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Multidimensional gas chromatography of oxidative degradation products in algae-derived fuel oil samples using narrow heartcuts and rapid cycle times

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ABSTRACT

To characterize a fuel's thermal and storage stability an understanding of the process of oxidation and oxidation pathways is essential. Oxidation pathways commence with hydroperoxides which quickly decompose to form a range of alcohols, acids and other oxygen-containing species. In the presence of significant levels of hydrocarbon-based matrix, analysis of these heteroatomic species is difficult. Applying multidimensional gas chromatography with very narrow heart-cut windows (0.20 min) minimizes the number of compounds transferred to the second dimension (^{2}D) column during each heart-cut. Successive heart-cuts every 2.00 min are taken throughout the analytical run, since each heart-cut has a maximum retention on ^{2}D of <2.00 min on the fast elution ^{2}D column. Subsequent analyses involve incrementing or offsetting the heart-cut windows by 0.20 min, so after 10 analyses, a complete coverage of the sample components can be obtained. On the polar ^{1}D and non-polar ^{2}D phase column arrangement, non-polar matrix compounds elute last on the ^{2}D column, and this determines the largest ^2t_R; i.e. $^2t_R < P_M$ to ensure retained components on ^{2}D will not overlap with subsequent heart-cuts. Heartcutting is supported by cryotrapping at the start of the ^{2}D column in order to provide significantly better resolution. Good quality MS library match data generally demonstrate the high resolution separation of oxygenates achieved. Whilst 1D GC–MS was unsuccessful in identifying any of the oxygen-containing compounds reported here, good correlation of MS data (with average MS library similarity data) for acids (903), alcohols (909), ketones (941) and aldehydes (938) in the sample is obtained. The method requires ten sequential runs, and this can be accomplished automatically once the events table is set up. However if fewer target compounds are to be transferred, a reduced number of sequential runs can be implemented.

1. Introduction

Thermal stability of aviation fuel is of great importance. Jet fuel is thermally stressed in military aircraft as it is used as a heat sink to cool oil and avionics, i.e. as a heat exchange medium for thermal management. Diesel fuel may become thermally stressed when used in common rail diesel engine fuel systems. As a result fuels undergo auto-oxidation to form a range of oxidation products which may then form gums that can block fuel nozzles and filters. Sooting tendency, surfactant formation and the formation of insoluble compounds are additional problems.

The move to synthetic (e.g. from the Fischer–Tropsch process) or renewable (e.g. algal-derived or biofeedstock) transportation fuels requires their reactivity towards thermal oxidation to be assessed. With increased heat demands for the fuels (e.g. as a heat sink), the formation of hydroperoxides becomes more likely, resulting in faster consumption of natural and/or synthetic antioxidant additives. Additionally, the lack of sulfur in neat synthetic fuels removes this natural scavenger of hydroperoxides [1]. This promotes oxidative instability, leading to a greater rate of formation for alkylperoxyl radicals and secondary oxidation processes. Methods for elucidation of the oxidation products from the hydrocarbon matrix remain an analytical challenge.

Methods to examine the thermal oxidation of fuels have focused on bulk fuel properties such as changes in total acidity or peroxide content, or require exhaustive pre fractionation via open column techniques [2]. Due to the complexity of the fuel matrix, methods may aim at group type quantification rather than isolation and characterization of the specific oxidation products [3–5].

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Current methods require high performance liquid chromatography (HPLC) fractionation and subsequent gas chromatography–mass spectrometry (GC–MS) analysis of the subfractions. Attempts to characterize the thermal oxidative degradation products of fuels have included use of GC–MS techniques with appropriate sample preparation, with quantification of the hydroperoxide [6] and HPLC and solid phase extraction (SPE) for quantification of total polar compounds in fuels [7–9]. Recent chromatographic methods for identification of polar – notably oxygen-containing – species, include multidimensional gas chromatography (MDGC) [10].

Sequential heart-cut (H/C) MDGC involving repetitive sample injection was introduced in 1958 [11]. Gordon et al. [12] applied this to tobacco essential oil analysis. Twenty-three individual cuts of different duration were selected from a primary (^{1}D) wide bore polar (P) column, cryotrapped, then released on a long second dimension (^{2}D) medium polarity column with oven temperature programming. Excellent separation of components comprising each H/C was achieved, with 306 identified components, however the total analysis required 48 h. Marriott et al. [13] demonstrated an automatic, sequentially time-resolved cryogenic modulation MDGC method using an on-line cryotrap system in a single analysis in 2000, providing improved resolution on a short fast elution ^{2}D column of various lengths (0.8, 2.0 and 5.0 m) for a semi-volatile sample mixture. Striebich et al. [14] applied a H/C method for combustion effluent analysis. A 3.0 min cut time was selected apparently from various locations in the chromatogram obtained on a long ^{1}D column, cryofocused and released on a short polar microbore ^{2}D column. Subsequent work by Marriott et al. and Dunn et al. incorporated switching valves and cryogenic modulation to pass specific regions of a ^{1}D GC analysis to a fast ^{2}D column, for pesticides [15], essential oils [16], and allergens [17]. In all these methods, compounds must be effectively retained in the cryotrapping device for the required duration. Rapid sequential heart-cut MDGC with 1.00 and 1.50 min on-line collection zones was applied in lavender oil analysis with parallel flame-ionization detection (FID) and quadrupole MS (qMS) detection [18]. An approximate 7-fold increase in peak capacity was estimated, due to the cryogenic focusing and fast ^{2}D column elution.

Recently, MDGC–time-of-flight mass spectrometry (TOFMS) has been applied for identification of polar species in conventional aviation fuels [10], after solid phase extraction on a silica gel cartridge, using a non-polar (NP)/P column set. Modulation was performed in a similar manner to that proposed by Marriott and Kinghorn [19] in 1997, either by moving the column through a fixed cryotrap, or moving the cryotrap over the fixed column segment towards the incoming carrier flow. The method closely resembles comprehensive two-dimensional gas chromatography (GC × GC) with a longer ^{2}D column than normally used, and a longer modulation period (P_M = 15 s). Hindered phenols and sulfurous components were not detected in analysed fuel samples due to their low polarity and inability to be retained by SPE. Aldehydes, ketones and acids were not evaluated in the proposed method. The additional SPE extraction step is one drawback of the method, and the fast acquisition TOFMS detector represents a considerable cost investment.

van der Westhuizen investigated oxygenates in Fischer–Tropsch-derived samples [20], comparing GC × GC, H/C MDGC and sequential MDGC analysis for these target compounds. The latter method collected and eluted 80 narrow H/C regions on a classical capillary column under a slow temperature program. Sciarrone et al. [21] applied multiple H/C MDGC to analysis of oxygenates in gasoline. Twelve cuts were selected from the ^{1}D ionic liquid polar column and diverted to a ^{2}D NP column of the same dimensions, located in a separate GC with a −25 °C temperature offset, to provide a refocusing effect. Component identification was by fast scanning qMS.

Here, we present a method that can be switched from GC × GC analysis with FID detection for general profiling of oil samples, to a sequential heart-cut MDGC–qMS method for detailed and high-resolution isolation and identification of oxygenates from saturates in algae-derived fuel oil. Very narrow H/C zones (0.20 min) from ^{1}D are used. The method allows bulk matrix-interference free identification of the target oxygenated compounds.

2. Experimental

2.1. Materials

Algae-derived jet fuel was supplied by the US NAVAIR Fuels Division. The fuel was used without any further blending or addition of antioxidant or other additives. This fuel consists of a mixture of straight chain and branched hydrocarbons but is free of aromatics and any oxygenated compounds. Current practice in the aviation community allows for a 50:50 blend of this algae-derived jet fuel with conventional jet fuel in accordance with the relevant specification.

2.2. Sample preparation procedure

Static thermal stressing was carried out according to ASTM D7545 [22] using a PetroOXY Oxidation Tester (PetroTest Instruments, Dahlewitz, Germany). This involved taking 5.00 mL of sample and heating it to 140 °C under an oxygen atmosphere at 700 kPa. The pressure is monitored until a pressure reduction of 10% is achieved (induction time). After the induction time was met, approximately 1 mL of fuel was removed from the vessel for analysis and replaced with 1 mL of fresh sample. This was repeated until four oxidation cycles had been performed. The sample reported here is from the 4th oxidation cycle.

2.3. Instrumentation

An Agilent 7890A GC coupled to an Agilent 5975C MS (Agilent Technologies, Burwood, Australia) was used for all GC–MS analyses with electron ionization (EI) mode at 70 eV over the mass range from 45 m/z to 350 m/z at 4.57 scans/s. A flame-ionization detector (FID) on the same system was used for all GC × GC-FID analyses. Injection and detection (FID) temperatures were 270 °C and 280 °C, respectively. The NIST08 MS database and NIST search algorithm (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used for peak identification. A Deans switch (DS) assembly (Part number G2855-60100, Agilent) enabled H/C in MDGC operation. Modulation for GC × GC-FID mode and cryofocusing of H/C in MDGC was performed by using the longitudinally modulated cryogenic system (LMCS, Doncaster, Australia), with liquid carbon dioxide as a coolant.

For MDGC, the ^{1}D column was 30 m × 0.25 mm I.D. × 0.25 μm film thickness (d_f) Supelcowax 10 (Supelco, Bellefonte, USA) with poly(ethylene glycol) as a polar (P) stationary phase, whilst the ^{2}D NP column was Rxi-5Sil MS (20.0 m × 0.18 mm × 0.18 μm d_f) with 5% phenyl (equivalent)/95% dimethyl polysiloxane (Restek, Bellefonte, USA). The usual DS restrictor column operates as the ^{2}D column in GC × GC mode, which in the present case was 2.0 m × 0.1 mm × 0.1 μm d_f of BPX5 phase (instead of a deactivated fused silica column) from SGE (Ringwood, VIC, Australia). The same column set and the same GC system was used for both MDGC and GC × GC modes, with only one operational difference: for MDGC mode modulation was performed on the beginning of the 20.0 m ^{2}D column (Rxi-5Sil MS), whilst for GC × GC modulation was performed on the beginning of the 2.0 m ^{2}D column (BPX5). Column configurations and a schematic of the systems used are given in Fig. 1.

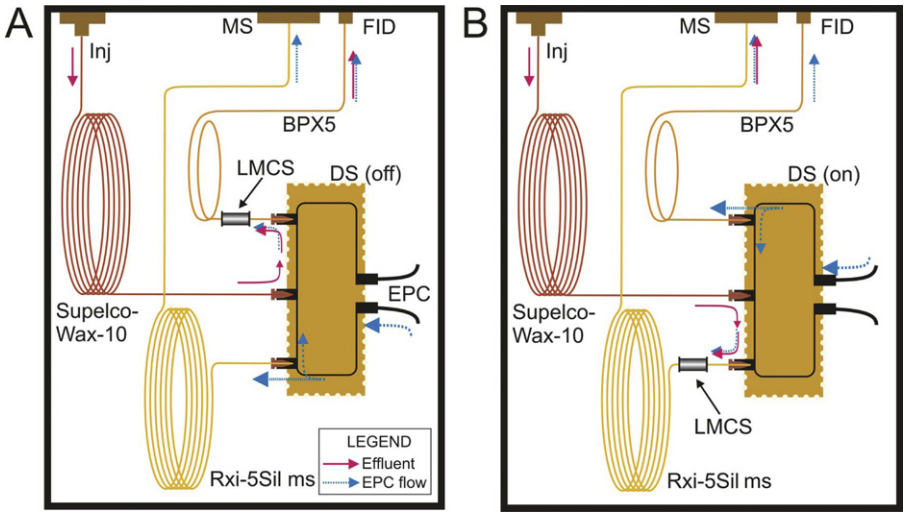

Fig. 1. Schematic of the instrumental arrangement. GC × GC-FID was performed using fast modulation (cryotrapping) applied on the beginning of the short ^{2}D column (A), and MDGC–qMS for multiple heart-cutting where target modulation occurs on the beginning of the long ^{2}D column (B). EPC: electronic pressure control for the Deans switch (DS) operation.

Due to the anticipated complexity of oxygenates and matrix in the sample it was decided to sample very narrow H/C of the ^{1}D eluate, for fast separation in ^{2}D. A wide H/C will potentially sample more oxygenates (and hydrocarbons) to the ^{2}D column, which may then be more difficult to resolve. Following preliminary experiments with different H/C durations, a H/C of 0.20 min was chosen here. From the maximum retention on the second column ($^2t_{R,max}$ value), the regular period H/C cycle can be set to be just greater than this value. Therefore, H/C were sampled every 2.00 min in order to allow repetitive sampling during a single GC run, to prevent components from a current H/C eluting after the commencement of the next H/C cycle. Incrementing the sampling procedure by 0.20 min for the next injection allows the next zone of the ^{1}D sample to be H/C. In total, 10 automated analyses provide full coverage of all compounds in the sample. Fig. S1 (Supplementary Information) is a representation of the sampling sequence and incremented injections.

The same oven temperature program was applied in both modes: 60 °C (1 min) to 280 °C (hold 2 min) at 8 °C/min. One μL of undiluted oil sample was injected at a split ratio of 50:1, or from a 10× and 100× dilution with hexane for comparison purposes. In GC × GC-FID mode, modulation was performed at −20 °C with 6 s modulation period (P_M), and a data acquisition rate for FID of 50 Hz. The H/C mode was performed by applying 10–13 H/C from ^{1}D in a single run, with cut duration of 0.20 min conducted periodically at a 2.00 min interval between each cut. Thus complete sample coverage requires 10 runs to acquire data for the total sample, giving in excess of 100 H/C. This is accomplished automatically. The transferred effluent from each H/C was collected (refocused) by cryotrapping at the LMCS (−20 °C) with a release step 6 s after each H/C was finished. One size G cylinder of liquid CO_2 is sufficient for about 30 analyses. For comparison purposes, H/C were also diverted to the long ^{2}D column without cryotrapping, and also in one instance the cryofocused heart-cut was analysed on the ^{2}D column by cooling the oven and slowly raising the temperature to provide greater separation.

3. Results and discussion

3.1. GC × GC-FID

A classical 1D GC-FID analysis of the sample (data not shown) revealed a reasonably good separation early in the chromatogram, but with many high abundance peaks superimposed on an unresolved baseline later in the chromatogram. A similar result was obtained using GC–MS (Fig. 2) where the last eluting high abundance peak was identified as n-C18 alkane, expected for an algal-derived fuel. Several straight chain or branched alkanes were tentatively identified although in general absolute identification is limited because of the heterogeneity of the sample, and the lack of precise mass spectra and authentic standards. Better identification mainly arises in the earlier part of the chromatogram however no oxygenated component(s) were positively identified in 1D GC–MS even though they were subsequently shown to be present; their satisfactory identification required a different methodology.

By contrast, GC × GC-FID on the P/NP column set (Fig. 3) of the same sample revealed a good class separation of the non-polar hydrocarbon fraction (eluting later in ^{2}D) from the more polar components (eluting earlier in ^{2}D), with oxygenates expected in the latter class. Furthermore, at least three homologue groups of polar components are distinguishable in the structured 2D plot, proposed as 2-alkylketones, acids and n-alkylaldehydes which were tentatively identified in the MDGC method later. Even though the presence of these homologues was confirmed in the sample, 1D GC–MS failed to positively identify any of these (even though they were suspected due to the sample's oxidative stress history, and were searched for), except for propanal which eluted early in the chromatogram and so exhibits little interference. However, due to poor specificity of fragmentation of the oxygenated molecules, and common fragment ions with hydrocarbons, identification cannot be certain; the match quality of nearly 900 (on a scale of 0–999) largely was ascribed to the overlapping interfering

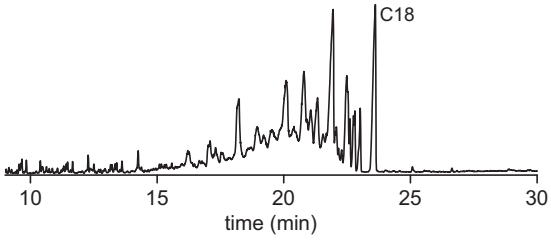

Fig. 2. GC–MS TIC chromatogram of an algae-derived fuel oil. The last major component is tentatively identified as n-octadecane (C18).

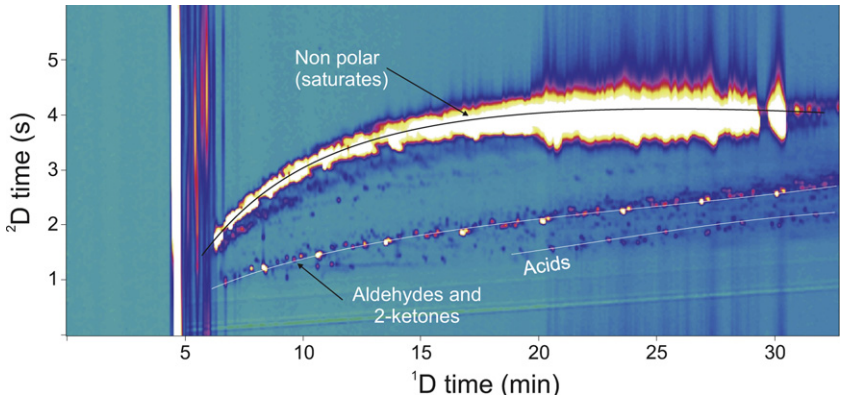

Fig. 3. GC × GC-FID 2D plot of an algae-derived fuel oil. Some suspected compound classes are noted. ^{1}D column: Supelcowax 10 (30 m × 0.25 mm; 0.25 μm); ^{2}D column: BPX5 (2 m × 0.1 mm; 0.1 μm).

hydrocarbon compound rather than the underlying oxygen-containing compound.

Whilst GC × GC reveals good separation between saturates and oxygenated compounds, separation within classes, i.e. aldehydes/2-ketones, and for the non-polar class (although this is not a goal of the present study of oxygenated products), was not satisfactory. The estimated peak capacity of the ^{2}D column (2 m × 0.1 mm) in GC × GC mode for the 6 s separation was ~30. Thus there is insufficient separation capacity on the short ^{2}D column for the plethora of different non-polar overlapping compounds throughout the sample, as well as for many oxygenated compounds in the sample, which were identified later. Further dilution of the sample (100 fold) slightly improved separation, but the polar compounds (and low abundance non-polar compounds) were not detectable due to their relatively low abundance. In order to more effectively resolve the target oxygen-containing compounds, a MDGC method was tested.

Peaks in GC × GC are on the order of ~100 ms wide at half-height, and the qMS scan rate is likely to be too slow for effective GC × GC analysis using the P/NP column set described in Fig. 3. The bias in spectra due to scan speed adds to the uncertainty of peak identification, although qMS does provide some measure of identification for GC × GC. The application of qMS to GC × GC of complex mixtures is possible, albeit with limited success due to its slow scanning property [23,24]. Since polar compounds are of interest here, three strategies are possible. (i) Use a NP/P column set. This will provide greater retention for polar compounds on the ^{2}D column, and also should separate the different classes of polar compounds better. This will also generate wider peaks on the ^{2}D column. (ii) Use a much slower T program rate in GC × GC with a longer ^{2}D column and slower P_M to broaden ^{2}D peaks to make them compatible with slower qMS scan rate; (iii) Alternatively, a MDGC method was tested according to Section 2.3, as further described below.

3.2. MDGC–MS

The H/C zone times and their frequency in MDGC are mostly defined by the sample complexity, the length of the ^{2}D column, and the desired separation and extent of retention of components on the ^{2}D column. The two extremes for separation maximization are (i) GC × GC where the whole effluent is submitted for additional separation on a very short ^{2}D column with rapid cycling, and (ii) when a single target cut is diverted, cryotrapped, then released on a long ^{2}D column and separated under a new oven temperature program commencing at low temperature. The advantage of the former approach is comprehensive analysis in one run, but with limited sample capacity and separation power on the (usually) very short ^{2}D column (0.5–2 m), although requiring a fast detector.

The second approach gives best separation for a target region, but it is not practical for closely sampled multiple H/C. 1D GC–MS may fail to detect the signal of minor components in presence of high abundance matrix without further sample pre-treatment or additional effluent sub-division (multi-column separation). This is exacerbated when there is a lack of uniqueness in target mass fragmentation. Introduction of prior extraction reduces sample turnaround, requires extra technical input, and may introduce contamination and possible sample loss. For these reasons on-line sample sub-division (commonly known as heart-cutting) is preferred for separation enhancement.

Preliminary results, when H/C of different duration were sampled, showed that most compounds had a ^2t_R of <1.4–1.9 min on the ^{2}D column. Thus a cycle period between sampled zones from ^{1}D of at least 1.90 min should be implemented so that prior H/C zones are fully eliminated from the ^{2}D column before the next is introduced. Subsequently, H/C events that differed by 2.00 min exactly were employed, with each analysed zone derived from a 0.20 min H/C sample. A typical multiple H/C MDGC chromatogram without any cryofocusing is given in Fig. S2A (Supplementary Information), where eleven H/Cs are presented usually as a major "peak" (more precisely – bunched co-eluting peaks) comprising non-polar components (saturates) and just prior to each of these are minor polar components (oxygenates), which elute earlier on the non-polar ^{2}D column.

A typical example of the separation obtained from one H/C of 0.20 min from the ^{1}D column, now eluted over a 1.4 min period on the long ^{2}D column, is shown in Fig. 4 (dotted line). The improvement in the separation is not as good as expected. Polar components are well resolved from NP components, but the peak shapes of both were unsatisfactory, especially for NP. A number of logical improvements are possible: either to preserve (cryotrap) the cuts whilst reducing the oven temperature and release the cuts starting at a new lower oven temperature; use a two-oven system with the ^{2}D column in the second oven held at lower temperature; or refocus the cuts at the prevailing elution temperature. The first does not allow application of a new oven temperature program for all individual cuts within one run. It is suitable for a single cut in target analysis, but it is not practical for multiple cuts or H/C where the entire sample is to be analysed. The second dual oven system option was not available. The third was expected to give the same refocusing effect that is achieved in GC × GC and reduces the band dispersion of a component arising from the first dimension column: after the transfer of effluent from ^{1}D to ^{2}D via the DS, the effluent is trapped at the LMCS for the H/C duration of 12 s, held for an additional 6 s, and then released in a sharp band to the long ^{2}D column. This allows modulation (cryotrapping and releasing) of all H/C within one run, to be individually separated on the long ^{2}D

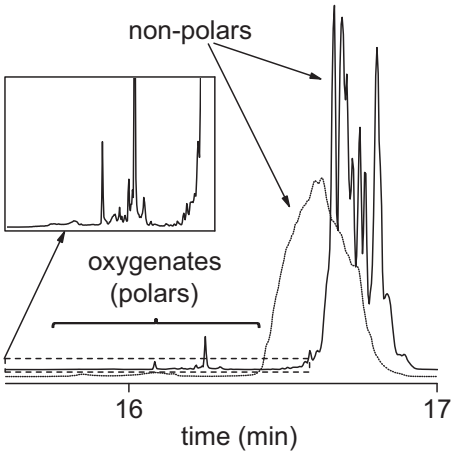

Fig. 4. MDGC–qMS result for comparison of a typical heart-cut of 0.20 min from ^{1}D analysed on the ^{2}D column, with (solid) and without (dotted) cryotrapping. Polar components largely comprising oxygenated components are effectively quantitatively separated from the very abundant non-polar compounds in both cases. However separation of all compounds is much better when cryotrapping is applied.

column. The estimated peak separation capacity of the ^{2}D column (20 m × 0.18 mm) in MDGC was ~120, noting that this is at isothermal conditions, and at a high prevailing oven temperature with a relatively high carrier flow.

When each H/C was first cryotrapped at −20 °C for the duration of the H/C event (12 s) and then released in a sharp band on the ^{2}D column, enhanced separation and increased signal was obtained, especially for polars (see Fig. S2B, Supplementary Information), as expected for a cryofocusing effect of this nature. The difference between a typical separation of the same H/C (14.8–15.0 min) without cryofocusing (dotted line) and with cryofocusing (solid line) is clearly illustrated in Fig. 4. The inset shows good separation of oxygenated compounds. Due to the improvement arising from the cryofocus step, this approach was implemented for each H/C event.

When the same H/C as in Fig. 4 (14.8–15.0 min) was diverted to the ^{2}D column, cryotrapped at −20 °C, held at the beginning of this column whilst the oven temperature was reduced to 80 °C, then released and separated under temperature programming at 4 °C/min, the separation was significantly improved (Fig. 5). The Fig. 5 result can be implemented at any stage, if desired, by simple variation of the sampling strategy. This process is informative and aids better characterization of individual peaks, but in the context of the present method employing multiple H/C events is not practical because the total turnaround of the analysis on the ^{2}D column has to be within 2.00 min (i.e. shorter than the sampling cycle time). The Fig. 5 result, however, serves an important role since it is a simple procedure that establishes a high resolution separation to improve characterization of less-resolved peaks arising in the Fig. 4 result. The calculated peak capacity of the same column (20 m × 0.18 mm) under this condition was ~600.

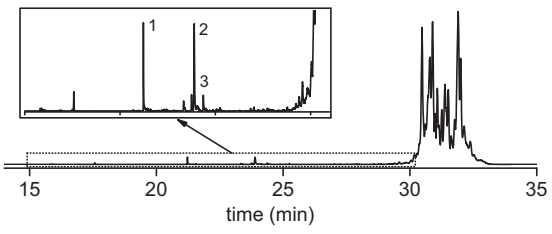

Fig. 5. MDGC–qMS result for a single H/C (same zone as shown in Fig. 4) which was cryotrapped, the oven cooled from 280 °C to 80 °C, and released onto the ^{2}D column for separation using programmed oven temperature of 4 °C/min to 280 °C. Better resolution is noted (refer to text). 1: 1-heptanol; 2: 2-decanone; 3: 4-decanone.

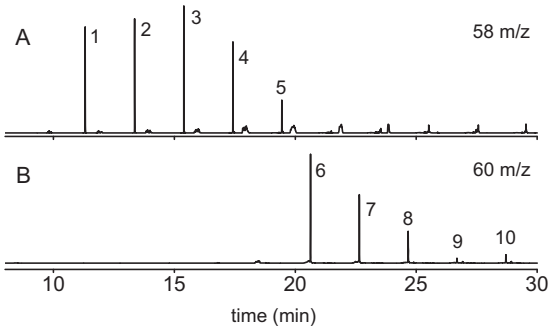

Fig. 6. MDGC–qMS chromatograms of elution of five 2-ketones (A) and five free fatty acids (B) by using the proposed strategy (0.20 min H/C; 2.00 min cycle time). Note the excellent peak shape of acids. It is simply fortuitous that the selected 0.20 min H/C regions here coincide with the elution of the ketones and acids. 1: 2-heptanone; 2: 2-octanone; 3: 2-nonanone; 4: 2-decanone; 5: 2-undecanone; 6: butanoic acid; 7: pentanoic acid; 8: hexanoic acid; 9: heptanoic acid; 10: octanoic acid.

3.3. Comments on heart-cut sampling

A full MDGC analysis of the sample can be covered with 10 runs provided the cut width from ^{1}D is 0.20 min and the ^{2}D duration for each H/C analysis is 2.00 min. The minimum number of repeat runs can be reduced if the maximum retention on ^{2}D column is less (therefore requiring a shorter interval between two consecutive cuts) or if the sampled H/C width is increased (e.g. 0.30 min or 0.40 min instead of 0.20 min). The latter option will reduce the separation achieved on the ^{2}D column because as the ^{1}D sampled zone becomes wider, more components will be potentially recombined at the cryofocusing stage, and transferred to the ^{2}D column, requiring greater separation capacity.

Twelve seconds is a reasonable time for the sampled H/C since it is comparable with the peak width on the ^{1}D column, but there are some cautions. Should a peak span two neighbouring H/Cs, this compound will appear spread across those two respective H/C in two different consecutive injections. This cannot be prevented, since the method cannot adjust the sampling zone to just select complete peaks. However, the peak's MS similarity (identity), the similar $^{2}t_{R}$ values, and the retention time difference of 0.20 min of the two modulations, is a strong indication that a double-sampling of the compound occurs. Narrowing the cut time might solve some of these problems, but will require many more runs to cover the whole sample and will increase the total runtime. In general, higher orthogonality between the two columns (^{1}D and ^{2}D), should mean wider H/C can be applied. The occurrence of peaks being spread across neighbouring sampled fractions is a normal process for GC × GC analysis.

In target analysis, depending on the relative retention times of the analytes and number of compounds to be targeted, the minimum number of cuts can be theoretically reduced to one (one compound, or a single zone targeted), as in Fig. 5, or just a few. If analysis of one class of compounds is required (i.e. 2-ketones), the H/C event times can be adjusted (based on the GC × GC profile) to include just those homologues within the sample, divert each to the ^{2}D column, and effectively separate them in a single run. This is provided the homologues can be resolved on the ^{2}D column. Fig. 6 shows fortuitous elution of five 2-ketones in chromatogram (A) and five acids in chromatogram (B) using the strategy outlined (0.20 min H/C; 2.00 min cycle time). Each H/C in the single injection was able to capture each homologue because the retention time difference between these homologues in these two chromatograms was approximately 2 min, and they were H/C to the ^{2}D column in successive 0.20 min H/C events. The result should be complete transfer of each targeted peak, with good resolution, and relatively good response since the peaks are narrow. Overlapped

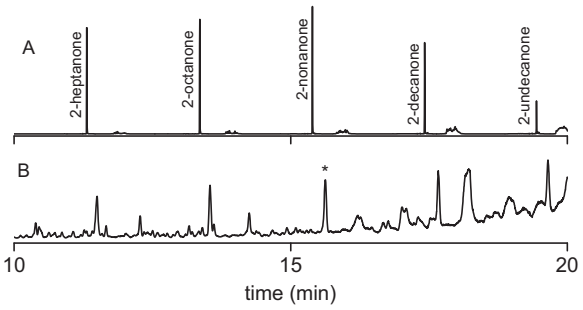

Fig. 7. (A) Expanded MDGC–qMS chromatogram of algae-derived jet fuel oil (similar to Fig. 6A). (B) The respective full 1D GC–MS result for this sample. An extracted ion plot of 58 *m*/*z* is shown in both traces. The 2-ketones contribution to the 58 *m*/*z* response using MDGC in (A) is now clearly separated from overlapping peaks and other large 58 *m*/*z* responses arising from non-2-ketone interferences seen in (B). The mass spectrum of component marked * is shown in Fig. 8.

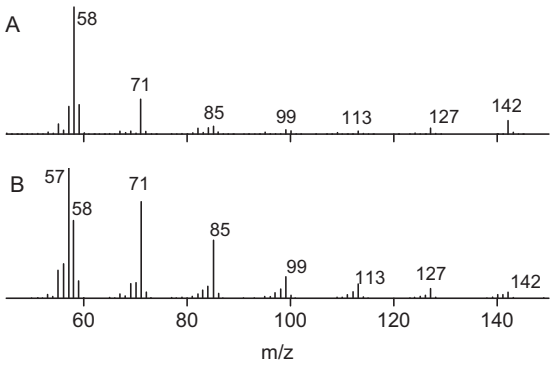

Fig. 8. Mass spectrum of 2-nonanone acquired in MDGC mode, with MS similarity of 960 (A), and mass spectrum acquired at the corresponding peak at 58 *m*/*z* from the GC–MS chromatogram in Fig. 7 (marked with asterisk). Note that 1D GC–MS did not give a match to a 2-ketone, but rather to an n-alkane.

extracted ion chromatograms (EIC) in Fig. S3 (Supplementary Information) complete the profile of 2-ketones in the analysed fuel. Note that 2-undecanone was sampled in two consecutive runs and consequently appeared in two different modulations differing by 0.20 min. In this case, if just the 2-ketone components were to be targeted in the analysis, then a sampling procedure to effectively H/C each of these to the ^{2}D column (in one run) would be a simple solution.

3.4. Analysis of target oxygenated products

As can be seen from figures above, all polar components (including oxygenates) are clearly separated from the high abundance saturated hydrocarbons, with very good peak shape. Fig. 7 displays an expanded chromatogram of the same result as Fig. 6A, along with the respective 1D GC–MS result, for the extracted ion 58 *m*/*z* (specific ion for 2-ketones). The advantage of MDGC is apparent here. In Fig. 7A, NP compounds are well resolved from the ketones which give narrow and tall peaks due to the combined effects of cryofocusing and resolution on ^{2}D. The mass spectra of alkanes give a very small 58 *m*/*z* response, but their high abundance leads to observable clusters of peaks in Fig. 7A. By contrast, the Fig. 7B 1D GC–MS result is indistinct. The total GC–MS trace has some measure of response at almost every position. The location of the ketones is not as clear, and there is no certainty that each ketone is a pure resolved peak. The non-2-ketone 'interference' responses in Fig. 7B are greater than the small peaks in Fig. 7A, since the H/C process is used in the Fig. 7A result to just extract a 12 s portion from the analysis. Consequently, taking a mass spectrum for the 2-nonanone peak in Fig. 7A gives MS similarity of 960 (Fig. 8A), but the MS result for the scan taken across the suspected 2-nonanone peak for the Fig. 7B gives a result dominated by the overlapping alkane spectrum (Fig. 8B). An MS similarity search of that peak (marked with asterisk in Fig. 7B) did not give a match for 2-ketones but rather was for an n-alkane component.

Free fatty acids often tail or generate overloaded peak shapes in GC, due to their polarity. Fig. S4 (Supplementary Information) shows the EIC 60 *m*/*z* result for the jet fuel obtained using 1D GC–MS on the same system. Component identification failed for each of the acids, despite the very characteristic 60 *m*/*z* ion, due to low abundance and matrix overlap. Since the peaks are wide and tailing on the ^{1}D column, up to four very sharp modulations are now seen (see Fig. S5, Supplementary Information) and so are produced in MDGC when each 0.20 min H/C was cryofocused and released on the ^{2}D column (see Fig. 6B; note that Fig. S5 data are from an overlay of all 10 incremented analyses). The clear separation from NP components is another benefit of the MDGC approach. As a consequence, very good match quality was now obtained (see Table 1).

MS detection in scan mode allows identification of oxygenated components with good match quality since they are now well resolved from the matrix. The use of EIC, or selected ion monitoring (SIM) in target analysis, for quantification is possible provided chemical standards are available. An expanded GC–MS TIC result for the zone between 20.0 and 21.5 min (one single H/C) is presented in Fig. 9A. A selection of components is identified here. Fig. 9B–E

Table 1
Selected major oxygenates tentatively identified in algae-derived fuel oil sample, with their retention times and MS similarity.

Class/compounds	t_R (min)[a]	MS similarity[b]
2-Alkyl ketones		
2-Hexanone	9.463	951
2-Heptanone	11.313	950
2-Octanone	13.356	943
2-Nonanone	15.392	955
2-Decanone	17.421	942
2-Undecanone	19.442	943
2-Dodecanone	21.267	930
2-Tridecanone	23.084	934
2-Tetradecanone	24.701	920
n-Aldehydes		
Pentanal	8.611	931
Hexanal	9.473	940
Heptanal	11.328	937
Octanal	13.371	952
Nonanal	15.410	944
Decanal	17.439	946
Undecanal	19.460	944
Dodecanal	21.474	932
Tridecanal	23.292	920
Alcohols		
2-Hexanol	11.637	922
2-Heptanol	13.476	923
2-Octanol	15.516	881
1-Heptanol	16.084	930
1-Nonanol	19.941	920
1-Decanol	21.766	887
1-Undecanol	23.390	901
n-Acids		
Butanoic	20.629	954
Pentanoic	22.650	953
Hexanoic	24.664	938
Heptanoic	26.682	879
Octanoic	28.507	765
Nonanoic	29.108	927

[a] t_R is the retention time of the peak on the two-column system with use of the cryogenic trapping method. If two peaks are generated by the sampling process, the retention time of the largest peak is given.

[b] MS similarity given on a scale 0–999 according to the NIST library match protocol.

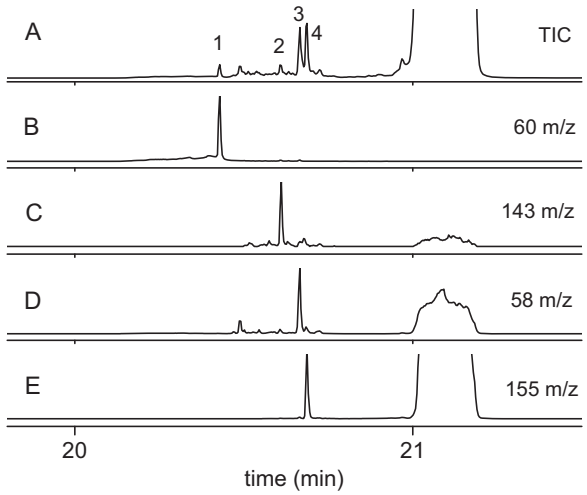

Fig. 9. (A) Total ion current chromatogram of one cryofocused modulation showing several oxygenated components, well separated from each other, as well as from the matrix (saturates; peaks at 21+ min). Peak identities are 1: butanoic acid; 2: 3-undecanol; 3: 2-dodecanone; 4: 3-dodecanone. The respective EIC scan values are B: 60 *m*/*z*; C: 143 *m*/*z*; D: 58 *m*/*z*; and E: 155 *m*/*z*. All marked components produced an excellent MS similarity to corresponding NIST08 entries. MS data and similarity values are shown in Fig. S5 (Supplementary Information).

shows the extracted ions 60 *m*/*z* (acids), 143 *m*/*z* (3-undecanol), 58 *m*/*z* (2-ketones), and 155 *m*/*z* (3-dodecanone), and includes the alkanes region and their responses for each extracted ion. This demonstrates the use of EIC ions for delineating the target compound in the presence of matrix when using 1D GC–MS (when there is no matrix response; 60 *m*/*z*) or the lack of specificity in EIC when there is a strong matrix response (58, 155 *m*/*z*). The mass spectrum of each of the oxygenated compounds is also presented (Fig. S6, Supplementary Information). Excellent match quality is achieved.

Table 1 reports representative components found in the oxidatively stressed jet fuel sample. The reported components include 1- and 2-alcohols, 2-ketones, n-aldehydes and n-acids. These are not the only oxygenated species present, and amongst others, 3- and 4-ketones are the most abundant oxygenated components not reported in Table 1. Note that these are largely based on NIST-library matching, in the absence of authentic standards, and so must be considered tentative identifications. Library match quality data are provided. In the case that a component locates across two neighbouring H/Cs they will have a retention time difference of 0.20 min; Table 1 reports the retention time corresponding to the largest peak obtained for the individual component.

Reproducibility of retention times of individual components was excellent. Measured from the release time of the cryotrapped species (rather than from the original injection point) the retention range was of the order of ±0.20–0.25% from the mean value, corresponding to ±0.1–0.3 s for early and late eluting peaks on the ^{2}D column.

The distributions of oxidized species including alcohols, ketones and acids is consistent with other reported analysis of polar compounds in jet fuels via SPE then HPLC subfractionation with GC–MS identification [9]. Oxygenates have been reported to have an impact on a fuel's thermal deposit formation and the identification of the various series of oxygenates will allow for a more detailed understanding of the oxidative mechanisms in thermally stressed fuels. The identification of aldehydes in oxidized fuels is not normally reported. These compounds are products of thermal degradation rather than oxidation under ambient conditions. The high temperature degradation process accelerates the rate of oxidation versus ambient conditions. Formation of the compounds identified shows the primary oxidation vulnerability of straight chain and branched alkanes under elevated temperatures. These primary oxidation products may be the precursors to other compounds that interfere with key fuel properties such as water separability and gum formation.

4. Conclusions

The proposed MDGC–qMS approach reported here is suitable for isolation and identification of minor oxygenated (polar) components in the presence of high abundance and complex matrix (saturates), as found in algae-derived jet fuel. The instrumental setup is readily converted from GC × GC-FID for general sample profiling, to MDGC–qMS for effective target component isolation and identification (conversion takes less than 1 h). The additional (third) method, of cryotrapping a single H/C whilst cooling the oven and releasing it under a slow temperature program, is also available without any variation to the setup. If the two columns are co-located through the cryotrap as proposed by Maikhunthod et al. [25], there will be no need to re-configure the columns. The width of the sampled H/C can be extended, and the interval between each cut can be reduced for maximum throughput if the GC × GC profile reveals that less than the entire region on ^{1}D is of particular interest. An initial GC × GC screening of samples aids optimization of conditions for a comprehensive analysis in fewer sample runs than that proposed here (ten incremented runs). One of the benefits of this method is that qMS can be applied for reliable identification since the peaks are wider (~1.0 s at base) than in GC × GC mode.

Cryofocusing at the beginning of the ^{2}D column produced much better peak shapes, enhanced signal, and better separation of target compounds. Several classes of oxygenated components were identified with excellent match similarity, some of them reported for the first time in this type of fuel.

The need for multiple runs from the same sample for complete sample analysis is a drawback. The search for a MDGC method best able to resolve all oxygenates from the matrix in a single run is continuing. Another drawback can be the lengthy time to initially enter all required flow switching and modulation events in the event table, since each H/C combined with the cryotrapping function requires up to seven event entries. However, once the table is completed, the process operates automatically.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.12.051.

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