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High-speed, low-pressure gas chromatography–mass spectrometry for essential oil analysis

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ABSTRACT

Analysis of parsley and fennel essential oils was performed by using low-pressure gas chromatography–mass spectrometry (GC–MS). The low-pressure instrument configuration was achieved by fitting a GC–MS instrument with a 530 μm I.D. capillary column and an appropriate capillary restrictor at the inlet of the column. Comparison of the performance of the low-pressure GC–MS setup was made with fast GC–MS using a narrow-bore capillary column. By comparing the two approaches side-by-side the benefits of low-pressure GC–MS for characterisation of moderately complex essential oils comprising less than 50 detectable components can be fully appreciated. Although efficiency is sacrificed, the improved sample capacity of the 530 μm I.D. column leads to higher peak intensities and in-turn better mass spectral library matching thus providing highly satisfactory results.

1. Introduction

There are a variety of practical routes for achieving high-speed separations of complex samples [1] and many of them have been employed for essential oil analysis. Most commonly 10 m × 100 μm I.D. columns (with appropriately reduced stationary phase film thickness) have been employed in place of 25 m × 250 μm I.D. columns [2] and it has been shown many times this approach leads to a significant speed gain while preserving resolution [3]. In a similar way Mondello et al. [4] demonstrated fast analysis of lime essential oil using a 5 m length of 50 μm I.D. capillary with a 0.05 μm stationary phase coating. Lime oil analysis was achieved in around 90 s by employing the fastest possible temperature program rate of the GC oven (50–150 °C in 75 s, 150–200 °C in 43 s, 200–250 °C in 55 s) as well as a higher than optimum average linear carrier gas velocity of 120 cm/s. An additional approach for achieving faster analysis includes direct resistively heated column GC [5] which, by marrying rapid temperature programming (up to 20 °C/s) with fast data acquisition (using flame ionization detection) and high split ratio [6] can lead to essential oil analysis times between 40 and 100 s [5,6].

Fast analysis approaches often try to maintain efficiency, however having highlighted that the efficiency of a capillary column often exceeds analytical requirements, Bicchi and coworkers investigated the use of short 250–320 μm I.D. columns with appropriate selectivity for the analysis of rosemary (*Rosmarinus officinalis* L.) and chamomile (*Matricaria recutita* L.) essential oils [7]. Both of these essential oils are considered as moderate complexity samples, and effective analysis was performed by substituting the standard (*ca.* 25 m) capillary column comprising around 150,000 theoretical plates with 5 m columns comprising 20,000–50,000 theoretical plates. A 5% phenyl- 5% vinyl-polydimethylsiloxane stationary phase was used for the separation of chamomile oil but lacked the selectivity to adequately resolve the key components of rosemary oil. Thus a polyethylene glycol stationary phase was used in its place. Analyses were performed 5–10 times faster than the corresponding analysis with conventional columns.

Our primary interest in fast GC relates to its application in comprehensive multidimensional gas chromatography (GC × GC) where fast operation of the second dimension columns is particularly important [8]. Short (*ca.* 1.5 m) narrow-bore (100 μm I.D.) columns have been utilised in more than 80% of published GC × GC applications [9] in order to produce chromatograms over the required retention window, which is typically 2–8 s. However, by considering the events taking place inside GC × GC columns, Beens and coworkers concluded that 100 μm I.D. second dimension columns may not be the best choice for GC × GC [9]. The use of a narrow second dimension column leads to very high average linear velocity in the second dimension column; high resistance to flow in these narrow columns leads to a high midpoint pressure, which in-turn reduces the optimum average linear carrier gas velocity in the first dimension column [9]. The combined result of these phenomena is slow total analysis time coupled with reduced second column efficiency. Thus we are interested in fast GC approach that utilises columns with low flow resistance. In practical terms, this means the use of wide bore and/or shorter columns. This topic

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is supported by outstanding theoretical and experimental works [10–12].

A straightforward means of operating 530 μm I.D. columns at reduced pressure was realised by de Zeeuw et al. [11]. This method directly couples the outlet of the column to a mass spectrometer and the entire length of the column is operated at very low pressure. A restrictor has to be applied at the inlet side of the system to ensure that the column head pressure can be precisely maintained by electronic pressure control. Later van Deursen et al. [12] explored three options for producing the restriction at the inlet of the wide-bore column, including (1) the use of a micro-injection valve (2) the use of a supercritical fluid chromatography restrictor and (3) the use of a narrow capillary, as employed by de Zeeuw and coworkers. Comparable performance was reported for the latter two options, both being slightly better than the micro-injection valve, which was thought to contribute to band broadening by additional dead-volume effects. Optimum average carrier gas velocity $\bar{u}$ is proportional to the average binary gas-phase diffusion coefficient and both of these vary inversely with pressure, so the low-pressure GC arrangement opens opportunity for fast separations. Low-pressure GC–MS has been used for analysis of lanolin steryl esters [13], pesticide analysis [14–17] and for environmental contaminants [18–21]. The authors know only of a single study of low-pressure GC–MS with 530 μm I.D. columns for essential oil analysis [22] in which the analysis of *Turnera diffusa* (Ward.) Urb. essential oil was performed in 3 min and compared to conventional analysis using a 30 min temperature program with a 200 μm I.D. column.

It is noteworthy that van Deursen and coworkers specifically stated "A distinct disadvantage of wide-bore columns is that the plate-number is not very high. This system therefore is not very suitable for complex separations" [12]. While this point may have discouraged the application of low-pressure GC for essential oil separations, we have found that highly satisfactory results are achievable. Thus the present study investigates the benefits of low-pressure GC for the analysis of essential oils, in terms of peak capacity, separation speed, and sample capacity. The work described here is important because it compares wide-bore columns with the more accepted narrow-bore columns in fast GC–MS analysis. Only by directly comparing the performance of these two separation systems side by side, as we have done in the present study can these benefits be truly appreciated. Translation of these findings to GC × GC–MS with 530 μm I.D. second dimension columns is currently underway and this will be reported in future correspondence.

2. Experimental

All analyses were performed using a Shimadzu QP2010 Plus GC–MS equipped with split/splitless injector and AOC20 autoinjector (Shimadzu Scientific Instruments Oceania, Mt Waverley, Australia). A 12 m × 530 μm I.D. capillary column coated with a thin layer (0.25 μm film thickness) of 5% phenyl polysilphenylene–siloxane (BPX-5) stationary phase (SGE Analytical Science, Ringwood, Australia) was employed throughout for the low-pressure GC separations. A 0.60 m × 100 μm I.D. length of deactivated fused silica tubing (SGE Analytical Science) was connected to the inlet of the analytical column using a stainless steel union and appropriately sized SilTite metal ferrules (SGE Analytical Science). The narrow-bore restrictor column was inserted a few mm into the wide bore analytical column to ensure that there were no dead-volume effects caused by the union. Narrow-bore GC–MS separations were performed using a 10 m × 100 μm I.D. capillary column coated with a thin layer (0.10 μm film thickness) of 5% phenyl polysilphenylene–siloxane (BPX-5) stationary phase (SGE Analytical Science). The chromatograms presented here were acquired using the following instrument settings. The injector temperature was 250 °C in all cases. An injection volume of 1.0 μL was delivered using the AOC20 autoinjector and a split ratio of 250:1 was employed for all injections. The carrier gas was helium and the average linear carrier gas velocity used was 89 cm/s for the 530 μm I.D. column and 33 cm/s for the 100 μm I.D. column. The MS transfer line was set at 250 °C and the MS ion source was set at 200 °C for all analyses. Full-scan mass spectra were acquired

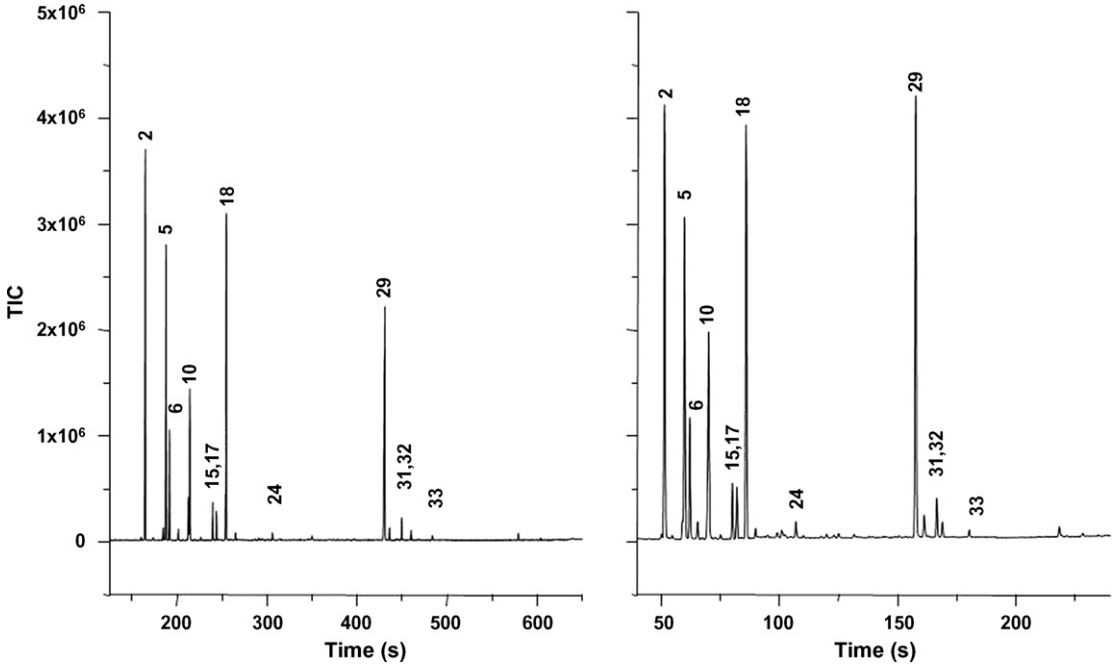

Fig. 1. GC–MS (TIC) chromatogram of parsley essential oil acquired using a 10 m × 100 μm I.D. BPX-5 capillary column (left) and using a 12 m × 530 μm I.D. BPX-5 capillary column (right). Peak numbers refer to those in Table 1. Expanded chromatograms with complete annotation can be provided by the corresponding author upon request.