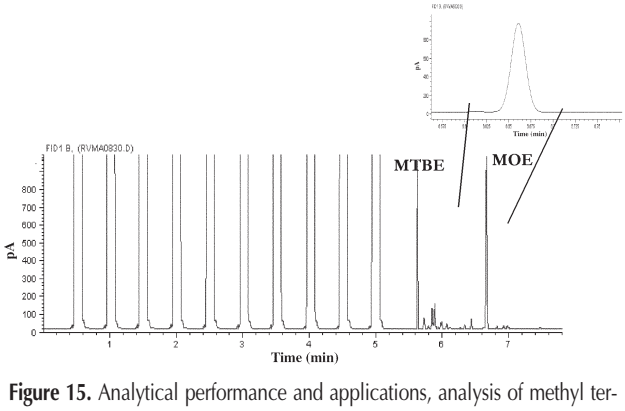

Figure 15. Analytical performance and applications, analysis of methyl tertiary butyl ether (MTBE) and methyl octyl ether (MOE) in hexane (10 injections). GC conditions listed in text

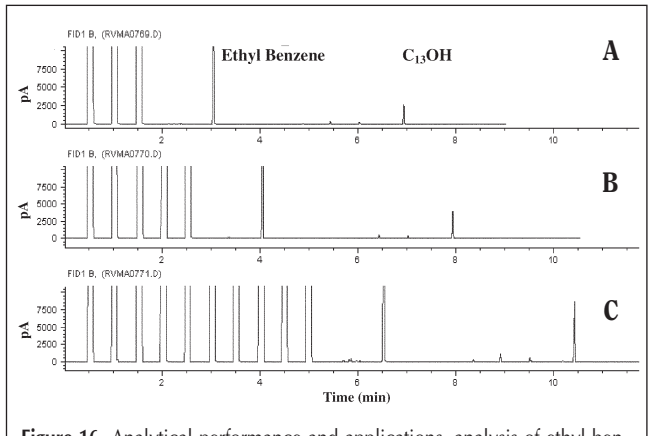

Figure 16. Analytical performance and applications, analysis of ethyl benzene and tridecanol in hexane, three injections (A), five injections (B), and 10 injections (C). GC conditions listed in text.

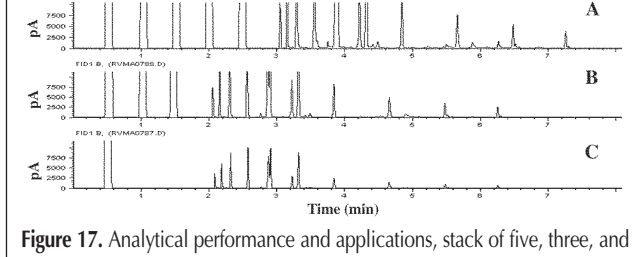

Figure 17. Analytical performance and applications, stack of five, three, and one injection, respectively, of C_2 to C_7 *n*-aldehydes in *n*-hexane, three injections (A), five injections (B), and 10 injections (C). GC conditions listed in the text.

ethanol, and 2-propanol was achieved. It was observed that good peak symmetry was obtained even for lower retention time solutes such as methanol for up to 10 stacked injections. Because of the quantitative nature of the method, by injecting 10 times within 1 analysis, the detection limit of the analytical system was lowered one magnitude. Although it was feasible to conduct analysis, which stacks more than 10 injections, there were three constraints: the gain in sensitivity was approaching diminishing return; the quality of chromatography might be compromised resulting in split peak; and the incurrence of analytical time. Table I lists results from 10 analyses, in which each analysis was stacked 10 times, of methanol, ethanol, and 2-propanol in *n*-hexanes using PLIS. A relative standard deviation of 3.7% or less was observed, and the concentrations obtained were cumulative of the number of injections made.

Using the technique described, it was feasible to attain ppb detection limits for oxygenated compounds such as alcohols. The high sensitivity of the method was further illustrated in the analysis of methyl tertiary butyl ether (MTBE). Figure 14 shows a stack of three, five, and 10 injections of a standard, and Figure 15 demonstrates the detection of 1 µL/L MTBE in hexane.

The applicability of this technique is not limited to just alcohols. Figures 16–18 show a series of stacked injections of one, three, five, and 10 injections of aromatics, aldehydes, and ketones, respectively. Figure 19 shows an overlay of stacks of three, five, and 10 injections of compounds commonly found in chemical industries such as 4-vinylcyclohexene, ethyl benzene, styrene, iso-propylbenzene, *n*-propylbenzene, 4-cyanocyclohexene, 2-ethylhexylacrylate, undecane, 2-ethylhexyl acetate, 2-ethylhexyl alcohol, and 4-phenylcyclohexene. Clearly, aromatic compounds such as these can be selectively enriched and measured at low detection limits. With its detection limit at the ppb range, stacked injection using the configuration described can be used as a complementary technique with headspace or even purge and trap analysis, especially when combined with mass spectrometry in selective ion monitoring mode.

Furthermore, LTMGC offers much faster cool down time when compared with conventional GC. In comparison with the classical stacked injection technique, which took 25 min to accomplish (1), only 5 min of analysis time was required with LTMGC, representing a throughput improvement of about five times.

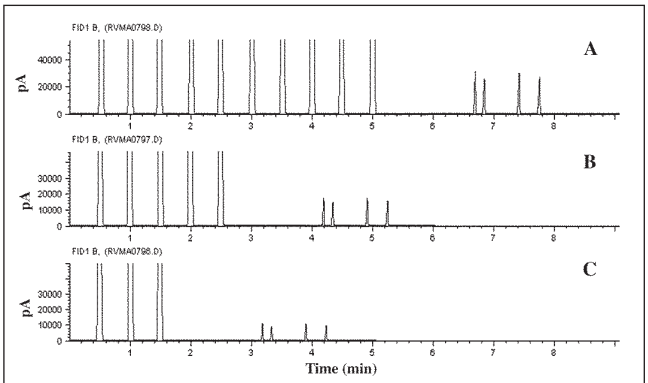

Figure 18. Analytical performance and applications, stack of 10, five, and three injections, respectively, of C_4 to C_7 *n*-ketones in hexane, three injections (A), five injections (B), and 10 injections (C). GC conditions listed in text.

Limitations

Although the CP-Lowox was highly selective towards oxygenated compounds, it did exhibit retention characteristics for components heavier than nC_{10} hydrocarbons. To avoid potential chromatographic interference(s) and false-positive identification, structural elucidation of analytes of interest with either a mass spectrometer or a mass selective detector is recommended. Should a coelution occur, it can be eliminated by reoptimizing the GC conditions of the analytical column or by selecting a column with different selectivity than the one employed. Alternatively, a less retentive trap than the CP-Lowox can also be employed.

Another limitation was that because of the high sensitivity of the technique, there was possible chromatographic interference either from impurities in the solvents, chromatographic system (i.e., carrier gas, septum, and liner), or sample. It was recommended that a blank run be made to rule out this possibility. If in doubt, the identification of the solutes should be confirmed by alternative means such as structural elucidation techniques.

Because of the limitation of the firmware used, the Agilent 7683 autosampler cannot be used for stacked injection with a split/splitless injector. It can, however, perform this task with a PTV injector. Alternatively, one can use a third party autosampler such as the LEAP Combi-PAL or PLIS.

Conclusion

A new and improved analytical approach based on stacked injection LTMGC and MDGC has been successfully developed for the analysis of oxygenated compounds in hydrocarbons. When compared with the classical stacked injection technique, the new analytical approach not only addresses the shortcomings cited, but also offers markedly higher flexibility in controllable variables.

In terms of sample introduction, the concept of stacked injection remained unaltered in that solutes are introduced successively with a gas sampling valve or a pressurized liquid injection valve, PLIS to a split/splitless injector and then onto a highly selective column used as a trapping medium.

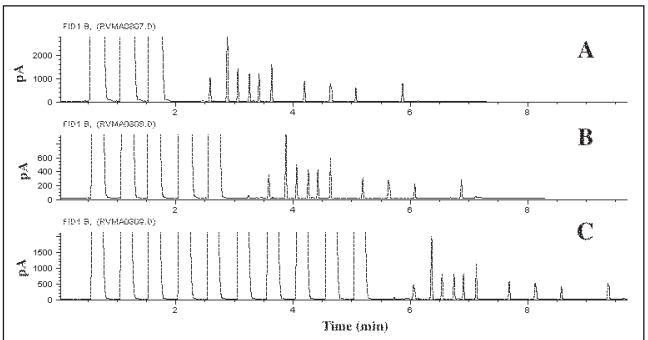

Figure 19. Analytical performance and applications, impurities (common organic compounds in chemical industries) stack of three injections (A), five injections (B), and 10 injections (C), respectively. Elution order: 4-vinylcyclohexene, ethyl benzene, styrene, *i*-propylbenzene, *n*-propylbenzene, 4-cyanocyclohexene, 2-ethylhexylacrylate, 2-ethylhexyl acetate, 2-ethylhexyl alcohol, 4-phenylcyclohexene. GC conditions are listed in text.

LTMGC, a radically new disruptive technology to achieve ultra fast temperature programming with an unprecedented cool down time and capability to control multiple GC column modules on a single GC was exploited to decouple the trapping medium from a separate analytical column, enabling enhanced throughput, chromatographic efficiency, resolution, and solute capacity.

With this new approach, a throughput improvement of up to 5 times, range extension of solutes amenable for this analysis of up to nC_{16} alcohols, and ppb levels of detection for oxygenated compounds were achieved. Apart from alcohols, this technique has been successfully employed for the ppb level analysis of other classes of oxygenated compounds such as ethers, aldehydes, and aromatics.

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