Comprehensive Two-Dimensional Gas Chromatography with Flame Ionization and Time-of-Flight Mass Spectrometry Detection: Qualitative and Quantitative Analysis of West Australian Sandalwood Oil

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Abstract

The use of gas chromatography (GC)–mass spectrometry (MS), GC–time-of-flight MS (TOFMS), comprehensive two-dimensional GC (GC×GC)–flame ionization detection (FID), and GC×GC–TOFMS is discussed for the characterization of the eight important representative components, including *Z*-α-santalol, *epi*-α-bisabolol, *Z*-α-*trans*-bergamotol, *epi*-β-santalol, *Z*-β-santalol, *E,E*-farnesol, *Z*-nuciferol, and *Z*-lanceol, in the oil of west Australian sandalwood (*Santalum spicatum*). Single-column GC–MS lacks the resolving power to separate all of the listed components as pure peaks and allow precise analytical measurement of individual component abundances. With enhanced peak resolution capabilities in GC×GC, these components are sufficiently well resolved to be quantitated using flame ionization detection, following initial characterization of components by using GC×GC–TOFMS.

Introduction

With the Australian standard for west Australian sandalwood essential oil currently under review (1), it is timely to consider some chromatographic analysis technologies available for fulfilling the requirements of successful characterization of the representative components in this complex oil. A widely used practice in the quality assurance analysis of essential oils involves the location of characteristic components within the separation space using gas chromatography (GC)–mass spectrometry (MS), followed by quantitation with GC–flame ionization detection (FID). Owing to the occurrence of peak overlap in these chromatograms, subsequent analysis using a capillary column with a dissimilar stationary phase is typically required to improve the separation of specific components in order to provide suitable analytical measurement of peak abundance (2). The abundance of each characteristic component within the sample will usually be compared with a recognized standard to measure the general quality of the sample.

It is recognized however that peak resolution in single dimension analysis is often inadequate to provide satisfactory analytical precision of individual components' abundances. There is often a requirement to use a multidimensional hyphenated analysis such as GC–spectroscopic detection, or coupled column methods the likes of liquid chromatography–GC or GC–GC, for the analysis of more complex samples. Suitable hyphenated techniques for essential oil analyses are GC–MS and GC–Fourier transform IR spectroscopy. The characteristic vibration frequencies of functional groups of organic compounds makes the IR spectrum the simplest, most rapid, and often the most reliable means for assigning a compound to its class, and the value of MS is usually related to its identification power over nonspectroscopic detection methods used in GC. Electron-induced ionization (EI) is the most widely used ionization technique for GC–MS analysis of essential oils, and the use of computerized MS of the experimental data to reference MS libraries is common. Although quadrupole and ion-trap mass analyzers are the most widespread instrument types available for GC–MS, recent technological advancemtents have lead to increasing popularity of time-of-flight (TOF) instrumentation. TOF mass spectrometry (TOFMS) has a higher spectral acquisition rate than quadrupole and ion-trap mass analyzers because the TOFMS does not involve the use of a scanning field for mass measurement. This offers improved performance in terms of sensitivity and speed (3). Having a maximum spectral acquisition rate of 500 spectra/s, the TOFMS instrument used in the present investigation offers a number of distinct advantages. The primary advantage here is the compatibility of TOFMS with fast GC. Further advantages of TOFMS lie in the ability of the instrument software to perform automated peak finding, spectral deconvolution, and component identification (4). Spectral deconvolution is possible because TOFMS produces constant ion-abundance ratios across the chromatographic pro-

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file (no spectral skewing) as the mass flux into the ion source varies.

An effective coupled-column alternative for the analysis of complex samples is the use of comprehensive two-dimensional GC (GC×GC), which offers a significantly greater peak capacity and, therefore, the opportunity for improved resolution of target components in a single analysis (5). Owing to enhanced peak separation capabilities achieved in GC×GC analysis, a genuine opportunity exists to perform quantitative analysis of complex samples using the more favorable FID response, with its well-known response factor relationship. Characterization of individual components within the 2D-separation space can be performed by quadrupole MS (6,7) or the preferred technique of fast data-acquisition TOFMS. It is known that very good first- and second-dimension retention time reproducibility is achieved in GC×GC-FID analysis, using the longitudinal cryogenic modulation approach (8,9), and it is expected that equivalent performance should be possible in GC×GC–TOFMS analysis. Dallüge et al. presented performance data for GC×GC–TOFMS recently (10). The suitability of GC×GC–TOFMS to characterize complex samples has been reported in the analysis of cigarette smoke (11,12) flavor mixtures in food (13), amongst other applications (14–17). Provided that GC×GC–FID and GC×GC–TOFMS chromatograms are highly correlated with one another, it will be possible to locate target analytes within the 2D-separation space using MS detection and quantitate them using FID.

The present study outlines such a comparative study for west Australian sandalwood (*Santalum spicatum*) essential oil and compares the GC×GC result with analysis using extracted ion GC–MS approaches as well as briefly investigating the performance of spectral deconvolution of GC–TOFMS data.

Experimental

Samples

West Australian sandalwood oil (*Santalum spicatum*) was provided by Australian Botanical Products (Hallam, Australia) and was diluted 1:10 in *n*-hexane prior to analysis. The injection volume in all experiments was 0.2 µL.

Instrumentation

All analyses were performed using Agilent 6890 GCs (Agilent Technologies, Palo Alto, CA). The GC temperature program was 60°C (held for 0.2 min) to 246°C at 3°C/min in all cases. All analyses were performed with the GC electronic pressure control operated in constant pressure mode. The use of constant flow maintained a constant mass flow of carrier into the MS, although it also provided adjustment for the increasing solute diffusion coefficients as temperature increased.

GC–MS

GC–MS analysis was performed using either an Agilent 5973MSD or a Pegasus III TOFMS (Leco Corporation, St. Joseph, MI) instrument. The GC–mass selective detector (MSD) was fitted with a 5% phenyl polysilphenylene-siloxane (BPX-5) capillary column (0.25-µm film thickness). The column dimensions were 30 m × 250 µm. The GC–TOFMS was fitted with a composite SolGel-polyethylene glycol (Solgel-wax) capillary column (0.25-µm film thickness). The column dimensions were 30 m × 250 µm. Both columns were from SGE International (Ringwood, Australia). In all experiments, He carrier gas was supplied at a nominal initial flow of 1 mL/min. The split/splitless injector was operated at 220°C, in split mode, with a split flow of 20 mL/min. The MS transfer line temperature in the MSD was 280°C, the quadrupole temperature was 150°C, and the source temperature was 230°C. The MS was operated in scan mode from 41–415 u. The detector voltage was –2235 V. The MS transfer line temperature in the TOFMS instrument was 250°C, and the source temperature was 200°C. Data were acquired between 41–415 u. The detector voltage was –1560 V.

GC×GC–FID

The GC was fitted with a 5% phenyl polysilphenylene-siloxane (BPX-5) first-dimension capillary column (0.25-µm film thickness), and a polyethylene glycol (BP-20) second dimension capillary column (0.10-µm film thickness). The dimensions of the first- and second-dimension columns were 30 m × 250 µm and 0.5 m × 100 µm, respectively. Both columns were from SGE International. The two columns were coupled using a zero dead volume capillary connector (SGE International). H_2 carrier gas was supplied at 15.8 psi. The split/splitless injector was operated at 220°C, in split mode, with a split flow of 200 mL/min. The FID data acquisition rate was 100 Hz, and the detector temperature was 250°C.

GC×GC–TOFMS

All analyses were performed using a Pegasus III TOFMS. The GC was fitted with the same column set described for GC×GC–FID analysis. The two columns were connected as mentioned previously. He carrier gas was supplied at 53 psi. The split/splitless injector was operated at 220°C, in split mode, with a split flow of 124 mL/min. The MS transfer line temperature was 250°C, and the source temperature was 200°C. Data were collected over a mass range of 41–415 u at a nominal data acquisition rate of 125 Hz. The detector voltage was –1560 V. The outlet pressure of the second dimension column was maintained at 18 psi using a modified MS No-Vent Interface (SGE International).

Modulation

A longitudinally modulated cryogenic system (Chromatography Concepts, Doncaster, Australia) was retrofitted to each instrument. The modulation period of 4.0 s was applied in all analyses, and the thermostatically controlled cryogenic trap was maintained at approximately 0°C for the duration of each analysis.

Results and Discussion

Qualitative analysis of west Australian sandalwood oil

GC retention and MS base peak details of the eight important characteristic components of *Santalum spicatum* essential oil, according to the draft of Australian Standard for oil of sandalwood

[AS 2112-2003 (1), which has been proposed to supersede AS 2112-1977 (18)] are listed in Table I. Linear temperature programmed retention indices (LTPRI) reported in Table I are approximately 10–20 index units higher than the respective reference values in Adams' compilation (19). The following discussion outlines the use of GC–MS, GC–TOFMS, GC×GC–TOFMS, and GC×GC–FID for the analysis of the listed components.

GC–MS

The characteristic components were located by first plotting an extracted ion chromatogram of the base ion for each component. Individual components were identified by comparison of their mass spectra with the Adams terpene library (19), and their retention indices were compared with Adams' (19) reference data. The total ion chromatogram (TIC) for the whole *Santalum spicatum* oil is presented in Figure 1, and a set of extracted ion chromatograms is shown in Figure 2. A list of the ions used for the preliminary screen of the whole chromatogram is given in Table I. Significant peak-overlap of the eight characteristic components was observed in the GC–MS (TIC) chromatogram, which was acquired using a 5% phenyl polysilphenylene-siloxane stationary phase. In fact only *Z*-α-santalol and *Z*-lanceol were observed as single component peaks in the TIC (see Figure 1, peaks 1 and 8). It should be noted that the TIC result does not guarantee the absence of peak overlap in single-column GC–MS analysis for these apparent single component peaks. Very few of the components in this sample exhibit truly unique mass fragment ions, and it is difficult to quantitatively de-convolute the peaks by plotting extracted ion chromatograms. *epi*-α-Bisabolol and *Z*-α-*trans*-bergamotol (Figure 1, peaks 2 and 3) are particularly problematic because they exhibit severe peak overlap (R_s = 0.17) and have few obvious unique ions. This will cause difficulty in quantitating these characteristic components for quality assurance purposes. Two extracted ion chromatograms are overlaid in Figure 3 to illustrate the extent of peak overlap of these components. This figure shows that the selected ions are likely to be unsuitable for quantitation of the respective components. The 204 *m/z* ion can serve as a suitable mass to locate the position of *epi*-α-bisabolol, but its relatively small abundance in the spectrum reduces the effectiveness of its use as a quantitation mass. The 145 *m/z* ion is useful for showing presence of the coeluting *Z*-α-*trans*-bergamotol peak, but this ion is also present in *epi*-α-bisabolol and will be unsuitable as a quantitation mass.

Table I. Important Characteristic Components in Oil of Sandalwood with Their Respective Retention Indices on Two Different Stationary Phase Columns*

	Component	LTPRI† BPX-5	LTPRI Solgel-Wax	Base ion (u)
1	*Z*-α-Santalol	1691	2316	93
2	*epi*-α-Bisabolol	1707	2197	43
3	*Z*-α-*trans*-Bergamotol	1707	2328	93
4	*epi*-β-Santalol	1721	2377	94
5	*Z*-β-Santalol	1732	2391	94
6	*E,E*-Farnesol	1735	2333	69
7	*Z*-Nuciferol	1747	2477	119
8	*Z*-Lanceol	1781	2453	43

* The base ion is given for each component.
† LTPRI = linear temperature programmed retention index

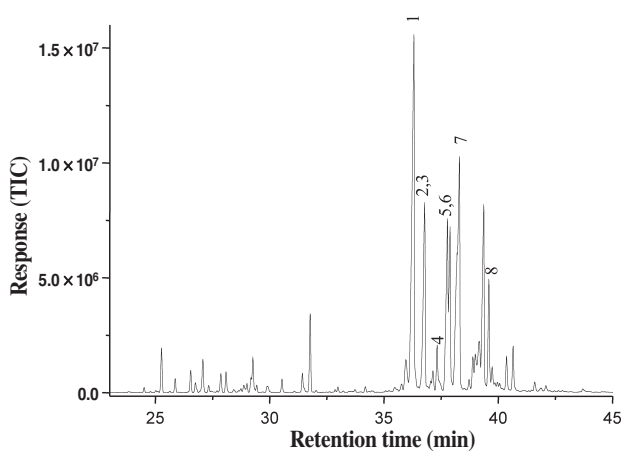

Figure 1. GC–MS TIC of *Santalum spicatum* essential oil using a 5% phenyl polysilphenylene-siloxane coated capillary column. For conditions, refer to the experimental section for all chromatograms.

GC–TOFMS

The separation of the characteristic components was marginally improved by the use of a polar polyethylene glycol

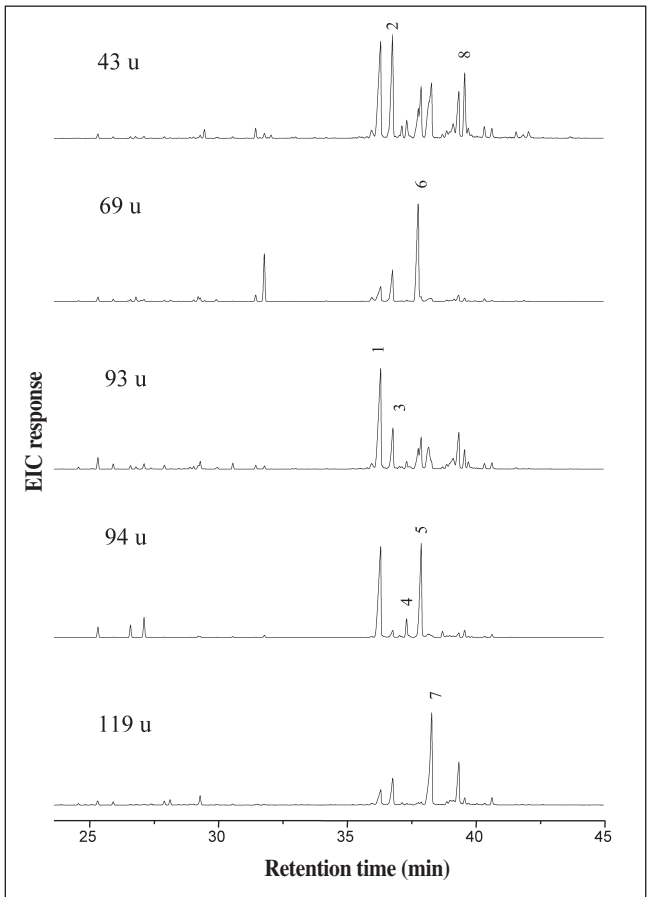

Figure 2. GC–MS extracted ion chromatograms (EICs) of *Santalum spicatum* essential oil using a 5% phenyl polysilphenylene-siloxane capillary column; selected mass ion indicated on each plot.

stationary phase column (Figure 4), in which case three of the eight characteristic components, *epi*-α-bisabolol (peak 2), *epi*-β-santalol (peak 4), and *Z*-β-santalol (peak 5) were reasonably well resolved from their neighboring components. The deconvoluted TIC response gives a signal that most closely resembles an FID response (20) and should also provide effective background correction. The performance of the instrument software for automated peak finding and spectral deconvolution was investigated. The ability of the TOFMS software to recognize overlapping peaks and apportion relative amounts of components where overlaps occur was hindered by the very close similarity of MS of the components eluting in the sesquiterpene region of the chromatogram. This is not surprising because it is well established that a great number of sesquiterpenes have identical or almost identical mass spectra. Greater (or complete) component resolution should still give more reliable quantitation.

GC×GC

A two-dimensional GC×GC separation offers a greater opportunity to resolve the target characteristic components into single component peaks and gives better insight into the number of true single component peaks that are (or should be) present in the one-dimensional column chromatogram. Overlapping components in the first dimension column will most often be separated in the second dimension column. Although every part of the sample is subjected to two different separations in a GC×GC analysis, by definition, the separation (resolution) obtained in the first dimension must be maintained (21). Thus, it is possible to directly compare the retention in a single-column GC–MS analysis with the first dimension retention time in GC×GC analysis,

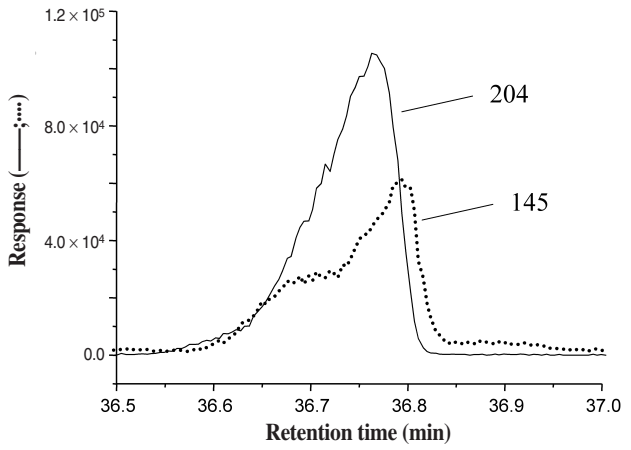

Figure 3. Overlay of an expanded section of two GC–MS (EIC) chromatograms of *Santalum spicatum* essential oil showing the overlap of *epi*-α-bisabolol and *Z*-α-*trans*-bergamotol. For the figure, (———) EIC 204 and (----------) EIC 145.

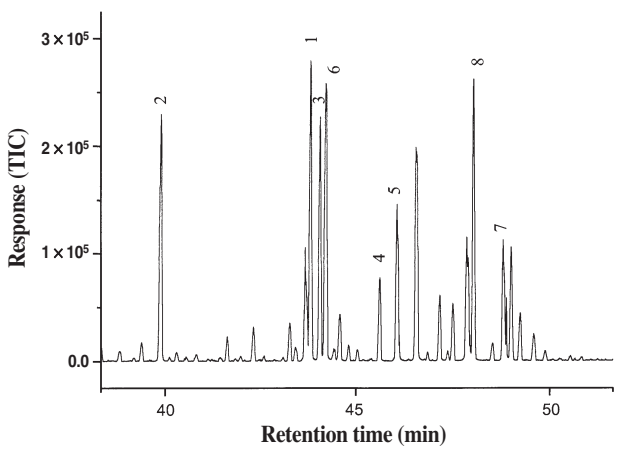

Figure 4. GC–TOFMS (TIC) chromatogram of *Santalum spicatum* essential oil using a polar SolGel + polyethylene glycol coated capillary column.

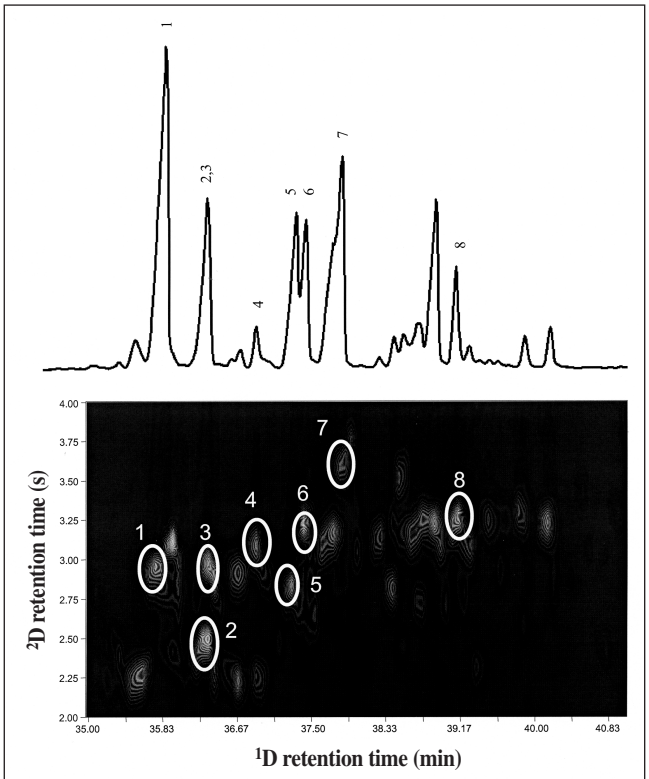

Figure 5. Comparison of an expanded GC–MS (TIC) chromatogram with the same region of the GC×GC–TOFMS (TIC) chromatogram for *Santalum spicatum* essential oil.

Table II. Measured Abundance of Each Characteristic Compound (as Determined Using GC×GC–FID)*

Component	Abundance (% area/area)	Library quality Match (/1000)
1 *Z*-α-Santalol	22	915
2 *epi*-α-Bisabolol	4.8	938
3 *Z*-α-*trans*-Bergamotol	5.2	907
4 *epi*-β-Santalol	1.7	961
5 *Z*-β-Santalol	5.2	865
6 *E,E*-Farnesol	5.8	887
7 *Z*-Nuciferol	2.8	869
8 *Z*-Lanceol	5.2	814

* The abundance of each component was determined by dividing the sum of the area of the individual slices for each respective peak by the total chromatogram peak area minus the solvent peak. Library quality matches were determined from the GC×GC–TOFMS experiment and were determined manually.

provided that an equivalent first dimension column (to the column used in the GC–MS analysis) is used. For essential oils this is particularly beneficial because the use of retention indices can still be incorporated to support identification based upon MS data. With maintenance of the first-dimension chromatogram integrity, existing retention index databases can be retained. Further work into the applicability of second-dimension retention indices (22,23) will be an important research direction. A comparison of the GC×GC and GC–MS chromatograms for *Santalum spicatum* oil is presented in Figure 5. The opportunity to spread components throughout the 2D-separation space in the GC×GC analysis, and the benefits that this holds over single-column analysis is apparent. The eight characteristic components are highlighted within the 2D-separation space by the numbered white peak markers. The expanded 2D chromatogram shows that the components thought to be single component peaks (labelled peaks 1 and 8) in the GC–MS analysis in fact have smaller underlying peaks. Using the current column configuration and operating conditions, the eight characteristic components are sufficiently well resolved from any neighboring peaks within the two-dimensional separation space to provide acceptable quantitation. Each component separated in the GC×GC–TOFMS analysis was computer matched to the Adams terpene library (19) and the spectrum matches (Table II) returned for each of the target components along with the indicated peak contours in the 2D plot provides a further indication that they were indeed single-component peaks; the excellent separation of components *epi*-α-bisabolol and *Z*-α-*trans*-bergamotol is indicative of the increased resolution capacity of the GC×GC experiment. The same observation was noted in GC×GC–quadrupole MS analysis of *P. graveolens* essential oil components, with approximately 80 compounds greater than 90% match quality (6).

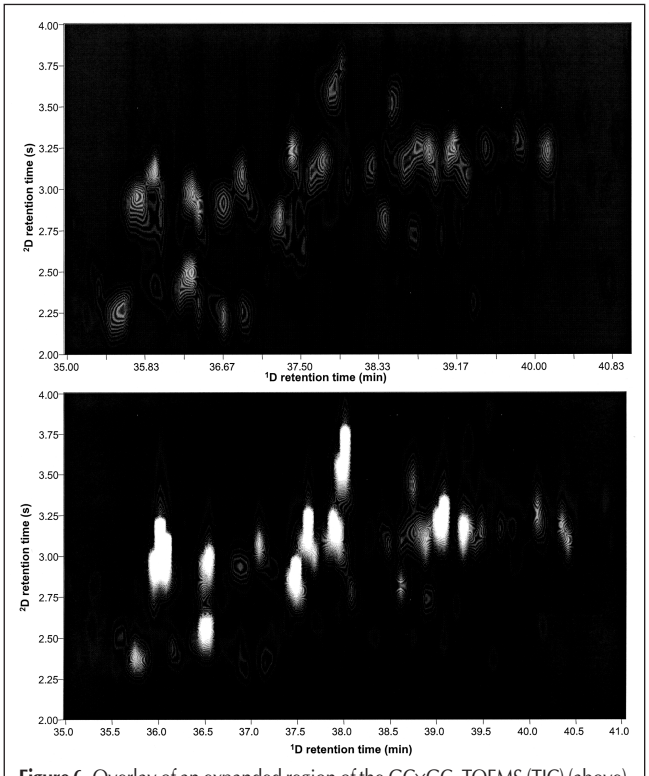

Figure 6. Overlay of an expanded region of the GC×GC–TOFMS (TIC) (above) and GC×GC–FID (below) chromatograms of *Santalum spicatum* essential oil.

Quantitative analysis of west Australian sandalwood oil

The abundance of each of the eight characteristic components in the oil was determined by GC×GC–FID and is reported in Table II. An expanded section of both the GC×GC–TOFMS and GC×GC–FID chromatograms are presented as two-dimensional plots in Figure 6. The peaks in the GC×GC–TOFMS chromatogram overlay those for the corresponding components in the GC×GC–FID chromatogram when the two plots are superimposed. Although this has been a general goal of the authors, a difficulty has previously arisen in obtaining such high correlation because of the differences in second dimension outlet pressures between the different detectors. van Stee also illustrated this problem recently in comparing GC×GC–MS and GC×GC–AED chromatograms (24). In a previous study by the authors (25) that compared GC×GC–MS and GC×GC–FID chromatograms, absolute retention time correlation was not achieved, although the overall peak distribution pattern was reproducible between the different analyses. Excellent retention time correspondence between the GC×GC–TOFMS and GC×GC–FID chromatograms in the present investigation was made possible by controlling the outlet pressure of the second-dimension column, as well as adjusting the inlet pressure of the first-dimension column, in the GC×GC–TOFMS experiment. With absolute retention time correspondence, components can be assigned within the GC×GC–FID chromatogram with much greater confidence. A detailed discussion regarding the procedure for achieving this high correlation has been described elsewhere (26).

Conclusion

The present study has offered further support to the contention that a single two-dimensional analysis is more powerful than two one-dimensional analyses because the GC×GC separation, which uses two dissimilar stationary phase columns, provides significantly more information than two GC analyses using dissimilar stationary phases. The complex nature of west Australian sandalwood essential oil makes quantitative analysis using GC–FID difficult. In investigating the use of GC–MS and GC–TOFMS for the characterization of some important components of the oil, some challenges that arise in performing a quality assurance test have been highlighted. However, with three independent parameters upon which to base component identity, namely first- and second-dimension retention times, as well as MS information, GC×GC–TOFMS can be used to characterize important components and they can be quantitated using the less expensive and simpler GC×GC–FID technique. Compound assignment in the FID 2D separation space can be made with confidence because retention time reproducibility is good, and it is now clear that absolute retention time correlation between the TOFMS and FID results is possible. With recent movements towards automating GC×GC data analysis, the use of GC×GC–FID for routine analysis of essential oils is nearing reality. Once a suitably large sample range has been characterized by GC×GC–TOFMS, it will be possible to use these data as a template for characterizing and quan-

titating important characteristic components in a wide range of essential oils using GC×GC–FID.

Acknowledgments

The authors gratefully acknowledge the generous support of SGE International and Leco Australia and also wish to thank Australian Botanical Products for providing essential oil samples.

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Manuscript accepted July 23, 2004.