



MONASH University

**Investigations of
Trace Oxygenates in
Middle Distillate Fuels using
Gas Chromatography**

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BSc (Hons)

A thesis submitted for the degree of Doctor of Philosophy at

Monash University in 2017

School of Chemistry

Dedicated to Brian Frank Jahn and Carla Ryan Downie

for Pop and Bear

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Abstract

There can be many thousands of different compounds in aviation or diesel fuels, making the analysis of trace components within the complex matrix highly challenging. Many small oxygenated compounds can be found in fuels, either included as additives, present as contamination, or generated as a result of thermal oxidation inside hot aircraft fuel systems and during storage. Although only present in trace amounts, such compounds can have dramatic effects on the physicochemical and fit-for-purpose qualities of a fuel. Detailed identification and quantitation of these compounds is critical for understanding the chemical reactions that form oxidised species and cause fuel system fouling, engine failure, and crashes. Aspects of these oxidation reactions are poorly understood, and a comprehensive understanding is crucial particularly as the uptake of alternate fuels increases, and modern high performance aircraft operate at ever hotter temperatures. This research informs and improves the use and storage of middle distillate fuels, contributing a critical understanding of the role of trace oxygenates on the chemistry of new and existing fuel types.

Gas chromatography is a well-established analytical chemistry technique suited to resolving complex mixtures such as fuels. Multidimensional gas chromatography further improves resolution and detection limits through the use of two orthogonal dimensions of separation resulting in increased peak capacity. This project used a variety of configurations of GC and MS technologies, taking full advantage of advances in multidimensional separations and the development of faster and more powerful tandem and high resolution detectors. The methods also incorporated careful selection of real fuels, covering conventional and alternate fuels which are approved for military or civilian use, or likely to be approved in the near future.

In this project, novel combinations of advanced gas chromatography and mass spectrometry techniques have enabled detection, identification and quantification of a broad range of target oxygenated species under a variety of conditions designed to simulate real-world fuel system operations. Antioxidant additives have been detected at low concentrations, along with minor components and impurities included in the additive. Contaminants from other fuel types were detected, and speciated in order to determine the feedstock and likely contamination sources. The progress of oxidation reactions has been characterised during thermal oxidative stressing. Several oxidised

molecules have been identified for the first time in this context, which are likely to play critical roles in fuel oxidation chemistry, aided by the fabrication of bespoke extractive media.

Quantitative associations between the presence of oxygenates and physicochemical properties of the fuels were also drawn, illuminating potential routes to simpler fit-for-purpose fuel assessments. Detailed analysis of oxidised species using advanced GCMS techniques has shown qualitatively and quantitatively the breadth of molecular functionalities produced under normal aircraft operating conditions. The presence of these compounds has been demonstrated to induce failure of some important specification and fit-for-purpose tests.

This work highlights key differences in the chemistry of emerging alternate fuels compared with traditional fuels derived from crude oil feedstocks. Knowledge of these molecular species ultimately increases productivity through decreased maintenance, fewer instances of engine and fuel system failures and enables the safe, efficient and timely uptake of new alternate fuels. Additionally, it is likely that these methods and knowledge can be translated to other fuel types such as light and heavy distillates.

Thesis Including Published Works Declaration

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes 6 original papers. Of these, 4 have been published in peer reviewed journals, 1 has been accepted for publication, and 1 has been submitted for publication. The core theme of the thesis is the application of advanced chromatographic and spectrometric techniques to the investigation of oxygen-containing compounds in aviation and diesel fuels. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the School of Chemistry under the supervision of Professor Philip Marriott.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

In the case of chapters 2-7 my contribution to the work involved the following:

Thesis Chapter	Publication Title	Status <i>(published, in press, accepted or returned for revision, submitted)</i>	Nature and % of student contribution	Co-author name(s) Nature and % of Co-author's contribution	Co-author(s), Monash student
2	Synthetic Phenolic Antioxidants in Middle Distillate Fuels Analyzed by Gas Chromatography with Triple Quadrupole and Quadrupole Time-of-Flight Mass Spectrometry	published	Proposed original idea, prepared and analysed samples, developed and validated methods, analysed and interpreted all data, fully drafted manuscript. 80%	1) Paul M. Rawson; Assisted interpretation of results, editorial assistance. 5% 2) David J. Evans; Supervision, assisted interpretation of results, editorial assistance. 5% 3) Philip J. Marriott; Supervision, assisted interpretation of results, editorial assistance. 10%	1) No 2) No 3) No
3	Quantification of Trace Fatty Acid Methyl Esters in Diesel Fuel by Using Multidimensional Gas Chromatography with Electron and Chemical Ionisation Mass Spectrometry	published	Proposed original idea, prepared and analysed samples, developed and validated methods, analysed and interpreted all data, fully drafted manuscript. 80%	1) David J. Evans; Supervision, assisted interpretation of results, editorial assistance. 5% 2) Philip J. Marriott; Supervision, assisted interpretation of results, editorial assistance. 10%	1) No 2) No

4	Detailed Chemical Analysis Using Multidimensional Gas Chromatography–Mass Spectrometry and Bulk Properties of Low-Temperature Oxidized Jet Fuels	published	Proposed original idea, prepared and analysed samples, developed and validated methods, analysed and interpreted all data, fully drafted manuscript. 80%	1) Paul M. Rawson; Assisted interpretation of results, editorial assistance. 5% 2) David J. Evans; Supervision, assisted interpretation of results, editorial assistance. 5% 3) Philip J. Marriott; Supervision, assisted interpretation of results, editorial assistance. 10%	1) No 2) No 3) No
5	Multidimensional Gas Chromatographic Analysis of Low-Temperature Oxidized Jet Fuels: Formation of Alkyldihydrofuranones	published	Proposed original idea, prepared and analysed samples, developed and validated methods, analysed and interpreted all data, fully drafted manuscript. 80%	1) David J. Evans; Supervision, assisted interpretation of results, editorial assistance. 5% 2) Philip J. Marriott; Supervision, assisted interpretation of results, editorial assistance. 10%	1) No 2) No

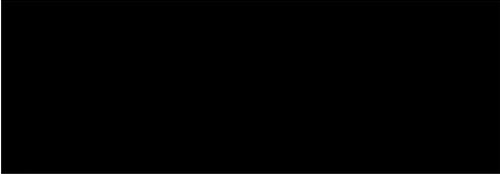
6	Identification of Oxidised Compounds in Aviation Fuels Using Nafion Fibre Solid Phase Microextraction	accepted for publication	Proposed original idea, partially prepared and analysed samples, developed methods, partially analysed and interpreted data, partially drafted manuscript. 70%	<p>1) Jonathan B. Mete; Partially prepared and analysed samples, partially analysed and interpreted data, partially drafted manuscript. 15%</p> <p>2) Paul M. Rawson; Assisted interpretation of results, editorial assistance. 5%</p> <p>3) David J. Evans; Supervision, assisted interpretation of results, editorial assistance. 5%</p> <p>4) Philip J. Marriott; Supervision, assisted interpretation of results, editorial assistance. 5%</p>	<p>1) Yes</p> <p>2) No</p> <p>3) No</p> <p>4) No</p>
7	Investigation of the Thermal Oxidation of Conventional and Alternate Aviation Fuels with Comprehensive Two-Dimensional Gas Chromatography Accurate Mass Quadrupole Time-Of-Flight Mass Spectrometry	submitted for publication	Proposed original idea, prepared and analysed samples, developed and validated methods, analysed and interpreted all data, fully drafted manuscript. 80%	<p>1) Paul M. Rawson; Assisted interpretation of results, editorial assistance</p> <p>2) Chadin Kulsing; Assisted experimental development</p> <p>3) David J. Evans; Supervision, assisted interpretation of results, editorial assistance</p> <p>4) Philip J. Marriott; Supervision, assisted interpretation of results, editorial assistance</p>	<p>1) No</p> <p>2) No</p> <p>3) No</p> <p>4) No</p>

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The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author I have consulted with the responsible author to agree on the respective contributions of the authors.

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Finally, to my husband Nathan, thank you for your enduring love and support, and for always believing in me.

List of Abbreviations

1DGC	One dimensional gas chromatography
2DGC	Two dimensional (comprehensive) gas chromatography
accTOFMS	Accurate mass quadrupole time of flight mass spectrometry
ASTM	American Society for Testing and Materials
ATJ	Alcohol to jet
CI	Chemical ionisation
CID	Collision induced dissociation
CW	Carbowax
DHA	Detailed hydrocarbon analysis
DSHC	Direct sugar to hydrocarbon
EI	Electron ionisation
EIC	Extracted ion chromatogram
eV	Electron volts
F-XX	NATO code generic designations for military fuels
F-34	A kerosene-type aviation turbine used primarily for Air Force and Army operations
F-44	High flashpoint kerosene-type aviation turbine fuel used for Navy operations
F-76	Military specification diesel fuel distillate with high storage stability
FAME	Fatty acid methyl ester
FSII	Fuel system icing inhibitor
FT	Fischer-Tropsch
GC	Gas chromatography
GC-MS	Gas chromatography mass spectrometry
GC/MS	Gas chromatography mass spectrometry
GC×GC	Comprehensive two-dimensional gas chromatography
HEFA	Hydroprocessed esters of fatty acids
HPLC	High performance liquid chromatography
HT	Hydrotreated
HTFT	High temperature Fischer-Tropsch
IPK	Isoparaffinic kerosene
JFTOT	Jet fuel thermal oxidation test(er)
LC	Liquid chromatography

LOD	Limit of detection
MDGC	Multidimensional gas chromatography
MRM	Multiple reaction monitoring
MS	Mass spectrometry
MS ⁿ	Tandem mass spectrometry
MSEP	Microseparator rating
<i>m/z</i>	Mass to charge ratio
NMR	Nuclear magnetic resonance spectroscopy
PEG	Polyethylene glycol
PFTBA	Perfluorotributylamine
P(DONA)	Paraffins, (isoparaffins), olefins, naphthenes, aromatics
RSD	Relative standard deviation
RSSOT	Rapid small scale oxidation test(er)
QCM	Quartz crystal microbalance
qMS	Single quadrupole mass spectrometer/spectrometry
QQQ	Triple quadrupole
QTOF	Quadrupole time of flight
R ²	Coefficient of correlation
RSD	Relative standard deviation
SEM	Scanning electron microscope
SIM	Single ion monitoring
SK	Synthetic kerosene
S/N	Signal to noise ratio
SPA	Synthetic phenolic antioxidants
SPK	Synthetic paraffinic kerosene
SPME	Solid phase microextraction
TOFMS	Time of flight mass spectrometer/spectrometry
TSR	Thermal stability rig

Style Notes

Chapters 2-5 of this thesis were all originally published as journal articles and have been reformatted to provide a consistent style throughout the document. Chapter 6 has been accepted for publication and Chapter 7 has been submitted and is being considered for publication.

References are renumbered throughout and are located at the end of the thesis, preceding the appendices.

Figures and Tables are presented in sequentially numbered order throughout the thesis, so have been re-numbered from the original manuscripts.

Abbreviations are redefined in each chapter to make them true transcripts of the manuscripts.

This thesis uses primarily Australian English; however, Chapters 2, 3, 4 and 5 were originally published in American English. The title pages for these chapters include the published titles of these chapters. For example, the word ‘analysed’ is spelled ‘analyzed’ in the titles but has been changed to ‘analysed’ for the text of these chapters for consistency with the rest of the thesis.

Figures in Chapter 4 were originally published in black and white but have been reproduced in colour here.

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1 Introduction

Liquid hydrocarbon fuels are a critical resource for energy and power generation. The unrivalled energy density and stability of liquid hydrocarbons ensures their continued use as transport fuels into the foreseeable future.¹ Despite concerted efforts across numerous sectors to shift away from fossil fuel use, liquid hydrocarbons will remain a crucial energy source for the propulsion of aircraft and other specialised platforms.

Middle distillate fuels is a term for refined hydrocarbon products which includes aviation and diesel fuels, as differentiated from lighter and heavier liquid fuel fractions such as petrol (gasoline) and fuel oils, respectively.² While the etymology of the term middle distillates is drawn from fractional distillation for the refining of crude fossil oil, the definition is not precise, and may refer to the distillation or carbon number range of the fuel. In a modern context it may also be applied to alternatively-derived fuels which are not produced by fractional distillation, but nevertheless to the same physicochemical properties, and therefore perform in the same applications, as conventional aviation and diesel fuels.

The chemical composition of fuels underpins their physical characteristics and hence, fit-for-purpose properties. “Fit-for-purpose” can be defined as refers to a property required for safe operation which is not directly controlled by the respective fuel specification. Characterisation of the bulk composition of fuels is an important step in the manufacture of refined liquid hydrocarbon products, providing part of the basis for meeting standard specifications and regulations prior to sale and use. Entities acquiring fuels rely on the results of standardised physical and chemical analyses to confirm that procured fuels meet specifications and are fit for purpose. While these validated methods can consistently and reliably determine bulk chemical composition of fuels, the contribution from trace, low concentration components is often overlooked.

There can be up to a million different components in a middle distillate fuel,³ making the analysis of trace components within the complex matrix very challenging. While trace inclusion of heteroatomic species may not strongly affect bulk properties such as density, they can significantly affect the thermal stability. Despite only making up a tiny proportion of the total, certain trace compounds can have significant and measurable effects on the physical and chemical properties of any given fuel and therefore warrant detailed investigation.

1.1 Heteroatomic species in fuels

Though comprised primarily of hydrocarbons, fuels can contain a variety of heteroatomic species, at trace to percent levels.⁴ Fuels from different sources, and used for different purposes, may contain a range of heteroatomic species incorporating nitrogen, sulfur, and oxygen.⁵ These may exist naturally in the fuel, be present in the original source material (e.g. crude oil), intentionally included as additives to serve a specific purpose, incorporated through contamination, or have been generated as a result of oxidation. The subject of this thesis falls in the three latter of these categories of oxygenated heteroatoms.

1.1.1 Fuel additives: Antioxidants

Additives are routinely included in fuels in order to meet performance specifications, improve fuel properties, or increase economic benefit. One of the most important fuel additive classes is antioxidants, which may be phenol or amine based, and are added to increase storage stability and inhibit the formation of solid deposits⁴ by preventing the proliferation of peroxides generated by oxidation while in storage.⁶ Labile hydrogens in antioxidants form stable radicals with peroxides, terminating the autoxidation chain reaction.⁷ The use of antioxidants is particularly important in a military context where fuels may be stored for years in accordance with operational requirements. Progress in fuel feedstocks and refining technologies has reinforced the need for antioxidants, as refining processes such as cracking remove compounds like olefins and sulfur and nitrogen heteroatoms which have natural antioxidant activity, from the fuel. Alternatively-derived fuels inherently lack these compounds also, and generate higher amounts of peroxides when in storage.⁸

The inclusion of synthetic phenolic antioxidants (SPAs) in hydroprocessed middle distillate fuels is mandated in many fuel specifications.⁹⁻¹⁴ Typically, SPAs are hindered phenols, with methyl or tertiary butyl substitutions at the 2, 4, and 6 positions on the ring (Figure 1). The use of SPAs is primarily encountered in aviation fuels, however the Australian specification for naval distillate fuel⁹ also includes provisions for SPAs. Trace amounts of SPAs (<25 mg/L) are sufficient to improve the stability of the fuel, although once consumed can have the opposite effect, and decrease thermal stability measured by rate of deposition of solids.¹⁵ The ability to positively identify and quantify the specific SPAs present in any given fuel is desirable, particularly when fuels experience stability and contamination problems

which may be treated with the re- addition of synthetic antioxidants. Advanced separation and detection techniques present promising routes for the detection of low concentration species such as SPAs in middle distillate fuels.

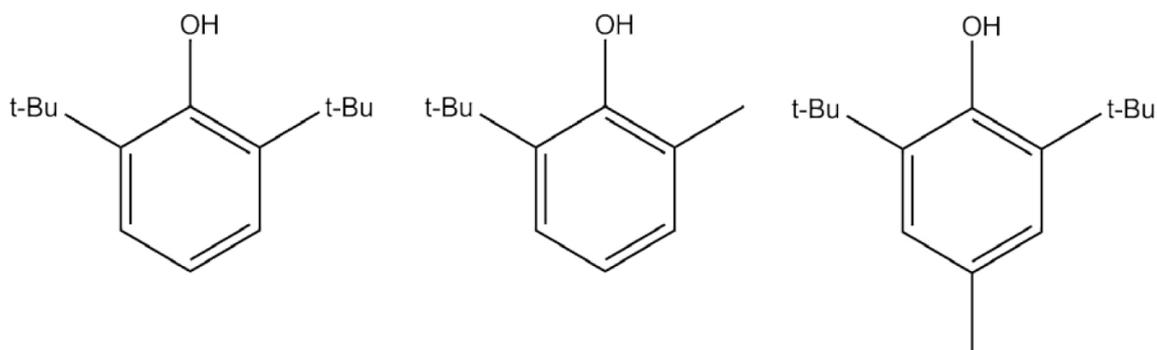


Figure 1. Examples of SPA compounds commonly permitted in military fuel specifications. From L-R: 2,6-di-*tert*-butylphenol, 2-(*tert*-butyl)-6-methylphenol, 2,6-di-*tert*-butyl-4-methylphenol

1.1.2 Fuel contaminants: fatty acid methyl esters

A popular non-petroleum alternate fuel is fatty acid alkyl esters, commonly known as biodiesel. The most common of these are comprised primarily of fatty acid methyl esters (FAME) and may be used as a neat fuel or blended with conventional petroleum fuels. FAME-containing fuels are one of the most widely used and well established renewable energy sources, and are made by the acid or base catalysed esterification of triglycerides from oils or fats (Figure 2). Primarily used as blending feedstock with diesel for ground applications, increased use and distribution has led to more incidents of cross-contamination and FAME is considered a contaminant in many fuels, particularly those used in aviation and other specialised fuels used by militaries. Even small amounts of FAME contamination are known to contribute to poor fuel properties including decreased thermal and storage stability, raised freeze point and poor water separability characteristics^{16, 17}.

Standards dictate that FAME content in jet fuels must not exceed 50 mg/kg¹⁸, which has recently been revised from 5 mg/kg¹⁹, and for naval distillate FAME content is not permitted^{9, 20}. Methods for the detection and quantification of low levels of FAME are generally applicable to aviation fuels only^{21, 22}. The wider cut, higher molecular weight components and increased complexity of naval diesel and heavy fuel oils has prevented quantification of low levels of FAME contamination in these matrices. Currently, the undesirable situation exists whereby there is a standard dictating a

zero level of FAME in a fuel, but there is no method available to determine whether this condition is satisfied. Multidimensional chromatographic techniques provide a promising route for the detection and quantification of low levels of FAME contamination that have not previously been achievable with conventional detection methods.

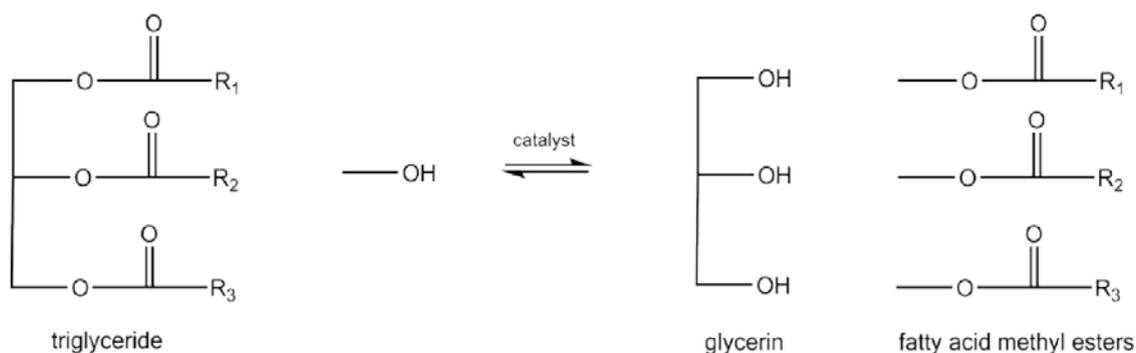


Figure 2. Generic reaction scheme for the production of FAME biodiesel. R indicates hydrocarbon chains of different carbon numbers and/or degree of saturation.

1.1.3 Oxidised species in fuels

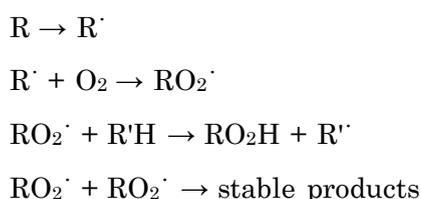
The final category of oxygenated heteroatomic compounds in fuel covered in this thesis is those generated through oxidation and instability reactions. Fuel hydrocarbons are susceptible to oxidation during either extended periods of storage, or through thermal stress. This results in the formation of a broad range of difficult to quantify oxygenated hydrocarbons which will be discussed in more depth in Section 1.2.

1.2 Thermal stability and oxidation of middle distillate fuels

Thermal stability refers to the resistance to decomposition of a molecule or mixture at elevated temperatures. This is a crucial operational and performance requirement for middle distillate fuels, in particular those used by the military in high performance air and sea vehicles. Fuels are routinely subjected to high heat loads and thermal stress when used in modern jet and high pressure common rail diesel engines. In jet aircraft, fuels may serve a dual purpose; in addition to propulsion, they also act as a heat sink to cool oil and avionics.²³ High pressure common rail diesel engines also return and reuse unspent fuel that may have been heated to temperatures above 120 °C.²⁴ When fuel is exposed to these elevated temperatures,

autoxidation and the formation of undesirable reactive compounds are accelerated. This leads to a decrease in engine operation efficiency, increased maintenance and possible engine failure.

Previous work on thermal stability of hydrocarbon fuels²⁵⁻²⁸ has determined that the first step in the degradation of fuels is the formation of reactive hydroperoxides (primary oxidation), which then initiates further reactions (secondary and tertiary oxidation) resulting in the formation of other oxygen-containing species.²⁹⁻³¹ A generic reaction scheme for a given hydrocarbon R, is given below.



adapted from Heneghan & Zabarnick³²

Once the peroxide is formed, myriad other oxidised species can be generated. Further reactions of these oxidised compounds have two significant effects on fuel which may render it unsuited to high performance operations; the formation of fuel- insoluble products, and changes to the fuel's physicochemical properties.

1.2.1 Assessment of fuel oxidation and degradation

Standardised physical and chemical test methods are currently the most commonly used tools to assess the extent of oxidation or degradation of a fuel. Tests may be carried out upon procurement of the fuel, or whilst the fuel is in service, to determine whether it is fit for purpose. These include the jet fuel thermal oxidation test (JFTOT),³³ acid³⁴ and base³⁵ number, peroxide content,³⁶ existent gum,³⁷ bromine number,³⁸ water reaction,³⁹ and water separability.⁴⁰ However, none of these methods can be used as a single indicator or predictor of the extent of oxidation of a fuel, do not allow for determination of the overall state of the fuel, and do not provide detailed information about the oxidative species that are in the fuel.

1.2.2 Fuel insoluble products

One significant deleterious effect of thermal oxidation of fuel is the formation of insoluble products including sediment, gums and lacquers (Figure 3). Continual thermal stressing is known to accelerate the formation of insoluble species⁴¹⁻⁴⁴ which may then reduce heat exchanger efficiency and cause engine system fouling including the blocking of nozzles, valves and filters.²³ The processes leading to the formation of insoluble products are complex and may include bulk liquid phase reactions, nucleation of particles via polymerisation, oligomerisation and agglomeration, solubility, surface and solvation reactions.⁴⁵ Previous analyses^{43, 46-48} of insoluble products have revealed that their elemental composition includes oxygen, sulfur and nitrogen, as well as carbon and hydrogen, and notably, cyclic and aromatic components. Although elemental analyses of insoluble products may allow inferences to be made as to their formation, the processes and reactions occurring in between the generation of oxygenated species, and the generation of insolubles, to this stage have not led to any concrete conclusions regarding the routes of their formation.

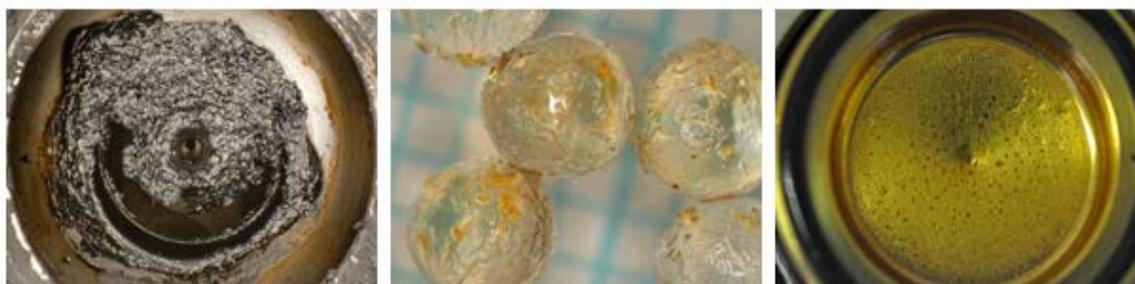


Figure 3. Examples of carbonaceous deposits (left), gums (centre) and lacquers (right) from thermally oxidised fuels. Photo credits (L-R) Qinetiq Group plc, P. Rawson., C. Stansfield

Much work has been undertaken to determine the fuel species and properties which are related to the formation of insolubles. Deposition is highly dependent on the availability of molecular oxygen⁴⁹ and it has been reported that it will cease once dissolved oxygen is consumed.⁵⁰ Antioxidants will also strongly influence the deposition characteristics of fuels, through their presence, consumption and depletion. It has also been shown that antioxidants are more effective at reducing deposits from storage instability, than thermal instability.⁵¹ Acid/base chemistry also influences deposition, but the relationships are not simple. Measurement of acid

and/or base content of a fuel is not a good indicator of deposit formation tendency, and attempting to negate the detrimental effect of acids with organic bases may actually increase the formation of insolubles.⁵² The method of refining and processing the fuel also has an effect, most notably due to the proportion of aromatic compounds. These electron-rich species react preferentially with oxygen, creating more radicals and hence oxidised species.⁵³ Refinery processing is also relevant to oxygenated species whereby the formation of insoluble precursors may be mitigated through the presence of dispersants introduced into fuels during processing.⁵⁴ The solubility of deposit precursors will also vary between fuels from different feedstocks, with some synthetic fuels shown to exhibit poor solubility for macromolecular oxidatively reactive species.⁵³

1.2.3 Physicochemical effects of oxidation

There exists documented cases of aircraft lost due to peroxide-induced degradation of fuel system seals.^{6, 55} Oxygen-containing compounds have also been demonstrated to contribute to poor thermal stability, water separability and emulsification tendency (Figure 4), higher wear, and increased conductivity (which leads to accumulation of static charge).^{56, 57}



Figure 4. Examples of poor water separability in fuels. Photo credits D. Evans, R. Webster.

There is a suite of heteroatomic additives routinely added to military middle distillate fuels, which have been known to cause fuel quality issues such as metal deactivator and thermal stability additive,^{15, 58} but it is likely that other heteroatomic compounds formed via fuel instability and oxidation reactions also contribute to deleterious effects on fuel physical and chemical properties. Identifying and quantifying the oxygenated compounds present in thermally oxidised or otherwise problematic fuels will be important in formulating strategies to mitigate their effects.

1.3 Considerations of alternatively derived middle distillate fuels

Increased global interest in liquid fuels derived from non-traditional sources has led to many developments in the processing, treatment and synthesis of non-crude oil sourced middle distillates. However, in order for new fuels to be successfully adopted, they must be ‘drop-in’ replacements. That is, alternatively-derived fuels must be indistinguishable from crude-derived in terms of requiring no alterations to equipment, operations, handling or transportation while meeting existing user specifications.⁵⁹ Several types of alternative feedstock fuels are currently approved for use in aviation or being investigated as fossil fuel replacements (Figure 5), including Fischer-Tropsch (FT) synthesis from coal, biomass or natural gas, hydroprocessed esters of fatty acids (HEFA) from algae and plant and animal-derived oils and fats, and conversion of alcohols via oligomerised olefins (alcohol to jet, ATJ), amongst others. Although not yet in widespread use, these three processing methodologies have already acquired certification, and may be used when blended at up to 50% by volume with conventional aviation fuel.⁶⁰

Alternatively-derived fuels, and fuels that have been hydrotreated, cracked or heavily processed, may differ in their chemical composition and therefore, in their oxidation and thermal stability characteristics. The feedstocks and methods of their production result in an end product that is inherently comprised of different compounds in different ratios to conventional fuels. Variation between fuels created through different processing routes is also expected. For example, fuels produced via cracking of heavy hydrocarbons will have different properties and composition compared with fuels produced via oligomerisation of 3- and 4-carbon monomers. Poor stability of these fuels is also in part due to the removal, or non-existence, of naturally occurring antioxidants such as olefins, aromatics and sulfur-containing compounds.⁶¹ Increased thermal stability and resistance to deposit formation of synthetic paraffinic kerosene at lower temperatures

has been observed using two different thermal stability test methods.⁵⁹ At temperatures above 350-400 °C however, these are far more reactive, and produce more deposits than conventional fuels.⁶² This suggests that there may be a different set of reactions taking place in these types of alternative fuels.

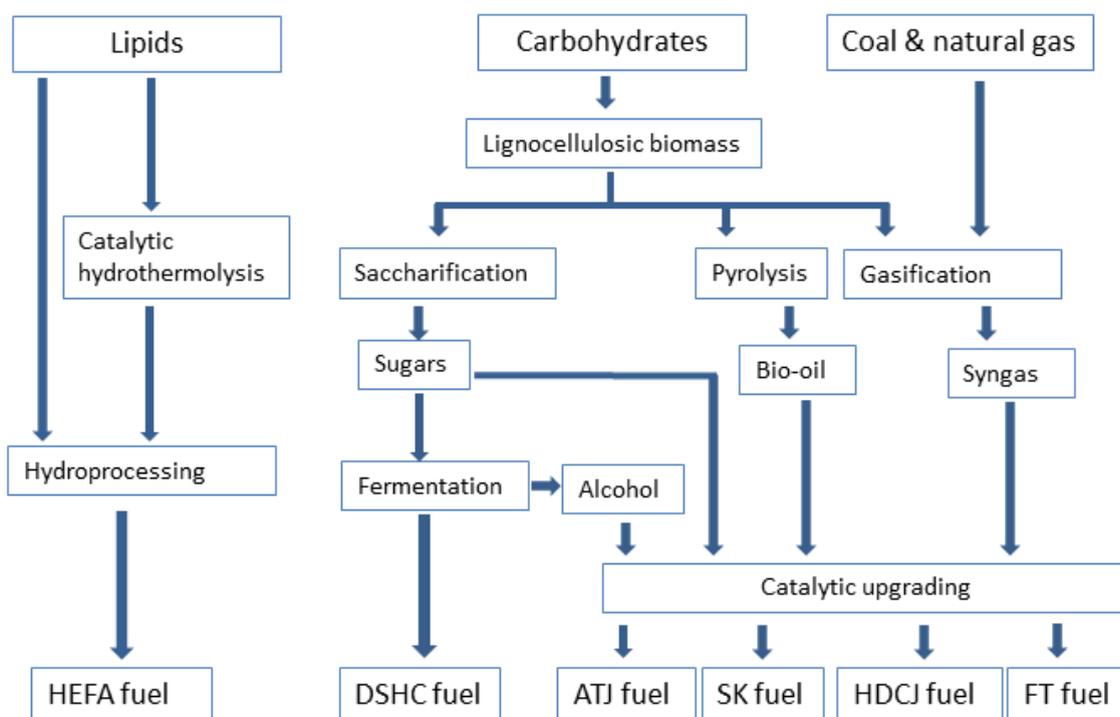


Figure 5. Pathways to alternate jet fuel production. Adapted from Rumizen⁶³

1.4 Analytical approaches to oxygenated compounds in fuel

Traditional methods for analytically investigating the thermal stability of fuels have generally relied on either bulk fuel property tests, gravimetric measurement of the formation of insoluble reaction products or time-consuming extraction and fractionation procedures. The complex nature of fuel has meant that crude functional group-type analyses have generally been popular, rather than a focus on the isolation and characterisation of specific molecules.^{32, 64, 65} Popular analytical methods such as high performance liquid chromatography (HPLC),⁶⁶⁻⁷⁰ gas chromatography (GC, Section 1.4.2), nuclear magnetic resonance (NMR),^{71, 72} and infrared spectroscopy, (IR)⁷³⁻⁷⁵ have all been implemented for the analysis of stability and/or polar species in fuels. However, these are plagued with problems such as poor compound resolution and specificity, and demanding with respect to time and resources. Modern column-coupled chromatographic techniques, such as multidimensional and comprehensive gas chromatography, present a much greater

potential for successful identification and quantitation of compounds in complex fuel matrices.

1.4.1 Extractive techniques for oxygenated compounds

In order to reduce interferences and lessen the influence of the hydrocarbon matrix, extractive or fractionating techniques are commonly applied to fuels prior to the analysis of oxygenated compounds. These may be broadly classified into three categories: liquid-liquid (solvent) extractions,^{76, 77} column-based extractions (e.g. preparative LC,⁷⁸⁻⁸⁰ solid phase extraction^{79, 81}) or micro-extractions (e.g. solid-phase microextraction; SPME). These procedures are both time and resource intensive and the risk of losing compounds of interest in the sample preparation processes is an ever present consideration. While the challenges of analyte loss and matrix interference must be kept in mind, sample extraction and pre-preparation techniques are still a valid approach⁸² to remove interferences and pre-concentrate target analytes. Indeed, studies have shown that compounds recovered in methanol extracts of fuel are directly implicated in the formation of insoluble products,⁵² and that the amount of polar species extracted using HPLC can be correlated with the amount of thermal oxidative insoluble deposit formed.⁸³ Prior to the development of high resolution chromatographs and spectrometers, extraction was the only feasible way analysts could probe the trace constituents of fuel.

SPME may be considered an underutilised extraction mode in this context, as the vast majority of applications are for analytes in polar matrices, usually water. Based on the selective extraction of volatile analytes sorbed onto a polymer-coated fibre, SPME concentrates target compounds from the headspace of a sample prior to further analysis.⁸⁴ Given that most SPME applications target relatively non-polar analytes in a polar matrix, the success of commercially available fibres to analytes in fuels has been limited.^{85, 86} Laboratory fabrication of bespoke fibres is a route to carry out SPME conducive to the extraction of polar analytes from fuels. Followed by an appropriate separation technique such as GC, such extractive approaches can provide valuable additional information about trace polar species which may not be gleaned using other analyses.

1.4.2 Gas chromatography of oxygenated compounds in fuel

Gas chromatography is a popular analytical technique for characterising either neat fuels, or following appropriate extraction/concentration techniques. When coupled with an appropriate mass (Section 1.4.3) or element selective detectors, GC is usually the preferred technique for analysing oxygenated compounds in fuels at low concentrations. Only at high, percent-level concentrations, is it possible to analyse oxygenated compounds in fuels using a single column GC separation. Analyses of extracted or derivatised oxygenated compounds in fuels has traditionally been the preferred approach.

Choice of column is often a critical step in developing GC analytical methods. Long, hydrocarbon specific columns of 100 or even 200 m in length provide a high number of theoretical plates and maximise resolution of the hundreds of thousands of components in complex fuel mixtures.^{87, 88} Polar column phases such as polyethylene glycol and cyanopropyl exhibit chemistries that have long been the most suited to resolving polar analytes from many matrices, including fuels. The advent of commercially available ionic liquid columns has added a new realm of polarity in column phases which further assists separations in non-polar matrices.⁸⁹ Applications of these columns to fuels and hydrocarbon mixtures have revealed high stability and suitability for these matrices.⁹⁰⁻⁹²

Another approach for identifying oxygen species in the carbon and hydrogen-rich fuel matrix is the use of element specific detectors, which are particularly useful when coupled with a separation technique such as GC. There is some work in the area of oxygen specific detection via oxygen-flame ionisation⁹³ or atomic emission^{5, 94} but these detectors are notoriously difficult to use for trace analysis, as they are prone to leaks and interference from atmospheric oxygen. A more popular approach in the modern laboratory is the use of mass spectrometric detectors.

1.4.3 Mass spectrometry for oxygenated compounds in fuel

Mass spectrometry is frequently used in conjunction with GC and other separation techniques to aid in the identification of groups and specific compounds of interest in fuels.⁹⁵ Applications of many varieties of mass spectrometers are published in the literature for the analysis of oxygenated compounds in fuels. Spectrometers with electron (hard) ionisation sources are robust, with large searchable libraries, and comparatively low cost contributing to their ubiquity in the modern chemical

analysis laboratory. Examples of these in the literature are many, with quadrupole and ion trap spectrometers used for the study of fuel instability reactions,^{96, 97} of *in situ* hydrocarbon oxidation,⁹⁸ and oxygen passivation at low temperatures.⁹⁹

Supersonic molecular beam (cold) ionisation has also been shown to be effective for characterising biodiesel, through the identification of molecular ions which is particularly useful for unreacted glycerides which are not well separated by GC.¹⁰⁰ Nominal mass time-of-flight mass spectrometry (TOFMS) has been used to identify oxygenates such as phenols in aviation fuels.⁸² For compounds with a molecular mass ideally of 100 or more and amenable to successive fragmentations, tandem mass spectrometry (MS^n) provides the benefits of low detection limits and the elimination of matrix noise, ideal for the analysis of trace oxygenates in fuels. Although analytes must be targeted, in order to set up reaction monitoring for secondary and further fragmentations, this limits its utility for elucidating unknowns. Triple quadrupole MS has been employed for the analysis of antioxidants in Naval fuels, with soft chemical ionisation to further improve detection limits.¹⁰¹

Alternate soft ionisation modes have been gaining traction in fuel analysis, including chemical ionisation, atmospheric pressure ionisation, electrospray ionisation, laser desorption ionisation, field ionisation and others. Soft ionisation techniques have shown special utility for the analysis of hydrocarbons, where molecular ion fragments provide far more revealing information about composition than hard ionisation fragments which are common amongst classes of hydrocarbons.¹⁰² Additionally, the polarisability of heteroatomic trace target analytes can be taken advantage of with techniques that do not readily ionise hydrocarbon species.¹⁰³ Electrospray ionisation has been used to identify heteroatomic nitrogen, sulfur and oxygen species in diesel^{104, 105} and aviation fuels.⁴⁵ Atmospheric pressure ionisation has been demonstrated to be more effective in identifying a broad range of heteroatoms in fuels but is not always the optimal technique for oxygenates.¹⁰⁶ Time of flight and Fourier transform ion cyclotron resonance spectrometry were used to detect four oxygenated groups in hydrocarbon mixtures, however some key oxygenates could not be resolved.¹⁰⁷ Combinations of different ionisation modes and mass analysers provide promising avenues for detailed investigations of trace oxygenates in fuels.

1.4.4 Multidimensional and comprehensive two dimensional gas chromatography of oxygenated compounds in fuels

Despite attempts to improve analyses by extraction and fractionation of the fuel, and low and high resolution separations, issues related to poor detection limits, matrix complexity and sample preparation persist. Multidimensional gas chromatography (MDGC) is a versatile and powerful technique based on two or more orthogonal dimensions of separation attained through the use of capillary chromatographic columns of different selectivities. The enhanced separation power of MDGC techniques over traditional one dimensional gas chromatography (1DGC) makes it ideal for the analysis of samples with highly complex matrices. Therefore, MDGC is a promising method of resolving the hundreds of thousands¹⁰⁸ of chemicals present in the complex fuel matrix. Indeed, there have been many prior studies applying MDGC techniques to fuel samples. Successful group-type or PIONA (paraffins, isoparaffins, olefins, naphthenes, aromatics) separations have been demonstrated, in good agreement with ASTM methods for hydrocarbon typing in middle distillates.^{109, 110} Addition of MS detection^{108, 111} as well as degree of branching and carbon number distribution³ lends further value for the analysis of middle distillates. More recent advances in this area incorporate GC systems with much faster detectors^{112, 113} allowing even more detailed analysis of the fuel group types.

There has been relatively little focus upon analysis of heteroatomic species and these are generally concerned with the analysis of trace heteroatomic compounds indigenous to the fuel or intentionally included as additives.^{82, 112, 114, 115} To date, research into the analysis of oxygenates via MDGC has concentrated on analysis of target oxygen-containing compounds, or homologous groups such as fatty acid methyl ester (FAME), for the identification and quantitation of biodiesel/diesel blends.¹¹⁶⁻¹¹⁸ The small group of oxygenates which are added to fuels in order to improve emissions have also been studied with MDGC, successfully isolating the target compounds from the fuel matrix.^{119, 120}

Comprehensive two-dimensional gas chromatography (GC×GC) is ideally suited for the analysis of complex mixtures such as hydrocarbon fuels.^{121, 122} Applications of GC×GC to fuels and other hydrocarbon mixtures are unique in that the matrix itself is often the analytical target. Group typing or fingerprinting of fuels is a common application of GC×GC, particularly PIONA-type (paraffins, isoparaffins, olefins, naphthenes, aromatics) analyses.^{123, 124} Other minor groupings or subsets of the

aforementioned classes are also possible where an even more detailed approach is warranted. Approaches for grouping aromatic and cyclic compounds in particular can be found in the literature, where compound classes such as polycyclic alkanes,¹²⁵ indanes/tetralins, naphthalenes, and fluorenes^{126, 127} were resolved in a variety of middle distillates.

Group typing or group targets of heteroatomic species has also been achieved; including of oxygenates which are indigenous to the fuel^{128, 129}, a by-product of the refining/synthetic process,^{112, 130, 131} performance additives¹¹⁹ or as blendstock.¹³² More popular are GC×GC analyses of the nitrogen^{114, 133-135} and sulfur^{115, 136-139} heteroatoms in middle distillates, although by their nature this often also includes compounds which contain oxygen. These approaches are often aided by employing an element-specific detector as discussed in Section 1.4.2. Targeted and trace compound analysis is another use of GC×GC, such as the resolution of mainly phenolic oxygenated compounds in fuel derived from coal.¹²⁸ However, in this example complete separation of oxygenates from nitrogenated and other polar compounds was not achieved. Quantitative analysis of trace species such as metal deactivator additive¹⁴⁰ and aromatics¹⁴¹ in fuels is also reported using GC×GC techniques. Another area where GC×GC has been applied in complex hydrocarbon mixtures is to identify products formed via the environmental degradation of crude oil. The oxygenates isolated included carboxylic acids, alcohols¹⁴², and ketones¹⁴³ derived from the biological and light-induced oxidation of the spilled oils.

1.5 Key objectives

The key objectives of this research were to:

- develop new gas chromatographic and mass spectrometric methods for the analysis of trace oxygenated compounds in conventionally and alternatively-derived middle distillates that are more efficient, more sensitive and with lower detection limits than existing methods. The oxygenated compounds of interest are:
 - Antioxidant additives in the form of synthetic methyl and tertiary butyl phenols
 - Fatty acid methyl ester contamination
 - A broad range of oxidised species generated via thermal oxidative instability reactions;

- implement and validate new GC and MS methods, with particular focus on multidimensional techniques, to identify and quantify oxygenated compounds inherently present in conventional and alternate middle distillate fuels;
- characterise the progress of oxidation reactions in conventionally and alternatively derived middle distillate fuels during thermal oxidative stressing;
- formulate quantitative associations between the presence of oxygenates in middle distillate fuels, and the physicochemical properties of the fuels.

Chapter 2: Publication 1

Webster, R. L.; Rawson, P. M.; Evans, D. J.; Marriott, P. J., *Energy Fuels* **2014**, 28 (2), 1097-1102

Synopsis

This work presents two new methods for the selective determination and quantification of specific SPA in jet and diesel fuels using gas chromatography-triple quadrupole (GC-QQQ) and quadrupole time-of-flight (QTOF) mass spectrometry. The goal was to improve the detection and quantitation of SPAs, broadening the scope of analytes to include compounds usually overlooked in antioxidant determination and also decreasing the detection limit to capture the minor constituents in SPA mixtures used in fuel finishing. Despite this expansion of the analyte set, the method is still highly targeted and focuses only on the compounds which are known, through being detailed in the relevant specifications, to be allowed in the SPA additive package. The analytical procedure is rugged and robust and involves no sample preparation, with direct injection of the diluted parent fuel into the GC column. It is a significant advance on other methods for determining synthetic phenolics in fuel matrices which have had only limited numbers of analytes, poor resolution, inadequate sensitivity/selectivity or loss-inducing sample extraction procedures. The power and limitations of the two separate advanced spectrometric techniques are demonstrated and also contrasted, each showing that the highest quality separations are not always required where highly selective mass spectrometry is available. Validation of the methods is achieved and authenticated through quantification of SPA concentrations in real fuel samples. The inclusion of several alternatively-derived fuels in the study lends a forward-looking focus to the work, and is the first published independent verification of SPA concentrations in these fuel types.

2 Synthetic Phenolic Antioxidants in Middle Distillate Fuels Analyzed by Gas Chromatography with Triple Quadrupole and Quadrupole Time-of-Flight Mass Spectrometry

Renée L. Webster, Paul M. Rawson, David J. Evans, Philip J. Marriott

2.1 Abstract

Methods for the selective determination and quantification of 10 synthetic phenolic antioxidants (SPA) in jet and diesel fuels have been developed. The analytical procedure involves no sample preparation, and uses direct injection of the diluted parent fuel into the GC column. Gas chromatography with both triple quadrupole and quadrupole time of flight mass spectrometry was used to quantify synthetic phenolic antioxidants in the range of 0.1-20 mg/L. Precision was in the range of 3-9%. The method is demonstrated to be rugged and robust, and since no extraction is required, does not require estimation of extraction efficiencies. It is generally suited to volatile SPA compounds included in jet and diesel fuel specifications. The method is appropriate for the estimation of SPA in fresh and in-service middle distillate fuels stored on military bases, tankers or in use on aviation or naval platforms.

2.2 Introduction

The inclusion of synthetic phenolic antioxidants (SPA) in hydroprocessed middle distillate fuels is mandated in jet fuel specifications.^{19, 144} Antioxidants were first introduced as fuel additives to increase fuel stability by preventing the build-up of peroxides, which are generated when the fuel experiences thermal stressing or oxidation during ambient storage.⁶ Peroxide formation may lead to damage of the fuel system elastomers and is also recognised in the initial phase of the oxidation process of fuels.^{145, 146}

The build-up of peroxides is increasingly important in fuel due to recent prevalence of hydroprocessing as a refinery finishing process, which removes naturally occurring antioxidant compounds from the fuel and promotes formation of peroxide-

forming compounds.^{32, 147, 148} Specifications mandate a maximum total SPA concentration of 24 mg/L. Currently it is not possible to analytically confirm the SPA concentration once SPA are added to fuel, given the many possible compounds which may be present in the antioxidant package, and the complexity of the base fuel which leads to considerable matrix interference. Methods that provide the ability to positively identify and quantify specific SPAs present in any given fuel is desirable, particularly when fuels experience stability problems and/or become contaminated and where these may be treated by addition of synthetic antioxidants. SPAs are primarily found in aviation fuels, however Australian specifications for naval distillate fuel also includes provisions for SPA addition.⁹ SPAs will continue to be important fuel additives in the future as the use of antioxidant-free synthetic, biological, and other types of alternatively derived fuels increases.

Gas chromatography (GC) is a popular analytical method for fuel.¹⁴⁹ In particular, GC/mass spectrometry (GC-MS) with selected ion monitoring has been used for SPA by Bartl and Schaff¹⁵⁰, Pearson¹⁵¹, Bernabei *et al.*¹⁵² and Shin *et al.*^{153, 154} but these methods were only applied to a small number of analytes. Methods based on GC separation with MS SIM detection generally persist as the most popular analytical methods for determining SPAs in fuels, despite suffering problems such as lack of baseline resolution from the fuel matrix, interferences, incomplete extraction and poor sensitivity and linearity. Multidimensional separation has been reported for analysis of SPAs in middle distillates^{155, 156} but requires sample preparation by liquid extraction, and applicability to middle distillates is not proven. Other identification methods for SPAs in fuels include HPLC,^{152, 157, 158} UV spectroscopy¹⁵⁹ and voltammetry.¹⁶⁰ These techniques suffer many of the same drawbacks as discussed previously.

Advances in commercial MS technology coupled with GC, such as quadrupole time of flight (QTOF) and triple quadrupole (QQQ), present promising routes for the detection of low concentration species such as SPAs in middle distillate fuels. GC/QQQMS is useful for analysis of complex matrices through multiple reaction monitoring (MRM), offering improved sensitivity, minimum background interference, and unambiguous identification of analytes through monitoring of specific precursor-product ion transitions. Specifically, MRM permits the analysis of 'known' analytes, where unique ion transitions may be selected after the collection of the compound's mass spectrum. Applications of GC/QQQMS to hydrocarbon fuel

analysis are scarce, possibly attributed to the recent popularity of the technique and high cost of the instrumentation. Older generation QQQ mass spectrometers were applied to various aspects of hydrocarbon analysis but apparently none to the analysis of SPAs.¹⁶¹⁻¹⁶⁴

Accurate mass QTOFMS is well suited to the analysis of trace compounds within a complex matrix, either when analytes are known or are unknown, and the mass therefore is also known or can be acquired with accuracy. In this case, an extremely narrow mass window greatly improves sensitivity by eliminating noise emanating from the matrix, or coeluting analytes. Omais *et al.*¹²⁸ applied GC×GC/QTOFMS to the analysis of oxygenated compounds in a coal middle distillate, which included naturally occurring phenolic compounds. The highly sensitive and selective nature of these techniques obviates the requirement for sample preparation, extraction or fractionation, which are time consuming and often lead to analyte losses.

Here, we present a new method of GC coupled to the MS/MS instrumentation - QQQMS and QTOFMS - for quantification of SPA in naval and aviation middle distillates. Various analytical figures of merit are presented. The method eliminates bulk matrix interferences to permit effective analysis of SPA in fresh and in-service middle distillate fuels.

2.3 Experimental

2.3.1 Samples and Standards

2.3.1.1 Middle Distillate Fuels

A set of eight middle distillate fuels were selected for this study and their details are given in Table 1. A selection of aviation and naval fuels were chosen in order to cover a variety of different refinery processing methods and fuels made from both conventional and alternatively-derived feedstocks. Samples were analysed as received unless otherwise specified.

Table 1. Details of the middle distillate fuels used in this study.

	Sample	Source	Processing/Refining Method
	A	Fossil	Hydroprocessed
	B	Fossil	Hydroprocessed (high flashpoint)
	C	Fossil	Merox
Aviation	D	Fossil	Straight Run
	E	Camelina	Hydroprocessed Esters of Fatty Acids
	F	Algae	Hydroprocessed Esters of Fatty Acids
	G	Coal/Syngas	High Temperature Fischer-Tropsch
Diesel	H	Fossil	Cracked/Hydrotreated Low Sulfur
	I	Fossil	Cracked/Hydrotreated High Sulfur

2.3.1.2 Synthetic Phenolic Antioxidants

Pure samples of individual SPA compounds were obtained from Sigma-Aldrich (Castle Hill, Australia), and commercial antioxidant mixture AO-32 from AS Harrison (Brookvale, Australia). For clarity and consistency, the notation used in this manuscript to refer to specific SPA compounds is similar to that used previously,^{153, 157} and will follow the example in Figure 6 derived from abbreviating the IUPAC name for each compound. The specific composition of AO-32 is proprietary but is known to contain 26dtb4mp, 6tb24dmp, dmp (positions of methyl substitutions not specified) and at least 25% unspecified constituents.

A mixed stock standard of the 10 SPAs was prepared in heptane, at a concentration of approximately 10,000 mg/L per individual compound. Working standards were prepared from this stock solution by diluting with heptane, with deuterated o-xylene (D-10) (Novachem, Collingwood, Australia) used as an internal standard at 4.85 mg/L. Spiked mixed SPA standards in heptane and SPA-free jet fuel revealed no significant matrix effects.

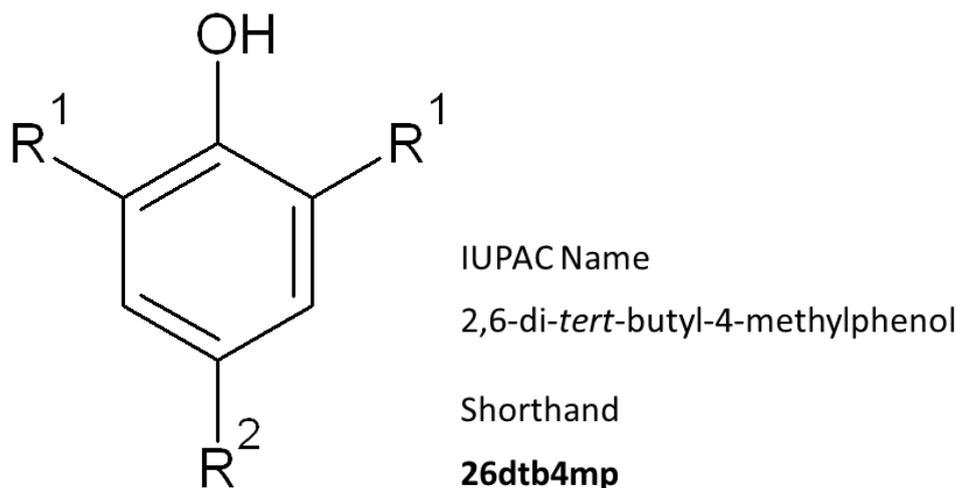


Figure 6. Naming example for SPAs in this study, where R1 and R2 represent tertiary butyl and methyl substitutions for the indicated compound, respectively.

2.3.2 Static Thermal Oxidation

Static thermal stressing was carried out as per ASTM D7545, using a PetroOxy Oxidation Tester (PetroTest Instruments, Dahlewitz, Germany).¹⁶⁵ 5.00 mL of sample under a limited oxygen atmosphere, charged to 700 kPa was heated to 140 °C and the pressure monitored until a pressure reduction of 10% was observed. An SPA-free fuel was spiked with a known amount of AO-32 commercial antioxidant mixture and submitted to static thermal oxidation using the PetroOxy system. As most modern middle distillates are produced with at least some degree of hydroprocessing, it is difficult to obtain fuels that are completely free of SPA and only one such fuel was available for this study. This serves to test whether determinations of SPAs are susceptible to any interferences which may arise through the process of fuel oxidation.

2.3.3 GC/MS Instrumentation

2.3.3.1 GC/QQQMS

Qualitative and quantitative sample analysis was carried out using an Agilent 7890A GC with 7000B triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, USA). Instrument control, data collection and processing were performed using MassHunter software (v. B.06.00). Samples were analysed

undiluted. GC and MS operating conditions are presented in Table 2. The QQQMS was operated in MRM mode with acquisition starting at 3 min. The spectrometer was in EI mode at 70 eV with the ion source at 280 °C. The collision cell was supplied with He quench gas at 2.25 mL/min and N₂ collision gas at 1.5 mL/min. Collision energy was adjusted as required for best sensitivity for the selected transitions

2.3.3.2 GC/QTOFMS

Qualitative and quantitative sample analysis was carried out using an Agilent 7890A GC with 7200 quadrupole - time of flight mass spectrometer (Agilent Technologies, Santa Clara, USA). The QTOFMS was calibrated daily with perfluorotributylamine (PFTBA), achieving a typical mass accuracy of <5 ppm. Instrument control, data acquisition and data analysis was carried out using MassHunter B.06.00. Samples were analysed undiluted. GC and MS operating conditions are presented in Table 2. The QTOFMS was operated in both targeted MS/MS (using extracted ion(s) for TOFMS data) and full scan modes at 5 GHz with acquisition starting at 3.9 min. Spectra were recorded from *m/z* 50-300, and MS/MS spectra from *m/z* 50-250.

Table 2. Operating parameters for GC/QQQMS and GC/QTOFMS analyses.

	QQQ	QTOF
Column	HP-5	HP-5ms
Length/ID/d _f	30 m / 0.25 mm / 0.25 µm	30 m / 0.25 mm / 0.25 µm
Oven	50 °C↑70 °C (7.5 °C/min) ↑120 °C (20 °C/min; 5 min hold) ↑180 °C (5 °C/min) ↑300 °C (20 °C/min)	50 °C↑120 °C (20 °C/min; 12 min hold) ↑220 °C (10 °C/min) ↑300 °C (20 °C/min)
Injector	300 °C	300 °C
Inj. vol. / split ratio	0.2 µL / 20:1	0.2 µL / 20:1
Carrier; flow; velocity	He; 1.2 mL/min;/ 39.9 cm/s	He; 1.0 mL/min ; 28.6 cm/s
Transfer Line; source	300 °C;230 °C	280 °C; 230 °C

Ionisation	EI, 70 eV	EI, 70 eV
Quadrupole	150 °C (Q1,2)	150 °C

2.4 Results and Discussion

2.4.1 Selection of Transitions for Multiple Reaction Monitoring (MRM) in GC/QQQMS

The SPAs in this study all exhibit two or three abundant peaks in their mass spectra, namely the molecular ion and one or two fragment peaks. The obvious strategy in a tandem MS experiment is to select the most abundant ions as precursor ion(s) for ions produced arising from further fragmentation. However, it became clear that almost all of these ions and their associated transitions to product ions were non-specific in the presence of the complex fuel matrix, and so non-SPA compounds also displayed similar transitions. Fuels spiked with known SPA compounds were used to conduct a thorough investigation of ion transitions which were specific only to the SPA compounds of interest, and not found in the bulk fuel matrix. In some cases, the ion transitions chosen were not those that were the most abundant, or displayed the strongest signal in the analysis of the SPA standard mixture. It was necessary for a compromise to be made with respect to the signal strength, in order to select ion transitions which were unique to the analytes and free of any interferences. Subsequent MS experiments encompassing a wider range of precursor ions, discovered precursor-product ion transitions that were unique to the SPAs and were free of interferences from other compounds in the fuel matrices studied. These transitions and SPA retention times are reported in Table 3. A chromatogram of the SPA standard mixture analysed by GC/QQQMS is displayed in Figure 7. Peak labels and transitions as given in Table 3.

2.4.2 Targeted MS/MS by QTOFMS

Table 3 summarises analyte retention times, optimised collision energies, target ion and quantifier ion mass values of the QTOFMS analytical method. The presence of an oxygen atom in SPAs allows differentiation from the hydrocarbon matrix by the

accurate mass capabilities of the QTOFMS instrument. For each SPA analyte, the molecular ion peak is present, as well as the base peak generated for the product ion $[M-CH_3]^+$. These two ions were utilised in the targeted MS/MS experiments, with extracted accurate mass fragment ions used as quantifier ions.

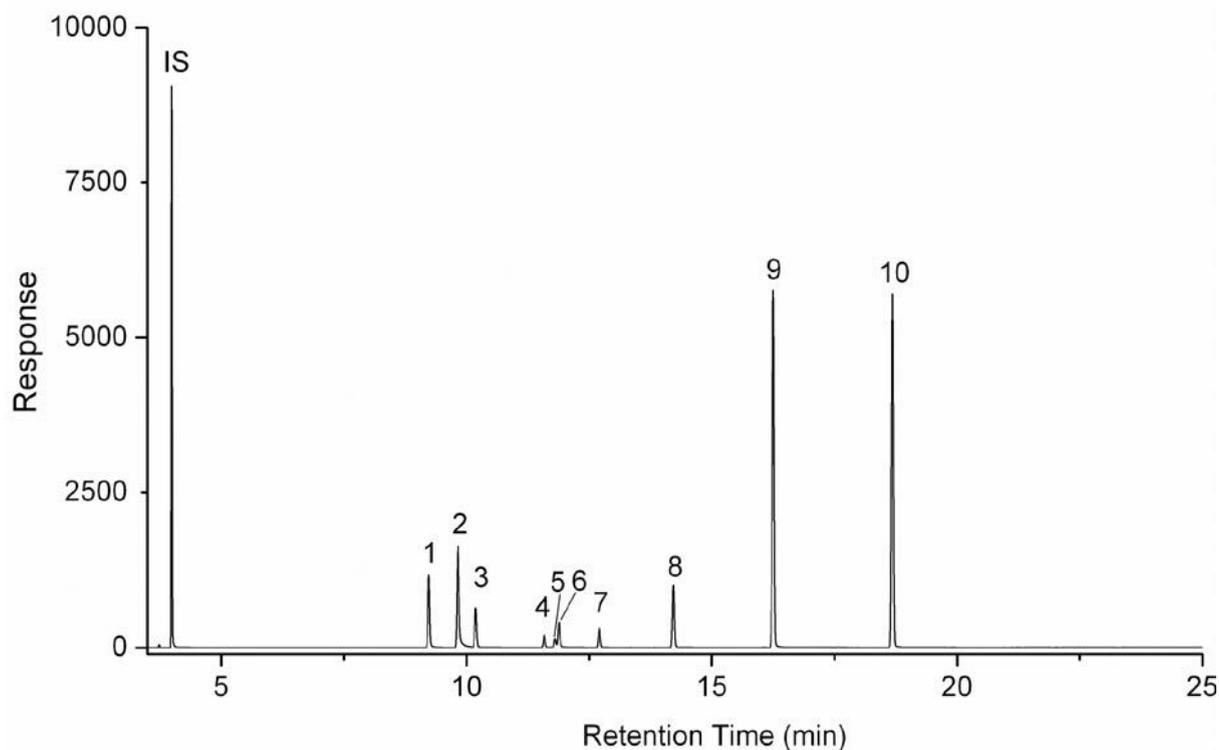


Figure 7. Chromatogram of SPA 10 mg/L standard by using selected MRM transitions in QQQMS. Peak labels and transitions as given in Table 3.

Mass deviation was less than 10 ppm for all analytes. Satisfactory mass accuracy and linearity of detector response were maintained up to the upper concentration solution investigated (20 mg/L). Where neat fuels are injected directly without dilution or extraction, it is necessary to take advantage of the tandem MS capability of the QTOFMS instrument. Despite accurate mass capabilities, the overwhelming number of compounds in the fuel matrix means that unique accurate mass ions of SPAs cannot be detected in TOFMS full scan mode alone. Utilization of the quadrupole mass filter to remove the bulk of interfering hydrocarbon matrix, is required in order to detect ppm-level concentrations of SPA compounds

Table 3. Parameters for MRM in QQQMS and targeted MS/MS by QTOFMS.

Number*	Analyte	Molecular Formula	QQQ			QTOF		
			Retention Time (min)	MRM transition (Q1→Q3)	Collision Energy (eV)	Retention Time (min)	Target ions (Q; <i>m/z</i>)	Quantifier ions (TOF; <i>m/z</i>)
int. std.	<i>o</i> -xylene (D-10)	C ₈ D ₁₀	3.99	116→98	20	3.92	98 116	70.07 98.0982
1	2tbp	C ₁₀ H ₁₄ O	9.23	135→115	30	10.38	135 150	107.0491 135.0804
2	4tbp	C ₁₀ H ₁₄ O	9.83	135→95	10	11.29	135 150	107.0491 135.0804
3	2tb6mp	C ₁₁ H ₁₆ O	10.19	149→116 149→115	10 10	11.82	149 164	121.0648 149.0961
4	2tb4mp	C ₁₁ H ₁₆ O	11.59	149→109	20	14.14	149 164	121.0648 149.0961
5	4tb2mp	C ₁₁ H ₁₆ O	11.81	149→116 149→115	10 10	14.57	149 164	121.0648 149.0961
6	2tb5mp	C ₁₁ H ₁₆ O	11.88	149→116 149→115	10 10	14.71	149 164	121.0648 149.0961
7	2tb46dmp	C ₁₂ H ₁₈ O	12.71	163→135	30	16.35	163 178	135.0804 163.1117
8	26dtbp	C ₁₄ H ₂₂ O	14.21	191→147	20	18.36	191 206	163.1117 191.1430
9	26dtb4mp	C ₁₅ H ₂₄ O	16.25	220→145 205→177	30 10	20.34	205 220	177.1274 205.1587
10	246ttbp	C ₁₈ H ₃₀ O	18.68	262→247 262→231	20 30	22.15	247 262	231.1743 247.2056

*Number according to chromatographic elution order – refer to Figure 7.

2.4.3 Quality Parameters

2.4.3.1 Linearity

The concentration range of standard solutions was chosen to encompass a range of concentrations in which each component is likely to be present in a typical middle distillate fuel meeting military specifications. Calibration curves were linear over the concentration range tested (0.1-20 mg/L), with correlation coefficients between 0.990 and 0.997 for all analytes. Parameters of linearity are given in Table 4. The sensitivity of both methods was sufficient to indicate that the limit of detection (LOD) is below 0.1 mg/L, defined as the lower limit required to be measured in this study.

Table 4. Linearity parameters for all 10 SPA analytes using QQQMS and QTOFMS; $n = 3$ for each analyte.

	QQQMS		QTOFMS	
	Regression equation ^a	R ²	Regression equation ^a	R ²
2tbp	$y = 0.143x - 0.017$	0.994	$y = 77.5x - 12.3$	0.995
4tbp	$y = 0.178x - 0.031$	0.993	$y = 43.8x - 7.56$	0.995
2tb6mp	$y = 0.089x - 0.015$	0.994	$y = 83.7x - 16.7$	0.993
2tb6mp	$y = 0.025x - 0.005$	0.990	$y = 79.3x - 15.3$	0.994
2tb4mp	$y = 0.016x - 0.003$	0.991	$y = 44.1x - 8.93$	0.993
4tb2mp	$y = 0.059x - 0.011$	0.993	$y = 73.2x - 16.3$	0.992
2tb5mp	$y = 0.053x - 0.010$	0.991	$y = 53.1x - 10.5$	0.993
26dtbp	$y = 0.154x - 0.028$	0.993	$y = 37.5x - 7.53$	0.992
26dtb4mp	$y = 0.833x - 0.162$	0.992	$y = 21.8x - 2.70$	0.997
246ttbp	$y = 0.768x - 0.141$	0.993	$y = 14.2x - 2.08$	0.996

^a Standard concentrations were: 0.1, 1.0, 2.5, 5.0, 10 and 20 mg/L. Slopes are related to the relative sensitivities of selected precursor and product ions of the CID process. x is SPA concentration in mg/L.

Differences in results obtained between the methods, and between analytes, in terms of analytical sensitivity of the calibration line can be attributed to the different ionization processes through the CID mechanism, and the relative responses of the precursor and product ions. Ionization in QQQMS is a dual stage SIM/SIM process, producing highly selective and sensitive detection of the specified ions. By contrast, QTOFMS is a SIM/scan process, which despite the accurate mass TOFMS capability, does not have the increased ion residence time of the second SIM stage of QQQMS.

2.4.3.2 Precision and accuracy of the analytical methods

In order to determine the precision of the methods, samples were examined for inter-day and intra-day variation. From an individuality prepared stock solution (10 mg/L) multiple repeat analyses were carried out on the same day and then on two subsequent days. Accuracy was assessed by a series of spikes, with the results expressed as mean recovery of the analyte, versus pure calibration standards. The results are presented in Table 5.

2.4.3.3 GC/QQQMS

The precision of the GC/QQQMS method was good, with relative standard deviations (RSD) for each analyte < 2% and < 5% for intra-day and inter-day variation, respectively. Accuracy was also good, with recoveries for each analyte between 92% and 104%

2.4.3.4 GC/QTOFMS

Both precision and accuracy of the GC/QTOFMS method were marginally poorer than the GC/QQQMS analysis. In this case, intra-day RSDs were < 3% and inter-day < 9% variation. While the recoveries of most analytes were good, in a few cases they were quite low.

Table 5. Results of method precision and accuracy for all 10 SPA analytes by using QQQMS and QTOFMS. RSD% values for absolute peak areas.

SPA	QQQMS			QTOFMS		
	Intra-day	Inter-day	Mean recovery	Intra-day	Inter-day	Mean recovery
	(n=6)	(n =18)	(n = 4)	(n =6)	(n =18)	(n = 4)
	average (RSD)	average (RSD)	%	average (RSD)	average (RSD)	%
2tbp	1390 (1.1)	1200 (3.4)	99	138000 (0.7)	126000 (6.3)	79
4tbp	2320 (1.2)	2240 (4.8)	104	73100 (2.3)	72800 (7.0)	86
2tb6mp	1150 (0.3)	1150 (0.3)	97	158000 (1.9)	155000 (5.7)	95
2tb4mp	342 (0.5)	333 (4.7)	96	145000 (2.6)	128000 (7.0)	98
4tb2mp	4590 (0.6)	4520 (2.5)	102	81700 (1.6)	72600 (6.2)	105
2tb5mp	2570 (1.0)	2550 (2.6)	97	78200 (1.2)	75200 (8.7)	106
2tb46dmp	965 (1.8)	921 (4.4)	92	91900 (1.6)	76400 (8.5)	103
26dtbp	2130 (0.3)	2090 (3.0)	94	53600 (2.5)	46500 (8.5)	100
26dtb4mp	10700 (0.4)	10400 (4.0)	96	47600 (1.8)	43700 (7.6)	64
246ttbp	10100 (1.5)	9580 (5.0)	98	43300 (2.9)	35400 (7.7)	75

2.4.4 Results of Analyses

2.4.4.1 Application to real samples

QQQMS and QTOFMS methods were successfully applied to the analysis of SPAs in all authentic middle distillate fuel samples. A range of middle distillate fuels were chosen for this study, encompassing both aviation and naval fuels, and fuels from conventional and alternative feedstocks.

Agreement between the two techniques was reasonable (Table 6), allowing for measurement errors, but the GC/QTOFMS method generally returned results lower than those returned by the GC/QQQMS analysis. This is consistent with the lower recoveries for SPA-spiked fuels discussed in Section 2.4.3.4. A statistical comparison

was made for each analyte for each method using an F-test based on the null hypothesis that the precision of each method is identical. At an uncertainty level of 5%, half of the analytes returned the results that the GC/QQQMS method is significantly more precise, while the other half did not. Both techniques can be effectively used for this application for the samples and concentration range studied.

Table 6. Results of SPA levels (mg/L) in authentic fuel samples. Data presented as GC/QQQMS value; QTOFMS value.

Sample	A	B	C	D	E	F	G	H	I
2tbp	1.8; 1.6	1.6; 1.5	ND	ND	1.3; 1.6	ND; 1.6	ND	ND	ND
4tbp	ND	ND	ND	ND	ND	ND	ND	ND	ND
2tb6mp	ND	ND	1.8; 1.4	ND	ND	ND	ND	ND	ND
2tb4mp	ND	ND	ND	ND	ND	ND	ND	ND	ND
4tb2mp	ND	2.5 3.3	ND	ND	ND	ND	ND	ND	3.5; 1.5
2tb5mp	1.3; 1.5	1.5; 1.5	ND	ND	ND	ND	1.1; 1.2	ND	4.7; 5.4
2tb46dmp	ND	ND	5.0; 4.2	ND	0.2; ND	ND; 1.4	8.3; 7.6	ND	ND
26dtbp	10.5; 7.8	8.3; 1.7	2.7; 1.2	ND	9.3; 3.9	8.5; 4.7	0.9; ND	ND	ND
26dtb4mp	1.0; 1.6	1.0; 1.7	2.0; 1.9	1.0; ND	0.9; ND	ND; 1.2	1.0; 1.7	1.1; 1.6	ND
246ttbp	2.6; 1.6	1.9; 1.4	1.1; 1.2	ND	3.1; 1.4	1.6; 1.9	0.9; 1.2	ND	ND
Total SPA	17.1; 14.1	16.8; 11.1	12.6; 9.9	1.0; ND	14.8; 6.8	10.1; 10.8	12.3; 11.7	1.1; 1.6	8.2; 6.9

Note: ND = not detected. Single ND means the analyte was not detected by either technique.

The concentrations of SPA present in the fuel samples are within the expected range. SPA concentrations are generally higher in fuels which are known to have

been hydrotreated, or blended with hydrotreated distillates. All of the fuels returned concentrations lower than that dictated as maximum SPA concentration by the relevant standards^{13, 19,144} however, the fuels analysed in this study were not ‘refinery fresh’, and antioxidant depletion is likely to have occurred through extended storage. No interferences from naturally occurring phenols were observed in the samples studied, although this cannot be ruled out altogether, given the variation between feedstocks used for producing fuels around the world. An example of the GC/QQQMS analysis of an authentic sample (camelina-derived jet fuel) is presented in Figure 8. This biologically derived synthetic paraffinic kerosene was chosen to demonstrate the applicability of these methods to new, non-fossil-sourced fuels.

Fuels C and D were refined without hydroprocessing and therefore retain natural antioxidant compounds. These returned lower SPA content, with D for example reported to only have one SPA (26dtb4mp) at low content by GC/QQQMS, than the other hydroprocessed fossil jet fuels (A, B). This may be due to consumption of SPA in storage, or that it was not added at the refinery as there is no requirement for SPA inclusion in these fuels. Naval distillates H and I also generally contained lower amounts of SPA.

2.4.4.2 Analysis of oxidised fuels

Concern that chromatographic methods for determining SPAs in middle distillate fuels may not be appropriate where the fuel has been degraded, either by thermal stress or extended storage, means that this valuable assessment tool has been underutilised. In these circumstances, it is possible that SPAs may be consumed entirely, or chemically degraded into phenolic or other degradation products. Such compounds may produce interferences in the chromatogram, and may share mass fragment ions in common with SPA compounds of interest. Analysis of a thermally oxidised fuel that was spiked with a known amount of commercial antioxidant mixture revealed that both the QQQMS and QTOFMS analytical methods are suitable for the determination of SPAs in heavily oxidised fuels; no interferences were encountered with the range of analytes studied.

Accurate mass scan mode only on QTOFMS (i.e. using total transfer of ions for operation of the Q sector) is not sufficient to differentiate the SPAs from the fuel

matrix, and targeted mode using the primary sector quadrupole filter is required. The distinction between the neat, SPA-free fuel and the fuel spiked with SPA was clear in the chromatograms obtained through QQQMS and QTOFMS analyses, and is demonstrated in Figure 9. The neat fuel, which contained no SPA, displays a flat baseline, whereas a significant SPA peak is clearly visible in the fuel which has been spiked with a commercial antioxidant. The spiked fuel which was subjected to accelerated storage stability testing reveals a heavily depleted SPA peak, and there were no interferences from any oxidation products arising from the depletion process.

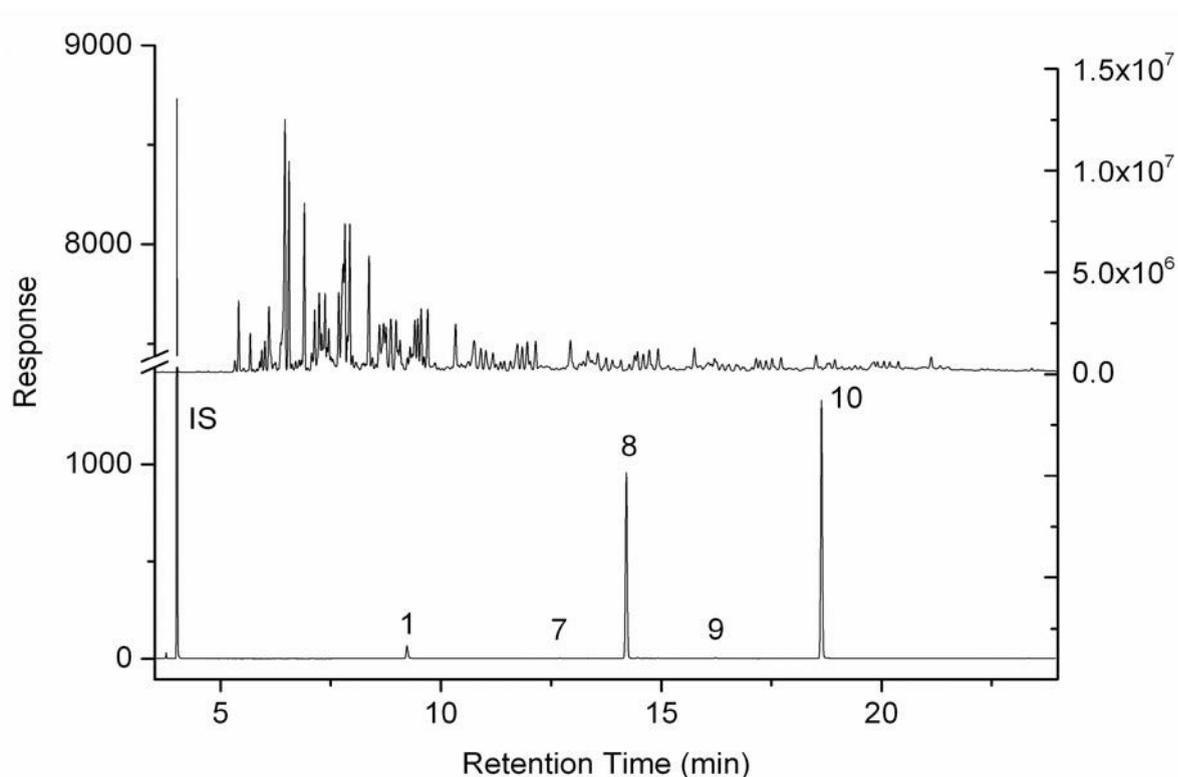


Figure 8. Chromatogram A: Chromatogram of SPA content in camelina-derived jet fuel (sample E), using GC/QQQMS and MRM analysis according to Table 3. Chromatogram B: The secondary (right) axis reports the total ion chromatogram (upper trace) of the same fuel using Q1 total transfer of ions and Q3 scan mode.

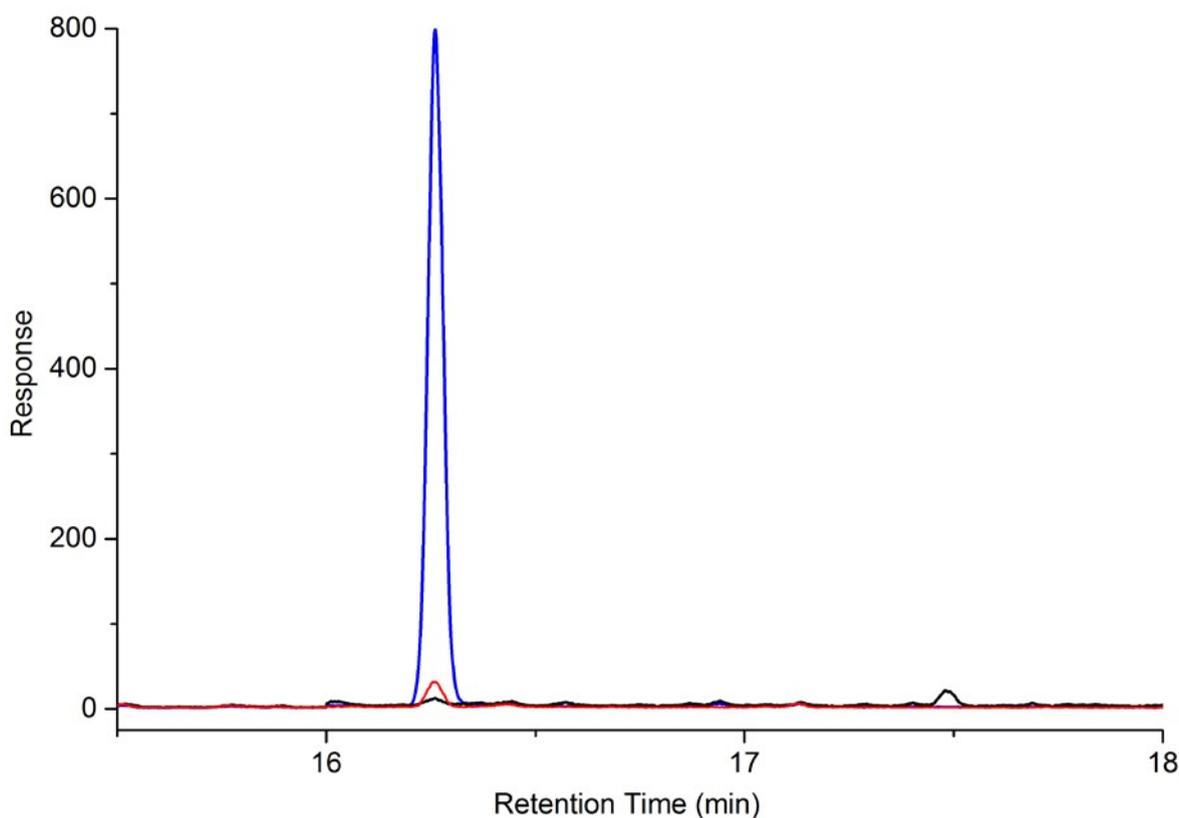


Figure 9. Overlaid GC/QQMS chromatograms of neat, (black line), SPA-spiked (blue line) and oxidised SPA-spiked jet fuel (red line) according to Section 2.3.2.

2.5 Conclusions

The analysis of SPAs in neat middle distillate fuels may be achieved via analysis with either GC/QQMS or GC/QTOFMS. These analyses can be carried out with no prior sample preparation which is extremely advantageous with cost savings in terms of time and reagents, and also prevention of analyte losses which may be incurred through extraction techniques. Both of these advanced MS detection methods have accommodated a significant expansion in the range of SPA analytes detected in a single method.

There is scope for routine analyses to be based on either of these methods which would be useful for determining in-service levels of SPAs in middle distillate fuels, however the GC/QQMS method would be preferred based on superior recovery and precision for this analytical method. Providing proper sample storage to limit storage-related oxidation, these methods could be employed in a fuel testing laboratory, to provide accurate information about the amount, and nature of SPAs

present in fuels that present with stability problems in the field. This information is vital when determining if additional dosage of SPA is required for in-service fuels, and if so, how much additive should be used. SPAs are also widely used in aerospace hydraulic fluids which undergo similar oxidation processes to middle distillate fuels. These methods may also be applicable to the analysis of SPAs in aircraft lubricants, or for the analysis of naturally occurring phenols present in conventional fuel feedstocks, providing known standards are available

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Chapter 3: Publication 2

Webster, R. L.; Rawson, P. M.; Evans, D. J.; Marriott, P. J., *J. Sep. Sci.* **2016**, 39 (13), 2537–2543.

Synopsis

This work presents a multidimensional gas chromatography/mass spectrometry (MDGC-MS) method with electron and chemical ionisation mass spectrometry to isolate and provide adequate analysis for fatty acid methyl esters in diesel samples. This analysis is difficult, due to the diesel matrix. The introduction of a middle distillate diesel fuel introduces an additional level of complexity from aviation fuels, where considerable resolution of the oxygenated constituents by means of separation is required, as well as a carefully chosen and optimised use of mass spectrometry as is demonstrated in the previous chapter. Statistical validation of the method is presented, with analytical figures of merit including detection limits, dynamic linear range, and reproducibility for approaches employing both electron and chemical ionisation techniques.

Here, the relevance to specific problems encountered in military applications on land and sea was a key driver to achieving the described analytical parameters. Similar to the previous chapter, the low detection limits required by these real world operational uses induced the need for a novel analytical approach and in this case, the optimisation of both the separation and detection components of the method. Whereas in the previous chapter a single dimension separation was sufficient, here a multidimensional approach was necessary. Most importantly, the technique permits the elucidation of potential FAME-based feedstock contamination based on the profile of the target analytes. This, in conjunction with knowledge of biodiesel feedstocks that may have been processed or pumped in the same facility, provides invaluable information for identifying contamination sources and subsequently formulating remediation strategies.

3 Quantification of Trace Fatty Acid Methyl Esters in Diesel Fuel by Using Multidimensional Gas Chromatography with Electron and Chemical Ionisation Mass Spectrometry

Renée L. Webster, Paul M. Rawson, David J. Evans, Philip J. Marriott

3.1 Abstract

Measurement of contamination of marine and naval diesel fuels (arising from product mixing or adulteration) with biodiesel or fatty acid methyl esters can be problematic, especially at very low levels. A suitable solution for this task for trace amounts of individual fatty acid methyl esters with resolution and quantification can be achieved by using a multidimensional gas chromatographic approach with electron and chemical ionisation mass spectrometric detection. A unique column set comprising a 100 m methyl-siloxane nonpolar first dimension column and high-temperature ionic liquid column in the second dimension enabled identification of individual fatty acid methyl esters at below the lowest concentrations required to be reported in a diesel fuel matrix. Detection limits for individual fatty acid methyl esters compounds ranged from 0.5 to 5.0 mg/L, with excellent linearity up to 5000 mg/L and repeatability of the method from 1.3 to 3.2%. The method was applied to the analysis of diesel fuel samples with suspected biodiesel contamination. Contamination at 568 mg/L was calculated for an unknown sample and interpretation of the results permitted the determination of a likely source of the contamination.

3.2 Introduction

Finite supplies of fossil fuels and concerns about their environmental impacts have led to an increase in the use of alternatively derived fuels across the globe. One such alternate fuel is fatty acid methyl esters (FAME) that comprise the molecular components of the alternate fuel most commonly known as biodiesel. Increased use of FAME-containing fuels has led to incidents of cross-contamination, particularly

where tankers and storage facilities are used for multiple fuel types. This can cause problems in cases where FAME is considered a contaminant; in particular, this is the case for fuels that are used in aviation and other specialised fuels used by defence forces. Even small amounts of FAME contamination are known to contribute to poor fuel properties including decreased thermal and storage stability, raised freezing point, and introduce poor water separability characteristics.^{16, 17, 166-168}

Standards dictate that the FAME content in aviation fuels must not exceed 50 mg/kg¹⁶⁹, and there are a number of analytical methods available for the detection and quantification of FAME in aviation fuels^{21, 170-173} to ensure that such standards are met. These are broadly either separation (particularly GC or LC) or spectroscopic (e.g. FTIR). The analysis of FAME in aviation fuels is comparatively simple, particularly with GC analysis. This is in the most part due to the relatively high volatility range of the hydrocarbons that comprise aviation fuel, ensuring resolution from later eluting FAME compounds commonly found in biodiesel using an appropriate column phase. Coupling GC with a polar column and MS permits sufficiently low detection limits through improved separation, and the use of selected ion monitoring techniques, respectively. Whilst some of the FTIR methods report the potential to achieve a detection limit below 50 mg/kg (particularly when data are interpreted using a chemometric approach), it is not possible when the speciation of the individual FAME compounds is required, which is often crucial information for determining the source of contamination.

Diesel fuel specifications for the marine environment dictate that FAME content is either not permitted at all (Australian naval distillate),⁹ or at a maximum of 0.1% by volume.^{20, 174, 175} Unfortunately, chromatographic methods for the analysis of FAME in aviation fuel (i.e. usually based on a single column separation) cannot be directly applied to the analysis of the same FAME compounds in a diesel fuel matrix, which has matrix interferences in the same elution region as FAME. The wider distillate cut, higher molecular weight components, high aromatic content and increased complexity of marine and naval diesel confounds the quantification of low levels of FAME contamination in these matrices, when using single capillary GC methods. Due to significant overlap of the complex hydrocarbon matrix with FAME analytes, it is impossible to resolve low levels of FAME contamination in diesel fuels with conventional chromatographic separations. Importantly, there are no published methods that can achieve the detection limits required to determine conformity of

FAME concentration in diesel range fuels that comply with certain fuel standards. Therefore, there is an urgent need to develop a reliable approach to measure these compounds, at the required levels.

Multidimensional and comprehensive 2D GC techniques provide a promising route for the resolution of trace FAME compounds from complex matrices.¹⁷⁶⁻¹⁷⁹ The improved peak capacity of multidimensional separations and especially the potential for structured separations, can alleviate many of the problems associated with 1-D GC analyses, in particular interferences caused by coeluting compounds. Seeley *et al.*,¹³² Tiyapongpattana *et al.*,¹¹⁷ and Adam *et al.*¹¹⁶ achieved separation of FAME compounds in a biodiesel matrix using comprehensive 2D GC, however the FAultraME component was quite high, at 1% or 5% (concentrations typical for automotive diesel). The development of extremely polar ionic liquid GC columns has also been effective for the analysis of FAME compounds,^{92, 180, 181} however, like other more established polar column phases, these are often temperature limited and not suitable for the analysis of diesel and higher boiling range fuels.

Given that even very low levels of FAME contamination can result in poor fuel quality parameters, it is critical to employ a method capable of providing a very low detection limit in even the most complex fuel matrices for the assessment of FAME contamination. Here, the use of a unique column set and two mass spectrometric modes as part of a multidimensional GC separation provides an excellent strategy for the resolution of low mg/L levels of FAME contamination in diesel.

3.3 Materials and methods

3.3.1 Samples and standards

Two different grades of diesel fuel were the test sample matrices in this study. Samples of commercially available marine diesel fuel, and military grade naval distillate (F-76) were obtained from local sources. Commercial marine diesel may contain a *de minimus* level of 0.1% v/v of FAME¹⁷⁴, while Australian F-76 naval distillate is required to be “free” from FAME contamination⁹. Samples of biodiesel were obtained from commercial suppliers; one was derived from a known feedstock (soy) whilst the other was from an unknown feedstock. A sample of suspected biodiesel-contaminated diesel fuel was obtained from a local Australian source.

Solvents and standards of single FAME compounds were obtained from Sigma–Aldrich (Castle Hill, NSW, Australia) as detailed in Table 7. A stock standard of approximately 60 000 mg/L total FAME was prepared in F-76, with exact concentrations for each component given in Table 7. Matrix matched standards were deemed necessary as enhancement was observed in comparison to samples of equal concentration prepared in *n*-dodecane. These FAME components were chosen due to their prevalence in biodiesels prepared using many common feedstocks.

Table 7. FAME standards used in this study

<u>FAME</u>	<u>Molecular Formula</u>	<u>Abbreviation</u>	<u>Concentration (mg/L)</u>
methyl tetradecanoate (myristate)	C ₁₅ H ₃₂ O ₂	C14:0	10,100
methyl hexadecanoate (palmitate)	C ₁₇ H ₃₄ O ₂	C16:0	9,600
methyl heptadecanoate (margarate)	C ₁₈ H ₃₆ O ₂	C17:0	9,900
methyl octadecanoate (stearate)	C ₁₉ H ₃₈ O ₂	C18:0	10,200
methyl octadecenoate (oleate)	C ₁₉ H ₃₆ O ₂	C18:1	9,600
methyl octadecadienoate (linoleate)	C ₁₉ H ₃₄ O ₂	C18:2	10,200

3.3.2 Multidimensional GC–MS analysis

The instrumentation used for multidimensional GC–MS analysis was an Agilent 7890A-5975C GC–MS (Agilent Technologies, Santa Clara, CA, USA). The GC–MS was capable of dual detection modes with flame ionisation and mass selective detectors installed. The GC–MS was also equipped with a Deans’ switch assembly, with the primary (¹D) column outlet and second (²D) column inlets each connected to the Deans’ switch. The ¹D column comprised a HP-1 PONA phase, (Agilent) of dimensions 100 m × 0.25 mm × 0.5 µm, as it is well suited to the detailed analysis of complex hydrocarbon mixtures. The ²D column was a SLB-IL60 phase (Sigma–Aldrich), 30 m × 0.25 mm × 0.2 µm, which is a highly polar and thermally stable ionic liquid (IL) phase column. The GC oven was programmed from 35 to 250 °C at 5 °C per min (hold 75 min), then ramped at 20 °C per min to 300 °C (hold 5 min). A deactivated fused-silica restrictor of dimensions 0.65 m × 0.1 mm was used to connect the Deans’ switch to the FID and provide pressure balancing for effective heart-cutting operations. Backflushing was not available on this instrument, but could feasibly be incorporated should the analysis require it, rather than flush heavier matrix material through the columns. The FID was operated at 300 °C with hydrogen and air supplied at 40 and 450 mL/min, respectively. Heart-cut regions of analytes were determined according to the retention times of FAME compounds in a

standard mixture made up inn-dodecane. Injections of 0.2 μL of undiluted sample were made with the injector operated in split mode at a ratio of 20:1.

Ultra-high purity He was used as carrier gas and for Deans' switch operation, supplied at constant pressure to the inlet and Deans' switch at 77.6 and 39.1 psi, respectively. MDGC analysis using a Deans' switch is commonly carried out in constant pressure mode due to GC firmware requirements, which results in a progressive decrease in flow rate over the course of a temperature programmed run. As the very long primary column requires a high head pressure to maintain a sufficient flow rate throughout the entire run, the calculated flow rate started at 10.7 mL/min (^1D column 3.6 mL/min + ^2D column 6.2 mL/min) and decreased to 3.5 mL/min (^1D column 1.3 mL/min + ^2D column 2.2 mL/min) over the course of the analysis. Ordinarily a flow rate this high would not be appropriate for an analysis employing a MS detector that must be kept under vacuum and standard turbo/roughing pumps cannot maintain a sufficient vacuum at total flow rates above 4.0 mL/min. To account for this the MSD remained switched off for the first 50 min of the run when the pressure inside the MS analyser chamber was at its highest, and switched on once the first analytes began to elute when the flow rate was low enough such that the vacuum could be maintained at a sufficiently low level with no damage or unnecessary wear caused to the detector. Dead time for the analysis was 11.5 min.

Table 8. Total retention times and SIM ions used for FAME analytes. The ions used for quantification are marked with asterisks

	t_R (min)	EI SIM ions m/z	CI SIM ions m/z
C14:0	52.4	74*, 87, 242	241*, 243, 271
C16:0	60.1	74, 87*, 270	269*, 271, 299
C17:0	65.1	74, 87*, 101	283*, 285, 313
C18:0	71.4	74*, 87, 298	297, 299*, 327
C18:1	69.8	74*, 87, 264	265, 297*, 325
C18:2	69.4	108, 162*, 294	263*, 293, 323

Mass spectrum data were collected in both electron (EI) and chemical (CI) ionisation modes, with methane used as the CI reagent gas. The suitability of each ionisation mode to the analysis of FAME compounds in a diesel matrix was assessed based on interpretation of analytical figures of merit. After determining appropriate ions by full scan analyses of standards in a diesel matrix, selected ion monitoring (SIM) mode was used to maximise sensitivity and selectivity. The SIM ions selected for

each analyte are given in Table 8, along with their total retention times. The set of three ions for each analyte were collected only in the window bracketing the retention times of the target compounds. Data were acquired by Agilent MSD Chemstation (version E.02.00) and analysed using Agilent MassHunter (version B.06.00) software packages respectively. FAME compounds were identified in the samples according to retention time matching with the known standard mixture, quantified using the ion with the highest S/N and confirmed by comparison with the three SIM target ions (Table 8) in a ratio corresponding to and in agreement with that of the compounds in the standard mixture.

3.4 Results and Discussion

3.4.1 Column selection

The success of this analysis largely depends on selection of two specialised capillary columns with specific features that have been effective in a previous analysis of slightly polar esters in a complex fuel matrix.¹⁸² For ¹D, a long nonpolar column was chosen to maximise peak capacity of the complex hydrocarbon matrix as a first step. Improving the resolution of the major n-alkane peaks, as well as the significant contribution of iso-alkanes and aromatic components is important to gain sufficient resolution in the subsequent ²D separation. Minimizing the transfer of potentially interfering compounds in the heart-cut regions is important to achieve the best possible separation of FAME compounds from other matrix hydrocarbons on the ²D column. Under these conditions, the heart cuts are sufficiently spaced to avoid interferences between adjacent cuts. Attempting this analysis using only the 100 m PONA column, even when coupled with selected ion monitoring, does not provide sufficient selectivity. This can be seen in Figure 10, where the first column was temporarily connected to the MS to demonstrate that interferences from the diesel matrix prevent identification of most target compounds below 100 mg/L. The converse is also true, as demonstrated in Figure 11, where multidimensional analysis alone is inadequate for resolving the FAME analytes without the addition of SIM operation with the MS detector.

An IL phase as the ²D column was also a crucial element of this separation. A degree of orthogonality is required between the ¹D and ²D columns to achieve a polarity-

based separation in the ²D column. This serves to resolve the slightly polar methyl esters from the nonpolar and aromatic hydrocarbon components that largely comprise the fuel matrix.

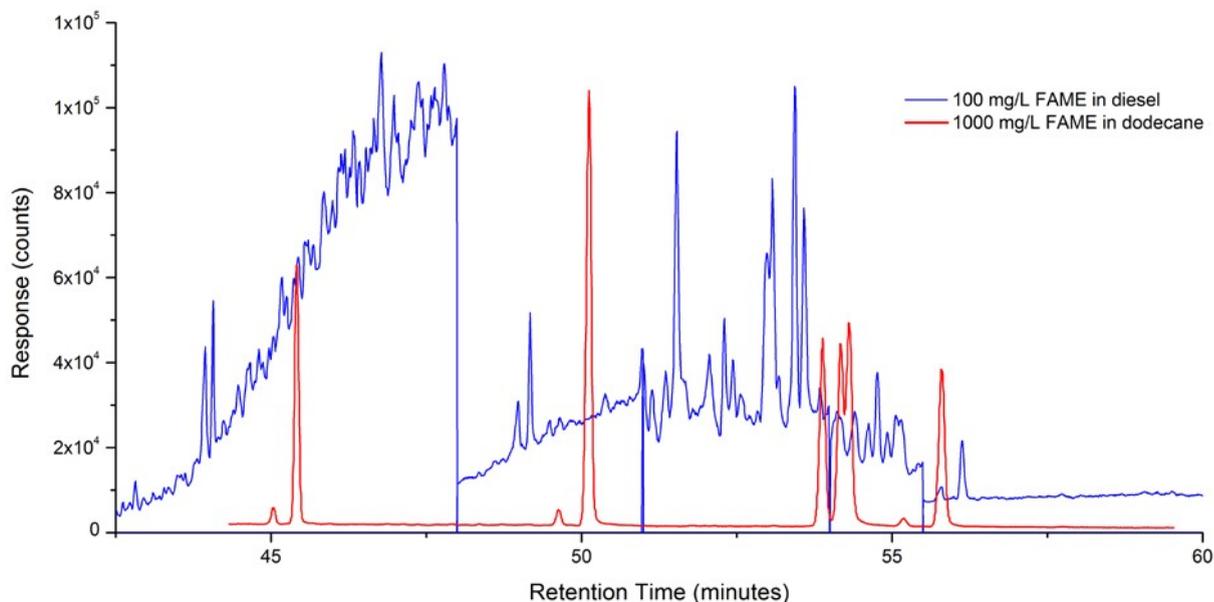


Figure 10. ¹D chromatogram of 1000 mg/L FAME standard in dodecane and 100 mg/L FAME standard in diesel fuel, demonstrating the need for a multidimensional separation. Breaks in the baseline are due to changes in SIM windows for each analyte.

It is likely that any highly polar column phase (for example PEG or cyanopropyl) would have sufficient polarity to achieve this. However, as the matrix in this case is diesel fuel with an upper boiling point limit in excess of 360 °C, both analytical columns must have an upper temperature limit of at least 300 °C to completely elute the matrix from the column. As a comparison, aviation fuel that has an upper boiling point limit of 300 °C is readily eluted under usual GC conditions at approximately 250 °C which also does not overlap with the elution of common FAME compounds. At the time of writing the only polar column available with an upper temperature limit of 300 °C was an SLB-IL60 ionic liquid phase column and hence was selected for this study.

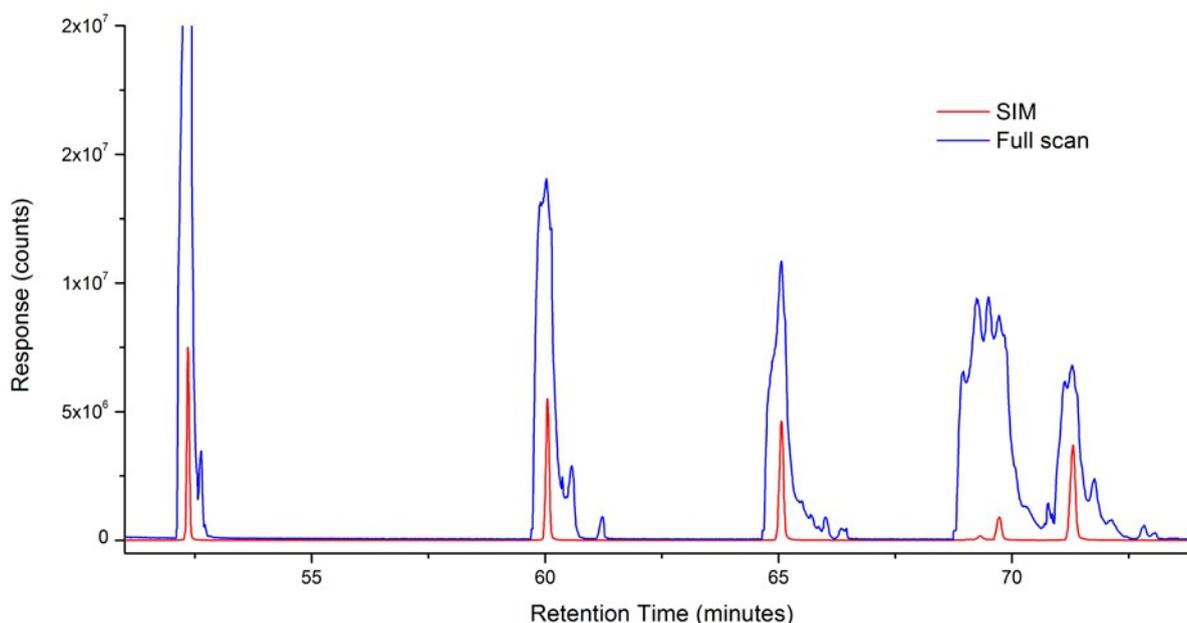


Figure 11. ²D chromatograms of 1000 mg/L FAME standard in diesel fuel, with the MS operating in full scan and SIM modes, illustrating that poor selectivity arises for full scan operation. SIM ions are as per Table 8.

3.4.2 Comparison of electron and chemical ionisation

While EI gives recognizable, library searchable mass spectrum data, low molecular ion stability may lead to low abundance upon fragmentation. This results in a mass spectrum that is often not unique, being shared by many fragment ions with the hydrocarbons comprising the matrix, and makes identification difficult. Interference from the numerous hydrocarbon fragments also means that it was more challenging to differentiate the signal from the matrix-generated noise at low concentrations. However, EI did produce higher overall abundance signals but they did not translate to a lower detection limit due to interferences from the fuel hydrocarbons.

The softer CI mode ensured that the protonated molecular ion $[MH]^+$ was in most cases the base peak in the resulting mass spectrum. However, it was not the only ion in the mass spectra for all FAME compounds as they each exhibited additional peaks due to further fragmentation and formation of adducts. The $[M-1]^+$ fragment was observed in the mass spectrum for some of the analytes, as is common where alkyl chains are present, and was found to be the base peak in the case of C14:0, C16:0 and C17:0.

Ethylation of the FAME compounds was also observed with $[M+CH_3CH_2]^+$ adduct ions present in the mass spectrum of all of the analytes. Low levels of ionisation of the sample matrix also ensured that the interference from the hydrocarbon background was minimised and signal-to-noise was in some cases improved.

3.4.3 Analytical figures of merit

3.4.3.1 Linearity and linear range

A set of six FAME standards from 10 to 5000 mg/L prepared by serial dilution of the stock standard were analysed in triplicate. Calibration curves constructed from the EI MS analysis were linear over the range 10–5000 mg/L for all FAME compounds except C18:2, which was linear from 50 to 5000 mg/L. The linear range for the CI analysis was inferior, with the upper linear range reduced by an order of magnitude, with sufficient linearity ($R^2 > 0.990$) achieved for the range of standards from 10 to 500 mg/L. This is not necessarily a concern as the upper limits of the calibration curve overlaps with the lower limits for other analytical methods. Increased specificity achieved through the use of CI MS analysis did result in improved performance at the lower concentration levels, where the lowest standard (10 mg/L) was easily quantified for each analyte. Linearity parameters are displayed in Table 9. Based on these regression equations, and that the response factor is less than half that for the other FAME analytes, the reliability of results for C18:2 is significantly lower than for the other analytes.

Table 9. Parameters of linearity for FAME analytes using EI and CI MS

<u>FAME</u>	<u>regression equation: EI</u>	<u>correlation coefficient: EI</u>	<u>regression equation: CI</u>	<u>correlation coefficient: CI</u>
C14:0	$y = 2082.7x + 763.24$	0.999	$y = 2417.8 x - 4157.4$	0.999
C16:0	$y = 1517.1 x + 82419$	0.999	$y = 1955.8 x - 15380$	0.999
C17:0	$y = 1575.4 x + 197769$	0.994	$y = 1828.7 x - 17644$	0.998
C18:0	$y = 1908.8 x + 132892$	0.998	$y = 2450.6 x - 23043$	0.997
C18:1	$y = 418.41 x + 43341$	0.996	$y = 1587.3 x - 15767$	0.997
C18:2	$y = 3.587 x + 4897.1$	0.998	$y = 715.6 x - 9089.5$	0.996

3.4.3.2 Limits of detection and repeatability

An assessment of the LOD for each individual FAME analyte was determined based on a measurement of the S/N of a blank sample compared with samples of known, low concentrations. The minimum concentration at which the analyte could be

detected with an S/N of at least 3:1 was determined to be the LOD. The LODs for each analyte under both ionisation modes are given in Table 10. It is important to note that the detection limits attained through CI analysis were superior for the C18 FAMEs that are generally the most problematic to resolve and quantify in GC analysis, including this method. It is possible that detection limits may be improved by further decreasing the split ratio or injecting more sample, however the peak shape for the highest concentration standard exhibited some fronting under these conditions that is due to the low sample capacity of IL columns for hydrocarbons. Peak shape would likely become worse for greater amounts of injected compound, so the linear range may need to be adjusted accordingly but for this study that is focused on trace analysis, there is no requirement for the upper end of the calibration curve to be especially high. The repeatability of the instrumental methods was also assessed through several replicate analyses ($n = 7$) of one of the calibration standards (50 mg/L for each component) with the results shown in Table 10. Repeatability was better for the EI analysis, as poor repeatability is a known drawback of chemical ionisation analyses.

Table 10. Limits of detection and repeatability using EI and CIMS

	LoD; EI (mg/L)	Repeatability; EI (% RSD)	LoD; CI (mg/L)	Repeatability; CI (% RSD)
C14:0	1	1.3	1	6.5
C16:0	2.5	1.4	2.5	5.9
C17:0	2.5	1.9	2.5	5.3
C18:0	1	1.4	0.5	5.7
C18:1	2.5	1.3	1	7.8
C18:2	5	3.2	2.5	5.8

3.4.4 Analysis of biodiesel contamination in conventional diesel fuels

A sample of diesel fuel with suspected biodiesel contamination was obtained from a local source. To apply the method to a broad range of samples, a naval diesel fuel was also spiked with two commercially obtained 100% FAME biodiesels at a total concentration of 750 mg/L (i.e. individual FAME will be at much lower concentration). One of the biodiesels was soy-derived, while the source of the other was unknown. The diesel samples were of a typical high complexity, with virtually no baseline resolution of any components. Separation of the saturated FAME compounds in the second dimension was good for all samples, even for C14:0 that elutes within a relatively complex part of the diesel chromatogram. Resolution of the

unsaturated C18 FAMEs was more difficult with some minor interferences preventing complete baseline resolution, but quantification is still achievable even though retention times of C18:1 and C18:2 are very close, and the mass spectra of these two compounds are less distinctive from the matrix than the saturated FAMEs. An example first dimension FID chromatogram displaying the heart-cut regions for each FAME compound is given in Figure 12. Chromatograms of the ²D SIM result for a FAME standard, contaminated diesel and spiked diesels are displayed in Figure 13.

The FAME content of a suspected contaminated sample and the two laboratory-spiked diesels were quantified using SIM EI MS. The calculated concentrations of each of the six target FAME analytes in all three samples are given in Table 11. The calculated amount of the soy-derived biodiesel is in excellent agreement with the known fatty acid composition of soybean oil, taking into account that roughly 10% of the FAME component would be the C18:3 linolenic acid methyl ester that was not analysed in this study. However, it would likely be relatively straightforward to include additional target FAME compounds as necessary for specific analysis requirements. The biodiesel with unknown provenance spike is possibly canola-derived, given the high concentrations of C18:1 and C18:2. It was found that the suspected contaminated sample was indeed adulterated with biodiesel. With a high concentration of C16:0 and C18:1, it is likely to have been contaminated with palm oil-derived biodiesel that is consistent with a possible source of contamination. This approach, targeting a small, but carefully chosen group of FAME compounds is preferred as contaminants typically consist of only a select group of FAME compounds found in the most common feedstocks. A blind or screening type analysis for all FAME in a sample would generally not be required as the potential contamination sources are anticipated to be limited, and known, in a typical fuel processing facility. For a case where identification of a FAME not shown here was required, the method could be adjusted to accommodate this to select desired FAME targets.

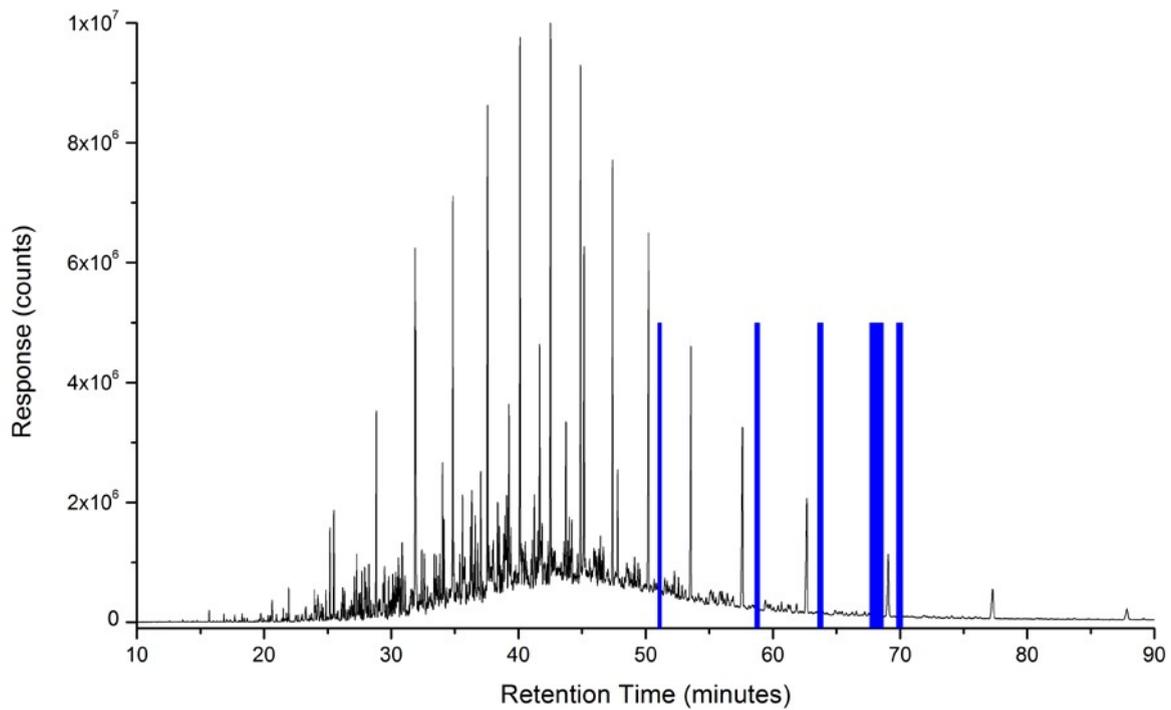


Figure 12. First dimension FID chromatogram with heart-cuts marked in blue at the retention times of the target FAME analytes.

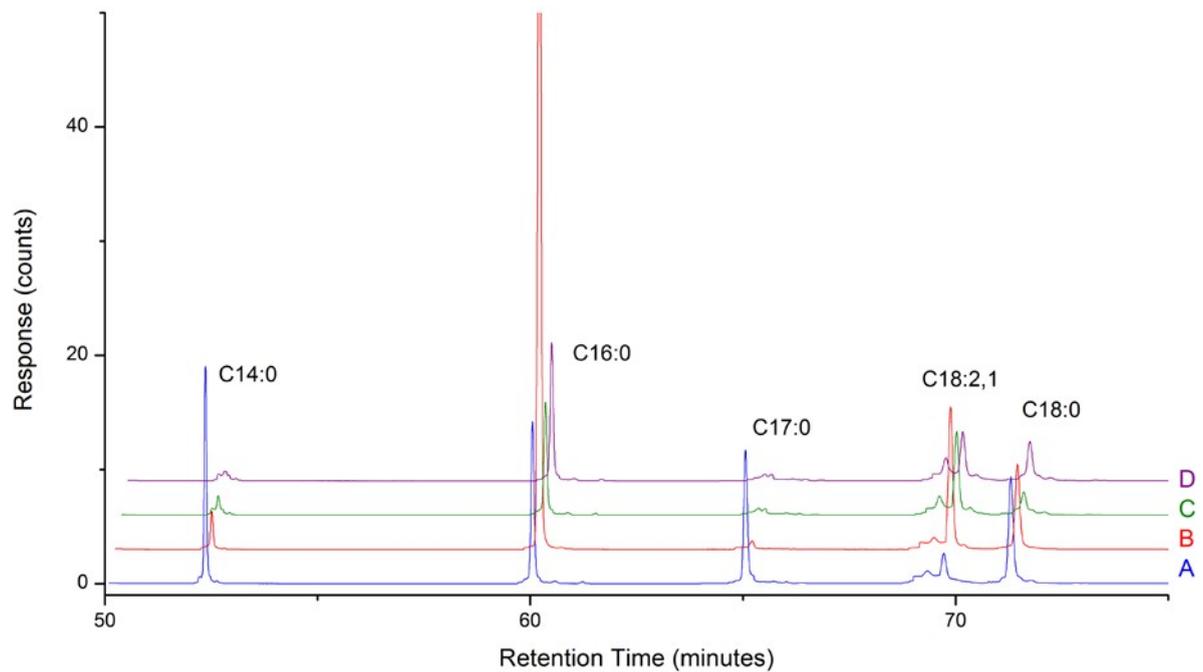


Figure 13. Second dimension stacked SIM chromatograms of (A): 100 mg/L FAME standard; (B): suspected contaminated sample; (C, D): samples spiked with commercial biodiesel. SIM ions are as per Table 8.

Table 11. Calculated amounts of FAME biodiesel contamination in mg/L. Letters correspond with chromatographic traces in Figure 16.

	Figure 16 trace	C14:0	C16:0	C17:0	C18:0	C18:1	C18:2	total
Suspect contaminated	B	14	400	2.7	64	85	2.4	568
Spike 1 (soy)	C	34	110	14	41	120	350	670
Spike 2 (unknown)	D	29	90	13	29	177	248	586

3.5 Concluding remarks

A multidimensional GC method has been developed to successfully identify and quantify trace contamination of diesel with individual fatty acid methyl esters at a level up to two orders of magnitude lower than any previously reported analysis incorporating FAME speciation. At the time of writing no other methods are capable of achieving detection limits of low percent level contamination for individual compounds, rather than a total summation of FAME content in a diesel fuel matrix. The selection of a unique column set was critical in achieving sufficient resolution and appropriate temperatures for complete elution of the analytes and matrix. Investigation of both electron and chemical ionisation modes has revealed a slight advantage for chemical ionisation with respect to detection limits; however, this is at the expense of linearity and repeatability. Partial method validation and application to real samples confirms the suitability of this analysis in real situations where the quantification of low levels of FAME is required to ensure safe and efficient operation of land and sea vehicles. This analysis will be valuable for determining trace amounts of biodiesel contamination in diesel fuel matrices where the presence of oxygenated compounds can be detrimental to engine performance.

Acknowledgments

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Chapter 4: Publication 3

Webster, R. L.; Evans, D. J.; Marriott, P. J., *Energy Fuels* **2015**, 29 (4), 2059-2066.

Synopsis

This work presents further chemical characterisation of conventional and alternative fuels using the method of multidimensional gas chromatography with mass spectrometry. Contrary to the previous 2 chapters where the target analytes were artificially introduced into the fuels, in this case the oxygenated species of interest are generated by thermal oxidative stressing. The fuels are subjected to thermal degradation using a customised stressing rig that mimics conditions in high performance aircraft as closely as possible. Repeated, sequential heart-cutting with GCMS offers the advantages of a multidimensional separation in resolving a great many compounds of interest from the fuel matrix without requiring the additional capability of a fully comprehensive two-dimensional approach. An extraordinary number of oxidation products were identified, and many were confirmed by comparison with authentic standards. Those which could not be matched with a standard were identified to a reasonable level by application of logical approaches, with respect to elution order and existing knowledge of low temperature thermal oxidation products in middle distillate fuels.

The results are further correlated with bulk methods of oxidative stability, demulsification and water separation. It is shown that some of these standard tests are very sensitive to changes caused by oxidative stress, while others do not recognise it at all. Additionally, under some circumstances, low-temperature oxidised fuels will fall out of specification very quickly after only a few minutes of heating. Inferences about corresponding effects in diesel fuels can be extrapolated from the results here, as some of the test methods are more commonly applied in a maritime environment. This publication represents a significant contribution to the understanding of complexity of thermally oxidised conventional and alternate aviation fuel samples.

4 Detailed Chemical Analysis Using Multidimensional Gas Chromatography–Mass Spectrometry and Bulk Properties of Low-Temperature Oxidized Jet Fuels.

Renée L. Webster, David J. Evans, Philip J. Marriott

4.1 Abstract

Sequential multidimensional gas chromatographic separations were used to identify secondary and tertiary oxidation products in a number of conventional fossil and alternatively-derived aviation fuels. The samples were produced by low temperature thermal oxidation of the fuels, and the higher dimensional separations were required due to the difficulty in quantification of the products at both bulk and molecular levels. The presence of certain oxidation products is a concern, due to functional similarities to restricted contaminants, contribution to solid deposit formation, and impact on physical properties. Accurate identification assisted in characterisation of the range of products. Primary alcohols dominated the secondary oxidation products in most cases, comprising 24-78% of the total oxygenated species identified in each fuel. Fuels were also subjected to several standardised physical property tests, showing that thermal oxidative stress affects certain fuel properties in a quantifiable manner which in some cases is comparable to the effect of adding polar dopants.

4.2 Introduction

Thermal stability of fuels is a property which is becoming increasingly important. Modern jet engines operating at increasingly higher temperatures employ fuel in a dual-use role; the second role is in a heat-sink capacity as a cooling fluid for hydraulics, avionics and engine lubrication systems. In these scenarios fuels may be heated to well over 100 °C, initiating auto-oxidation reactions which are known to contribute to the formation of gums, sediment and other insoluble species which block fuel nozzles and filters. Thermal oxidation may also affect other fuel

characteristics including sooting tendency, surfactant formation and water separability.²³

The increasing uptake of synthetic and biologically derived fuels adds further complications. Their suitability in high heat-demand applications is potentially diminished due to a lack of naturally-occurring antioxidants,¹⁸³ which mitigate the effects of peroxides and radical species, and potentially leads to oxidative instability. The initial stages of fuel oxidation are well understood,³² with hydroperoxides being the primary products, and alcohols, carbonyls and carboxylic acids the secondary products. The subsequent formation of tertiary oxidation products such as heterocycles and anhydrides has not been thoroughly explored. Methods of fuel production and processing will also affect the chemical composition, and therefore may affect the formation of oxidation products, thermal stability characteristics and properties.¹⁸⁴

Of particular interest are those secondary and tertiary oxidised species which are likely to have an effect on the water shedding and separation characteristics, since they possess a variety of oxygen-containing polar functional groups. Previous work¹⁸⁵ has identified furanones as a class of compounds that may be of concern, due to the similar functionality shared with fatty acid methyl esters (FAME). FAME are considered contaminants which are not tolerated in jet fuels, due to deleterious effects on the fuel's stability and water separability.¹⁶⁷ Interactions of fuel and water are undesirable due to effects on the fuel system, particularly the coalescer. The presence of water in fuels may also accelerate corrosion and microbial growth. The presence of other oxygen containing compounds generated through low temperature thermal oxidation on fuel properties is an area that has not yet been thoroughly investigated.^{59, 186-188}

There are a multitude of methods in use for isolating and quantifying oxidation products in the complex fuel matrix. Fuel oxidation is commonly assessed via a number of bulk chemical and physical property tests (including but not limited to, the jet fuel thermal oxidation test (JFTOT), automatic accelerated oxidation or quartz crystal microbalance), with varying degrees of suitability towards the parameter being measured. Complications arise in the analysis of trace compounds where specificity, selectivity and carryover from the matrix become problematic. Additionally, there is no consensus on which, if any, of the available bulk fuel property tests are suitable indicators as to the degree of oxidation of a fuel. Trace

oxidised species have generally been analysed through the use of lengthy separation processes such as column chromatography, liquid–liquid extraction, solid phase extraction and preparative high performance liquid chromatography. While group-type analyses, which focus on analysis of particular functional groups, can be useful, they do not allow for the precise analysis of individual oxidised compounds.

Multidimensional gas chromatographic (MDGC) separations provide a suitable technique for the detection of individual compounds of interest within the complex fuel matrix. An increase in the available separation space permits improved resolution of trace compounds in complex fuels, allowing for the identification of oxidised species without the extent of interferences, analyte losses and researcher time accompanying other analytical techniques. It has been demonstrated previously^{189, 190} that sequential heart-cut techniques are well suited to the analysis of trace compounds in complex matrices, particularly fuels.^{120, 189} Previous work by Mitrevski *et al.*¹⁹¹ combined MDGC and GC×GC separations, affording the advantages of each in the isolation and identification of trace oxygenated species and broad sample profiling, respectively. This study expands upon the previous work, utilising multiple heart-cut separations to identify a range of oxidation products, including tertiary oxidation products which have not been reported before using a comparable technique. Physical properties of a number of thermally stressed fuels are also reported for the first time, with insights into possible consequences of the presence of oxidation products.

4.3 Experimental

4.3.1 Samples and Standards

4.3.1.1 Standards

A selection of oxygenated compounds covering the main classes of anticipated secondary oxidation products were employed as qualitative reference standards for development of the gas chromatography-mass spectrometry (GC-MS) analytical method. The components of this standard mixture are given in Table 1 of the Supporting Information (Appendix A). All oxygenated compounds except FAMEs were obtained from Sigma-Aldrich (Castle Hill, Australia) and used without further purification. The FAME mixture used in demulsification and separability analyses

was obtained from a commercial biodiesel facility and consisted primarily of C16.0, C18.0 and C18.2 FAMEs. The furanone mixture used in these tests contained approximately equal volumes of each furanone from the methyl through to octyl substituted analogues, and was diluted to the given concentration in the same fuel to which it was added.

4.3.1.2 Fuel Samples

A total of seven aviation fuels were used in this study, details of which are given in Table 12. Samples were selected to include a range of processing technologies, and new generation alternatively derived fuels (Fuels A-D) to compare with more established conventional fuels (Fuels E-G). Fuels E-G are certified for use in jet engine aircraft, whilst fuels A-C meet the requirements of Annex A1 and A2 in ASTM D7566¹⁴⁴ for synthetic aviation fuels. Fuel D utilises a new pathway for production and has not been certified at the time of publication. The fuels were used ‘as-is’, with no blending with other feedstocks, and contained such additives that may have been included at the refinery. No sample cleanup or preparation was carried out in order to represent ‘real-world’ usage. All fuels and samples were stored at -18 °C.

Table 12. Summary of jet fuel samples used in this study.

Sample	Feedstock	Processing/Refining Method
A	Camelina	Hydroprocessed Esters of Fatty Acids
B	Coal/Syngas	High Temperature Fischer-Tropsch
C	Algae	Hydroprocessed Esters of Fatty Acids
D	Biogenic Isobutanol	Alcohol to Jet
E	Fossil	Merox
F	Fossil	Hydroprocessed
G	Fossil	Straight Run

4.3.2 Thermal stressing

Fuels were subjected to dynamic thermal stressing by circulating through a custom-built thermal stability rig (TSR) described previously¹⁸⁵. Fuel samples were sparged with air for 60 min at ambient temperature before the cyclic thermal stressing commenced. The fuels flowed through a heated stainless steel tube 5 m long, with the sand bath temperature adjusted to provide a bulk fuel temperature of 180 °C.

Fuel temperature is measured from inside the stainless steel tube directly after the portion submerged in the heated sand bath. The fuel was supplied at 18,600 kPa at a flow rate of 40 mL/min and collected in a separate flask, resulting in a residence time of 120 s for each pass. The fuel was returned to ambient temperature between each pass through the heated tubing by a small length of tubing being immersed in a recirculating chilled water bath.

A sample of fuel was removed from the TSR at eight intervals throughout the thermal stressing period for analysis of thermal oxidative degradation products and fuel properties. The sampling interval became progressively longer throughout the duration of the experiment, in order to more effectively capture changes that occur in the earlier stages of thermal oxidation. Table 13 shows the protocol describing the sampling intervals and residence times. Fuel is returned to the collection reservoir every 20 min at the beginning of the experiment, gradually shortening to every 5 min by the end.

Table 13. Sampling protocol for fuels during thermal stressing experiment.

Sample Number	Residence Time (min)	Number of passes through heated zone
0	0.00	0
1	2.79	1
2	8.43	3
3	16.7	6
4	27.9	10
5	47.4	17
6	66.9	24
7	89.2	32
8	111.5	40

4.3.3 Instrumentation

MDGC analysis was carried out on an Agilent 7890A gas chromatograph with a model 7000 triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). The spectrometer was operated in single quadrupole mode only by using total transfer of ions at the first quadrupole. Operating conditions and instrumental set up are given in Table 14. A traditional non-polar/polar column set was selected in order to aid identification of compounds by order of elution on the 2D column based on their increasing polarity. A 30 m 5% phenyl column was used in the first

dimension, with a 30 m wax column in the second dimension. Heart-cutting was performed using a Deans' switch assembly, with a liquid CO₂-cooled cryogenic tee trap at the beginning of the second column for cryofocussing. Data collection, processing and analysis were performed with MassHunter version B.06.00.

Our previous work on sequential heart-cutting of an algae-derived jet fuel¹⁹¹ determined that under these conditions, optimum resolution of the significant complexity in the fuel matrix was achieved using narrow heart-cuts of 12 s taken from the first dimension, and the column dimensions allows the selected heart-cuts to elute within a 2 min time period on this column. As this study incorporates conventional fossil-derived fuels, which are even more complex than the neat alternatively derived fuels, a similarly narrow heart-cut region of 12.5 s was chosen for this analysis. However, successive heart-cuts were made 2.5 min apart in each run such that 12 – rather than 10 – successive injections would sample the entire chromatogram. This slightly longer elution region was required for the more complex fossil-derived fuels, the heart-cuts of which did not always elute from 2D in <2 min. Thus each analytical run with one series of selected heart-cuts takes 26 min. Each sample is analysed using 12 repeat injections, with heart-cut series moved progressively by 12.5 s, to give a total of about 300 min.

Table 14. GC-MS operating parameters.

Column 1	HP-5
Length/ID/ <i>d_f</i>	30 m / 0.25 mm / 0.25 μm
Carrier; flow; velocity	He; 1.0 mL/min;/ 13.5 cm/s
Column 2	Supelcowax
Length/ID <i>d_f</i>	30 m / 0.25 mm / 0.2 μm
Carrier; flow; velocity	He; 2.5 mL/min;/ 59 cm/s
Restrictor Length/ID	0.9 m / 0.1 mm
Oven	50 °C↑280 °C (10 °C/min; 3 min hold)
Injector	280 °C
Inj. vol. / mode	1 μL / split, 20:1
Transfer Line; source	300 °C; 230 °C
T	
Ionisation	EI, 70 eV
Quadrupole	150 °C (Q1)

4.3.4 Bulk Property Testing

A number of standardised test methods were applied to the neat and thermally stressed fuels with a view to investigating the effect of oxidised species on certain fuel properties. Of particular interest were properties related to stability, emulsification and water separation.

4.3.4.1 Water Separation (MSEP)

Water separation or MSEP analyses were carried out using a portable separometer (EMCEE Electronics, Venice, FL, USA) in accordance with ASTM D3948¹⁹². A 50 mL sample of fuel was stirred at high speed with 1 μ L of deionised water at room temperature and then passed through a pre-calibrated coalescer cell. A 15 mL sample of the effluent was then analysed by light transmission for uncoalesced water, which is indicative of the fuel's surfactant characteristics. Water separation analyses were carried out on the neat fuels, the full regime of thermally stressed fuels, and also two doped fuels. One representative each of the alternative and fossil fuel (Fuels A and F) were separately spiked with 1% of FAME mixture, and 1% of furanone mixture to determine the effect of these contaminants on water separation characteristics, and as a comparison against the thermally stressed fuels. Fuels were considered to have met the water separation specification if the separometer returned a value of 70 or higher. This limit is taken from the lower limits of the Australian¹⁰, UK¹¹ and US¹³ military specifications for aviation turbine fuel (NATO F-34).

4.3.4.2 Demulsification

Demulsification analyses were carried out in accordance with ASTM D1401⁴⁰ using a Herschel Emulsifier (Anton Paar GmbH, Graz, Austria). A 40 mL fuel sample was stirred with 40 mL of deionised water at 1500 rpm for 5 min at 54 °C. The volume of fuel-water interface was then measured and the characteristics (e.g. lacing, bubbles, haze, cloudiness) visually examined every 5 min over a total period of 30 min.

Demulsification analyses were carried out on the neat fuels, thermally stressed fuels, and fuels doped with a variety of oxygen-containing compounds. Fuels A and F were separately doped with 1% each of mixed n-carboxylic acids, primary alcohols, carbonyls, furanones and FAME to determine the effect of these contaminants on

water demulsification properties, and as a comparison against the thermally stressed fuels. In order to pass the demulsification test, the fuel-water interface must have a volume ≤ 3 mL once the test sample has been standing for 30 minutes, which is the demulsification limit detailed in the ASTM.

4.3.4.3 Oxidative Stability

Accelerated stability analyses were carried out in accordance with ASTM D7545¹⁶⁵ using a PetroOxy rapid small scale oxidation tester (Anton Paar GmbH, Graz, Austria). 5.0 mL of fuel was heated to 140 °C under an atmosphere of O₂ at 700 kPa. The time taken for a 10% drop in the O₂ pressure to occur was measured, and is indicative of the oxidative stability of the fuel. The neat and thermally stressed fuel samples were both subjected to oxidative stability testing, in order to quantitatively assess the effect that thermal stressing had on the stability of the fuels.

4.4 Results and Discussion

4.4.1 MDGC

4.4.1.1 Identification of oxygenated compounds

This technique permits the broad identification of a range of compounds with different functionalities, which traditionally were only analysed via group-type, employing fractional or functional group-specific techniques whereby only a sub-set of compounds are scrutinised at any one time. A broad range of secondary and tertiary oxidation products anticipated in a low temperature oxidised fuel sample are readily identifiable by this technique. Although time consuming to complete the analysis, with 12× 30 min runs required to fully analyse each sample, the amount of the analyst's time once the system is set up is low as the GC-MS instrument can be set up to automatically run the samples in the required manner.

The oxidised species are completely masked by the bulk hydrocarbon matrix in one dimension, and even with the heart-cut multidimensional separation, there can still be a significant amount of interference from alkanes in the second dimension. In one dimension, even using specialised hydrocarbon analysis columns, i.e. 100 m detailed hydrocarbon analysis (DHA) or paraffin, olefin, naphthene and aromatic (PONA)

columns, the likelihood of identifying a trace oxygenate is very low, in the most part due to interferences from the major alkane components. Figure 14 shows an entire chromatogram from one multiple heart-cut event run (A), as well as a more detailed view of one of the heart-cut segments, selected for the region 15-17 min (B). This sample, which is one of the conventional fossil fuels, has a high degree of complexity in the chromatogram due to the presence of a number of aromatic species which are not present in typical alternative fuels. Major alkane and aromatic compounds are present in high proportions and elute as large, sometimes unresolved peaks at the beginning of the heart-cut section. Despite this, a majority of the oxidised species can be separated and identified by utilising the second dimension separation space which is able to resolve the heart-cut compounds based on their relative polarities (Figure 14B).

Many of the oxidised species could be identified with a satisfactory degree of certainty based on a) matching via searching the NIST11 Mass Spectral Search Program, b) comparison of retention times and mass spectra with the small number of standards available and then extrapolating to similar homologous compounds, and c) background subtraction of the interfering alkane mass spectral peaks from the mass spectrum of interest using MassHunter's built-in background subtraction feature. A portion of peaks remained, which could not be even tentatively identified, likely due to coelution of two or more compounds which were not amenable to deconvolution, or which did not adequately match database record spectra. A list of all the oxygenated compounds that were identified in the fuels is given in the Supporting Information (Appendix A).

An example of the increased complexity observed in conventional fuels compared with alternative fuels is shown in Figure 15. It is likely that there are a greater proportion of oxidised species that were successfully identified in the alternative fuels as there are virtually no interferences, with the major alkane components eluting prior to the polar oxidised species. In this case, data from the alternative fuels may serve as a reference for the conventional fuels. Conventional fuels however, suffer from overlap of the substantial aromatic content with many of the oxidised molecules of interest. Key differences between the alternative and conventional fuels were easily observed in the chromatograms of the oxidised fuels of each. Many oxygenated aromatic compounds were identified in the conventional fuels, which naturally include a significant proportion of aromatics derived from crude fossil oil.

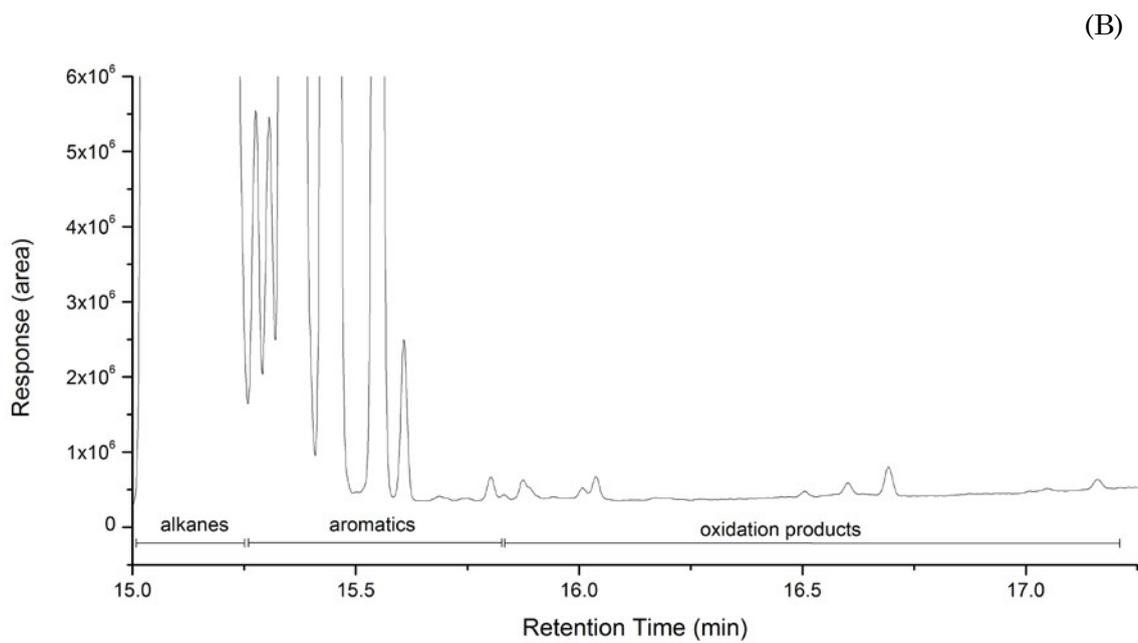
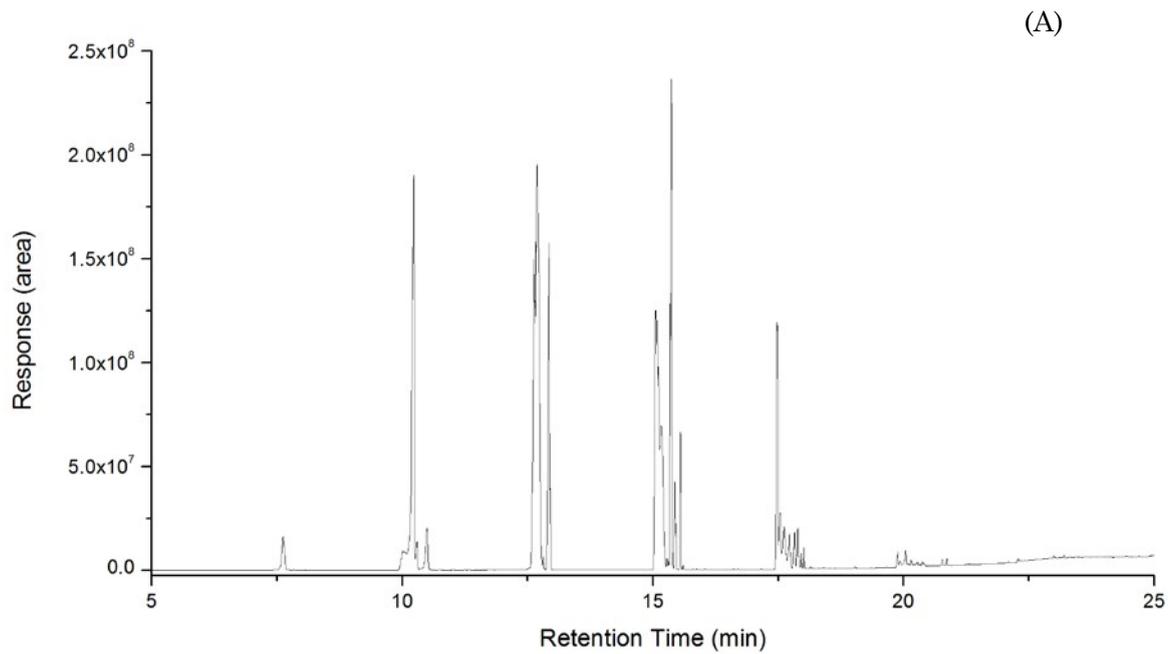


Figure 14. (A) Chromatogram of one multiple heart-cut run with the full chromatogram shown, and (B) zooming in on the region between 15-17 min to show the elution of smaller oxygenated species after the hydrocarbon matrix.

The alternative fuels however, do not contain aromatics other than what may have been added during the manufacturing process as additives, for example synthetic phenolic antioxidants. Strong positive library matches (match quality ≥ 700) in alternatively derived fuels for aromatic oxidised species as indicated in Table 15 are likely the result of oxidation of the additives included in the product, and is supported by previous analyses of antioxidant content in these fuels¹⁸³. Chromatograms of the alternatively derived fuels were generally far less complex, with fewer large peaks eluting after the dominant alkanes at the beginning of each heart-cut (Figure 15).

Table 15. Oxygenated compounds identified in the fuels by functional group class (most fuels also had compounds which contained multiple functional groups on the one molecule). Aromatic compounds identified in fuels A-D are additives, or oxidised additives.

class/functional group		A	B	C	D	E	F	G
alcohols	<i>n</i> -alcohol	x	x	x	x	x	x	
	<i>n</i> -diol	x	x	x	x	x	x	x
	cyclic diol	x					x	
	cyclic alcohol	x	x	x	x	x	x	x
	aromatic alcohol					x	x	x
aldehydes	<i>n</i> -aldehyde	x	x	x	x	x	x	x
	aromatic aldehyde	x		x		x	x	x
	dial							x
ketones	<i>n</i> -ketone	x	x	x	x	x	x	x
	dione	x	x	x	x	x		x
	cyclic ketone		x	x		x	x	x
	aromatic ketone	x				x	x	x
acids	<i>n</i> -carboxylic acid	x	x		x			
	aromatic acid							x
esters	<i>n</i> -ester	x		x	x	x	x	x
	cyclic ester	x		x		x		
	diester			x				
	aromatic ester						x	
ethers	<i>n</i> -ether	x	x	x		x	x	x
	cyclic ether	x						
	aromatic ether					x	x	x
heterocycles	furan	x	x	x	x	x	x	x
	pyran	x			x		x	x
	furanone	x	x	x	x	x	x	x
	pyranone	x			x	x	x	

Secondary oxidation compounds consisting of diols and diones were present in most of the analysed fuels. These are of particular interest as they are suspected to undergo an intramolecular ring closure reaction to form lactones.^{30, 185, 193} Table 15 shows the presence of certain major classes of oxidation products in each of the conventional and alternative fuels. In addition to the identification of secondary oxidation products, was the appearance of tertiary oxidation compounds such as lactones and anhydrides which can be considered likely precursors to soluble macromolecular oxidatively reactive species (SMORS);^{41, 52, 194, 195} it is therefore important to understand their formation in order to consider and test methods to prevent formation of insolubles.

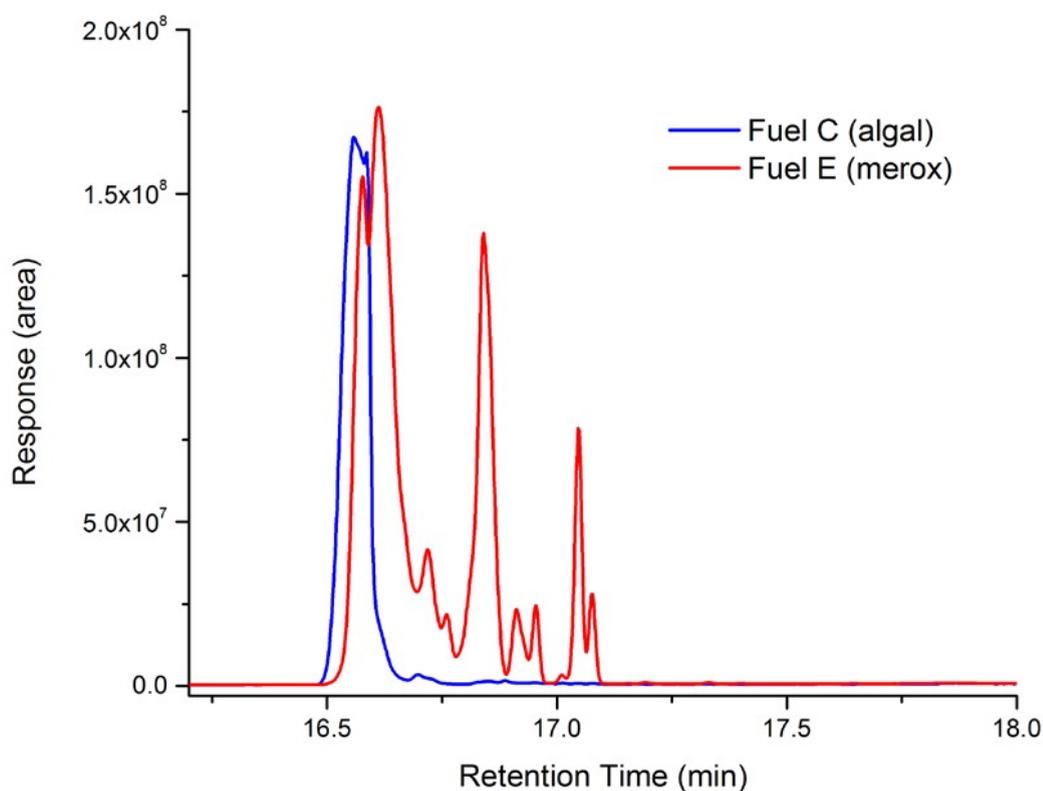


Figure 15. Overlay of a heart-cut segment for an alternative fuel and conventional fuel demonstrating the increased complexity of the conventional fuels. The later eluting compounds are the aromatic components.

In agreement with previous findings, the major products of low temperature oxidation reactions are alcohols, carbonyls and oxygen-containing heterocycles.¹⁹⁶ As shown in Table 16, in many of the fuel samples, secondary alcohols dominate the

oxidation products, formed by the creation of alkylhydroperoxy radicals which can then decompose to the alcohol.¹⁹⁷ Where the fuels contain alkanes that are of sufficient length and without steric hindrance arising from branching, ring closure reactions occur with the products dominated by furans, followed by pyrans. At the low temperature of this study, these 5- and 6-membered rings are favoured over oxiranes and oxetanes which are observed in the higher temperature oxidation regimes.¹⁹⁸⁻²⁰⁰

Table 16. Percentage of the total identified oxidation product content containing certain functional groups of interest.

	Fuel						
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>
Alcohols	72	24	60	56	72	78	58
Ketone	10	47	18	30	3	6	37
Aldehyde	1	4	1	<1	9	9	4
Acid	4	6	<1	<1	<1	<1	<1
Other	12	19	20	14	16	6	1

Note: The “other” category includes esters, ethers, anhydrides and heterocycles.

4.4.2 Bulk Fuel Properties

4.4.2.1 Water Separation (MSEP)

This method determines the ease with which a fuel releases entrained water on passing through a coalescing medium. The presence of molecules with surfactant characteristics will affect the result; hence the thermally oxidised fuels may be expected to exhibit differences in water separability due to the presence of oxygenated compounds generated over the course of the thermal stressing experiment. Analyses with the microseparometer revealed all of the fuels failed to meet the water separability specification from sample #2 onwards, i.e. after only eight min of thermal stressing. The neat fuels which had not undergone any thermal stressing all met the water separability requirement. One fuel (G1) failed to meet the specification at sample #1, after only one min of thermal stressing.

Previous work has shown that separometer values of thermally stressed fuels continue to decrease once peroxide concentrations have reached a maximum²⁰¹, which suggests that secondary and/or tertiary oxidation products with hydrophilic

character are likely to be responsible for this effect. Doping with FAME at 1% caused both fuels A and F to fail the water separation test, which is unsurprising given the known surfactant properties of FAME molecules. Doping the same fuels with 1% furanone mixture however, caused only the hydrotreated fossil fuel to fail. This is likely explained by the fact that this fuel already contained an additive package that is known to increase the propensity towards poor water separability. Fuel F contained lubricity improvement, static dissipater and icing inhibitor additives, all of which have significant polar functionalities which can affect water separability properties. Indeed, the separometer value of the neat fuel was already at the limit of 70 without any thermal stressing, or dopants, whereas all other samples except fuel E returned values above 90 at this stage. The addition of further polar compounds in this case, pushed the fuel beyond the specified limit.

The presence of a number of alcohols, in particular where they are multifunctionalised onto an alkane chain, is likely to significantly affect water separability properties and Table 15 shows that all fuels generated single and multiple alcohol functionalities during thermal stressing. Esters, ethers and carbonyls are also likely to affect this property, although to a lesser extent. Any acids generated, although not measured here, are also likely to have an effect (in particular the formation of soaps at high pH²⁰²) given their highly polar nature.

4.4.2.2 Demulsification

All neat fuels, and their corresponding sample #8 (thermally stressed for 112 min), met the demulsification standard. The oxidised species generated in the thermal stressing experiment were significant enough to influence the demulsification properties of these particular fuels, in that the volume of the fuel-water interface is clearly increased in the early stages of the demulsification experiment. Results at the beginning of the stabilisation time for the neat samples and those that have been thermally oxidised are clustered together in these two groups (Figure 16).

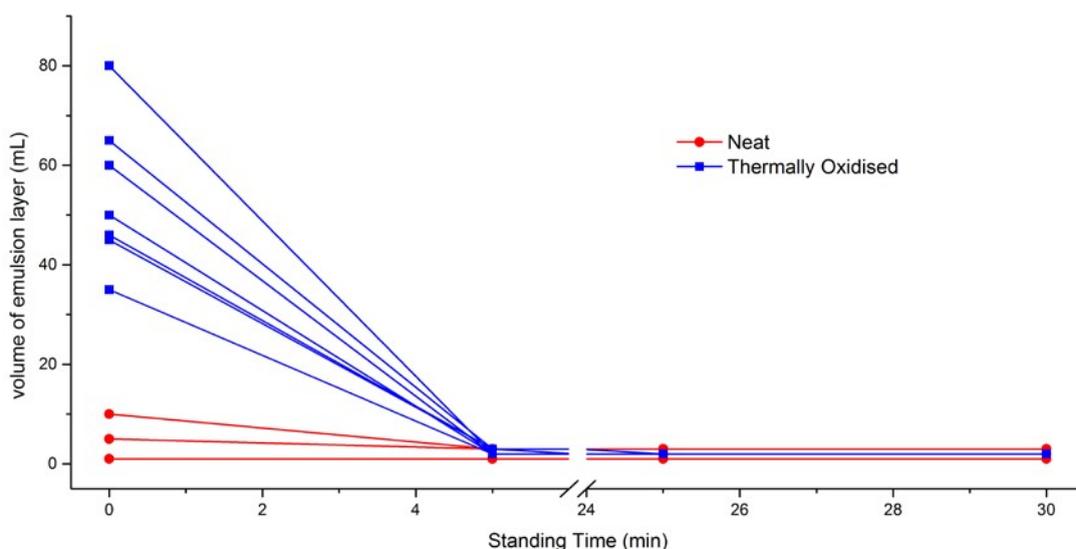


Figure 16. Results for the demulsification of the neat and thermally oxidised fuels, showing the increased volume of emulsion layer for fuels that have undergone 112 min of thermal oxidative stress compared with the neat fuels.

By the end of the designated standing time (30 min), all thermally stressed fuels had separated into fuel and water phases enough to pass the demulsification specification. Fuels A, B and F, when doped at 1% with five different classes of oxygenated compounds, all passed except for fuels A and B when doped with 1% FAME. Similar to the separometer results in the previous section, it was expected that the FAME would have an effect on the emulsifiability of the fuels. The failure of fuels A and B to meet this specification when the FAME contaminant was introduced may demonstrate the inability of less complex, alternatively-derived fuels to counteract the effect of contaminants compared with the traditional fuel types which are generally more complex and potentially able to offset the effects of contamination through a combination of antioxidant and solubilising interactions. Whilst the addition of many of the oxygenated compounds to the fuels did result in a quantitative increase in the volume of the fuel-water interface, they all still passed the specification with the exception of the aforementioned FAME doped samples. The development of lacing at the interface, as well as water haze within the fuel phase was common to virtually all of the samples tested, but generally cleared within the 30 min standing period. All fuels failed to meet the water separability specification after 8 minutes of thermal stressing, yet all fuels passed the demulsification standard even after 2 h of thermal stressing. Taking into account

The results of both the separability and demulsification analyses, it seems that under the conditions investigated in this study, the parallel between FAME and furanones is not a significant concern. Furanones do not significantly impact the coalescence or water shedding properties of a fuel under these conditions, which may be indicative of weaker hydrogen bonding compared with the FAMEs.

4.4.2.3 Oxidative Stability

A clear trend was observed whereby the thermally stressed fuels had a considerable decrease in their oxidative stability as measured by the PetroOxy tester. The production of oxidised species during the thermal stressing experiment limits the capacity of the fuels to resist further oxidation. One of the major concerns about non-petroleum based liquid fuels is their poor stability, and this is clearly evident here. All of the alternatively-derived fuels display substantially poorer stability than the conventional fuel types (Figure 17). Indeed, the neat alternatively-derived fuels even had stability which was comparable to, or worse than, the thermally stressed conventional fuels. This decline in oxidative stability can be attributed to the consumption of antioxidants, and those fuels with the most effective natural or synthetic antioxidants display a higher degree of oxidative stability. Fuels typically become coloured and/or generate insoluble gums or sediment during this stability test, and it was noted that the colour of the thermally stressed samples was significantly intensified, and only the conventional fuels generated solid deposits while undergoing oxidative stability testing. The likely explanation for this is the lack of heteroatomic species in the alternative fuels, as heteroatomics, particularly those containing nitrogen and sulfur, have a far greater propensity to form sediment.³²

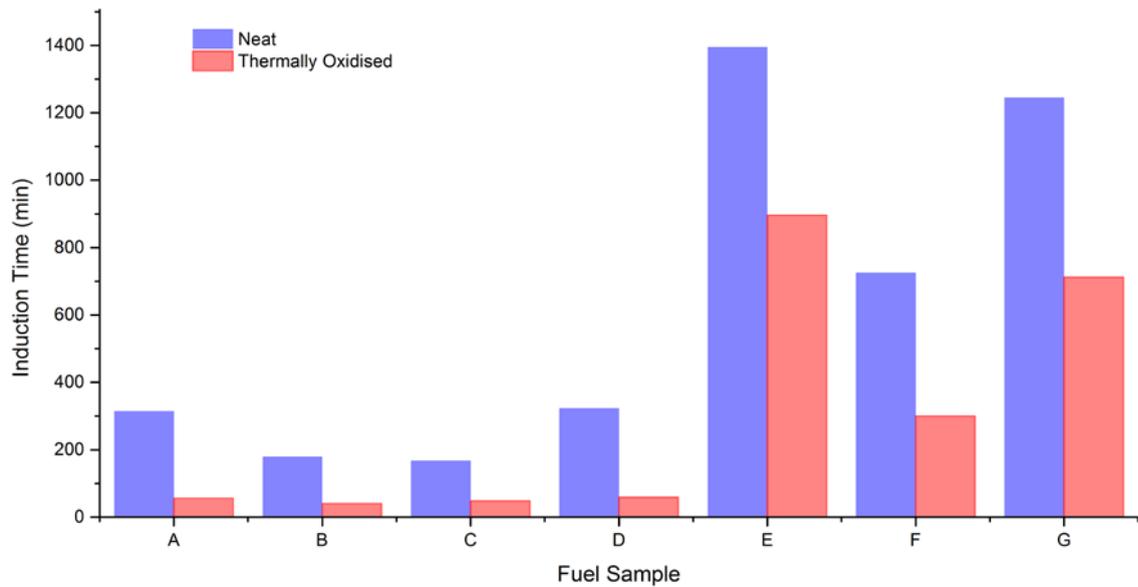


Figure 17. Accelerated stability tests of the neat and thermally oxidised fuel samples showing decreased stability for those fuels that have been exposed to prior thermal stress.

4.5 Conclusions

The sequential heart-cut MDGC method used here permits the identification of a range of oxygenated species, including tertiary oxidation products in thermally stressed fuel by utilising the increased separation space of a multidimensional separation. Use of a dynamic thermal stressing method replicates aircraft fuel system conditions as closely as possible and allows for samples to be taken at intervals over the oxidation period, which is useful for monitoring the process over time.

Standardised test methods are useful to provide supporting information and supplementary evidence for the oxidative history of a given fuel, but none of the tests here gives an accurate indication of the extent of oxidation on their own, and whether a fuel is fit-for-purpose based on these measured properties.

Acknowledgments

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Chapter 5: Publication 4

Webster, R. L.; Evans, D. J.; Marriott, P. J., *Energy Fuels* **2015**, 29 (4), 2067-2073.

Synopsis

This work builds on results reported in the previous publication by using a multidimensional gas chromatography/mass spectrometry (MDGC-MS) method to isolate furanones for a range of fossil and alternatively-derived jet fuels. While Chapter 4 was very broad in terms of the oxidised species identified in thermally stressed fuels, this publication has much narrower focus. Here a single class of oxidised compounds, furanones, are selected for isolation based on chemical similarity to known fuel contaminants. Quantification is also carried out, with excellent analytical figures of merit achieved. The same set of fuels is used as the previous study, but with a time series constructed along operationally-relevant periods of thermal oxidative stress.

A similar approach is taken as Chapter 3 in the instrumental parameters adopted for the analysis. Once again the very long first dimension column coupled with the highly polar ionic liquid second dimension column has proven advantageous. Similarly the analysis is conducted with both electron and chemical ionisation mass spectrometry. Measurement of the concentrations of eight substituted furanones reveals linear increases in their concentration over time, and final concentrations which are worthy of concern given the results of some of the physicochemical properties tests in the previous chapter. Additional evidence from the previous study, in the form of stable intermediates identified in the heart-cuts of oxidised fuels, are presented as part of a proposed mechanism for furanone formation. Such mechanistic insights are crucial for future development of strategies to mitigate the effects of fuel oxidation.

5 Multidimensional Gas Chromatographic Analysis of Low-Temperature Oxidized Jet Fuels: Formation of Alkyldihydrofuranones

Renée L. Webster, David J. Evans, Philip J. Marriott

5.1 Abstract

Liquid hydrocarbon fuels are complex hydrocarbon mixtures, made even more complex when oxidation reactions produce a variety of oxygenated species. Heart-cut multidimensional gas chromatography coupled with chemical ionisation mass spectrometry was applied to the quantification of alkyldihydrofuranones in several fossil and alternatively-derived jet fuels. The fuels were then subjected to thermal oxidative stress for extended times using a purpose-designed experimental system. The concentration of furanones in all fuels increased over the course of the experiment, to a maximum of 7.5 mg/L in a hydrotreated fuel. The analytical method is robust with R^2 for all analytes above 0.9993, and RSD below 6%. A mechanism for the formation of these compounds via intramolecular cyclisation is also postulated.

5.2 Introduction

In modern aircraft platforms, middle distillate fuels are being subjected to increasingly high thermal loadings.²⁰³ Thermal stability is a crucial performance characteristic of fuels, particularly in aircraft where fuel is used as a heat sink for the cooling of avionics and lubricants. Poor thermal stability is known to contribute to the formation of gums and other solid residues in fuel.²³ as well as an increased propensity towards undesirable qualities such as surfactant tendency and poor water separability.¹⁸²

Low temperature (<180 °C) regime oxidation has not been fully investigated in the literature, with much of the research into thermal stability carried out in the middle and high (pyrolytic) temperature regimes.^{59, 204-206} Not only has the bulk of the work

in thermal stability of fuels been carried out at higher temperatures, it has also been for long periods of time, significantly longer than the typical flight time of a high-performance jet aircraft. There is also a dearth of experimental data from dynamic fuel stressing experiments; the majority are performed under static conditions where the fuel is heated in a single flask, without circulation or temperature variation. Although there are sound practical reasons for accelerated stability testing, these factors may contribute to a picture of fuel oxidation which is not representative of real-life usage.

Whilst the early (primary and secondary) stages of fuel oxidation have been extensively characterised and are well understood,^{26, 186, 207} the formation of tertiary and further oxidation products have been investigated to a much lesser extent. The characteristics of some tertiary oxidation products such as alkyldihydrofuranones (furanones), are worthy of further investigation due to the presence of polar functional groups in these molecules. Previous work in this area has focused on isolation of these compounds from the complex fuel matrix, and investigating whether the similar functionality to the known contaminant FAME (fatty acid methyl esters), impacts upon fuel quality.^{16, 185} The latter study employed HPLC for furanone isolation, although the method is rather tedious. Furanones are also likely to be involved in the formation of soluble macromolecular oxidatively reactive species (SMORS), which are known to be precursors to solid deposits in fuels.^{41, 195}

Until recently, fuel oxidation was normally assessed via bulk physical or chemical property tests. Heart-cutting gas chromatographic techniques were first applied to the separation of low molecular weight oxygenated fuel additives by McCurry and Quimby²⁰⁸, and then by Luong *et al.*²⁰⁹, and Sciarrone *et al.*¹²⁰ some years later. Compounds arising from oxidation reactions however, are generally of higher molecular weight, less volatile and substantially more difficult to isolate from the fuel matrix via chromatography or other techniques. However, with further development of multidimensional separation techniques, it has become possible to isolate individual oxidation products from the complex fuel matrix.^{101, 185, 210} Detection of oxygenated compounds has also been problematic, as mass spectra often lack signals that are concentrated or distinct enough from the fuel matrix to positively identify these compounds. Oxygen-specific detectors such as atomic emission (AED) or oxygen flame ionisation (O-FID) have also been unsuccessful in

this arena as they are plagued with difficulties relating to leaks and poor detection limits, which renders them impractical for trace compound analysis.

This work proposes a mechanism of formation for furanones in middle distillate fuels formed via low-temperature thermal stressing. These tertiary oxidation products can be isolated and quantified from the complex hydrocarbon matrix by using multidimensional gas chromatography with chemical ionisation mass spectrometric detection.

5.3 Experimental

5.3.1 Samples and Standards

5.3.1.1 Fuel Samples

Seven aviation fuels were used in this study, details of which are given in Table 17. Samples were selected to include a range of processing technologies, and new generation alternatively derived fuels (A-D) to compare with more established conventional fuels (E-G). Fuels E-G are certified for use in jet engine aircraft, whilst fuels A-C meet the requirements of Annexes A1 and A2 in ASTM D7566¹⁴⁴ for synthetic paraffinic kerosene (SPK). Fuel D utilises an alcohol oligomerisation synthetic pathway which has not been certified at the time of publication. The fuels were used ‘as-is’, with no blending with other feedstocks, and contained any additives that may have been included at the refinery. No sample cleanup or preparation was carried out. All fuels and samples were stored at -18 °C. Water content of the neat fuels was determined by automated Karl-Fischer titration and was between 9 and 28 ppm for all samples.

Table 17. Details of the jet fuels used in this study.

Sample	Source	Processing/Refining Method
A	Camelina	Hydroprocessed Esters of Fatty Acids
B	Coal/Syngas	High Temperature Fischer-Tropsch
C	Algae	Hydroprocessed Esters of Fatty Acids
D	Isobutanol	Alcohol to Jet
E	Fossil	Mercox
F	Fossil	Hydrotreated
G	Fossil	Straight Run

5.3.1.2 Standards

All furanone standards were commercially purchased from Sigma-Aldrich (Castle Hill, NSW, Australia) and used without further purification. For the purposes of this work, the furanones studied were a homologous series of *n*-alkyldihydrofuranones, with alkyl chain substitutions of methyl through to octyl. Standards were prepared in chromatography grade heptane (Merck, Kilsyth, VIC, Australia) from a stock solution containing approximately 1000 mg/L of each analyte. The exact concentrations of each analyte in the set of calibration standards are given in Table 18.

Table 18. Furanone standard concentrations.

	standard concentration (mg/L)					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	5	6
methyl-	0.0121	0.0605	0.121	0.303	0.605	1.21
ethyl-	0.0121	0.0605	0.121	0.303	0.605	1.21
propyl-	0.0104	0.0520	0.104	0.260	0.520	1.04
butyl-	0.0115	0.0575	0.115	0.288	0.575	1.15
pentyl-	0.0112	0.0560	0.112	0.280	0.560	1.12
hexyl-	0.0102	0.0510	0.102	0.255	0.510	1.02
heptyl-	0.0118	0.0590	0.118	0.295	0.590	1.18
octyl-	0.0088	0.0440	0.088	0.220	0.440	0.88

5.3.2 Dynamic Thermal Stressing

Fuels were subjected to dynamic thermal stressing by circulating through a custom-built thermal stability rig described previously¹⁸⁵. This unique cyclic dynamic stressing technique offers several advantages over other static and small scale fuel stressing methods. The rig is designed to simulate the movement of fuel through a real fuel system by subjecting it to short, repeated thermal stressing events followed by quenching and mixing with ambient temperature fuel.

Fuel samples of 1000 mL were sparged with air at room temperature for 60 min before commencing cyclic thermal stressing. The fuel was continually sparged with air throughout the thermal stressing experiment. A heated tube length of 5 m was utilised with the sand bath temperature adjusted to provide a bulk fuel temperature within the heated zone of 180 °C. The fuel was supplied at 18, 600 kPa (\pm 200) and 40 mL/min and collected in a separate flask resulting in a residence time of 170 s for each pass. The fuel completed 40 passes through the heated zone, with a subsequent

total stressing time of 113 min which is within the time range of a typical sortie for a high-performance aircraft. The fuel was returned to ambient temperature by passing through a chilled water bath between each thermal stressing period to create a heating/cooling cycle where $\Delta T \approx 160$ °C. Aliquots of sample of approximately 100 mL of fuel was removed from the rig at each of eight intervals during the stressing period for analysis of thermal oxidative degradation products, resulting in a final volume of 200 mL at the end of the experiment.. The sampling interval became progressively longer throughout the duration of the experiment, as previous work indicated that changes may be more rapid in the earlier stages of thermal oxidation.

An additional, significantly longer thermal stressing experiment was carried out on Fuel A only, in order to further investigate the continued formation and subsequent degradation of furanones. The conditions were the same as for the experiment above, except that the starting volume was 250 mL and the fuel completed 293 passes through the heated zone, for a total stressing time of 814 min. A small sample (<1 mL) was removed approximately every hour for monitoring the furanone concentration over time.

5.3.3 Gas Chromatography-Mass Spectrometry

Furanones were analysed in the thermally stressed fuels using multidimensional gas chromatography with chemical ionisation mass spectrometry (MDGC-CIMS).

Quantitation of the eight homologous furanone compounds was achieved via a multi-point external standard calibration. Analyses were carried out on an Agilent 7890A-5975C (Agilent Technologies, Santa Clara, CA, USA) gas chromatograph-mass spectrometer equipped with a Deans' switch assembly. Operating parameters of the MDGC-CIMS system are given in Table 19.

Table 19. GC-MS conditions and operating parameters

Column 1	HP-1
Length/ID/d _f	100 m / 0.25 mm / 0.5 µm
Column 2	SLB-IL60
Length/ID/d _f	30 m / 0.25 mm / 0.2 µm
Restrictor Length/ID	0.7 m / 0.1 mm
Oven	50 °C ↑ 300 °C (5 °C/min)
Injector	300 °C
Inj. vol. / split ratio	0.5 µL / 20:1
Carrier gas	He

Flow; velocity (col. 1)	1.1 mL/min; 12.7 cm/s
Flow; velocity (col. 2)	2.5 mL/min; 58.5 cm/s
Transfer Line	300 °C
Ionisation	CI (methane), 70 eV
Quadrupole; source T	150 °C; 300 °C (230 °C for EI)

Conditions for the comparison with EI mass spectrometry were the same, except for the change in ionisation mode and source temperature. Mass spectral detection was performed in selected ion monitoring (SIM) mode on two ions for each analyte of interest in CI, and one in EI. Analytical parameters for the furanones are supplied in Table 20. MSD Chemstation version E.02.00 was used for data collection and processing.

Table 20. Chromatographic parameters for the analysis of furanones by MDGC-CIMS, conditions are the same for the comparison with EI, except for that the SIM ion is m/z 85 for all analytes.

Compound (furanone)	¹ D Retention Time (min)	Heartcut Window	² D Retention Time (min)	CI SIM ions (m/z)
methyl-	25.17	25.10 – 25.30	27.93	83, 101
ethyl-	28.65	28.55 – 28.75	31.24	97, 115
propyl-	31.89	31.80 – 32.00	34.37	111, 129
butyl-	35.14	35.00 – 35.20	37.52	125, 143
pentyl-	38.21	38.10 – 38.30	40.51	139, 157
hexyl-	41.14	41.05 – 41.25	43.38	153, 171
heptyl-	43.97	43.90 – 44.10	46.14	167, 185
octyl-	46.72	46.65 – 46.85	48.84	181, 199

5.4 Results and Discussion

5.4.1 GC Column Selection

The choice of GC columns in this analysis is crucial. The complexity of the fuel matrix prevents identification of trace compounds in one dimension; there are simply too many interferences. The 100 m non-polar first dimension column is essential for

achieving a high degree of separation in the complex fuel matrix, and to decrease the number of compounds transferred in each heart-cut. The second dimension column must be highly polar, in order to separate the non-polar hydrocarbons in the heart-cut region from the polar analytes with minimal interferences and baseline resolution. The ionic liquid column SLBIL-60 is the commercially available column appropriate in this context due to its very high polarity and high temperature limit of 300 °C. The final analyte in this study does not elute until an oven temperature above 290 °C.

5.4.2 Choice of Ionisation Mode

The use of soft chemical ionisation in this study offers many advantages over conventional electron ionisation. The main ion in the EI mass spectrum of each of the furanones included in this study is 85 m/z , which is an ion also common to alkane fragmentation patterns. This makes it difficult to identify trace furanones in a matrix consisting primarily of alkanes. However, CI fragmentation of furanones generates two strong ions unique to each analyte, permitting a highly specific SIM analysis, with few, if any, interferences from the fuel hydrocarbons. Chemical ionisation also eliminates virtually all background associated with column bleed and baseline noise is solely electronic. Despite a higher overall analyte response from EI, CI also offers improved signal to noise (Figure 18) and therefore, better detection limits than EI by an order of magnitude. The detection limit for furanones under chemical ionisation conditions is less than 5 $\mu\text{g/L}$.

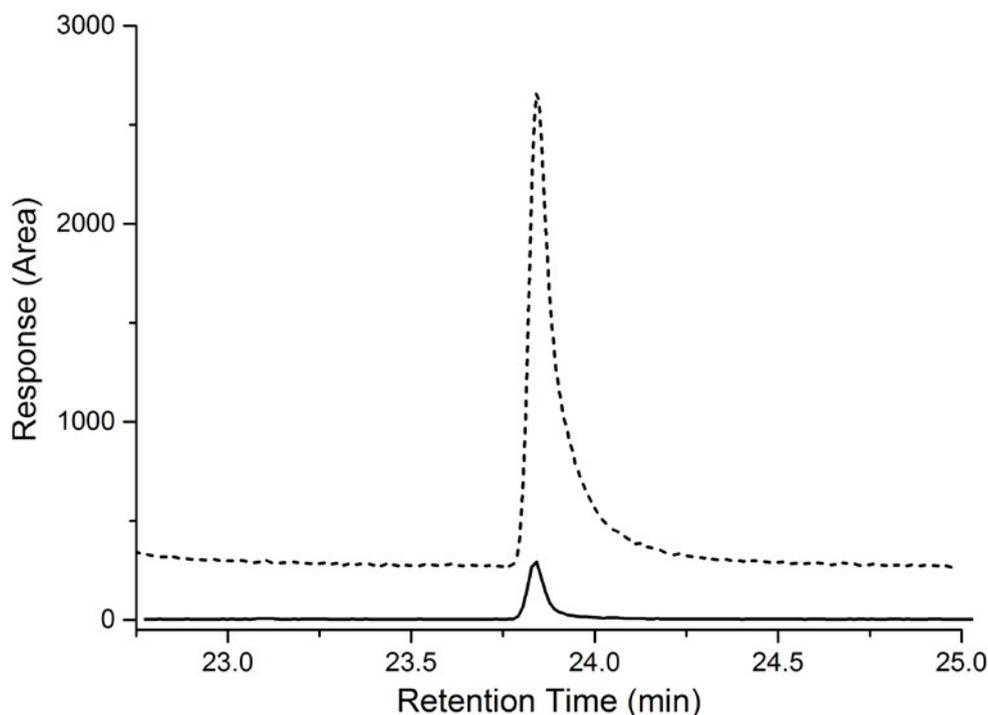


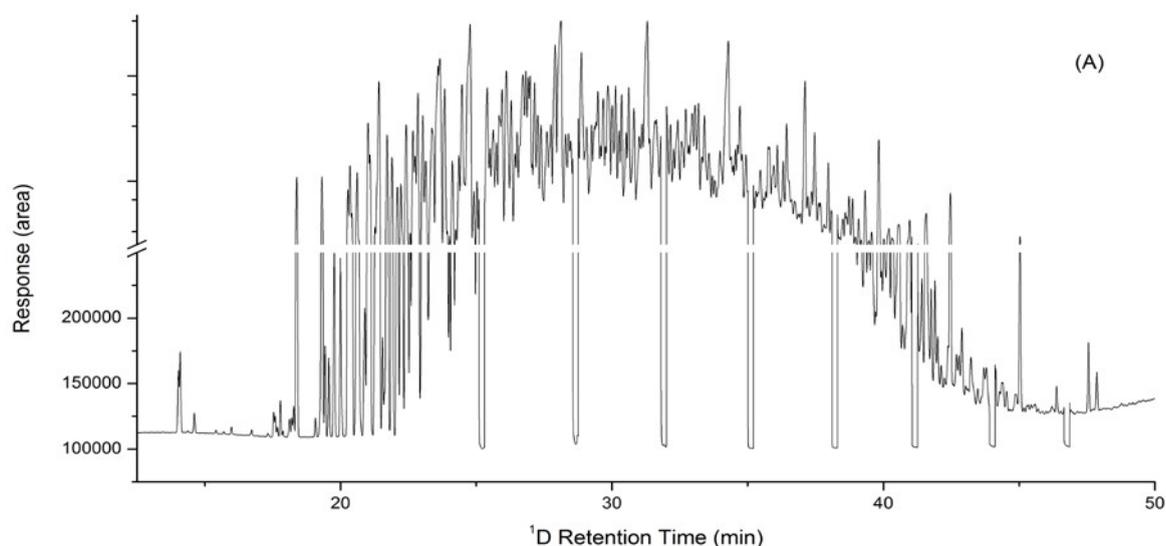
Figure 18. Response of octyl-furanone in electron ionisation (dashed) and chemical ionisation (solid) modes. Signal-to-noise for the peak in EI = 530, and in CI = 1200 (as calculated by MSD Chemstation).

5.4.3 Quantification of Furanones in Thermally Stressed Fuels

The eight furanone compounds of interest were quantified against a multiple point external standard calibration curve, covering a concentration range of approximately 0.01–1 mg/L for each analyte. The regression analysis showed a high degree of linearity, with minimum R^2 value for each curve of 0.9993. Reproducibility was assessed through seven replicate analyses of the second lowest concentration standard and was determined to be less than 6 % for all analytes.

An increase in furanone concentration was observed in all of the fuels over the thermal stressing period, clearly visible with the representative set of chromatograms given in Figure 19. The growth of methyl and ethyl furanone concentration with thermal stressing time demonstrated in this chromatogram is illustrative of similar increases in the other furanones in five of the other six fuels. Figure 20 displays the increase in furanone concentration for six of the seven fuels in this study, fuel D (alcohol to jet) is omitted due to negligible furanone content generated in this sample. The highest overall concentrations were observed in the

conventional fuels, with final total furanone concentrations of 4.5, 5.5 and 7.2 mg/L in the Merox (E), hydrotreated (F) and straight run (G) fuels, respectively. With the exception of the camelina SPK (A), the alternative fuels all had significantly lower concentrations than this by the end of the thermal stressing period. Initially this appeared counterintuitive, as the conventional fuels are generally regarded as being more stable, and have a greater ability to resist oxidation due to the presence of naturally occurring heteroatomic compounds which contribute antioxidant character, and these compounds are lacking in the alternative fuels. However, the alternative fuels are known to contain a large proportion of branched alkanes²¹¹, in contrast to the conventional fuels where the alkane component is primarily straight chain hydrocarbons. A higher degree of branching may inhibit the initiation of cyclisation reactions, which is discussed further in Section 5.4.5. Furanones with branched alkyl substitutions were also identified but not targeted for quantification in this study. These are generally seen in lower abundance than their straight-chain analogues, but are the most prevalent in the alternative fuels with a high degree of branching, i.e. the Fischer-Tropsch (B) and alcohol to jet (D) fuels. Standards of the branched alkylfuranones were not available for these compounds, but if they were at hand, they could be targeted and quantified in the same manner as the straight-chain furanones, by simple adjustment of the heart-cut regions and SIM ions.



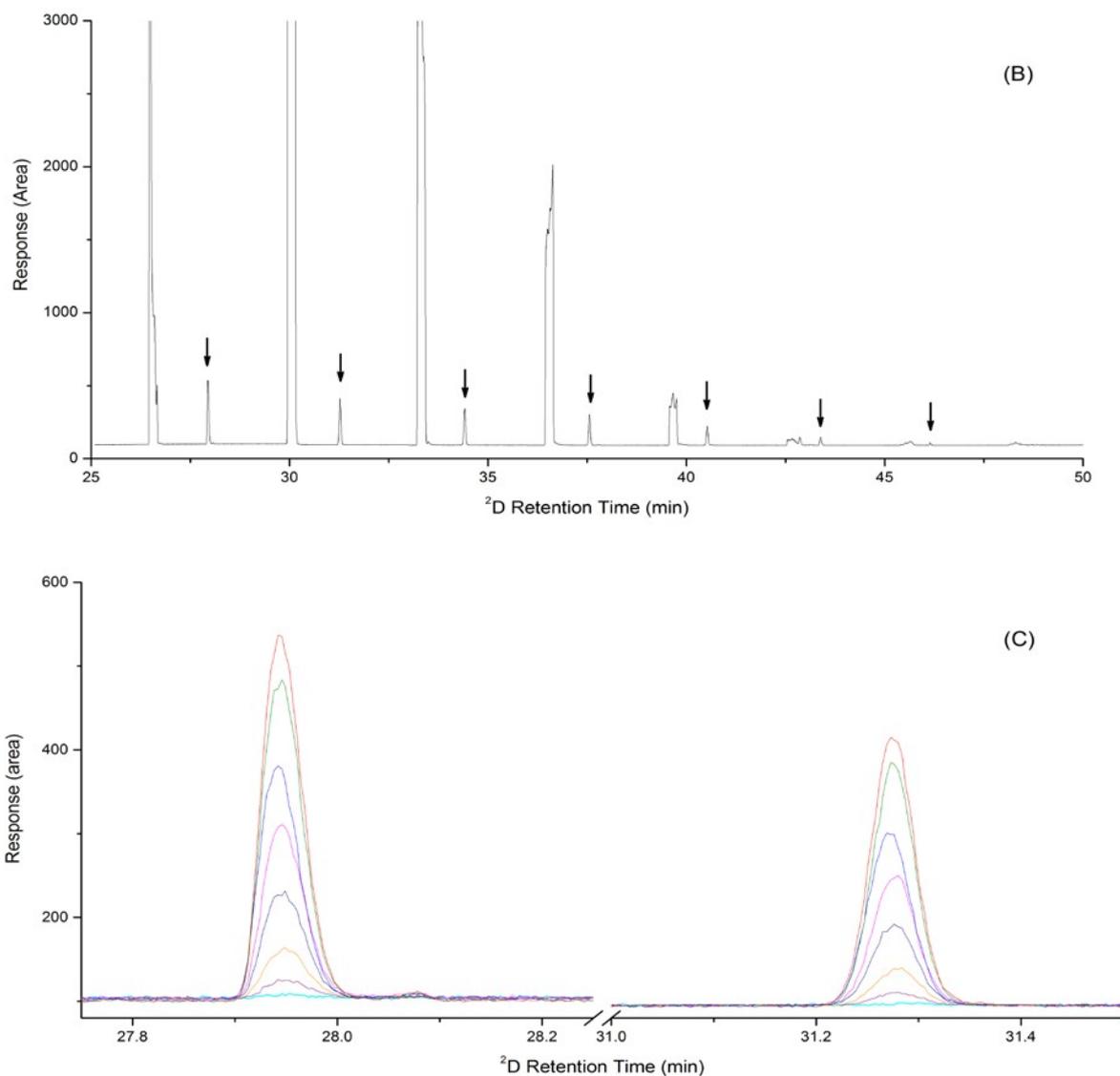


Figure 19. (A) 1D chromatogram (FID channel) of Fuel E (hydrotreated conventional jet fuel) showing heart-cuts located at regions where furanones elute. Break in y-axis signifies shift from linear to log scale. (B) 2D SIM chromatogram corresponding to sequential heart-cuts transferred to the second dimension; homologous furanones indicated by arrows. (C) Overlaid 2D chromatograms showing progressive increase in concentration of methyl (tr 27.95 min) and ethyl (tr 31.27 min) furanones over 113 min of thermal stressing time for Fuel E. Note: x-axis break omits the large hydrocarbon peak heart-cut from the first dimension.

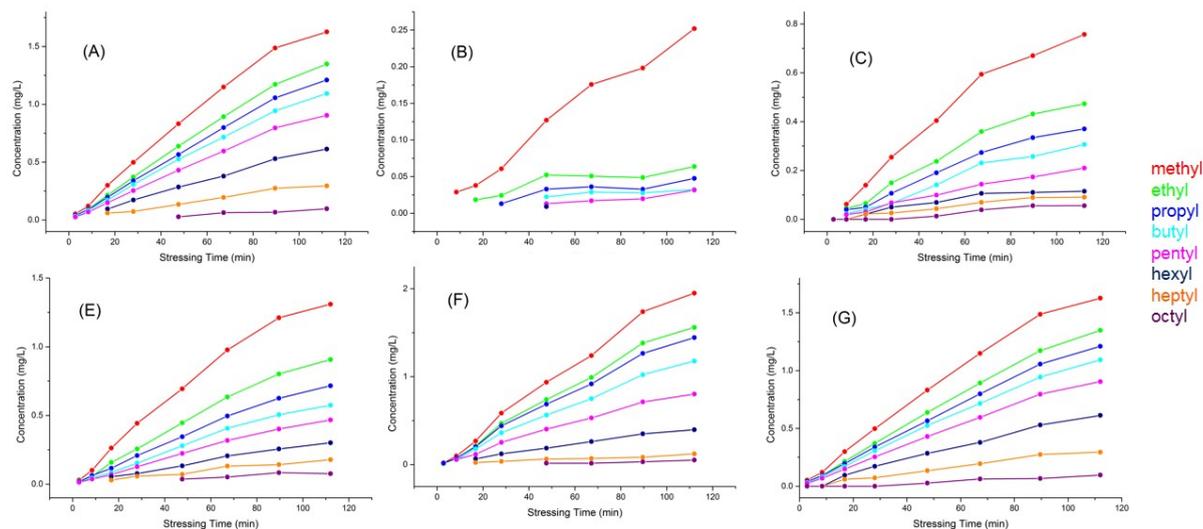


Figure 20. Concentrations of furanones in Fuels A-C, E-G over 113 minutes of thermal stressing. Fuel D is excluded due to negligible furanone content generated in this sample.

5.4.4 Extended Thermal Stressing Experiment

An extended thermal oxidation experiment on Fuel A only was carried out in order to investigate for how long the furanone concentration would continue to rise. The fuel was subject to thermal stress for well past the time corresponding with a typical high-performance aircraft flight time, and subsequent GC analysis revealed that the concentration of furanones in this sample continued to increase for many hours. Furanones did not begin to degrade until around 1500 min of exposure, after reaching a peak total concentration of approximately 45 mg/L (Figure 21).

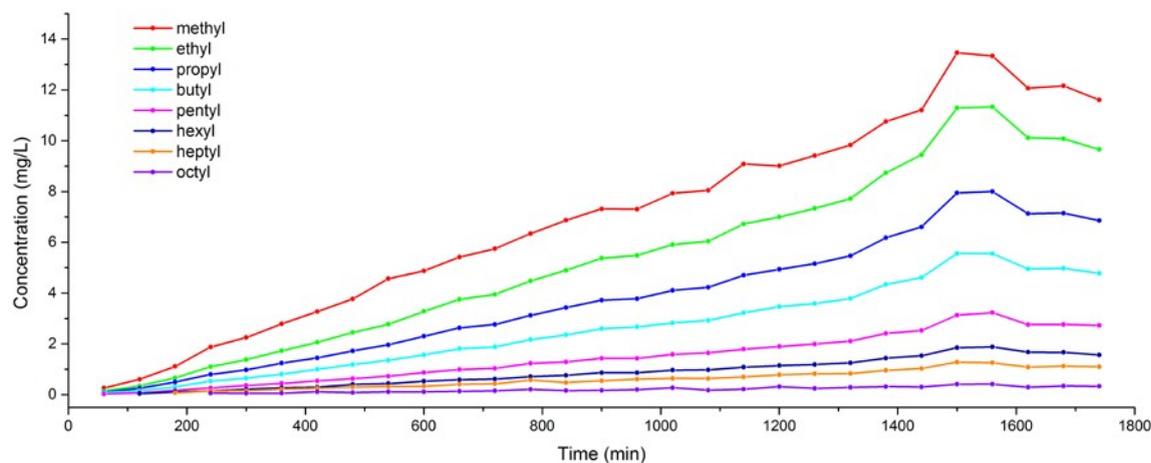


Figure 21. A consistent increase in furanone concentration occurs with time, over an extended period of thermal stressing, for camelina-HEFA (Fuel A).

5.4.5 Mechanism of furanone formation

It is well established that the initial stages of oxidation proceed via the production of hydroperoxides, as detailed by Heneghan and Zabarnick³² and Morley.²¹² We have previously postulated a mechanism for the formation of aromatic benzofuranones via intramolecular Fischer esterification¹⁸⁵, based on the work of Goosen and Kindermans²¹³ and Stark *et al.*³⁰ While there are reports of the formation of lactones from the oxidation of alkanes,²¹⁴ there appears to be a general reluctance to propose mechanisms for their formation. Although no mechanistic studies are included to support it here, we present in Figure 22 a proposed mechanism for furanone formation in this study, based on the aforementioned work of Goosen and Kindermans. Secondary hydroperoxides (1) formed in the first stages of oxidation undergo heat-induced homolysis of the O-O bond, which is often the first step in ring-closure reactions.¹⁹⁷ This is followed by intramolecular hydrogen abstraction to create 1,4-diols (4). One of the hydroxyl groups is then further oxidised to a carboxylic acid (7), creating a hydroxy acid and enabling the final step of the ring closure reaction. There are many and varied acidic species present in the oxidised fuels²³ as well as ongoing generation of peroxide species, both of which are available to participate in the reaction displayed. Sufficient water was also present in the fuels as per Section 5.3.1 to enable this reaction to occur. Further support for this mechanism comes via identification of some likely reaction intermediates in the same thermally stressed fuels using a different multidimensional chromatographic analysis. Stable intermediates in this reaction scheme, specifically difunctionalised alcohols and alcohol/carboxylic acids were identified in our previous study¹⁶. Indeed, one of the major classes of oxidation products identified was secondary alcohols (Figure 22, compound 3). Also identified were compounds conforming to the generic structures of compounds 4 and 7, for example hexane- and octane-diol and hydroxy-dodecanonic acid. This mechanism would also help to explain the fact that the more highly branched synthetic fuels have a lower concentration of furanones, as the hindrance induced by a greater degree of branching would prevent the cyclisation reaction from proceeding. The alcohol to jet fuel which is comprised primarily of branched alkanes, has generated virtually no furanones at all.

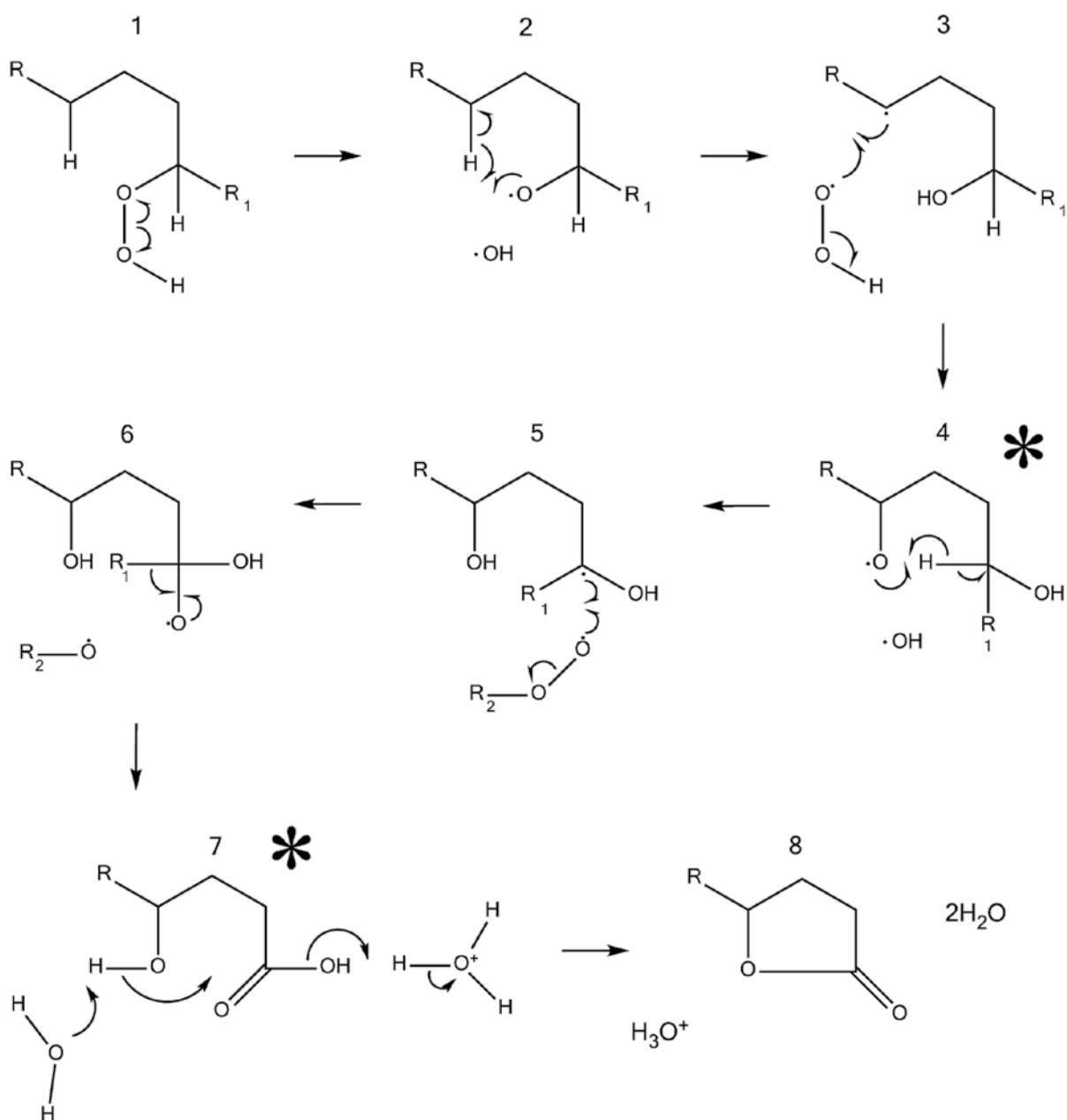


Figure 22. Proposed mechanism for furanone formation. Examples of the stable versions of the intermediates marked with asterisks have been identified in a previous study.

5.5 Conclusion

Gas chromatography coupled with chemical ionisation mass spectrometry is a highly suitable technique for the analysis of trace furanones in a complex fuel matrix. The analytical method eliminates interferences, requires no sample preparation and affords good sensitivity and exceptional linearity. It follows that a similar approach

could ostensibly be used for the targeted analysis of other groups of trace compounds that are otherwise difficult to analyse in fuels, or other complex matrices.

Conventional fossil fuels generally produced higher concentrations of furanones when subjected to low temperature thermal stressing, which can be explained by the fact that the more highly branched synthetic fuels are less amenable to cyclisation reactions. The intramolecular cyclisation reaction that may be a possible route of formation for these furanones is initiated by the formation of hydroperoxides, which go on to form hydroxy acid intermediates preceding the final step of furanone formation.

Acknowledgments

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Chapter 6: Publication 5

Webster, R. L.; Mete, J. B.; Rawson, P. M.; Evans, D. J.; Marriott, P. J., *Fuel* **2017**, 197, 226-231.

Synopsis

Taking a slightly different approach to the rest of the thesis, in this chapter sample extraction is employed to facilitate the characterisation of trace oxygenates in fuel. Custom-made, Nafion-coated SMPE fibres were created in order to investigate the formation of volatile species produced on thermal oxidation of fuels. Previous unpublished experiments in our laboratory with some alternate fuels had produced unusual and distinctive odours which warranted further investigation.

Here, the analysis of some selected oxygen-containing compounds first in solvent, and subsequently in conventional and alternate fuel matrices, demonstrates proof-of-concept; that the fibre offers improved selectivity towards target analytes compared with polar fibres already on the market. Once efficacy was confirmed, application of the fibre to thermally oxidised conventional and alternate fuel establishes the value of the technique with the identification of numerous volatile oxygenated species. Single dimension and multidimensional GC separations are applied here, as in the rest of the thesis, to achieve optimal resolution of target compounds from the fuel matrix.

This can be considered complementary to the other approaches, such as multiple sequential heart-cuts (Chapter 4), pre-fractionation or advanced mass spectrometry (Chapters 2,7), as compounds are identified that are unique to the SPME approach. Specifically, those which are particularly volatile, or highly polar and are less likely to be recovered and identified in a standard liquid injection GC.

6 Oxidised Compounds in Aviation Fuels Using Nafion Fibre

Solid Phase Microextraction

Renée L. Webster, Jonathan. B. Mete, Paul M. Rawson, David J. Evans,
Philip J. Marriott

6.1 Abstract

Nafion solid-phase microextraction fibres were prepared and applied to the analysis of polar oxygenated analytes in non-polar aviation fuel matrices. The performance of the Nafion fibres was investigated and exhibited higher extraction efficiencies for polar analytes spiked into a reference non-polar fuel, compared with a commercially available polar (carbowax) phase fibre. Oxygen-containing compounds were also tentatively identified in thermally oxidised aviation fuels using both single column and multidimensional gas chromatography with mass spectrometry.

6.2 Introduction

Thermal stability of aviation fuels is a key consideration facing the operation of high performance aircraft. As modern aircraft engines and fuel systems are required to operate at increasingly high temperatures and employ fuel as a coolant for hydraulic and avionics systems, fuel thermal instability and oxidation reactions are of growing concern. Thermal oxidation in fuel is a problem as oxygenated species are known to attack engine components,¹⁸⁴ form solid deposits,³² and increase the solubility of water in the fuel.¹⁶ The increasing introduction of alternatively derived fuels in aircraft is also an important consideration; even when stringent performance specifications are met, their oxidative chemistry can be different from conventional fossil crude derived fuels,¹⁸⁵ and so strategies to assess oxidation of such fuels are required.

Identification of oxygenated compounds is an important aspect of assessing the serviceability of the fuel, and to formulate strategies to mitigate the effects of the oxidised species. However, the identification of oxidised species in fuels can be

complicated due to the complex nature of the fuel and low concentration of the compounds of interest.¹⁸² A high resolution separation technique, coupled with sensitive and selective detection is required for the analysis of trace analytes in fuels, and for this task gas chromatography-mass spectrometry (GC-MS) is often used. To further improve the resolution and hence the identification of target analytes in the fuel mixture, multidimensional gas chromatography (MDGC) can be very effective to identify more analytes by reduced overlap with interfering peaks, and improved resolution of target components.

Solid-phase microextraction (SPME) is a technique used to selectively extract compounds usually from the headspace of a sample, based on sorption of volatile compounds to a fibre.⁸⁴ Most SPME fibres are applied to the extraction of analytes in polar matrices such as water²¹⁵ and applications for non-polar matrices (e.g. as represented by fuels) are scarce.²¹⁶ The most suitable commercially available fibre for the extraction of polar analytes is 'carbowax-polyethylene glycol' (CW/PEG), but optimal performance remains to be achieved in a non-polar matrix. Gorecki *et al.*²¹⁷ produced a Nafion-coated fibre for the extraction of polar compounds from non-polar matrices. However, the Gorecki *et al.* study only aimed to identify target alcohols in hexane and gasoline. Nafion fibres have also been applied to the analysis of polar aromatics such as phenols,^{218, 219} and composite Nafion fibres for extraction from aqueous and biological fluids.²²⁰⁻²²² A more extensive analysis of Nafion fibres to other, more complex non-polar matrices would be beneficial based on this demonstrated affinity and preferential sorption of target polar compounds. Here, Nafion SPME fibres were prepared in the laboratory and applied to the analysis of oxygenated compounds in conventional and alternatively-derived aviation fuels.

6.3 Experimental

6.3.1 Preparation of Nafion Fibres

Bare fused silica fibre (Institute for Photonics and Advanced Sensing, University of Adelaide, Australia) of 100 μm was coated with a solution of ca. 5% Nafion® 117 in a mixture of lower aliphatic alcohols and water (product code 70160; Sigma Aldrich, Castle Hill, Australia) using a Pasteur pipette. This procedure was repeated 15-20 times to build up a coating thickness of approximately 100 μm diameter, measured

by digital optical microscopy (Supporting Information, Appendix B Figure B1).

Fibres that measured between 200 and 300 μm diameter once coated were selected for use, to maximise the amount of coating material without exceeding the inner diameter of the protective sheath (stainless steel needle) of the SPME holder.

6.3.2 Samples and Standards

6.3.2.1 Fuel Samples

Three different aviation fuels were selected for investigation; a conventional fossil crude oil derived Jet-A1 fuel (Jet-A1), a synthetic isoparaffinic kerosene derived from Fischer-Tropsch processing (FT-IPK), and a biologically derived paraffinic kerosene from hydroprocessing of fatty acids (HEFA-SPK). All fuels were filtered through a column of 70-230 mesh silica gel (Merck, Kilsyth, Australia) to remove any additives or impurities such as icing inhibitor that may have been present. An aliquot of each of the three fuel samples was also subjected to accelerated oxidation using a PetroOxy rapid small scale oxidation tester (Anton-Paar, Graz, Austria) to induce the formation of oxidised species.

6.3.2.2 SPME Standard Solution

A stock standard solution of approximately 10,000 mg/L each of 11 oxygenated compounds (all from Sigma Aldrich, Castle Hill, Australia) was prepared in heptane. A wide range of model analytes were selected in order to cover many of the functional groups that have been previously found in oxidised fuels. Preparations of these fuels spiked with oxygenates at known concentrations were used in a method validation study in order to assess the performance of the Nafion fibre against a commercially available CW/PEG fibre (Sigma-Aldrich, Castle Hill, Australia).

6.3.3 Solid Phase Microextraction for Gas Chromatography-Mass Spectrometry

To perform SPME, 20 mL of sample was added to a 40 mL headspace vial and placed in an oven at 40 $^{\circ}\text{C}$ for 30 min to reach thermal equilibrium, then the fibre inserted into the headspace where samples were extracted for 5 min. Chromatographic analysis was carried out on an Agilent 7890A-5975C GC-MS (Agilent Technologies,

Santa Clara, CA), with details of 1 dimensional and multidimensional GC conditions given in the Supplementary Information (Appendix B1).

6.4 Results and Discussion

6.4.1 Fibre performance for extraction of oxidised compounds A heptane solution was spiked with standard oxygenate solution, with concentrations of each component approximately 100 mg/L. Extractions were performed in triplicate using both Nafion and CW/PEG fibres, to compare the performance of both fibre types towards oxygenate extraction. The result is illustrated in Appendix B, Figure B2. These results demonstrate that the Nafion fibre coating provides considerable enhancement of sorption for most of the oxygenate compounds. The excellent affinity of Nafion towards polar analytes is likely due to a combination of its highly electronegative fluorinated polymer backbone and sulfonic acid functional groups that participate in cation exchange. The same samples were also analysed by direct liquid injection into the GC-MS in order to determine the SPME enrichment factors for each compound (Table 21). Enrichment factors for the Nafion fibre varied over a range from 10 to 20,000 (depending on the matrix and compound) compared with direct liquid injection. In contrast, the CW/PEG fibre proved unsuitable, with responses for some compounds considerably reduced than even those found for liquid injections (Table 21). The SPME method using the Nafion fibre proved to be the most successful for the majority of target compounds, while CW/PEG had higher enrichment factors for naphthaldehyde and naphthol only. Overall, the Nafion fibre outperformed the CW/PEG fibre for extraction of polar oxygenates from all three spiked fuel samples, however different phase volumes are loaded onto the respective fibres, which needs to be taken into account to estimate comparative enrichment factors.

It was noted that the Nafion fibres began to discolour after several uses. Therefore, the stability of the fibre and hence repeatability of the extraction and analysis was tested by conducting 10 replicate measurements of the oxygenate standard mixture spiked at 100 mg/L in HEFA-SPK fuel matrix. The relative standard deviations of these measurements ranged from 7-14% and can be found in Table 21.

Table 21. Enrichment factors (EF) of target oxygenates analytes for the 3 aviation fuel matrices studied. Relative standard deviations for a 100 mg/L spiked standard of target oxygenated compounds in HEFA-SPK fuel matrix are also included.

Target Compound	HEFA-SPK			FT-IPK		Jet-A1		RSD (%) <i>n</i> =10
	Quant ion ^a	EF Nafion	EF CW/PEG	EF Nafion	EF CW/PEG	EF Nafion	EF CW/PEG	
Methyl ethyl ketone	72	3300	<1	6300	<1	13,000	<1	11
2-Ethoxyethanol	59	>20,000	<1	>20,000	<1	>20,000	<1	7.2
Methyl isobutyl ketone	58	930	<1	3700	8	2000	<1	14
Cyclohexanol	82	>20,000	<1	>20,000	>20,000	>20,000	<1	12
Benzaldehyde	106	34	<1	1500	520	<1	<1	13
Phenol	94	1130	572	8300	4200	10,000	1700	10
Hexanoic acid	60	<1	<1	<1	<1	<1	<1	8.7
Salicylaldehyde	122	>20,000	>20,000	>20,000	>20,000	>20,000	>20,000	15
Benzoic acid	105	<1	<1	<1	<1	<1	<1	ND
1-Naphthaldehyde	156	45	113	260	710	260	280	11
1-Naphthol	144	1100	7058	2200	11,000	1000	2700	11

n=3, ND = not detected

^a 'Quant ion' indicates the ion mass (m/z) used for response measurement.

Importantly, the performance did not deteriorate over the course of this experiment, with peak areas for analytes fluctuating between extractions but with no obvious decreasing trend observed in data points. According to the details in Section 6.3.1, the fibre was coated manually, to an approximate thickness of 100 μm . Whilst variation in volume of Nafion coating will lead to variation in total sorption amount, and hence extraction efficiency, a rigorous study on reproducibility with which fibres can be coated was not undertaken here.

6.4.2 Analysis of Thermally Oxidised Fuels

The three fuels were each subjected to rapid small scale oxidation in order to induce the formation of oxidised species under controlled conditions. This process creates a variety of oxidised compounds, many of which are volatile, amenable to headspace SPME, and readily observed eluting in the 2-7 min region of the chromatogram (Figure 23). The fuel matrix however, is still sorbed onto the fibre and contributes a significant response in the total ion chromatograms. The excellent enrichment of these polar, volatile components of the oxidised fuel by the Nafion fibre permits tentative identification via mass spectral library searching. The compounds tentatively identified are listed in the caption to Figure 23.

The response for the oxidised compounds was much improved for analyses employing the Nafion fibre as opposed to the CW/PEG fibre. Many of the oxidised compounds were observed using the Nafion fibre only and could not be visualised in the data for extractions using CW/PEG fibres. Despite the considerably improved performance using the Nafion fibre, there was still substantial matrix coelution and the peaks arising from many of the oxidised species were not sufficiently resolved by using a one dimensional chromatographic separation, hence their identities could not be confirmed.

To overcome this, a MDGC-MS procedure was employed. One of the oxidised fuels (FT-IPK) was selected for a more detailed investigation of the polar volatile components extracted by the Nafion fibre. Selected regions of 30 – 100 s were chosen based on the appearance of numerous small, unresolved peaks and heart-cut to a polar column. Chromatograms of 8 selected heart-cut regions are displayed in Figure 24. It is clear that the additional resolution provided by the second dimension separation is desirable for reducing coelution of target analytes, and this aids in

tentative identifications through mass spectral library searching and estimation of retention indices.

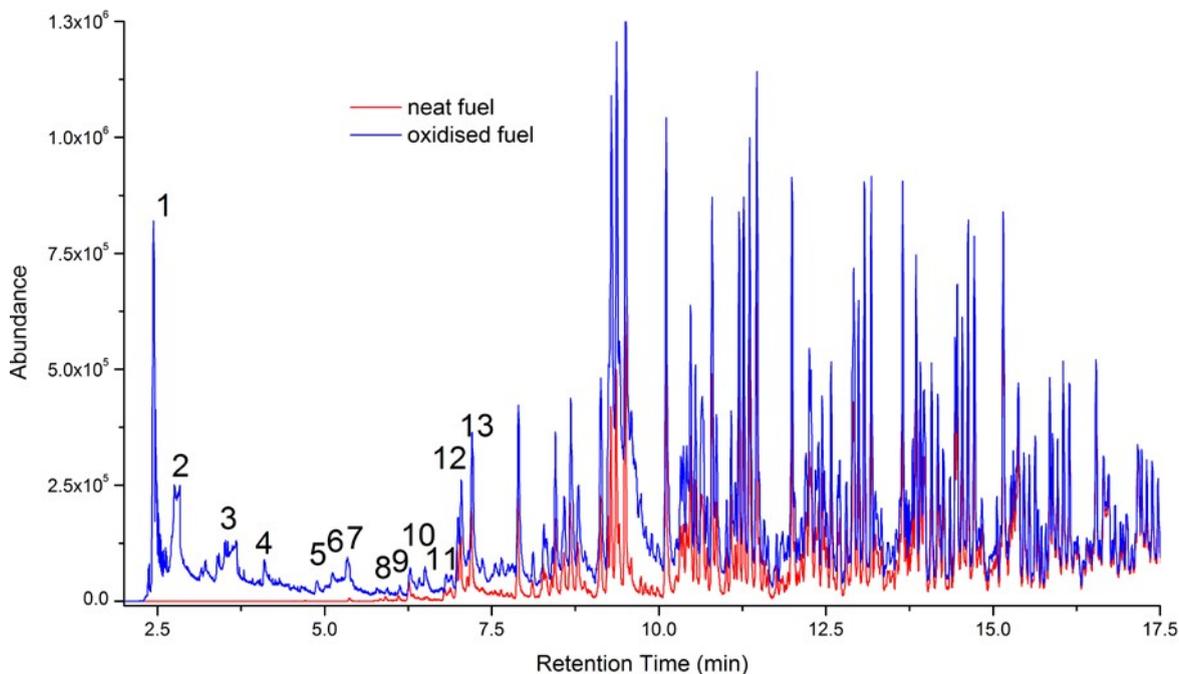


Figure 23. Total ion chromatograms of neat (red) and thermally oxidised (blue) HEFA-SPK extracted with Nafion fibre, using 1D GC-MS. Most of the chromatographic response here corresponds to the fuel matrix.

Tentatively identified compounds are: 1) 1,4-Dimethoxy butane, -; 2) 2-Propenoic acid; 3) 3-Pentanone; 4) Propanoic acid; 5) 1-Penten-3-one; 6) 1-Propoxypropan-2-yl 2-methylbutanoate; 7) Valeric anhydride; 8) 2,2-Dimethyl-3-heptanone; 9) 5-Ethenyldihydro-5-methyl-2(3H)-furanone; 10) 1,1'-Oxybisheptane; 11) 2-(1-Methylheptyl)-cyclopentanone,; 12) 2-Pentoxy-tetrahydropyran; 13) 3,4-Hexanedione. Extracted ion chromatograms of these oxidised species can be found in Appendix B, Figure B3, with compound data listed in Appendix B, Table B1.

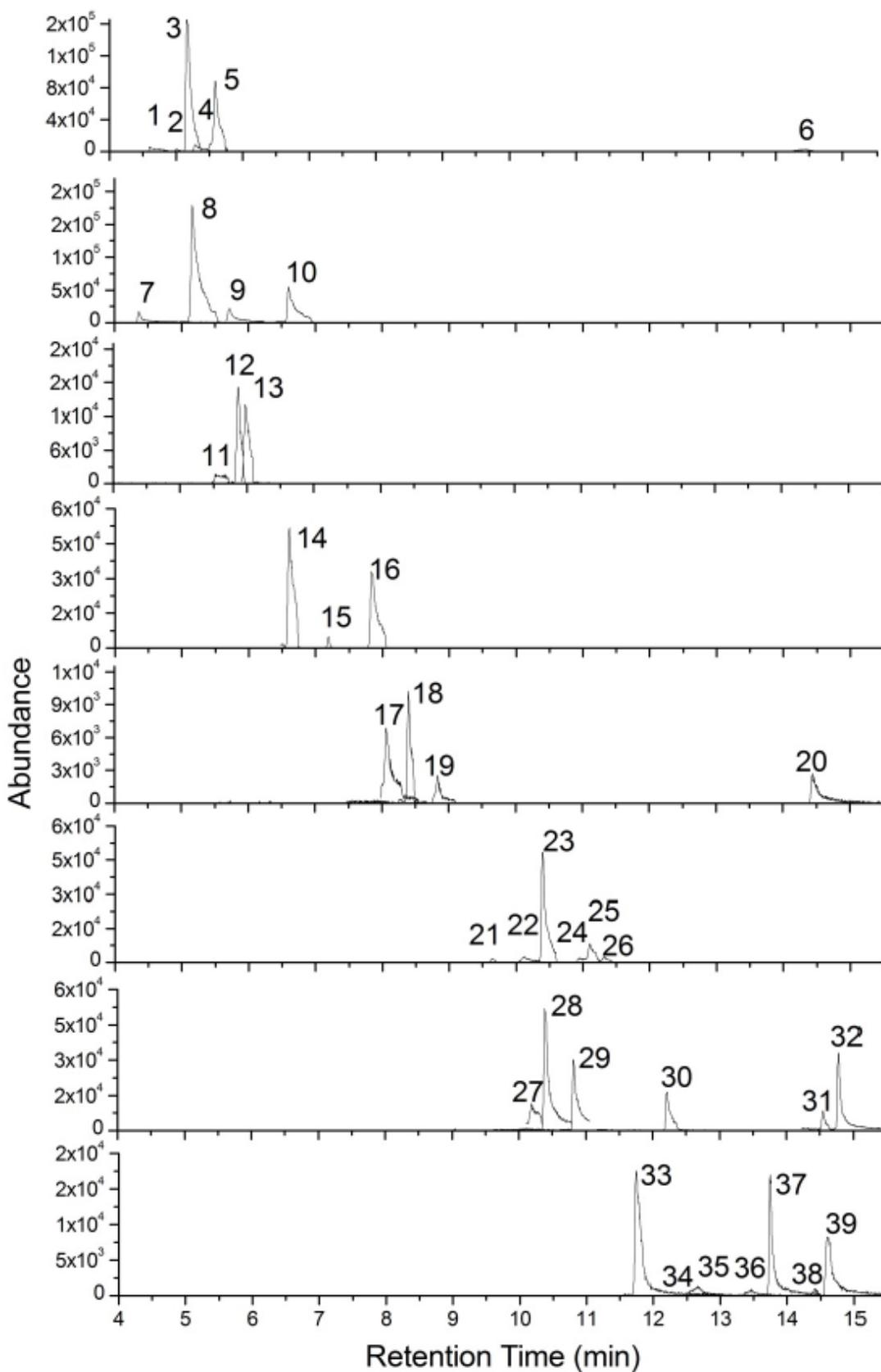


Figure 24. Extracted ion chromatograms of 8 heart-cut regions from MDGC analysis from the oxidised FT-IPK fuel; peak identities are given in Table 22.

Table 22. Oxidised species tentatively identified in successive heart-cuts of oxidised FT-IPK fuel in Figure 24. Most proposed compounds pass the two criteria of (i) acceptable mass spectrum quality and (ii) agreement with the retention index on the first column.

Peak #	Heart-cut region	Total t_R (min) ^a	Alkane index range ^b	Name of tentatively identified compound	Formula	Match quality	extracted ion (m/z)	Retention index (literature) ^c	Accept ID based on RI
1	3.7-4.2	4.59	500-600	2-Propenal	C ₃ H ₄ O	712	56	498	Yes
2	3.7-4.2	5.09	500-600	3-Buten-2-ol	C ₄ H ₈ O	691	67	536	Yes
3	3.7-4.2	5.16	500-600	Propanal	C ₃ H ₆ O	825	58	508	Yes
4	3.7-4.2	5.37	500-600	Formic acid	CH ₂ O ₂	745	46	543	Yes
5	3.7-4.2	5.59	500-600	2-Butanol	C ₄ H ₁₀ O	518	45	581	Yes
6	3.7-4.2	14.46	500-600	Ethyl propyl ether	C ₅ H ₁₂ O	768	59	594	Yes
7	4.3-6.0	4.36	550-650	Oxirane, (1-methyl ethyl)	C ₅ H ₁₀ O	812	56	612	Yes
8	4.3-6.0	5.16	550-650	Butanal	C ₄ H ₈ O	607	57	607	Yes
9	4.3-6.0	5.72	550-650	Ethene, (2-methoxy ethoxy)	C ₅ H ₁₀ O ₂	739	59	660	Yes
10	4.3-6.0	6.60	550-650	2-Methyl butanal	C ₅ H ₁₀ O	584	57	643	Yes
11	4.6-4.8	5.53	650-700	2-propyn-1-ol, acetate	C ₅ H ₆ O ₂	806	45	683	Yes
12	4.6-4.8	5.79	650-700	1-Propen-1-ol, formate	C ₄ H ₆ O ₂	774	58	650	Yes
13	4.6-4.8	5.87	650-700	2-Methyl pentanone	C ₆ H ₁₂ O	637	57	690	Yes
14	5.2-5.4	6.61	700-750	2-Propen-1-ol, 2-methyl acetate	C ₆ H ₁₀ O ₂	786	57	752	Yes
15	5.2-5.4	7.20	700-750	3-Methoxy-2-butanol	C ₅ H ₁₂ O ₂	560	59	692	Yes
16	5.2-5.4	7.92	700-750	2-Pentanone	C ₅ H ₁₀ O	769	86	654	Yes
17	6.5-7.1	8.07	800-950	Propanoic acid anhydride	C ₆ H ₁₀ O ₃	686	57	921	Yes
18	6.5-7.1	8.40	800-950	2-Octen-4-one	C ₈ H ₁₄ O	770	84	960	Yes
19	6.5-7.1	8.82	800-950	2,2-dimethyl-3-hydroxypropionaldehyde	C ₅ H ₁₀ O ₂	790	56	865	Yes
20	6.5-7.1	14.44	800-950	Acetophenone	C ₈ H ₈ O	873	105	1029	No
21	8.5-9.1	9.79	950-1050	3-Octanone	C ₈ H ₁₆ O	679	57	952	Yes
22	8.5-9.1	10.12	950-1050	1-Butyl-cyclobutanol	C ₈ H ₁₆ O	674	58	989	Yes
23	8.5-9.1	10.40	950-1050	2-Octen-4-one	C ₈ H ₁₄ O	685	69	960	Yes
24	8.5-9.1	10.82	950-1050	3-Hydroxy-3,5-dimethyl-2-hexanone	C ₈ H ₁₆ O ₂	792	59	980	Yes

Peak #	Heart-cut region	Total t_R (min) ^a	Alkane index range ^b	Name of tentatively identified compound	Formula	Match quality	extracted ion (m/z)	Retention index (literature) ^c	Accept ID based on RI
25	8.5-9.1	11.31	950-1050	3- <i>n</i> -propyl-5-methylhexan-2-one	C ₁₀ H ₂₀ O	695	114	1023	Yes
26	8.5-9.1	11.41	950-1050	2-Methyl-5-nonanone	C ₁₀ H ₂₀ O	687	71	1087	Yes
27	8.6-9.9	10.11	950-1100	5-Nonanone	C ₉ H ₁₈ O	527	57	1052	Yes
28	8.6-9.9	10.39	950-1100	3-Methylnon-1-yn-3-ol	C ₁₀ H ₁₈ O	578	69	1105	Yes
29	8.6-9.9	10.81	950-1100	2,5-Dihydroxyheptane	C ₇ H ₁₆ O ₂	577	85	1042	Yes
30	8.6-9.9	12.29	950-1100	Methoxyacetic acid, butyl ester	C ₇ H ₁₄ O ₃	690	57	960	Yes
31	8.6-9.9	14.53	950-1100	Heptanoic acid	C ₇ H ₁₄ O ₂	681	60	1073	Yes
32	8.6-9.9	14.73	950-1100	5-Methyl-1-phenyl-1-hexanone	C ₁₃ H ₁₈ O	673	105	1462	No
33	9.1-10.1	11.74	950-1100	7-Methyloctane-2,4-dione	C ₉ H ₁₆ O ₂	781	85	1112	Yes
34	9.1-10.1	12.49	1050-1300	2-Ethyl hexanoic acid, 1,1-dimethylethyl ester	C ₁₂ H ₂₄ O ₂	753	99	1233	Yes
35	9.1-10.1	12.53	1050-1300	2,2-Dimethylpropanoic anhydride	C ₁₀ H ₁₈ O ₃	690	57	1150	Yes
36	9.1-10.1	13.47	1050-1300	2-Methyl-octanoic acid	C ₉ H ₁₈ O ₂	539	74	1208	Yes
37	9.1-10.1	13.74	1050-1300	2-Ethyl-heptanoic acid	C ₉ H ₁₈ O ₂	723	73	1208	Yes
38	9.1-10.1	14.42	1050-1300	1-Phenyl-1-pentanone	C ₁₁ H ₁₄ O	848	105	1327	Yes
39	9.1-10.1	14.60	1050-1300	2-Propyl malonic acid	C ₆ H ₁₀ O ₄	870	84	1266	Yes

^a Total time is that for the analyte passing through both columns, as recorded at the detector.

^b Alkane range is the suggested range of alkanes, expressed as the alkane index, that corresponds to the heart-cut times on the first column. This is used to accept or reject possible tentative identifications since a proposed compound must have a RI within the suggested alkane range on the first column.

^c Example literature retention indices on an equivalent first dimension column phase. Since experimental data correspond to elution through both columns here, data are only expected to be an imprecise relative retention order.

Table 22 shows additional oxidised species (i.e. not present in the standard mixture) that were tentatively identified through this process, with the match quality threshold set at 600. Match quality is scored out of 1000 and is calculated by an algorithmic search function of the measured spectrum compared with library reference spectra. Here a threshold of 600 was selected, to minimise false positive matches but also take into account the small number of peaks and therefore non-unique spectra of some of the low molar mass analytes. Also shown in Table 22 is an interpretation of tentatively identified compounds based on retention index on the first dimension phase. This is used as a further criterion for acceptance/rejection of proposed compound identities. The heart-cut time window correlates with an approximate alkane index (the expected alkane retention times) as indicated, and a compound must have a first dimension index (on the non-polar column) within this range in order to be tentatively identified. If the RI is outside this range, the compound is rejected. Ideally the MS match list can be interrogated to find a compound that has acceptable MS threshold, and retention index. Peaks 20 and 32 do not pass the RI criterion, and no other compounds could be found that agreed with the two criteria; the two peaks are included in the Table to illustrate where an adequate match cannot be found.

These particular small organic acids and ketones are not easily identified in chromatographic analyses of oxidised fuels and reports of such compounds in the literature are scarce compared with the less polar and volatile components that are more amenable to standard chromatographic conditions. Despite that they are infrequently reported, one must suspect that these or similar species are present in many samples of oxidised fuels. This may be of considerable importance to the understanding of fuel breakdown and deposit formation, and some examples of these should be selected for inclusion in the standard oxygenate test mixture. We have previously¹⁹¹ identified small straight-chain organic acids and ketones in an algae-derived synthetic kerosene, but branched and di-functionalised oxidised species have proved more elusive.⁸³ The estimation of retention indices in the second dimension in the method used here, employing multiple heart-cuts each of relatively narrow duration, leads to considerable uncertainty. Chin *et al.*²²³ proposed a method to transfer alkanes to a ²D column to allow calculation of retention indices, however this incorporated an oven

cooling step and slow chromatographic elution on the ²D column, with easy interpolation of target compound within the alkane series. Since the rapid transfer here will most likely not collect successive alkanes in the heart-cut event, indices cannot be reliably measured. Nor can they be estimated on the first column, since it is only the heart-cutting process which allows them to be adequately identified by MS. An obvious future study will be to test the tentatively identified components under the same heart-cut process, to confirm retention times and mass spectrum match quality.

6.5 Conclusions

Application of a laboratory-made Nafion SPME fibre was shown to be a valuable tool for the analysis and identification of oxygenated compounds in complex matrices such as aviation fuels. Application of the Nafion fibre to thermally oxidised aviation fuels revealed many small oxygenated organic compounds which may be significant in fuel oxidation chemistry and have not been well characterised or investigated to date. The performance of this fibre offers a vast improvement on the best commercially available fibre for this application, and shows promise for the analysis of other polar analytes in non-polar matrices. This demonstrates the applicability of a Nafion fibre as an effective new way to enrich and isolate oxidised compounds from fuels that are otherwise difficult to analyse using traditional methods.

Acknowledgements

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Chapter 7: Publication 6

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Synopsis

This final research chapter, brings together many aspects of the work in the preceding chapters, as well as introducing some new advanced techniques. Prior approaches using multidimensional gas chromatographic separations are built upon to inform and optimise the comprehensive GC separation with a view to further elucidating trace oxygenates generated during thermal stress. A particularly attractive aspect of GC×GC in this case was ordered elution which delivers a global view of fuel composition by molecular functionality that simply can't be obtained with single dimensional or heart-cutting approaches. Accurate mass spectrometry contributes additional value in elucidating isobaric compounds which may have been overlooked or misidentified in previous studies.

Bringing together the physicochemical properties of the fuel in measures of oxidative stability with molecular level details of thermally oxidised fuels obtained using GCMS is the other pillar of this study. In contrast with the previous chapters, where oxidative stress has been applied to fuels simply to generate the oxygenated species of interest for further study, here these standardised methods are used in a manner more aligned with their usual intention, that is, to indicate the oxidative stability of a given fuel. Although only preliminary results are presented here, this lays foundations for further investigation into correlations between chromatographic and physicochemical data, most likely with robust and well-established chemometric approaches such as principal component analysis or partial least squares regression.

7 Investigation of the Thermal Oxidation of Conventional and Alternate Aviation Fuels with Comprehensive Two-Dimensional Gas Chromatography Accurate Mass Quadrupole Time-Of-Flight Mass Spectrometry

Renée L. Webster, Paul M. Rawson, Chadin Kulsing, David J. Evans, Philip J. Marriott

7.1 Abstract

Oxidation of aviation fuels affects the safe operation of high performance aircraft. This study reports the use of comprehensive two-dimensional gas chromatography (GC×GC) with accurate mass quadrupole time of flight mass spectrometry (accTOFMS) to study oxidised species in complex fuel matrices. GC×GC-accTOFMS was applied to the analysis of thermally oxidised conventional and alternate aviation fuels. A range of oxidised species were isolated and identified, and in a conventional fuel, a series of homologous aldehydes and 2-ketones were discovered. 4-Methyl-2-hexanone and 1-pentanol were found to be strongly correlated with established methods for quantitatively assessing fuel stability.

7.2 Introduction

Stability is a critical performance requirement of fuels used in modern jet aircraft and refers to the ability of a fuel to resist oxidation during heating or extended storage.²⁰⁵ The use of fuels as cooling fluid in high performance jet aircraft means that they are being exposed to increased heat loads which induces autoxidation reactions of the fuel hydrocarbons.³² The formation of oxidised species generated in these oxidation reactions is implicated in the formation of insoluble deposits in fuel systems, and also the development of undesired fuel properties such as poor water separability.¹⁶ Synthetic and other alternatively-derived fuels have been reported as having good thermal stability properties, resisting thermal oxidation much better than conventional jet fuel.⁵⁹ As the use of these fuels increases around the world, it is important to understand the process occurring at a molecular level. Thus it is important that molecular speciation of the fuel is well characterized.

Jet fuels from both conventional and alternate feedstocks are complex mixtures and it is difficult to identify oxidised species amongst the bulk hydrocarbon matrix.^{182, 183} Coelution of oxidised species and other trace heteroatomic compounds with hydrocarbons is impossible to avoid, and oxygen-specific detectors lack the sensitivity and robustness required to successfully characterize these analytes. Comprehensive two-dimensional gas chromatography (GC×GC) is a technique that is becoming increasingly utilised in the analysis of complex hydrocarbon mixtures such as found in jet fuels.¹²¹ The advantages of GC×GC, which include high peak capacity, increased resolving power, and improved sensitivity, make it ideally applicable to the resolution of both the bulk and trace components of complex matrices.¹⁰⁸ Useful information about the composition of fuels, particularly the type and amount of the many different hydrocarbon and heteroatomic species may be obtained using GC×GC, such that a group-type or “fingerprinting” type analysis is attainable for distinguishing between different fuel types.^{211, 224, 225}

Traditionally, detailed information about the trace and non-hydrocarbon species in fuels has been acquired via lengthy and resource-intensive approaches. Poor selectivity, incomplete separations and inadequate removal of interfering compounds have made detailed analysis of the trace components of fuels challenging. Employing a GC×GC approach addresses and may negate the need for extensive sample preparation and pre-treatment techniques, such as fractionation or solid phase or liquid extractions. GC×GC hyphenated with time-of-flight mass spectrometers (TOFMS) providing unit mass resolution has previously been demonstrated as a worthwhile technique for the analysis of middle distillate fuels.^{112, 118, 226} The data acquisition rate of these detectors permits sufficiently fast sampling of the narrow peaks generated through modulation of first dimension peaks, usually at least 50 Hz, required to obtain high quality data.²²⁷ More recently, accurate mass capability TOFMS has been shown to contribute additional identification, particularly where analytes and fragments share similar unit masses and/or fragmentation patterns. Differentiation between different compound classes can be gleaned, as well as a more informed approach to structural elucidation based on the accurate masses of fragment ions.

GC×GC studies of oxygenates in fuels have generally focused on the analysis of indigenous oxygen-containing compounds such as phenols derived from the crude feedstock.^{5, 107} To date there has been little investigation using comprehensive 2DGC

separations, of the species formed via oxidative instability reactions. There has been some study of the role sulfur compounds play in thermal stability using GC×GC-TOFMS¹¹² but the investigation of oxygenated species remains largely unreported. Here, we report the use of GC×GC with accurate mass spectrometry for fingerprinting and identification of trace oxidised species in conventional and alternate aviation fuels. Along with comparison of established stability test methods, this may provide a path forward to a GC-based assessment of oxidative stability.

7.3 Experimental

7.3.1 Fuel Samples

Four aviation fuels were used in this study (Table 23). Samples were selected to include a range of processing technologies, and new generation alternatively derived fuels. Fuels A and B were synthetic paraffinic kerosenes (SPK), meeting the requirements of Annexes A1 and A2 of ASTM D7566¹⁴⁴ for synthetic aviation fuel blend stock. Fuels C and D were conventional, fossil crude oil-derived jet fuels sourced from refineries known to use two different refining technologies. The fuels were used ‘as-is’, containing any additives that may have been included at the refinery. No sample cleanup or prior preparation was carried out. All fuels and samples were stored at -18 °C.

Table 23. Details of fuels used in this study

Label	Source	Processing method
A	Camelina	Hydroprocessed esters of fatty acids
B	Syngas	High temperature Fischer-Tropsch synthesis
C	Fossil crude oil	Merox
D	Fossil crude oil	Hydroprocessed

7.3.2 Standard oxygenate mixture

A standard stock solution containing approximately 10,000 mg/L of selected polar and oxygenated compounds, representing classes expected to be found in oxidised fuels was prepared in chromatography grade dichloromethane (Merck, Kilsyth, Australia). All standard compounds were purchased from Sigma-Aldrich (Castle Hill, Australia) and used without further purification. A standard of approximately 100 mg/L for each component concentration was prepared by 100× dilution of the stock

solution with chromatography grade dichloromethane. The exact concentrations and retention times of each analyte in the reference standard is given in Table 24 along with the chromatogram in Figure 25.

Table 24. Details of the standard oxygenate mixture.

Peak#		concentration (mg/L)	$^1t_{R}$ (min)	$^2t_{R}$ (s)
1	toluene	103.3	6.51	0.9
2	octanal	100.9	11.51	1.4
3	cyclohexanone	99.9	11.52	1.0
4	benzaldehyde	105.4	16.02	1.0
5	octanol	94.9	16.42	1.1
6	methyl furanone	110.2	17.71	0.8
7	dodecanal	103.1	19.2	2.0
8	naphthalene	93.8	19.92	1.2
9	hexanoic acid	98.0	21.82	1.0
10	phenol	115.3	24.11	2.6
11	pentadecanone	100.4	24.14	0.8

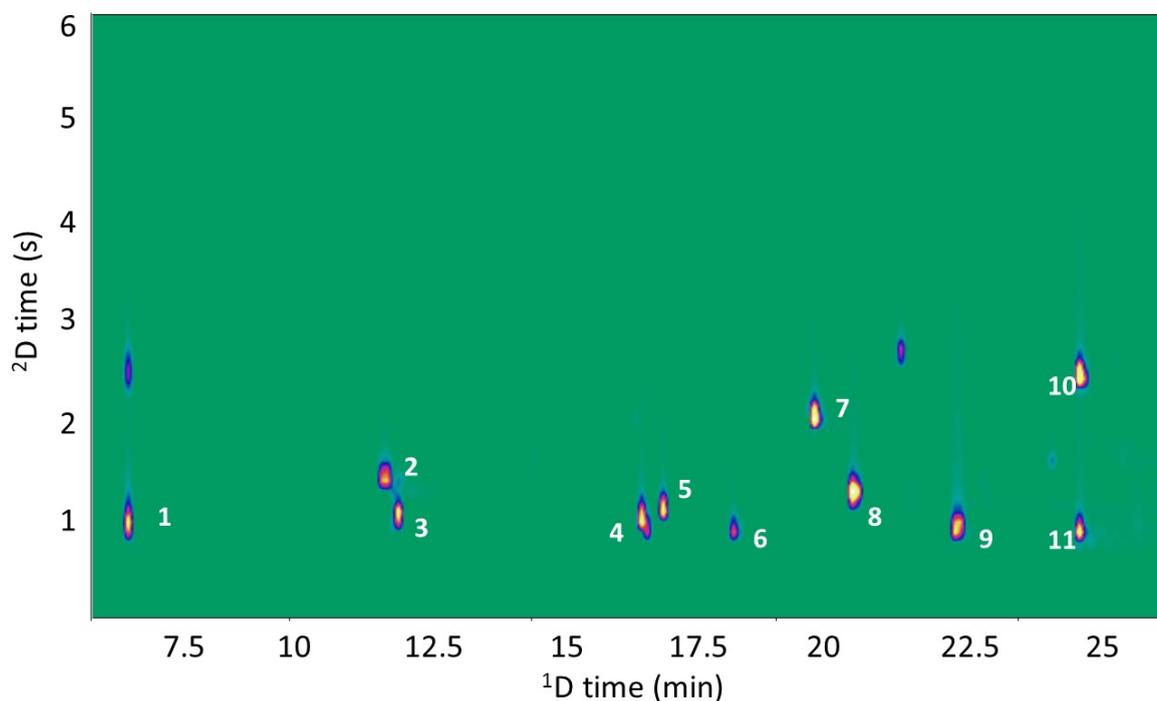


Figure 25. GCxGC-QTOFMS total ion chromatogram 2D plot of the standard oxygenate mixture, peaks numbered as per Table 24. Unlabelled peaks are unidentified contaminants.

7.3.3 Evaluation of Oxidative Stability

Two separate techniques were used to assess the oxidative stability of the neat fuels. These were both static, isothermal, oxygen headspace methods that have been previously demonstrated^{204, 228, 229} to be a measure of the oxidative stability of middle distillate fuels. The neat fuel samples were subjected to oxidative stability testing, in order to quantitatively assess the stability of the fuels.

7.3.3.1 Rapid Small Scale Oxidation Testing (RSSOT)

Accelerated stability analyses were carried out in accordance with ASTM D7545¹⁶⁵ using a PetroOxy rapid small scale oxidation tester (Anton Paar GmbH, Graz, Austria). 5.0 mL of fuel was heated to 140 °C under an atmosphere of O₂ at 700 kPa. The time taken for a 10% drop in the O₂ pressure was measured, and is indicative of the oxidative stability of the fuel. The oxidised fuel sample was also retained on completion of these tests for analysis by GC×GC-QTOFMS.

7.3.3.2 Quartz Crystal Microbalance (QCM)

Thermal oxidative stability measurements were carried out using a modified version of ASTM D7739.²³⁰ 60 mL of fuel was heated to 140 °C under an atmosphere of air for 15 hr. The fuel was not exposed to a 30 min saturation phase prior to heating as prescribed in ASTM D7739. The deposition of solid material on the surface of the oscillating crystal was measured to provide information about the thermal oxidative behaviour of the fuel.

7.3.4 Instrumentation

GC×GC analysis was carried out on an Agilent 7890A GC with a model 7200 quadrupole-time-of-flight mass spectrometer (Agilent Technologies, Santa Clara, CA). Separations were performed using a polar/non-polar column arrangement with a SolGel-WAX column in the first dimension (¹D; 30 m × 0.25 mm × 0.25 μm) and BPX5 (SGE, Ringwood, Australia) column in the second dimension (²D; 1 m × 0.1 mm × 0.1 μm). The columns were connected using a deactivated pressfit union. Undiluted samples of volume 0.05 μL were injected with a split ratio of 500:1 (except

for the standard mixture where the split ratio was 50:1). Helium carrier gas was supplied in constant flow mode at 1.2 mL/min. The MS transfer line temperature was 280 °C. The GC oven program began at 50 °C to 225 °C at 6.5 °C/min, then 20 °C/min to 265 °C for a total run time of 29 min. Modulation was carried out with a longitudinally modulated cryogenic system (LMCS) at 0 °C with a modulation ratio (P_M) of 6 s. The MS was operated in total transfer of ions mode through the quadrupole, which was held at a temperature of 150 °C, with the ion source at 280 °C. An ionization voltage of 70 eV was used, and data were collected over a mass range of 43-400 m/z . Data acquisition was set at a nominal 50 Hz, which equated to an actual acquisition rate of approximately 47.4 Hz. Data collection, processing and analysis were performed with MassHunter (Agilent Technologies) version B.06.00. GC×GC plots were generated following conversion of exported CSV data to a 2D matrix and visualized with Transform (Fortner Research LLC, USA).

7.4 Results and Discussion

7.4.1 GC×GC of thermally oxidised fuels

The use of a polar/non-polar column set in GC×GC is a well-established strategy for the analysis of fuels and other complex hydrocarbon mixtures.²³¹ This column arrangement increases resolution of straight chain and branched alkanes from one another, and from the aromatic hydrocarbons which elute at a smaller 2t_R (i.e. earlier on the 2D column), and aids in group-typing of the fuels. In this case, saturated alkanes define the latest eluting 2t_R band of compounds in the 2D plot. Groupings of polar and oxidised compounds were aided by comparison with the external standard, chromatographic deconvolution, and searching of mass spectral data with the NIST 2011 library. The modulation period of 6 s was selected to minimize wrap-around and ensure 2D elution within a single modulation cycle.

Total ion chromatograms (TIC) for the alternate and conventional fuels are displayed in Figure 26. The 2D plots reveal features and compound classes which can't be readily distinguished into groups using 1D GC. The relatively simple chromatograms of the SPKs on the left of Figure 26 are contrasted with the highly complex chromatograms of the conventional fuels on the right. While both the HEFA and FT SPKs meet the physical and performance specifications detailed in ASTM D7566,¹⁴⁴

their chemical composition is quite different, specifically with respect to the *iso*- and *n*-paraffin content. The HEFA SPK is dominated by saturated *n*- and *iso*-alkanes, eluting in a continuous band from $^1t_R = 4.5$ - 15 min. There is a small contribution from saturated branched cycloalkanes in the HEFA SPK, which has excellent separation in the 2D plot from the straight chain and branched alkanes where they are poorly indistinguishable in the 1D chromatogram. These monocycloalkanes can be seen eluting in a small band below the straight chain alkanes (i.e. at smaller 2t_R) from $^1t_R = 4.5$ -8 min. Separation of the cycloalkane content of SPK fuels, permitting its accurate quantification, is important given that the content must not exceed 15% w/w.¹⁴⁴

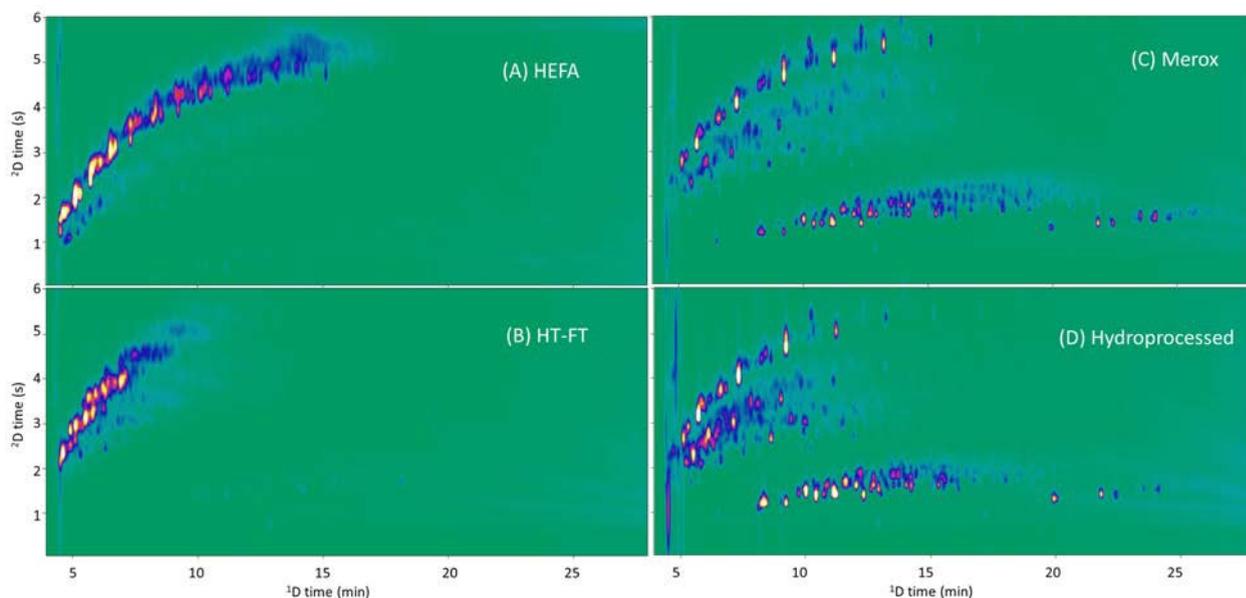


Figure 26. GC×GC-QTOFMS total ion chromatogram 2D plot of fuels A-D (refer to Table 23 for fuel identifications). A is comprised primarily of saturated straight chain alkanes and alkanes with limited branching, along with a small contribution of cycloalkanes. Fuel B is predominantly highly branched short chain saturated alkanes. For fuels C and D, both fuels are separated into distinct classes of normal alkanes, *iso*-alkanes, single ring and double ring aromatics.

The FT SPK consists almost exclusively of branched saturated alkanes eluting from 1t_R 4.5-11 min, with a tighter boiling point range, higher degree of branching, and also a broader distribution of cyclic alkanes. Confirmation of the exact identities of the saturated alkanes and cycloalkanes is tentative, based on library searching and molecular ion fragments, and has not been confirmed through comparison with authentic standards due to the enormous breadth of compounds present, and the

limited availability of authentic standards. Determination of their exact identities is outside the scope of this study, but would not be readily achievable due to shared fragmentation and structural isomerism producing ambiguous mass spectrum data. Trace amounts of aromatic compounds were also observed in the two alternate fuels, which are generally considered to be free of aromatics but we were unable to confirm whether they were present in the fuel as received, or arose from contamination with another fuel type.

Bulk compositional differences can also be observed for the two conventional fuels. Clear groupings of the straight chain and cyclic alkanes are visible, along with single and double ring aromatics. The most obvious difference between the SPKs and conventional fuels is the substantial concentration of single and double ring aromatics. There is also a much lesser contribution from branched alkanes in the conventional fuels, which are dominated in the non-aromatic region by normal and cyclic paraffins. The hydroprocessed fuel can also be distinguished from the Merox processed fuel by comparing the relative amount of mono- and di-aromatic components. There are fewer di-aromatics in fuel D as hydroprocessing has fully or partially saturated these to mono-aromatics or cycloalkanes. The saturated linear alkanes are also of shorter chain length in this fuel due to cracking of the larger paraffins.

The standard mixture of oxygenated compounds was used as a reference to assist in identifying the oxidised species in the thermally stressed fuels. While good class separation of the polar and non-polar constituents of the fuels was achieved with the polar/non-polar column set, the response of the oxidised species was not as intense as observed in our previous study of an algae-derived alternate fuel, using GC×GC-FID.¹⁹¹ Here we aimed to maintain good group-type separation without overloading the hydrocarbons. The reduced response of oxygenates may be due to their poorer or inconsistent relative response factor in the QTOFMS compared with FID. Issues with poor resolution within the broad group of oxygenates, were also observed due to insufficient peak capacity of the 2D column. In some cases, oxygenates co-eluted with other polar compound classes, specifically the mono- and di-aromatics. Homologous groups of oxygenated compounds were not readily visible in the full scan 2D chromatogram, although tentative identifications of some compounds could be made from mass spectrum library searching and by comparison with the standard solution. In contrast, while groups of peaks were observed in our previous GC×GC-

FID study, compound classes such as ketones, aldehydes and acids could not be positively identified using the complementary 1D GC-qMS analysis. Here, the comprehensive separation and accurate mass detection has enabled identification of many such compounds and will be discussed further, below.

7.4.2 Analysis of oxidised group types with GC×GC-QTOFMS

The chromatographic conditions provided excellent separation of the saturated hydrocarbons, and also of single- and multiple-ring aromatic compounds. There was however, some overlap and co-elution of some of the oxidised species with the aromatic compounds present in the two conventional fuels. Groups of oxygenated compounds that are of particular interest, namely carbonyls, alcohols and carboxylic acids which are often difficult to resolve in 1D GC as they are not concentrated enough, nor dissimilar enough from the bulk hydrocarbon matrix, were sufficiently separated to make tentative groupings of these following deconvolution and peak identification procedures. Classifications were also guided through the generation of extracted ion chromatograms (EIC) and by comparison of retention times with the chromatogram of the standard oxygenate mixture using the principle of ordered elution. Generating EICs is particularly useful in differentiating mass fragments containing oxygen from those containing carbon and hydrogen only, due to mass defect. This is especially helpful in fuels analysis, where a background of hydrocarbons is present throughout the entire chromatogram.

Accurate masses for fragments corresponding to alkanes (C_4H_9 , 57.0699) and oxygenates (C_3H_5O , 57.0335) were each extracted with a mass selection with ± 20 ppm uncertainty, with the resulting chromatograms shown in Figure 27. It is clear in this example that in a nominal mass EIC the contribution from the hydrocarbons would completely mask the signal of the oxygenated components, whereas here peaks for oxygenated species can be observed. Additionally useful is the ability to rule out contributions from common siloxane peaks generated by column and septum material using filtering of exact masses. Where there is overlap of masses from genuine target analytes by column and septum bleed, (e.g. m/z 73, 147, 207 etc.), again mass defects can be exploited to differentiate between those compounds. Ions that are known to be characteristic of certain function groups (i.e. m/z 60 for acids, m/z 58 for 2-ketones) can be used, but are not always universally valuable since

branching affects fragmentation patterns. The consequence of this is that despite being less complex overall, oxidised species can be more difficult to isolate in the more highly branched alternate fuels. Contributing to this is that fewer branched oxidised species have mass spectra in the reference libraries, and hence may not return a positive match during peak identification.

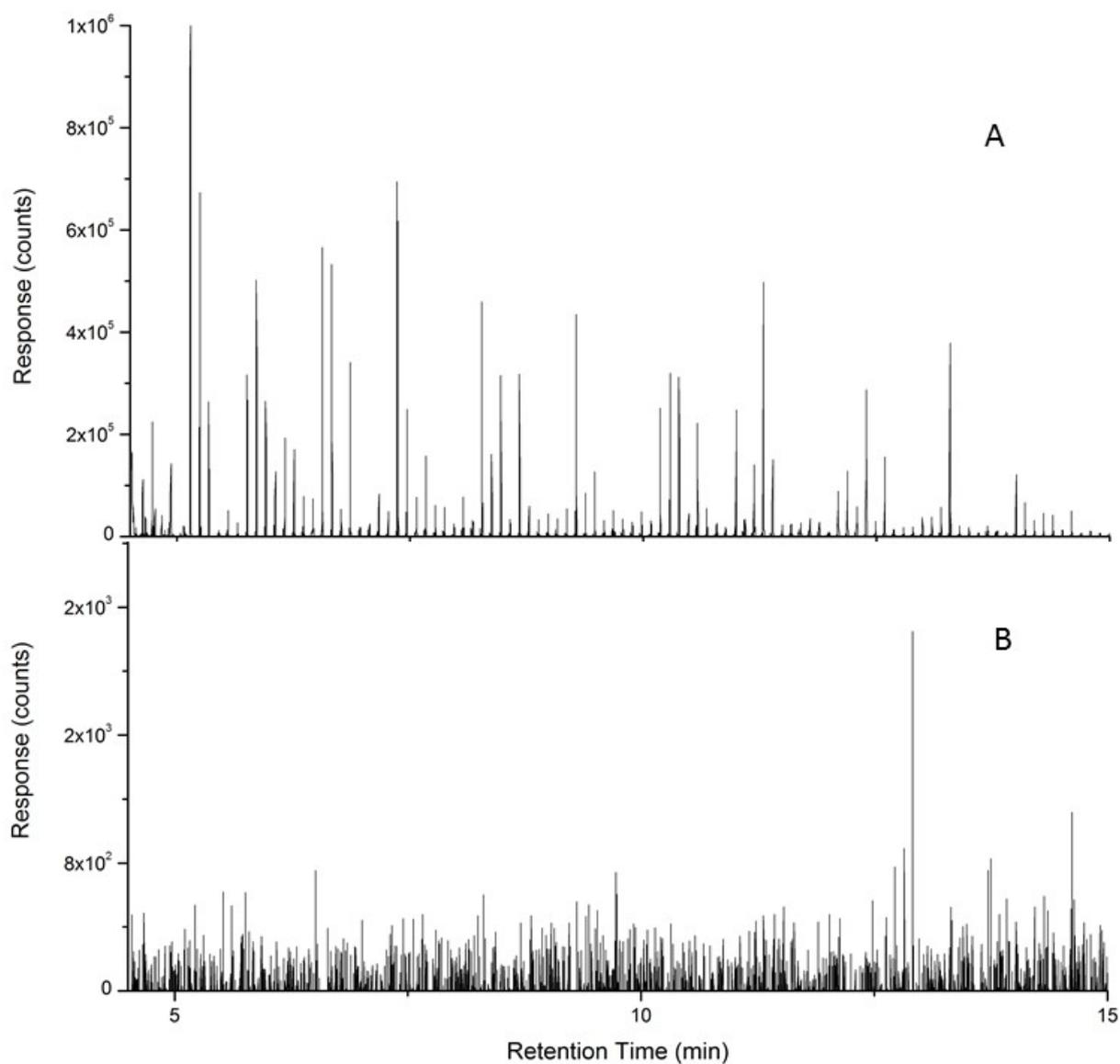


Figure 27. Modulated 1D extracted ion chromatograms of ions with equal nominal mass of 57 u. Chromatogram A is of 57.0669 ± 20 ppm, originating from C_4H_9 alkanes and chromatogram B is 57.0335 ± 20 ppm originating from C_3H_5O oxygenates. Note the difference in scale on the ordinate axis.

7.4.3 Analysis of target oxidised species with GC×GC-QTOFMS

It has proved difficult to resolve and positively identify unknown oxidised compounds in neat fuels using 1D GC-MS analyses, even with accurate mass spectrometry. Ions generated from the major alkane components of the fuels tend to swamp the detector, counteracting its sensitivity and making the identification of the trace compounds of interest often impossible. The task is markedly more challenging in a conventional fuel matrix which has much greater complexity than alternate fuels. Nominal mass resolution is not sufficient for the analysis of oxygenates in a bulk hydrocarbon fuel matrix due to shared ion fragments with non-oxygenated compounds, making identification virtually impossible. The accurate mass capabilities of the QTOFMS enables differentiation between organic compounds with carbon and hydrogen only, and carbon, hydrogen, and oxygen-containing molecular and fragment ions. The fast scan rate (approaching 50 Hz) also generates ample data across the narrow modulated peaks, increasing the likelihood of a response from trace compounds, reducing co-elution, and improving conditions for deconvolution.

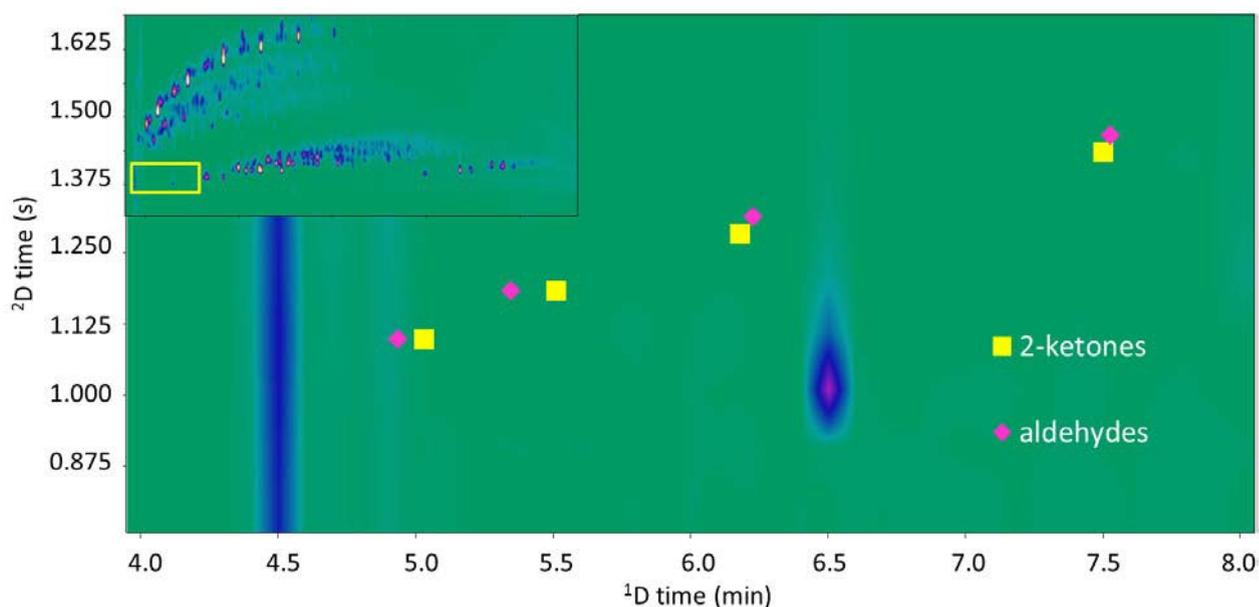


Figure 28. Partial peak apex plot 2D chromatogram of the area identified by the yellow box in the inset, of thermally oxidised conventional fuel with the positions of homologous series of 2-ketones (■) and *n*-aldehydes (◆) marked. Compounds were not readily visible in the full scan chromatogram, and were identified after applying deconvolution and peak identification algorithms and extracting accurate mass ion chromatograms.

Although not prominent in the full scan GC×GC plots, many oxidised compounds were identified in the thermally stressed fuels. Fuel C, the Merox-processed conventional jet fuel was selected for a more detailed analysis of the oxidised species present. This was chosen as it was considered the most challenging of the samples in this study, owing to its high degree of complexity. Thousands of unique compounds were identified in the oxygenates elution region by the software deconvolution and peak identification algorithms. A total of 10,439 oxidised species were identified in the Merox fuel, and 4,915, 3,785 and 8,526 peaks in fuels A, B, and D, respectively. Due to the sheer number of compounds identified, for brevity only a subset are shown here. A small region of the 2D chromatogram indicated in Figure 28 was selected for more detailed investigation, with the identified compounds presented in Table 25. Oxidised species spanning a range of functional groups were identified in this region, including aldehydes, ketones, lactones, acids and alcohols. A homologous series of aldehydes and 2-ketones were revealed, eluting in a band very close together as shown in Figure 28.

It was noted that in some cases, the library matched compound was incorrectly assigned to a peak, which would otherwise go unnoticed if not for accurate mass information provided by the spectrometer. For example, peak 1528 returns a library match of 2-(vinyl-2-ethoxy)ethanol with match quality 712. However, closer investigation of the library search results revealed the second highest quality match at 693, was 3-methyl-2-butanol. The mass spectra of these two compounds are very similar (Figure 29). The accurate mass capability of the QTOFMS enables differentiation of these isobaric compounds. 3-methyl-2-butanol, with a molecular formula of $C_5H_{12}O$ has an exact mass of 88.0883, and 2-(vinyl-2-ethoxy)ethanol with a molecular formula of C_4H_8O has an exact mass of 88.0519. Similarly, the shared fragments at 73 corresponds to a loss of CH_3^{\bullet} in each case, leaving $C_4H_9O^+$ (73.0648) and $C_3H_5O_2^+$ (73.0284) respectively. The compound in question had masses of 88.0863 m/z and 73.0654 m/z respectively, thus suggesting 3-methyl-2-butanol.

Table 25. A selection of oxidised species tentatively identified in thermally stressed Mercox conventional jet fuel (Fuel C) eluting in the space indicated by the yellow rectangle in Figure 28 (approximately from $^1t_R = 4.9-7.7$ min and $^2t_R 1.0-1.6$ s).

Name	match	1t_R	2t_R	formula	exact	base peak	fragment ions
Propanal	816	4.92	1.1	C ₃ H ₆ O	58.0413	58.0413	[C ₃ H ₆ O] ⁺
Dihydro-2-methyl-3-(2H)-Acetoin	654	5.08	1.3	C ₅ H ₈ O ₂	100.0519	43.0178	[C ₂ H ₃ O] ⁺ 100.0519 [C ₅ H ₈ O ₂] ⁺
Methoxy acetaldehyde	924	5.12	1.5	C ₄ H ₈ O ₂	88.0519	45.0335	[C ₂ H ₅ O] ⁺ 88.0519 [C ₄ H ₈ O ₂] ⁺
2(5H)-Thiophenone	765	5.13	1.5	C ₃ H ₆ O ₂	74.0362	45.0335	[C ₂ H ₅ O] ⁺ 74.0362 [C ₃ H ₆ O ₂] ⁺
1-Methylethyl ester formic acid	723	5.17	1.3	C ₄ H ₄ OS	99.9977	99.9977	[C ₄ H ₄ OS] ⁺ 72.0028 [C ₃ H ₄ S] ⁺ 70.995
1,2-Propanediol	896	5.18	1.2	C ₄ H ₈ O ₂	88.0519	45.0335	[C ₂ H ₅ O] ⁺ 59.0491 [C ₃ H ₇ O] ⁺
2-Methyl-furan	790	5.28	1.5	C ₃ H ₈ O ₂	76.0519	45.0335	[C ₂ H ₅ O] ⁺ 61.0284 [C ₂ H ₅ O ₂] ⁺
Butanal	803	5.30	1.2	C ₅ H ₆ O	82.0413	82.0413	[C ₅ H ₆ O] ⁺ 53.0386 [C ₄ H ₅] ⁺
2-(Vinylxy)-ethanol	899	5.35	1.2	C ₄ H ₈ O	72.0570	44.0257	[C ₂ H ₄ O] ⁺ 43.0542 [C ₃ H ₇] ⁺ 57.0335
2,3-Epoxybutane	819	5.43	1.5	C ₄ H ₈ O ₂	88.0519	45.0335	[C ₂ H ₅ O] ⁺ 73.0289 [C ₃ H ₅ O ₂] ⁺ 88.0519
Isopropyl acetate	852	5.47	1.5	C ₄ H ₈ O	72.0570	45.0335	[C ₂ H ₅ O] ⁺ 43.0178 [C ₂ H ₃ O] ⁺ 72.057
2-Butanone	917	5.50	1.3	C ₅ H ₁₀ O ₂	102.0675	43.0542	[C ₃ H ₇] ⁺ 87.0446 [C ₄ H ₇ O ₂] ⁺
3-Methyl-2-butanol	900	5.52	1.2	C ₄ H ₈ O	72.0570	43.0178	[C ₂ H ₃ O] ⁺ 57.0335 [C ₃ H ₅ O] ⁺
2-Methyl-butanal,	814	5.53	1.5	C ₅ H ₁₂ O	88.0883	45.0335	[C ₂ H ₅ O] ⁺ 73.0648 [C ₄ H ₉ O] ⁺
Ethenyl ester formic acid	798	5.62	1.3	C ₅ H ₁₀ O	86.0726	57.0335	[C ₃ H ₅ O] ⁺ 86.0726 [C ₅ H ₁₀ O] ⁺
3-methyl-butanal	764	5.63	1.2	C ₃ H ₄ O ₂	72.0206	43.0178	[C ₂ H ₃ O] ⁺ 72.0206 [C ₃ H ₄ O ₂] ⁺
Isopropyl alcohol	785	5.67	1.3	C ₅ H ₁₀ O	86.0726	44.0257	[C ₂ H ₄ O] ⁺ 57.0335 [C ₃ H ₅ O] ⁺ 71.0491
Acetate-1-propen-2-ol	981	5.72	1.1	C ₃ H ₈ O	60.0570	45.0335	[C ₂ H ₅ O] ⁺ 59.0491 [C ₃ H ₇ O] ⁺ 60.057
1-Methylethyl ester propanoic	841	5.77	1.3	C ₅ H ₈ O ₂	100.0519	43.0178	[C ₂ H ₃ O] ⁺ 72.0206 [C ₃ H ₄ O ₂] ⁺ 100.0519
Acetic acid	839	6.03	1.5	C ₆ H ₁₂ O ₂	116.0832	57.0335	[C ₃ H ₅ O] ⁺ 101.0597 [C ₅ H ₉ O ₂] ⁺
Pentanal	763	6.12	1.4	C ₂ H ₄ O ₂	60.0206	43.0178	[C ₂ H ₃ O] ⁺ 60.0206 [C ₂ H ₄ O ₂] ⁺
Bicyclo[2.2.2]oct-5-en-2-ol	922	6.27	1.3	C ₅ H ₁₀ O	86.0726	44.0257	[C ₂ H ₄ O] ⁺ 57.0335 [C ₃ H ₅ O] ⁺ 86.0726
1-methoxy-2-propanol	822	6.70	1.3	C ₈ H ₁₂ O	124.0883	80.0621	[C ₆ H ₈] ⁺ 81.0699 [C ₆ H ₉] ⁺ 78.0464 [C ₆ H ₆] ⁺
3,4-Dimethyldihydrofuran-2,5-	774	6.77	1.2	C ₄ H ₁₀ O ₂	90.0675	45.0335	[C ₂ H ₅ O] ⁺ 75.0441[C ₃ H ₇ O ₂] ⁺
3-Hexanone	825	6.93	1.5	C ₆ H ₈ O ₃	128.0468	56.0257	[C ₃ H ₄ O] ⁺ 128.0468[C ₆ H ₈ O ₃] ⁺
	810	7.17	1.5	C ₆ H ₁₂ O	100.0883	43.0178	[C ₂ H ₃ O] ⁺ 71.0491 [C ₄ H ₇ O] ⁺ 100.0883

Name	match	¹ t _R	² t _R	formula	exact	base peak	fragment ions
L-Lactic acid	792	7.33	1.3	C ₃ H ₆ O ₃	90.0311	44.9971 [CHO ₂] ⁺	90.0311 [C ₃ H ₆ O ₃] ⁺
2-Hexanone	901	7.60	1.5	C ₆ H ₁₂ O	100.0883	43.0178 [C ₂ H ₃ O] ⁺	57.0335 [C ₃ H ₅ O] ⁺ 100.0883
Hexanal	900	7.63	1.5	C ₆ H ₁₂ O	100.0883	44.0257 [C ₂ H ₄ O] ⁺	57.0335 [C ₃ H ₅ O] ⁺ 72.057

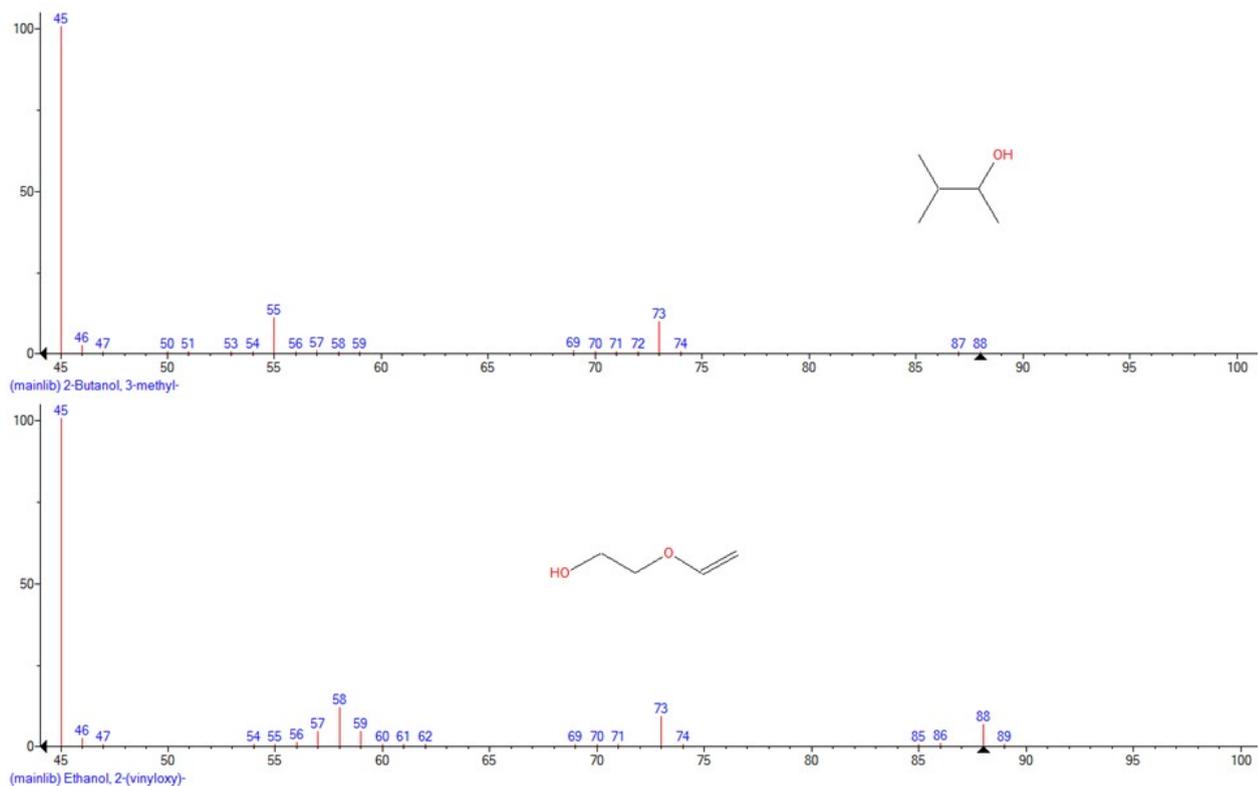


Figure 29a. NIST library mass spectra of 3-methyl-2-butanol and 2-(vinylloxy)ethanol demonstrating the similarity of their mass spectra.

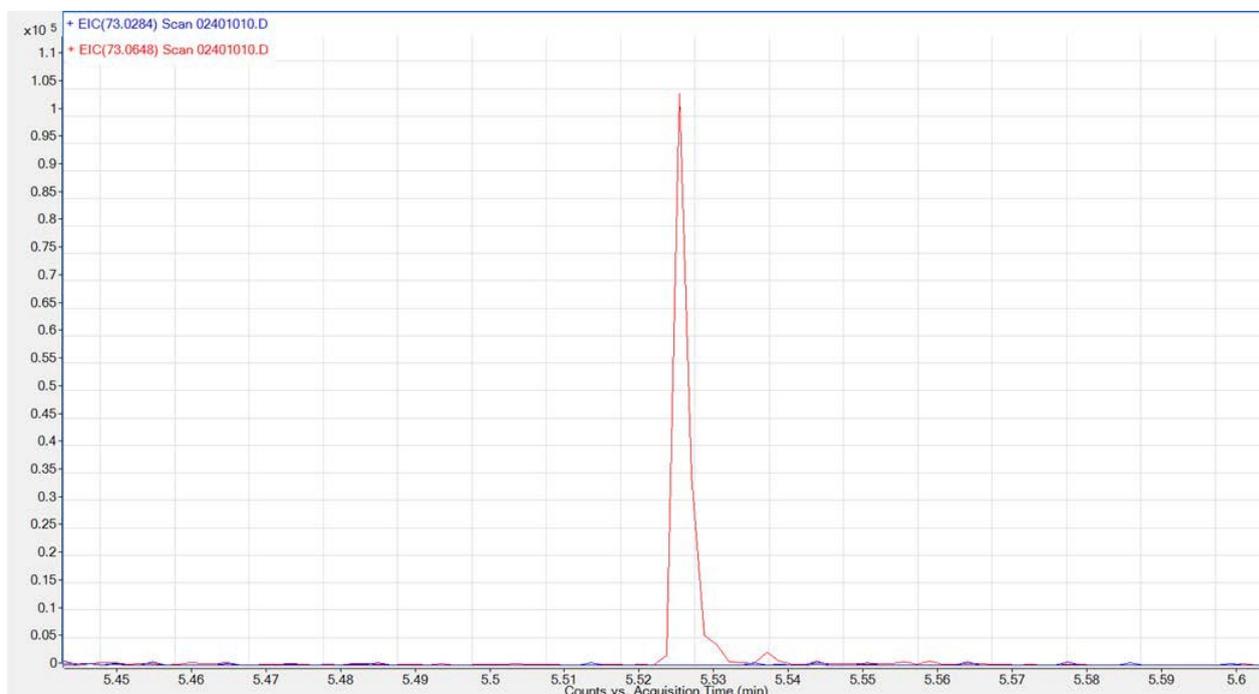


Figure 29b. Extracted ion chromatograms of the region where the peak identified as 2-(vinylloxy)ethanol elutes. Extraction of exact masses 73.0284 (blue line; no response noted) and 73.0648 (red line; corresponding to the large peak) reveals that the peak identity has been wrongly assigned.

7.4.4 Using GC×GC to Inform Oxidative Stability

Oxidative stability is an important characteristic for fuels, and is assessed using a range of direct and proxy test methods. Often these tests deliver contradictory results, and many are not suitable for determining the oxidative stability of alternatively-derived or extremely hydroprocessed fuels, having been developed in an era prior to introduction of these new generation fuels. Whether characterisation of stability is made gravimetrically, chemically, visually, or by any other means, the root of any measurable change lies ultimately with the formation of oxidised species in the fuel. Hence, should oxidised species be analysed with suitable precision it should be feasible to derive a stability assessment from the determination of oxygenated compounds in a stressed fuel. It is possible that “marker” oxidised compounds may be identified that link the stability of a fuel without the time and large volumes required for traditional testing, while also delivering a more reliable result. Attaining this goal is complicated by the surprisingly few specific oxidised compounds that were common to all fuels in this study, even with this limited sample set.

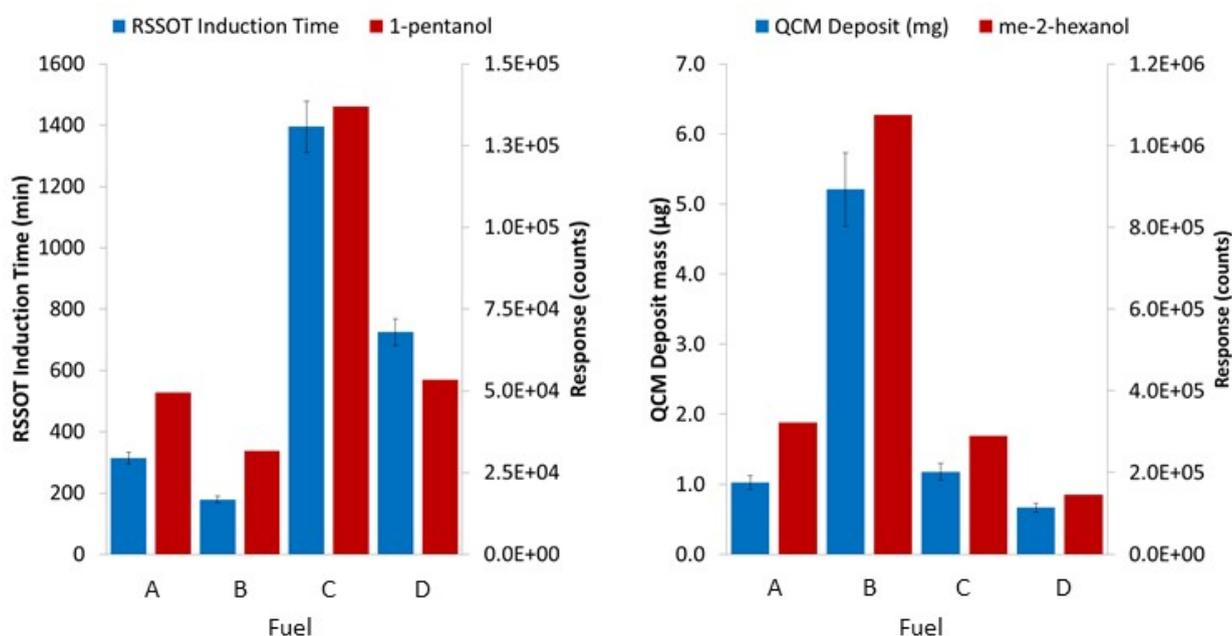


Figure 30. Correlation of specific oxidised species measured by GC×GC-QTOFMS with physical measures of oxidative stability. Refer to Table 23 for fuel identification.

For the fuels in this study, only 4 compounds were identified in common across the four fuels (4-methyl-2-hexanone, hexanal, 1-pentanol, and 2-methyl-4-heptanol).

Most of the deviation in this respect came from the highly branched FT-SPK, which did not generate the preponderance of oxygenated *n*-alkanes found in the other fuels. Nevertheless two of these compounds found in all four fuels, 4-methyl-2-hexanone and 1-pentanol, each showed a strong correlation with established oxidative stability test methods across the range of fuels in this study, as shown in Figure 30. The concentration of 4-methyl-2-hexanone was strongly correlated with the mass of solid deposit generated during QCM testing. The concentration of 1-pentanol was strongly correlated with the rate of oxygen consumption by the fuels during RSSOT testing. While no definitive causality can be determined here, nor concrete conclusions drawn from such a small sample set, this approach may provide an avenue for development of a fuel stability test based on comprehensive GC separations, or even a simpler target method based on multidimensional GC with accurate mass measurement.

7.5 Conclusions

When coupled with accurate mass spectrometry, GC×GC offers unparalleled insights into trace oxygenated species present in oxidised aviation fuels. Ordered elution of compound classes in the 2D chromatogram offers rapid visual identification of conventional and alternate fuels, which are much more difficult to distinguish using 1D GC. A faster and more inclusive analysis of oxidised species is possible, with more reliable identification of unknowns due to improved resolution, minimization of interferences, and accurate mass spectral data. Data gleaned from the GC×GC analysis of oxidised fuels is also correlated with some standardized fuel stability test methods and may present a means for a chromatographic method for assessing a fuel's oxidative condition.

Acknowledgements

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Chapter 8: Conclusions and Future Work

8 Conclusions

The primary objective of this study was to probe trace oxygenates in middle distillate fuels using advanced gas chromatography methods. A number of different chromatographic approaches were taken to resolve specific target analytes, and also broader groups of compounds of interest. The implications of the presence of these compounds in middle distillates were also investigated. It should also be noted that the developed analytical methodologies presented here could be successfully translated to other fuel types, namely light (petroleum) and heavy (oils and lubricants) distillates.

Single dimension chromatography was shown to be a suitable way to analyse trace synthetic phenolic antioxidants in a range of middle distillate fuels, but only if suitably selective MS was employed. The use of advanced MS techniques can overcome the difficulties of a complex matrix providing the target analytes are known and confirmed with authentic standards. Validation of the methods demonstrated that the required detection limits can be readily achieved with excellent precision and accuracy, of an expanded range of analytes which included isomers and impurities. Immediate applications are obvious, as SPA concentrations should be known before and after fuels are re-treated with antioxidant.

Despite the demonstrated power of tandem and accurate mass spectrometry coupled to GC, often the characterisation of trace fuel constituents does require an additional degree of separation. Here, multidimensional separations have proved to be instrumental in improving the analysis and characterisation of trace oxygenates in fuels. Heart-cuts made in selected regions for targeted analytes such as FAME and furanones, have enabled speciation and the achievement of very low detection limits. In the case of FAMEs, analysis of these compounds at low concentrations in heavier middle distillates like diesel has been neglected in the past due to seemingly insurmountable difficulties encountered with the matrix and analytical conditions. With MDGC these problems have been overcome, demonstrating a route for validating that fuels meet specified limits, and also determining the provenance of contaminants. For the study on furanones, this approach permitted quantification of a defined homologous series at trace levels. This was a step forward in the characterisation of stable oxidised species generated *in situ*, and the measurement of their concentration endorses previously unconfirmed suspicions that at these low levels such species can affect the physicochemical properties of fuels.

Non-targeted sequential heart-cutting also demonstrates excellent utility for broad assessment of a large range of polar and oxidised species in fuels. Complications associated with sample extraction or pre-treatment arising from the loss of analytes of interest, or insufficient removal of matrix interferences are largely negated when the sample is sent through two successive high resolution orthogonal separations. A variety of different functional groups can be identified in a single analysis, rather than focussing on a narrow subset by extraction or derivatisation. The results of a single analysis reveals the number and breadth of oxidised compounds generated via thermal oxidation exposing a level of complexity accepted by those in the field, but not explicitly laid out in this manner before. This approach came to the fore in isolating a series of precursors possessing different functionalities to the formation of furanones in thermally oxidised aviation fuels. As a result, a plausible mechanism for the generation of these lactones was postulated, providing valuable information for future development of strategies to mitigate the effects of fuel oxidation.

The characterisation of highly volatile polar species extracted from oxidised fuels is also assisted by multidimensional separations. Laboratory fabricated Nafion SPME fibres showed good efficacy for enrichment of the volatile oxygenates formed during thermal oxidation, and with both single and multidimensional GC analysis, also revealed a range of interesting products complementary to those identified in the other studies. Formation of these low molecular weight species provides additional evidence for chain breaking alkane reactions and the identification of potential marker compounds for simple headspace assessment of a fuel's oxidative condition. The concept of a molecular marker for fuel oxidation is touched on in the final study, but results at this stage are preliminary, and reliable conclusions will require further study.

Comprehensive 2DGC separations provide complementary capability to heart-cutting operations, where a more global view of the fuel's composition including the major alkane and aromatic constituents can be obtained. Rapid visual assessment of fuel composition by hydrocarbon type is invaluable, especially for alternate fuels which proved to be chromatographically distinct using this method as opposed to single dimensional separation where differences are less apparent. Trace components are more difficult to reveal in neat fuels, although are still identifiable when assisted by software algorithms and the ordered elution patterns inherent to GC×GC. The fast mass spectrometer required for GC×GC analysis has the additional

advantage in the present study of accurate mass capability which helps to distinguish between isobaric compounds, whether they are hydrocarbons and oxygenates, or oxygenates with different amounts of oxygen. This also provides assenting evidence of compounds which were tentatively identified with nominal mass resolution in the sequential heart-cutting study. Exploiting different mass spectrometry techniques has also proved advantageous through the use of chemical ionisation. Challenges relating to common fragmentation and shared ions between major and trace fuel components were suitably tackled using CI. In the case of furanones CI generated a unique molecular ion for each target analyte, enabling quantification at very low concentrations. For FAME, a similar outcome was achieved, removing interferences from shared ion fragments with both the matrix and also other target analytes. And for each of these examples, the additional benefit of improved signal-to-noise through reduced response from the hydrocarbon background due to poor ionisation was also realised.

8.1 Future work

There is great potential for follow up research on all work reported in this thesis, largely as a result of the new information that multidimensional GC separations provide. New routes of fuel production present the most obvious opportunities for future directions. As additional pathways are approved, the fuels generated by each of these will be chemically different from those already in the specification. MDGC and GC×GC profiling of such fuels can provide a reference database and comparative composition in a facile manner. Long standing issues related to fuel contamination and the effect of additives also remain unsolved, and warrant further attention. Additionally, while oxygen-containing heteroatoms have been the focus here, there is a substantial body of work in the literature on the sulfur- and nitrogen-containing compounds in middle distillates. Parallel studies on these species, employing similar approaches as explored in this thesis would certainly be a worthwhile avenue for pursuit.

8.1.1 Fuel additives

The additives studied in Chapter 2 were limited to a very specific subset of phenolic antioxidants. Resolution of specific molecular components in fuel additives continues to be a pressing issue as commercial formulations are not divulged beyond the requirements of safety data sheet reporting. As additives are often implicated in fuel quality issues, characterisation of their exact composition including isomers and impurities could provide vital insights into the causes and resolutions of such issues when they arise. In cases where additives react to form new compounds while fuels are in use or storage, the characterisation of these breakdown and/or transformation products would also be a worthwhile exercise. Where phenolic antioxidants are consumed or otherwise rendered ineffective, a molecular assessment of the inactivity may provide useful information about counteracting these effects. The publication in Appendix D1 takes some preliminary steps towards achieving this. It may be valuable to expand the scope of the study here to additives such as fuel system icing inhibitor, lubricity improver, metal deactivator, static dissipater, and the isomers, impurities and reactants thereof. The potential to apply a similar approach to other matrices, for example heavier distillates and synthetic fluids should also be investigated. For each of these future directions, new chromatographic techniques will be required, along with possible extraction and derivatisation of target analytes.

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8.1.3 Fuel oxidised species

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Chapter 8: Conclusions and Future Work

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Appendices

Appendix A: Supporting Information for Chapter 4

Table A1. Compounds included in mixed oxygenates standard solution

functional group	compound
alcohols	heptanol
	octanol
	nonanol
	decanol
	undecanol
	dodecanol
aldehydes	octanal
	decanal
	dodecanal
ketones	octanone
	decanone
carboxylic acids	pentanoic acid
	hexanoic acid
	heptanoic acid
	nonanoic acid
	decanoic acid
furanones	5-methyltetrahydro-2-furanone
	5-ethyltetrahydro-2-furanone
	5-propyltetrahydro-2-furanone
	5-butyltetrahydro-2-furanone
	5-pentyltetrahydro-2-furanone
	5-hexyltetrahydro-2-furanone
	5-heptyltetrahydro-2-furanone
	5-octyltetrahydro-2-furanone

Table A2. Full list of oxygenated compounds in the thermally oxidised fuels tentatively identified by the NIST11 mass spectral library with match quality >700. Names of compounds are as presented by the NIST11 database.

t_R (min)	compound	t_R (min)	compound
5.96	2-Pentanol, formate	15.33	Benzofuran, 2-methyl-
6.13	Ethanol, 2-methoxy-, acetate	15.36	Propane-1,1-diol dipropanoate
6.27	n-Butyric acid 2-ethylhexyl ester	15.37	Dodecanoic acid, 3-hydroxy-
6.39	(S)-3,4-Dimethylpentanol	15.38	2,5-Dimethyl-2-(2-tetrahydrofuryl)tetrahydrofuran
6.41	1-Pentanol, 2-methyl-, acetate	15.38	Benzenemethanol, α -methyl-, (R)-

6.43	1-Hexanol	15.38	Benzofuran, 2-methyl-
6.6	Formic acid, 1-methylethyl ester	15.4	2-Pentanol, 4,4-dimethyl-
6.64	2-Hexanol, 3,4-dimethyl-	15.41	9-Hexadecenoic acid
7.17	meso-2,5-Dimethyl-3,4-hexanediol	15.41	Benzenemethanol, α -methyl-, (R)-
7.31	Butanal, 3-methyl-	15.42	2-Undecanol
7.55	Pentanal	15.42	Benzofuran, 7-methyl-
7.62	2-Pentanone	15.43	3-Nonanone
7.62	2-Butanone, 3,3-dimethyl-	15.51	2-Decanone
7.77	2-Pentanone, 3-methyl-	15.56	(6-Hydroxymethyl-2,3-dimethylphenyl)methanol
7.78	Butanal, 2-methyl-	15.57	3-Octanol, 2,6-dimethyl-
7.82	formic acid butyl ester	15.57	6-Dodecanol
7.89	4-Heptanol,	15.59	3-Decanol
8.15	2-Butanone, 3-ethoxy-3-methyl-	15.59	7-Tetradecanol
8.19	Methyl Isobutyl Ketone	15.62	3-Octanol, 6-ethyl-
8.22	2-Hexanone	15.62	Cyclohexanol, 4-(1-methylethyl)-
8.22	Furan, tetrahydro-2,2,5,5-tetramethyl-	15.63	4-Decanone
8.23	3-Heptanol	15.64	1-Dodecanol, 3,7,11-trimethyl-
8.23	2-Butanone, 3-ethoxy-3-methyl-	15.67	Benzoic acid, 2-methyl-, anhydride
8.24	Methyl Isobutyl Ketone	15.67	Cyclododecaneacetaldehyde
8.28	3-Hepten-2-one	15.69	2-Undecanol
8.38	3-Pentanone, 2-methyl-	15.7	3,7-Dimethyl-2,3,3a,4,5,6-hexahydro-1-benzofuran #
8.4	Hexanal,2-methyl-	15.72	Cyclohexanol, 4-(1-methylethyl)-
8.41	2-Hexanol, 3,4-dimethyl-	15.76	2,2,3,3,4,4-Hexamethyltetrahydrofuran
8.42	2-Hexanone, 5-methyl-	15.78	Cyclohexanone, 3-butyl-
8.42	2-Pentanone, 3-methyl-	15.78	5-Hepten-2-one, 7-phenyl-
8.47	2-Butenal, 2-methyl-, (E)-	15.84	1-Nonanol
8.51	1-Pentanol	15.85	4-Heptanol, 3,5-dimethyl-
8.56	3-Penten-2-one	15.87	Cyclohexanol, 4-(1-methylethyl)-
8.56	2-Pentanone, 4,4-dimethyl-	15.87	Phenol
8.61	trans-13-Octadecenoic acid	15.87	Ethanone, 1-(4-methylphenyl)-
8.63	meso-2,5-Dimethyl-3,4-hexanediol	15.9	Phenol
8.64	2-Pentanone, 4,4-dimethyl-	15.91	meso-3,4-Hexanediol
8.66	Propane, 2,2'-[methylenebis(oxy)]bis-	15.93	Phenol
8.76	1-Butanol, 2-methyl-, (S)-	15.94	Methoxyacetic acid, 1-adamantylmethyl ester
8.76	2-Hexanol	15.95	Phenol
8.82	2-Pentanone, 4,4-dimethyl-	15.96	Ethanone, 1-(4-methylphenyl)-
8.83	2-Pentanone, 4,4-dimethyl-	15.98	Cyclohexanemethylpropanoate
8.86	Furan, tetrahydro-2,2,4,4-tetramethyl-	15.99	5-Decanol
8.95	2-Hexanone, 4-methyl-	15.99	5-Tridecanol
8.97	2-Hexanone	16.01	1-Nonanol
8.98	1-Pentanol	16.01	Benzofuran, 2-methyl-
8.99	3-Pentanone, 2,2-dimethyl-	16.01	3,4-(Methylenedioxy)toluene
9.12	Hexanal	16.03	2,2,3,3,4,4-Hexamethyltetrahydrofuran
9.12	RS-2,3-hexanediol	16.03	3-Ethyl-5-hexen-3-ol
9.15	1-Pentanol, 2,2-dimethyl-	16.03	1,4-Methanonaphthalen-9-one, 1,2,3,4-tetrahydro-
9.2	3-Hexanol	16.04	2,5-Dimethyl-2-(2-

			tetrahydrofuryl)tetrahydrofuran
9.21	2,3-hexanediol	16.04	4-Heptanol, 3,5-dimethyl-
9.21	3-Hexanol	16.04	2,6-Dimethylbenzaldehyde
9.25	2-Pentanol, formate	16.08	2-Hexanone, 4-methyl-
9.26	2-Pentenal, (E)-	16.09	Octanoic acid, 7-oxo-
9.29	3-Hexen-2-one	16.11	2-Decanol, methyl ether
9.3	(S)-3-Ethyl-4-methylpentanol	16.11	2-Undecanol
9.34	2-Pentanol, 4,4-dimethyl-	16.11	2-Hydroxy-5-methylbenzaldehyde
9.34	Furan, 2,3-dihydro-4-methyl-	16.13	2-Decanol, methyl ether
9.35	2H-Pyran, 3,4-dihydro-	16.13	6-Methyl-4-indanol
9.35	2-Hexanol	16.14	3-Methyl-2-(2-oxopropyl)furan
9.44	1-Butanol, 3,3-dimethyl-	16.16	Benzofuran, 2-methyl-
9.44	4-Heptanol, 2-methyl-	16.17	3,7-Dimethyl-2,3,3a,4,5,6-hexahydro-1-benzofuran
9.45	2-Pentanone, 3-ethyl-3-methyl-	16.17	1,4-Methanonaphthalen-9-one, 1,2,3,4-tetrahydro-
9.49	2-Hexanone, 3-methyl-	16.18	1,4-Methanonaphthalen-9-one, 1,2,3,4-tetrahydro-
9.54	Dodecanoic acid, 3-hydroxy-	16.2	3-Decanol
9.61	2-Pentanone, 3-ethyl-3-methyl-	16.21	3-Heptanone, 4-methyl-
9.66	2-Hexanone, 4-methyl-	16.22	1,4-Methanonaphthalen-9-one, 1,2,3,4-tetrahydro-
9.67	3-Pentanone	16.23	2-Decanol
9.71	2-Methyl-2,3-pentanediol	16.24	Phenol, 2-methyl-
9.72	2-Hexanol, 2-methyl-	16.24	Phenol, 2,3-dimethyl-
9.72	2-Hexanol, 2-methyl-	16.24	Phenol, 2,3-dimethyl-
9.72	1,8-Nonanediol, 8-methyl-	16.25	2-Decanol
9.76	meso-2,5-Dimethyl-3,4-hexanediol	16.25	1-Octanol, 2-butyl-
9.76	3-Pentanol, 2,3-dimethyl-	16.27	Benzaldehyde, 3-ethyl-
9.77	3-Hexanol, 3-methyl-	16.28	3-Tridecanol
9.88	4-Penten-2-one, 3-methyl-	16.28	Benzaldehyde, 4-ethyl-
9.88	2-Hexanone, 6-hydroxy-	16.31	2-Methyl-1-undecanol
9.95	2-Hexanone, 4-methyl-	16.32	Phenol, 3-methyl-
9.98	2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one	16.36	6-Methyl-4-indanol
10.01	2-Hexanone, 5-methyl-	16.37	2-Hexyl-1-octanol
10.02	1-Pentanol, 4-methyl-	16.37	Benzaldehyde,
10.04	2-Hexanone, 5-methyl-	16.38	1,4-Methanonaphthalen-9-one, 1,2,3,4-tetrahydro-
10.07	Ethanol, 1-methoxy-, acetate	16.42	Benzaldehyde, 3-ethyl-
10.13	1-Pentanol, 4-methyl-	16.43	Benzaldehyde, 3-ethyl-
10.15	3-Hexanone, 2-methyl-	16.45	4-Hepten-2-one, (E)-
10.19	Pentyl glycolate	16.45	1-Propanone, 1-phenyl-
10.21	(S)-3,4-Dimethylpentanol	16.46	1-Decanol, 2-hexyl-
10.28	Cyclopentanol, 2,4,4-trimethyl-	16.5	2,6-Dimethylbenzaldehyde
10.28	Cyclopentanone,2-methyl-	16.52	3-Methyl-2-(2-oxopropyl)furan
10.35	3-Pentanone, 2,4-dimethyl-	16.52	2,6-Dimethylbenzaldehyde
10.45	5-Methyl-1-heptanol	16.52	2,6-Dimethylbenzaldehyde
10.45	2,4-Heptanedione	16.53	2-Octanol, 2,6-dimethyl-
10.45	2-Heptanone	16.56	Ethanone, 1-(4-methylphenyl)-
10.54	2-Hexanone, 4-methyl-	16.57	Adamantane, 1,3-dimethyl-

10.56	Pentanal, 2-methyl-	16.57	Ethanone, 1-(4-methylphenyl)-
10.57	2-Methyl-2,3-pentanediol	16.59	2-Hexyl-1-octanol
10.58	3-Heptanone	16.6	2,6-Dimethylbenzaldehyde
10.59	5-Hexen-2-one, 5-methyl-	16.6	1-Phenyl-1-decanol
10.63	1-Hexanol	16.61	3-Methyl-2-(2-oxopropyl)furan
10.64	2-Heptanone	16.63	2,6-Dimethylbenzaldehyde
10.64	2-Hexanone, 4-methyl	16.65	2,6-Dimethylbenzaldehyde
10.65	2-Heptanone	16.66	Ethanone,1-(3-methylphenyl)-
10.65	Pentanal,2-methyl-	16.66	2,6-Dimethylbenzaldehyde
10.69	Benzeneethanol, α,β -dimethyl-	16.69	Methyl m-tolyl carbinol
10.71	3-Tetradecanol	16.69	Benzaldehyde, 4-ethyl-
10.71	2-Heptanol, 2-methyl-	16.7	2,6-Dimethylbenzaldehyde
10.72	2-Butanol, 3-methyl-	16.71	2-Decanol, methyl ether
10.73	1-Hexanol	16.73	2,6-Dimethylbenzaldehyde
10.73	Hydroperoxide,	16.74	Benzaldehyde,2,5-dimethyl-
10.73	Hydroperoxide, hexyl	16.74	2,6-Dimethylbenzaldehyde
10.74	Pentane, 3-ethoxy-	16.75	2,4-Heptanedione
10.75	2-Hexanone, 3,4-dimethyl-	16.76	Benzaldehyde,2,5-dimethyl-
10.76	Pentane, 3-ethoxy-	16.77	Benzenemethanol, 4-methyl-
10.78	Pentyl glycolate	16.78	Benzaldehyde, 4-(1-methylethyl)-
10.81	5-Methyl-1-heptanol	16.78	6-Methyl-4-indanol
10.82	3,4-Dimethyl-3-hexanol	16.78	Phenol, 2,4,6-trimethyl-
10.83	Heptanal	16.79	2-Methyl-1-undecanol
10.85	3-Heptanol	16.79	2,2,3,3,4,4-Hexamethyltetrahydrofuran
10.86	Pentane,3-ethoxy-	16.79	Ethanone, 1-(4-methylphenyl)-
10.87	3-Heptanol	16.8	2,6-Dimethylbenzaldehyde
10.89	Furan, 3-pentyl-	16.8	Ethanone, 1-(4-methylphenyl)-
10.92	5-Hexen-2-ol, 5-methyl-	16.81	Methyl m-tolyl carbinol
10.92	2,4-Heptanedione	16.83	2,5-Dimethyl-2-(2-tetrahydrofuryl)tetrahydrofuran
10.92	5-Methyl-1-heptanol	16.83	Benzaldehyde,2,5-dimethyl-
10.93	2-Heptanol	16.87	Benzenemethanol, 4-methyl-
10.96	3-Hexen-2-one, 5-methyl-	16.88	Benzenemethanol, 4-methyl-
10.98	2-Cyclopenten-1-one, 2-hydroxy-	16.89	m-Methylacetophenone
10.98	3-Penten-2-one, 3,4-dimethyl-	16.89	Benzenemethanol, 4-methyl-
10.98	5-Hexen-2-one, 5-methyl-	16.91	Methyl m-tolylcarbinol
11.02	1-Pentanol, 2,3-dimethyl-	16.92	2,2-Dimethyl-3-octanone
11.13	Trimethylene glycol monomethyl ether	16.92	3-Methylbenzyl alcohol
11.15	Cyclopentanone, 2-methyl-	16.92	Benzaldehyde, 4-(1-methylethyl)-
11.17	1-Propene, 3-propoxy-	16.93	3-Methylbenzyl alcohol
11.17	Cyclopentanone, 2-methyl-	16.95	1-Undecanol
11.21	2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one	16.96	2-Undecanone
11.23	Cyclopentanol, 2-methyl	16.96	2,6-Dimethylbenzaldehyde
11.24	2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one	16.97	1-Decanol
11.25	Cyclopentanone,	16.97	6-Tridecanol
11.25	Cyclopentanol, 2-methyl-	16.97	2-Undecanone
11.26	Hexanal, 5,5-dimethyl-	16.97	5-Hexen-2-one, 5-methyl-
11.28	4-Heptanol, 3,5-dimethyl-	16.98	Benzenemethanol, 4-methyl-

11.32	5-Hexen-3-ol, 2,3-dimethyl-	17.01	6-Methyl-4-indanol
11.33	2,4-Heptanedione	17.02	Benzaldehyde, 4-(1-methylethyl)-
11.34	2-Heptanone, 4-methyl-	17.02	Benzaldehyde, 4-(1-methylethyl)-
11.35	2-Heptanol, 2-methyl-	17.02	Phenol, 2-methyl-
11.37	2-Methyl-2,3-pentanediol	17.03	Benzenemethanol, 4-methyl-
11.38	2-Heptanone, 5-methyl-	17.04	Benzenemethanol, 2-methyl-
11.39	5-Hexen-2-one, 5-methyl-	17.05	1H-Indene-4-carboxaldehyde, 2,3-dihydro-
11.41	2-Heptanone, 4-methyl-	17.06	2-Heptanol, 5-methyl-
11.41	Butanoic acid, 3-hydroxy-3-methyl-, methyl ester	17.07	5-Ethyl-4-octanone
11.43	2-Heptanone, 5-methyl-	17.08	Phenol, 3-methyl-
11.48	2-Methyl-2,3-pentanediol	17.09	Phenol, 3-methyl-
11.49	1-Hexadecanol, 2-methyl-	17.09	5-Hepten-2-one, 6-methyl-
11.51	3-Heptanone, 6-methyl-	17.11	1H-Indene-4-carboxaldehyde, 2,3-dihydro-
11.52	SS)- or (RR)-2,3-hexanediol	17.13	Benzenemethanol, 2-methyl-
11.52	3-Pentanone, 2,2-dimethyl-	17.13	Benzenemethanol, 2-methyl-
11.53	3-Heptanol, 2,4-dimethyl-	17.13	Benzaldehyde, 4-(1-methylethyl)-
11.55	4-Nonanone, 7-ethyl-	17.15	Methoxyacetic acid, 1-adamantylmethyl ester
11.57	2-Heptanone, 6-methyl-	17.16	Benzenemethanol, 2-methyl-
11.59	2-Hexanone, 3,4-dimethyl-	17.18	Benzaldehyde, 2,5-dimethyl-
11.59	4-Hepten-2-one, (E)-	17.24	1-Dodecanol, 3,7,11-trimethyl-
11.6	3-Heptanone, 6-methyl-	17.24	Benzaldehyde, 4-(1-methylethyl)-
11.64	2,7-Octadiene-1,6-diol, 2,6-dimethyl-, (E)-	17.24	1H-Indazole, 3-methoxy-
11.65	2-Heptanone, 6-methyl-	17.28	2,6-Dimethylbenzaldehyde
11.66	2-Heptanone, 6-methyl-	17.28	2,6-Dimethylbenzaldehyde
11.66	3-Hepten-2-one	17.29	Phenol, 2-(1-methylethyl)-, acetate
11.67	9-Hexadecenoic acid	17.29	Phenol, 2,4,6-trimethyl-
11.67	2-Heptanone, 6-methyl-	17.33	3-Methyl-2-(2-oxopropyl)furan
11.72	1-Nonanol	17.37	3-Methyl-2-(2-oxopropyl)furan
11.72	2,5,10-Undecanetrione, 6,6-dimethyl-	17.38	Phenol, 2,4,6-trimethyl-
11.73	2(5H)-Furanone, 3,5,5-trimethyl-	17.39	2,4-Heptanedione
11.76	Pentanoic acid, 1,1-dimethylethyl ester	17.41	2,6-Dimethylbenzaldehyde
11.79	4,5-Dihydro-2(1H)-pentalenone	17.42	2,6-Dimethylbenzaldehyde
11.82	2-Nonen-4-one	17.43	2,6-Dimethylbenzaldehyde
11.83	4-Heptenal, (E)-	17.46	2H-1-Benzopyran, 3,4-dihydro-2,2-dimethyl-
11.89	2-Heptanone, 5-methyl-	17.47	1-Allyl-cyclohexane-1,2-diol
11.89	1-Hexanol, 4-methyl-	17.47	Undecanol-3
11.91	Ether, hexyl pentyl	17.48	3,4-Hexanedione, 2,2,5-trimethyl-
11.92	Cyclohexanol, 2-methyl-, cis-	17.48	1-Naphthalenol, 1,2,3,4-tetrahydro
11.95	1-Hexanol, 4-methyl-	17.49	Benzenemethanol, 4-methyl- α -(1-methyl-2-propenyl)-
11.98	2-Heptanol, 5-methyl-	17.51	2,6-Dimethylbenzaldehyde
12.01	2,4,4-Trimethyl-1-pentanol	17.53	Ethanone, 1-(3,4-dimethylphenyl)-
12.01	Cyclohexanemethyl propanoate	17.53	Benzaldehyde, 4-(1-methylethyl)-
12.02	3-Octanol	17.55	1-Undecanol
12.02	Cyclohexanone, 2-methyl-	17.56	7-Tetradecanol
12.08	2-Heptanol, 5-methyl-	17.56	Benzaldehyde, 2,5-dimethyl-
12.1	1-Hexanol, 4-methyl-	17.57	1-Decanol

12.1	Cyclohexanone, 3-methyl-	17.58	9-Hexadecenoic acid
12.13	trans-3-Methylcyclohexanol	17.59	1-Adamantanecarboxylic acid, 2-adamantyl ester
12.14	2H-Pyran-2,6(3H)-dione	17.6	4-Nonanone, 2,6,8-trimethyl-
12.17	2-Octanone	17.62	Phenol, 3-ethyl-5-methyl-
12.19	cis-3-Methylcyclohexanol	17.63	2-Hexyl-1-octanol
12.21	4-Hepten-2-one, (E)-	17.65	2,6-Dimethylbenzaldehyde
12.22	cis-3-Methylcyclohexanol	17.65	1,2-Benzenedicarboxaldehyde
12.22	trans-3-Methylcyclohexanol	17.7	Phenol, 2,4,6-trimethyl-
12.23	threo-2,5-Dimethyl-2-(2-methyl-2-tetrahydrofuryl)tetrahydrofuran	17.72	Phenol, 3-ethyl-5-methyl-
12.23	3-Pentanone, 2,2-dimethyl-	17.73	Benzofuran,4,7-dimethyl-
12.27	2H-Pyran-2-one	17.74	Phenol, 2,4,6-trimethyl-
12.28	trans-3-Methylcyclohexanol	17.76	4-Methylphthalaldehyde
12.28	2-Heptanol, 5-methyl-	17.79	Ethanone, 1-(3,4-dimethylphenyl)-
12.28	trans-3-Methylcyclohexanol	17.8	Undecanol-3
12.31	4-Heptanol, 2-methyl-	17.8	Cyclohexanecarboxylic acid, heptadecyl ester
12.32	3-Heptanol, 2-methyl-	17.82	2-Undecanol
12.32	2,5-Dimethyl-2-(2-tetrahydrofuryl)tetrahydrofuran	17.82	Phenol, 2,4,6-trimethyl-
12.33	2,5-Hexanedione	17.83	2-Methyl-1-undecanol
12.37	4-Penten-1-ol, 2,2,4-trimethyl-	17.84	2-Undecanol
12.37	2-Heptanone, 4,6-dimethyl-	17.84	Phenol, 2,4,6-trimethyl-
12.4	3-Methyl-2-(2-oxopropyl)furan	17.86	Pivalic acid vinyl ester
12.41	2-Heptanone, 4,6-dimethyl-	17.86	Benzaldehyde, 4-propyl-
12.41	Formic acid, heptyl ester	17.87	2-Decanone, 5,9-dimethyl-
12.42	3-Heptanone, 5-methyl-	17.89	Benzaldehyde, 4-(1-methylethyl)-
12.43	2,4-Heptanedione	17.95	Phenol, 3-ethyl-5-methyl-
12.46	2(3H)-Furanone, dihydro-5-pentyl-	17.96	Phenol, 3-ethyl-5-methyl-
12.48	1-Heptanol	17.97	Ethanone, 1-(2,4-dimethylphenyl)-
12.49	2,4-Heptanedione	18.01	6,10,14-Trimethyl-pentadecan-2-ol
12.49	1-Heptanol	18.04	Ethanone, 1-(3,4-dimethylphenyl)-
12.51	2-Heptanol, 2,6-dimethyl-	18.09	Ethanone,1-(3,4-dimethylphenyl)-
12.52	1-Hexadecanol, 2-methyl-	18.09	5,10-Pentadecadien-1-ol,(Z,Z)-
12.54	1,7-Octanediol, 3,7-dimethyl-	18.11	Ethanone, 1-(3,4-dimethylphenyl)-
12.59	2-Butenoic acid, 2-methoxy-, methyl ester, (Z)-	18.12	Benzenemethanol, 4-ethyl-
12.61	4-Heptanol, 2-methyl-	18.12	Benzaldehyde, 2,4,6-trimethyl-
12.63	3-Octanol	18.13	1-Adamantanol
12.64	1,7-Octanediol, 3,7-dimethyl-	18.13	Phenol, 2,3-dimethyl-
12.69	2-Octanol, (R)-	18.15	5,10-Pentadecadien-1-ol,(Z,Z)-
12.71	2-Octanol, (S)-	18.15	Phenol, 3,4-dimethyl-
12.71	Pentane,3-ethoxy-	18.17	Phenol, 3-ethyl-
12.72	4-Heptenal, (E)-	18.19	Phenol, 3-ethyl-
12.79	2(3H)-Furanone, 5-butyl-dihydro-	18.19	Benzaldehyde, 4-propyl-
12.79	Bicyclo[3.2.2]nona-6,8-dien-3-one	18.2	4-Ethylbenzoic acid
12.82	3,4-Dimethylcyclohexanol	18.21	Benzenemethanol, 4-ethyl-
12.9	2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one	18.21	Benzenemethanol, 4-ethyl-
12.93	3-Octanol, 6-ethyl-	18.21	Phenol, 2,4,6-trimethyl-

12.98	Cyclohexanone, 3,5-dimethyl-	18.24	1-Adamantanol
13.05	Benzaldehyde	18.24	Ethanone, 1-(3,4-dimethylphenyl)-
13.09	Cyclohexanol, 2,4-dimethyl-	18.25	2-Hexanol, 2,5-dimethyl-, (S)-
13.11	2(3H)-Furanone, dihydro-5-pentyl-	18.25	Benzenemethanol, 4-ethyl-
13.11	Cyclohexanone, 3,5-dimethyl-	18.27	4,5-Dimethyl-3H-isobenzofuran-1-one
13.12	4-Octanol, 4-methyl-	18.28	Phenol, 2,4,6-trimethyl-
13.12	Methyl 5-methoxy-3-oxovalerate	18.29	Benzenemethanol, 3,5-dimethyl-
13.13	Cyclohexanol, 1-methyl-4-(1-methylethenyl)-, acetate	18.29	Ethanone, 1-(3,4-dimethylphenyl)-
13.16	2-Heptanol, 2,6-dimethyl-	18.3	Benzoic acid, 4-methyl-, 1-methylethyl ester
13.18	2-Octen-1-ol, 7-[(tetrahydro-2H-pyran-2-yl)oxy]-, (E)-	18.31	3-Tridecanol
13.19	2-Heptanone, 4,6-dimethyl-	18.31	Phenol, 2,4,6-trimethyl-
13.2	4,4-dimethyl-5-oxo-tetrahydrofuran-3-carboxylic acid	18.31	3,5-Dimethyl-1-adamantanol
13.2	Cyclohexanol, 3,5-dimethyl-	18.32	1(2H)-Naphthalenone, octahydro-3,8a-dimethyl-, (3 α ,4 α ,8 α)-
13.23	2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one	18.32	Phenol, 2-(1,1-dimethylethyl)-
13.25	Butanoic acid, 3-oxo-, 2-propenyl ester	18.33	1-Phenyl-1-decanol
13.26	Bicyclo[2.2.2]octane-1,4-diol	18.33	Phenol, 2-propyl-
13.26	2-Heptanone, 4,6-dimethyl-	18.33	1-Phthalanol, 1,3,3-trimethyl-
13.26	2,2-Dimethyl-3-octanone	18.34	Naphthalene, 1,2-dihydro-7-methoxy-
13.29	Undecanol-3	18.35	1-Phenyl-1-decanol
13.31	Eucalyptol	18.36	Phenol, 2,4,6-trimethyl-
13.31	3-Methyl-2-(2-oxopropyl)furan	18.38	Benzenemethanol, 2,5-dimethyl-
13.31	Cyclohexanol, 2,3-dimethyl-	18.39	Benzenemethanol, 3,5-dimethyl-
13.31	1-Hexanol, 2-ethyl-	18.39	2 α , 4 α , 8 α -Decahydro-2-naphthalenol
13.33	3-Octanol, 3-methyl-	18.41	Phenol, 2-propyl-
13.34	3-Octanol, 3-methyl-	18.41	Phenol, 2,4,6-trimethyl-
13.36	(S)-3-Ethyl-4-methylpentanol	18.42	2-Methyl-6-propylphenol
13.37	Benzofuran	18.45	Benzyl alcohol, 2,3-dimethyl-
13.38	2(3H)-Furanone, dihydro-5-propyl-	18.46	Phenol, 2,4,6-trimethyl-
13.39	3-Pentenoic acid, 4-methyl-	18.46	Benzyl alcohol, 2,3-dimethyl-
13.39	δ -Nonalactone	18.48	Benzaldehyde, 4-butyl-
13.42	Cycloheptanone	18.49	Methyl 6-oxoheptanoate
13.42	2-Heptanone, 4,6-dimethyl-	18.49	Phenol, 2,4,6-trimethyl-
13.43	2-Butanone	18.5	2,5-Hexanedione
13.43	1-Cyclohexyl-2,2-dimethyl-1-propanol	18.51	2-Methyl-6-propylphenol
13.46	3,4-Dimethylcyclohexanol	18.51	Phenol, 2,4,6-trimethyl-
13.5	2-Nonanone	18.52	2 α , 4 α , 8 α -Decahydro-2-naphthalenol
13.5	1-Nonanol	18.53	9-Heptadecanol
13.52	3,4-Dimethyl cyclohexanone	18.53	2-Methyl-6-propylphenol
13.55	5-Nonanol	18.54	9-Hexadecenoic acid
13.58	3-Heptanol, 2,4-dimethyl-	18.56	Phenol, 2,4,6-trimethyl-
13.59	2-Hexanone, 3,4-dimethyl-	18.57	2,5-Dimethylphenyl methyl carbinol
13.59	3-Octanol, 2-methyl-	18.59	2-Methyl-6-propylphenol
13.64	1-Hexadecanol, 2-methyl-	18.61	Pentanoic acid, 2-methyl-, anhydride
13.65	2H-Pyran-2-one, tetrahydro-6-tridecyl-	18.61	Phenol, 2,3,4,6-tetramethyl-
13.67	Cyclohexanone, 3,3,5-trimethyl-	18.63	Phenol, 2,3,5,6-tetramethyl-

13.7	2-Nonanone	18.66	Phenol, 2,4,6-trimethyl-
13.75	5-Methyl-1-heptanol	18.67	Phenol, 3,4-dimethyl-
13.81	3-Nonanol	18.67	Phenol, 3-ethyl-5-methyl-
13.81	2-Propionyloxytetradecane	18.67	Phenol, 3,4-dimethyl-
13.82	2(5H)-Furanone, 3,5,5-trimethyl-	18.71	2-Tetradecanol
13.84	2-Dimethylcyclopentanol	18.71	Benzaldehyde, 2,4,6-trimethyl-
13.85	7-Tetradecanol	18.71	Phenol, 2,4,6-trimethyl-
13.85	3-Octen-1-ol, (Z)-	18.73	Phenol, 2-ethyl-4,5-dimethyl-
13.87	2-Nonanol	18.74	Phenol, 3-ethyl-5-methyl-
13.91	2,5-Dimethyl-2-(2-tetrahydrofuryl)tetrahydrofuran	18.75	Phenol, 3,4-dimethyl-,
13.92	2(3H)-Furanone, 5-(acetyloxy)dihydro-5-methyl-	18.75	Benzenemethanol, 3,5-dimethyl-
14.05	2(3H)-Furanone, 5-ethyl-dihydro-	18.77	Phenol, 2,4,6-trimethyl-
14.06	1-Undecanol	18.81	Phenol, 2,4,6-trimethyl-
14.07	1-Hexadecanol, 2-methyl-	18.82	4-(t-Butyl)benzaldehyde
14.08	4-Ethylcyclohexanol	18.83	Phenol, 2,4,6-trimethyl-
14.09	4-Ethylcyclohexanol	18.84	<i>p</i> -Cymen-7-ol
14.1	3-Hexanone, 4-methyl-	18.85	Ethanone, 1-(2,4,6-trimethylphenyl)-
14.11	2-Methyl-5-nonanol	18.86	Phenol, 2,4,6-trimethyl-
14.16	1-Octanol	18.87	Benzaldehyde, 2,4,6-trimethyl-
14.16	4-Ethylcyclohexanol	18.88	1-Phenyl-1-decanol
14.21	4-Heptanol, 2-methyl-	18.92	Phenol, 2-(2-methylpropyl)-
14.21	5-Methyl-1-heptanol	18.92	<i>p</i> -Isobutylbenzaldehyde
14.22	3-Methyl-2-(2-oxopropyl)furan	18.95	Benzene, 2-methoxy-4-methyl-1-(1-methylethyl)-
14.24	2-Methyl-2,3-pentanediol	18.98	Ethanone, 1-(3,4-dimethylphenyl)-
14.24	1-Octanol	19.01	1H-Inden-1-one, 2,3-dihydro-
14.25	Cyclohexanol, 2,3-dimethyl-	19.02	Thymol
14.25	1-Octanol	19.02	1H-Inden-1-one, 2,3-dihydro-
14.29	meso-3,4-Hexanediol	19.05	<i>p</i> -Cymen-7-ol
14.35	3-Heptanone, 4-methyl-	19.06	2,3,5-Trimethylanizole
14.39	2,4-Pentadien-1-ol, 3-propyl-, (2Z)-	19.08	Benzylalcohol, 2,3-dimethyl-
14.41	3-Nonanol	19.12	Benzyl alcohol, 2,3-dimethyl-
14.42	Benzene, (2-methoxy-2-propenyl)-	19.14	Phenol, 2,4,6-trimethyl-
14.42	3-Nonanol	19.15	5-Dodecanol acetate
14.43	Cyclohexanone, 4-ethyl-	19.15	α -Methoxy- β , β -dimethylstyrene
14.47	1-Hexadecanol, 2-methyl-	19.21	Phenol, 2,4,6-trimethyl-
14.47	2-Nonanol	19.24	Phenol, 2,4,6-trimethyl-
14.48	3-Octanol, 3,6-dimethyl-	19.25	3-Methylbenzothiophene
14.5	3-Octanol, 3,6-dimethyl-	19.25	Ethanone, 1-(4-ethoxyphenyl)-
14.5	Cyclohexanemethanol, 4-methyl-, cis-	19.25	Phenol, 2-ethyl-4,5-dimethyl-
14.51	3-Octanol, 3,6-dimethyl-	19.31	Phenol, 2,4,6-trimethyl-
14.56	2-Heptanone, 6-methyl-	19.31	Phenol, 2,4,6-trimethyl-
14.62	2-Cyclohexen-1-one, 3-methyl-	19.32	1H-Indene-1-methanol, α -methyl-, acetate
14.63	1-Allyl-cyclohexane-1,2-diol	19.34	α -Methoxy- β , β -dimethylstyrene
14.65	2-Nonanol	19.34	Phenol, 2-ethyl-4,5-dimethyl-
14.7	2-Cyclohexen-1-one, 3-methyl-	19.36	2-Methyl-6-propylphenol
14.72	Benzaldehyde, 3-methyl-	19.36	1H-Inden-1-one, 2,3-dihydro-3-methyl-

14.74	Acetophenone	19.37	3(2H)-Benzofuranone, 4,7-dimethyl-
14.78	Benzaldehyde, 4-hydroxy-	19.37	Phenol, 2-ethyl-4,5-dimethyl-
14.79	Benzaldehyde, 3-methyl-	19.38	Phenol,2,4,6-trimethyl-
14.8	2-Butene, 1-propoxy-, (E)-	19.4	Phenol, 2,4,6-trimethyl-
14.82	Acetophenone	19.41	Ethyl mesitylglyoxylate
14.82	Acetophenone	19.45	Phenol, 3-methyl-6-propyl-
14.88	Benzaldehyde, 3-methyl-	19.46	Phenol, 2-methyl-5-(1-methylethyl)-
14.88	Benzaldehyde, 4-methyl-	19.46	2-Methyl-6-propylphenol
14.89	4-Nonanol, 4-methyl-	19.47	3,4-Hexanedione, 2,2,5-trimethyl-
14.89	Acetophenone	19.52	2-Tetradecanol
14.93	meso-3,4-Hexanediol	19.54	2-Methyl-6-propylphenol
14.93	1,2-Cyclohexanedimethanol	19.64	2-n-Propylthiolane,S,S-dioxide
14.94	2-Octanol, 2,6-dimethyl-	19.66	2,4,6-Trimethylbenzyl alcohol
14.96	heptyl furanone	19.68	2,4,6-Trimethylbenzyl alcohol
14.97	Acetophenone	19.77	Benzaldehyde, 2,4,6-trimethyl-
14.98	Octadecanedioic acid	19.84	1-Heptatriacotanol
14.98	5-Methyl-2-(2-methyl-2-tetrahydrofuryl)tetrahydrofuran	19.85	Benzaldehyde, 2,4,6-trimethyl-
14.98	Acetophenone	19.89	2,6-Dimethyl-4H-furo[3,2-c]pyran-4-one
14.98	o-Toluic acid, 2-methylphenyl ester	19.92	Phenol, 2,3,5,6-tetramethyl-
14.99	1,2-Dimethylcyclopentanol	19.95	Benzeneacetic acid, α -methoxy-, methyl ester
15.02	1-Methylcycloheptanol	19.95	2-Methyl-6-propylphenol
15.03	2-Methyl-3-phenyl-2-propen-1-ol	19.96	2,6-Dimethylbenzaldehyde
15.03	Benzaldehyde, 3-methyl-	20.01	2-Methyl-6-propylphenol
15.04	Benzaldehyde, 4-methyl-	20.12	Naphthalene, 1,7-dimethoxy-
15.1	3-Dodecanol	20.14	1-Hexadecanol, 2-methyl-
15.12	3-Octanol, 3,6-dimethyl	20.14	Ethanone, 1-(4-ethoxyphenyl)-
15.14	Benzaldehyde, 3-methyl-	20.17	2,6-Dimethyl-4H-furo[3,2-c]pyran-4-one
15.14	Benzaldehyde, 4-methyl-	20.19	2-Pentanone, 4-methyl-4-phenyl-
15.15	6-Dodecanol	20.2	Thymol
15.21	2H-Pyran-2-one, 6-hexyltetrahydro-	20.3	2,4,6-Trimethylbenzyl alcohol
15.22	2H-Pyran-2-one, tetrahydro-6-nonyl-	20.32	Diphenyl ether
15.22	1-Nonanol	20.34	2,4,6-Trimethylbenzyl alcohol
15.23	2H-Pyran-2-one, 6-hexyltetrahydro-	20.42	2,4,6-Trimethylbenzyl alcohol
15.23	Benzaldehyde, 3-methyl-	20.43	1(2H)-Naphthalenone, 3,4-dihydro-
15.24	1-Nonanol	20.69	3-Tetradecanol
15.24	2,5-Octanedione	20.74	7-Tetradecanol
15.28	2-Decanone	20.89	2-Tetradecanol
15.28	Benzaldehyde, 3-methyl-	21.07	7-Methylindan-1-one
15.29	Benzofuran, 2-methyl-	21.3	Phenol,2,5-bis(1-methylethyl)-,
15.3	2-Decanone	21.36	Benzenemethanol,2-hydroxy-5-methoxy- $\alpha,\alpha,4$ -trimethyl-
15.31	Benzenemethanol, α -methyl-, (R)-	22.53	Naphtho[2,1-b]furan
15.33	4-Octanol, 2,7-dimethyl-	23.04	2-Tetradecanol

Appendix B: Supporting Information for Chapter 6

B1 Experimental Conditions for Gas Chromatography-Mass Spectrometry

SPME injections were performed manually using splitless mode, with the inlet at a suitable operating temperature for each fibre; 150°C and 240°C for the Nafion and CW/PEG fibres, respectively. Fibres were thermally desorbed in the inlet for 5 min. Liquid injections were performed via an autosampler, with the injector in split mode (200:1) and an injection volume of 0.2 µL. The column used was an Agilent HP-5ms with dimensions 30 m × 250 µm × 0.25 µm. The oven program started at 50 °C, with a hold time of 5 min, then ramped at a rate of 10 °C/min to 240 °C. Helium was used as the carrier gas at 1.2 mL/min. The mass spectrometer was operated in electron ionisation mode at 70 eV, and set with a scan range of 45-350 m/z and a scan rate of 5 scans /s. Data were acquired and analysed using Agilent MSD Chemstation (version E.02.00).

B1.1 Experimental Conditions for Multidimensional Gas Chromatography-Mass Spectrometry

The same model GC-MS was used for multidimensional separations, except with a Deans' switch installed. A flame ionisation detector was employed as the primary detector with the MS as the second detector. A non-polar/polar column setup was used with a primary column of DB-5ms 30 m × 250 µm × 0.5 µm (Agilent), and a SolGel-WAX 30 m × 250 µm × 0.25 µm second column (SGE Analytical Science, Ringwood, Australia). A 0.6 m length of 100 µm internal diameter deactivated fused silica was used as the restrictor. The MDGC-MS used the same oven programme as used for the 1D analysis. The Deans' switch was programmed to heart-cut target analytes, with various cuts selected each of 30 - 100 s duration. Helium was supplied to the inlet at 31.0 psi and to the Deans' switch at 22.7 psi (constant pressure mode).

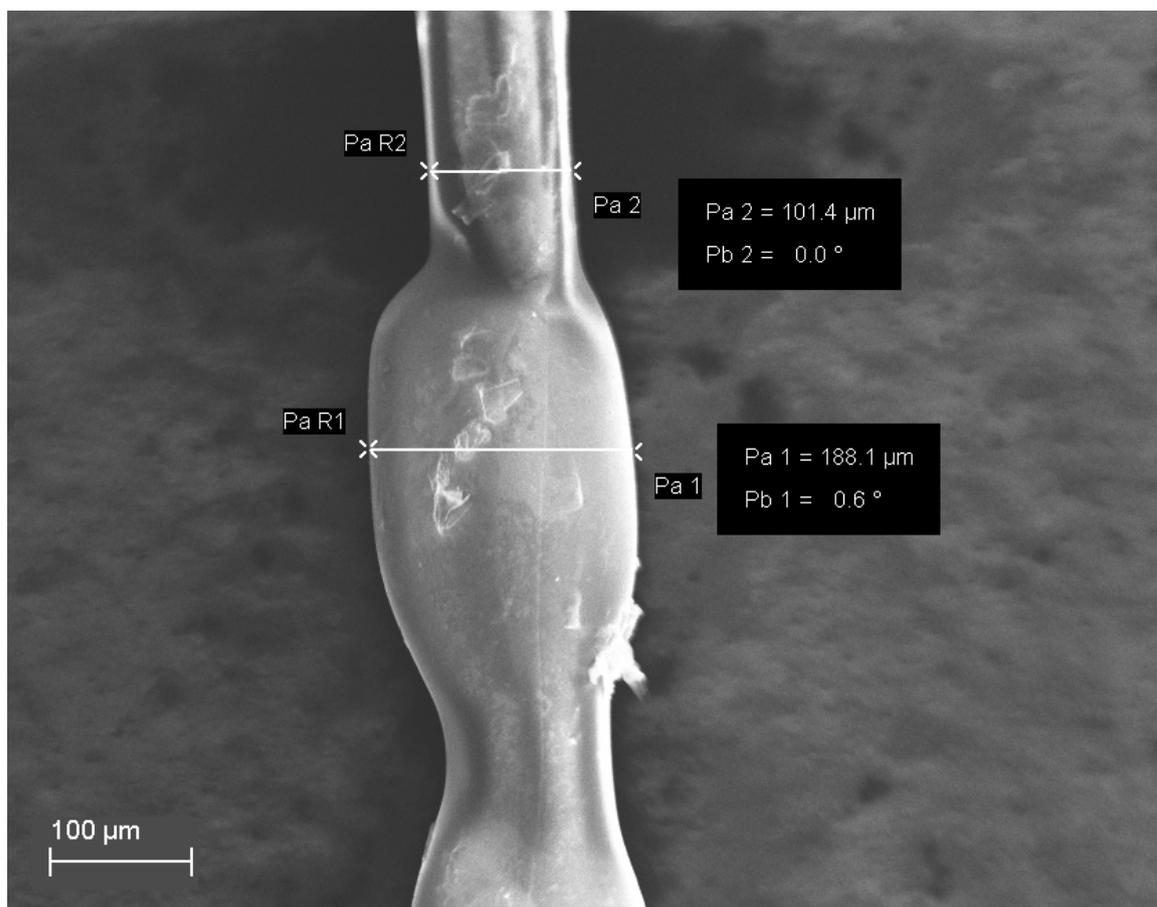


Figure B1. SEM image of a typical fibre showing the Nafion coated (lower section) and bare (upper section) of the silica fibre and measured diameters.

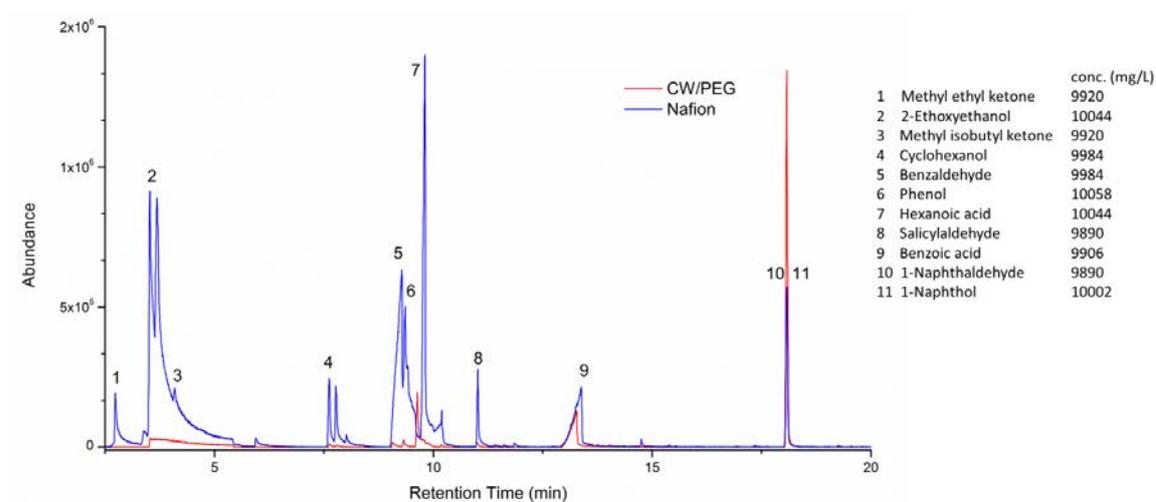


Figure B2. Total ion chromatogram comparison of the 1D GC-MS comparison of the extraction performance of Nafion and PEG fibres for the analysis of 100 mg/L oxygenate mixture in heptane.

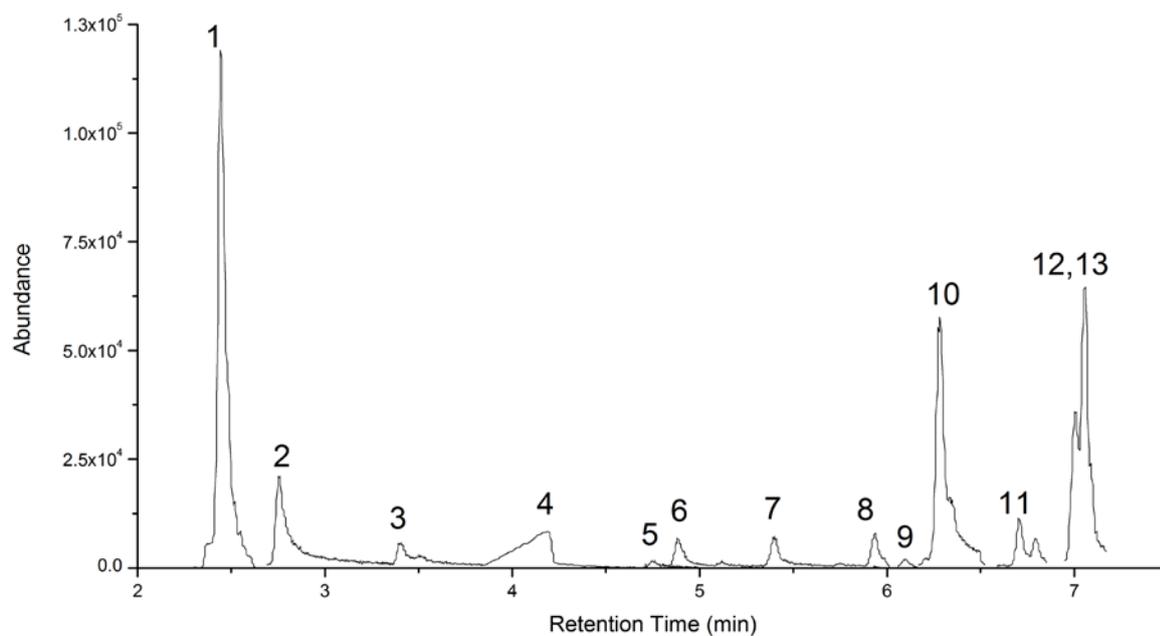


Figure B3. Zoomed region of the oxidised HEFA-SPK fuel in MDGC analysis, displaying extracted ion chromatograms for compounds tentatively identified with numbering as per Table B1.

Table B1. Oxidised species tentatively identified in the 0.0-7.1 min region of the oxidised SPK fuel after extraction with Nafion fibre.

Peak #	t_R	Name	Formula	Match quality	Extracted ion (m/z)
1	2.44	Butane, 1,4-dimethoxy-	$C_6H_{14}O_2$	614	45
2	2.75	2-Propenoic acid	$C_3H_4O_2$	601	72
3	3.21	3-Pentanone	$C_5H_{10}O$	744	86
4	4.23	Propanoic acid	$C_3H_6O_2$	673	74
5	4.75	1-Penten-3-one	C_5H_8O	625	84
6	4.88	1-Propoxypropan-2-yl 2-methylbutanoate	$C_{11}H_{22}O_3$	606	85
7	5.42	Valeric anhydride	$C_{10}H_{18}O_3$	638	85
8	5.94	2,2-Dimethyl-3-heptanone	$C_9H_{18}O$	640	85
9	6.12	2(3H)-Furanone, 5-ethenyldihydro-5-methyl-	$C_7H_{10}O_2$	679	111
10	6.28	Heptane, 1,1'-oxybis-	$C_{14}H_{30}O$	775	57
11	6.82	Cyclopentanone, 2-(1-methylheptyl)-	$C_{13}H_{24}O$	643	84
12	7.01	2-Pentoxy-tetrahydropyran	$C_{10}H_{20}O_2$	640	85
13	7.06	3,4-Hexanedione	$C_6H_{10}O_2$	604	85

Appendix C: Co-authored papers published during candidature

Three additional co-authored papers were published during my candidature. Two are presented here as appendices.

Appendix C1: Re-addition of antioxidant to aged MEROX and hydroprocessed jet fuelsxiii

Appendix C2: The oxidative stability of synthetic fuels and fuel blends with monoaromatic blending components xx

The third publication is under embargo and cannot be reproduced here.

Yildirim, U.; Webster, R.; Evans, D.; Rawson, P., Derived Cetane Number, Distillation and Ignition Delay Properties of Diesel and Jet Fuels Containing Blended Synthetic Paraffinic Mixtures. SAE International Journal of Fuels and Lubricants 2016, 9 (2016-01-9076).



Re-addition of antioxidant to aged MEROX and hydroprocessed jet fuels



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HIGHLIGHTS

- Effect of re-addition of antioxidant to aged and processed fuels.
- Addition of antioxidant to hydroprocessed fuel past mandated time.
- Antioxidant depletion rates for aged fuels.
- Influence of readdition of antioxidant on induction times.

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ABSTRACT

Long term storage of aviation turbine fuels often requires the use of antioxidants with many military fuel specifications mandating its addition for hydroprocessed fuels. This work examines the influence of antioxidants on aged and freshly refined aviation turbine fuels of various types, some containing antioxidant at manufacture and others not. The rate of antioxidant depletion is reported along with the re-stabilised fuel's oxidation induction periods. It was found that some fuel types do not benefit from re-addition of antioxidant and no improvement was observed for inhibition of hydroperoxide formation in aged fuels, however oxidation induction times were improved for re-addition of antioxidant for all fuels examined. A simple method for assessing the degree of hydroprocessing of an unknown fuel was also examined with limited success.

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1. Introduction

Storage stability is a significant concern for long term and strategic storage of jet fuels. Storage stability is defined as a fuel's resistance to peroxide and sediment formation. Other measures of stability also exist and include oxygen induction times. Jet fuels are manufactured by various processing methods including straight run, MEROX and hydroprocessing [1]. Different fuel refinery processing methods are known to affect the storage stability of fuels. Some fuels are known to have poor storage stability based on their processing such as hydroprocessed fuels which are generally considered to be fast oxidisers [2,3]. Hydroprocessing will remove naturally occurring antioxidants including oxygen, sulfur and nitrogen heteroatoms [4]. Unstabilised fuels will tend to react with oxygen to form hydroperoxides which will affect aircraft fuel system seals, diaphragms and materials made of neoprene, nitrile

rubber and Buna-N [5–9]. Rates of formation and decomposition of peroxides are driven by storage temperatures, duration and the availability of oxygen [10,11]. Peroxides once formed in a fuel, will initiate autoxidation reactions ultimately forming sediments and gums which lead to increased maintenance, poor performance and engine failures [3,12,13].

To ensure satisfactory storage stability and inhibit peroxide formation, some military and civil fuel specifications require the addition of antioxidant to hydroprocessed fuels immediately after processing and before the fuel is exposed to the atmosphere [14,15]. This is done with the purpose of preventing gum formation and peroxidation after manufacture [16]. Previous studies have shown that hydroprocessed fuels will exhibit peroxide formation rates 200 times greater than a non hydrotreated fuel [9]. Once all available antioxidants are depleted the rate of formation is so rapid that for the antioxidant to be effective it should be added at the time of processing.

Synthetic phenolic antioxidants have routinely been used to stabilise fuels by preventing peroxide build up [17–19]. Synthetic phenolics act to disrupt the chain of peroxidation reactions by

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Table 1

Ambient aged fuels peroxide concentrations pre and post addition of antioxidant and measured after 26 weeks aging at 43 °C. Note PV = peroxide value.

Sample name	Fuel type	Finishing process	Years in ambient storage	PV initial	PV 26 weeks at 43 °C with 25 ppm antioxidant added (ppm)	Initial antioxidant present (ppm)
Aging 7	F-34	MEROX blend	0.5	0.0	0.0	0.0
Aging 6	F-34	MEROX blend	3	0.0	7.2	0.0
Aging 5	F-34	MEROX Blend	10	0.5	8.5	0.0
Aging 4	F-34	MEROX blend	11	0.0	6.4	0.0
Aging 3	F-34	MEROX blend	12	0.0	7.4	8.1
Aging 2	F-34	MEROX Blend	17	0.0	7.3	9.4
Aging 1	Jet A1	MEROX blend	17	0.0	3.4	0.0

forming a stable radical but are not known to be effective in inhibiting those peroxides already in the fuel [20].

Work by Love et al. [7] on fuel related problems in gas turbine engines summarised the effect of peroxide formation finding the following:

- “Fuels that contained peroxide that attacked rubbers showed little or no improvement following addition of antioxidant, as the useful properties of the additive were quickly absorbed without a reduction in peroxide content.
- Little improvement was achieved when all traces of existing peroxides were removed from the fuel by chemical treatment as they quickly reform.
- Removal of existent peroxides from the fuel, followed by immediate addition of an antioxidant inhibited peroxide reformation.
- Blending of fast oxidising fuels with non-hydroprocessed fuels improved resistance to peroxide formation.”

Normally once a jet fuel has been stabilised with antioxidant it has no further requirement for re-addition under normal storage conditions. Fuels in storage have no defined in-service deterioration limits with respect to peroxide formation, but the deterioration may be monitored via other properties such as existent gum formation. Currently for some fuels in long term storage there is no limit placed on life as long as those fuels pass periodic recertification testing.

Fuel samples of uncertain provenance may be mixtures of fuels produced by varied finishing processes. Currently there is no simple method for determining the level of an unknown fuel's hydro-treatment, or the degree of hydroprocessed component of a mixture. A simple method to establish unknown fuels level of hydro-treatment based on the conversion of naphthalene to tetralin and decalin as a guide was examined.

This work explores the potential for re-addition of antioxidant to aged hydroprocessed fuels and to a hydroprocessed fuel that did not have antioxidant added during production. These hydro-processed fuels are compared with a range of straight run and MEROX fuels of various ages.

2. Experimental

2.1. Samples

Three different fuel types were examined plus a ‘model fuel’ assessed as a possible reference fuel. Fuel samples used in the experiment were either Jet A-1, F-34 (Jet A-1 plus military additive package) or F-44 (military aviation fuel for use on ships with additive package). The F-34 and F-44 all met the DEF(AUST) 5240D aviation turbine fuel specification [16] and all had the fuel system icing inhibitor (FSII), static dissipater additive and corrosion inhibitor additive package. All samples were taken either directly from the refinery or from air base tankage where the fuel was supplied

to the base consistently from a single refinery. All were stored in 1 L amber glass bottles at ambient conditions.

2.1.1. MEROX fuels

Seven ambiently aged fuels were included from a refinery known to use a MEROX finishing process. These fuels have no requirement for antioxidant addition. The Aging 1 and Aging 2 samples were the same fuel with Aging 2 containing the military additive package. It was found that Aging 2 still contained 9.4 ppm of antioxidant even after 17 years in ambient storage, Table 1.

2.1.2. Hydrotreated fuels

A range of ambient aged hydrotreated jet fuels, and a fresh 100% hydrotreated fuel with no antioxidant added was used as a reference standard. The reference hydroprocessed fuel, designated AO-24, was obtained from a local refiner and was 1 day old when received; this sample was subsequently stored at –18 °C. All of the F-44 samples were taken from a single location and known to be 100% hydrotreated, Table 3.

2.1.3. Model fuel

The model fuel composition was chosen to examine storage stability of the alkane and aromatic fractions of fuel and did not contain any diaromatics as added to other model fuels compositions [21]. The model fuel used was as that of Webster et al. [22] and was made up of the following components;

- 50 mL methyl cyclohexane.
- 50 mL 2,2,4-trimethylpentane.
- 100 mL toluene.
- 100 mL *o*-xylene.
- 100 mL nonane.
- 50 mL decane.
- 100 mL undecane.
- 250 mL dodecane.
- 200 mL tetradecane.

Table 2

MEROX and model fuel PetroOxy results.

Sample	Years in ambient storage	PetroOxy time, min
Model fuel	0	297
Model fuel + 24 ppm AO	0	1356
Aging 6 – MEROX	3	1715
Jet A1 69% MEROX	6	923
Aging 5 – MEROX	10	1760
Aging 4 – MEROX	11	1790
Aging 3 – MEROX	12	1417
Aging 1 – MEROX	17	974
Aging 2 – MEROX	17	1734

Note Aging 2 sample is Aging 1 that had the military additive packed added when produced.

Table 3
Ambiently aged hydrotreated fuels peroxide concentrations pre and post addition of antioxidant and measured after 13 weeks aging at 43 °C.

Sample name	Fuel type	Years in ambient storage	PV initial (ppm)	PV 13 weeks at 43 °C with 25 ppm AO added	PV 26 weeks at 43 °C with 25 ppm AO added (ppm)	Initial AO present (ppm)	Sulfur concentration (ppm)
AO-24	Jet A1	0.01	0.6		15.7	0.0	11
AO-10	F-34	0.5	0		12.2	14.2	85
AO-34	F-34	0.5	0.1	3.3		13.1	297
AO-35	F-34	0.5	1.3	2.5		16.9	304
AO-18	F-44	2	1.6		13.1	6.5	9
AO-11	F-44	2	1		14	8.8	10
AO-05	F-44	2	3		15.9	10.2	95
AO-14	Jet A1	3	0.4		7.2	2.3	185
AO-06	F-44	3	0		15.4	0.0	14
AO-33	F-34	7	0	1.6		13.7	19
AO-19	Jet A1	9	3.1		9.7	13.5	9

2.2. Assessment of storage stability

Two methods were used to assess the stability of fuels storage stability, a modified ASTM D4625 Standard Test Method for Distillate Fuel Storage Stability at 43 °C with subsequent peroxide analysis and without analysis of insolubles, and ASTM D7545 Oxidation Stability of Middle Distillate Fuels–Rapid Small Scale Oxidation Test (RSSOT). Fuels were aged using ASTM D4625 which has been reported to correlate well with fuels in field storage [23]. Peroxide concentration of the fuel was tested before aging and prior to addition of antioxidant and then again after the addition of 25 ppm of 2,6-di-*tert*-butyl phenol and subsequent aging at 43 °C. Samples were tested at 13 or 26 weeks. Peroxide testing was performed using ASTM D3703 standard test method for hydroperoxide number of aviation turbine fuels, gasoline and diesel fuels applied to a Mettler Toledo T50 titrator (Mettler-Toledo International, Columbus, Switzerland).

Induction time testing was undertaken by ASTM D7545 using a PetroOxy instrument (PetroTest Instruments, Dahlewitz, Germany) which determines oxidation stability by heating 5.0 mL of fuel at 140 °C under an oxygen atmosphere at 700 kPa. The stability result is the time taken for a 10% drop in the oxygen pressure. The PetroOxy instrument is normally used for diesel fuels, however, when used for a range of jet fuels it has been found to have good repeatability for jet fuel induction period assessment at ±6%. This repeatability value was generated by running the three different fuel samples five times each. Sulfur contents were measured following a method based on gas chromatography–atomic emission detection [24].

2.3. GCMS analysis of antioxidants

Antioxidant concentrations were quantified using an Agilent 7890A-5975C GCMS (Agilent Technologies, Santa Clara, USA) operating in selected ion monitoring (SIM) mode and equipped with a split/splitless inlet and a HP-5 ms column (30 m × 0.25 mm I.D. and 0.25 μm). Automated sample preparation and injection was performed using an Agilent 7693 automatic liquid sampler; 8 μL of internal standard was dosed into 92 μL of sample and mixed at 3000 rpm for 13 s in a bidirectional mixing mode. 0.7 μL injections of sample were made with the autosampler.

The analytical conditions were based on GC–MS–SIM methods described by Bernabei et al. and Morris [25,26]. The measurements were carried out with a 50:1 split and an injection temperature of 250 °C. The oven temperature profile was as follows: an initial temperature of 60 °C, held for 1 min; then 8 °C/min to 130 °C and held for 3 min; 10 °C/min to 171 °C and held for 1 min; and 30 °C/min to 310 °C and held for 3 min. The total run time was

25.5 min. A solvent delay of 11 min was used. The carrier gas was helium and the average velocity was 29.6 cm/s.

The operating conditions of the mass selective detector (MSD) were as follows: the mass transfer line temperature was 280 °C, electron impact ionisation in positive mode (EI+) with 70 eV ionisation energy. The following ions were acquired in SIM mode to measure the concentration of the phenolic antioxidants:

Standard	Ions, <i>m/z</i>
2,6-di- <i>tert</i> -butyl-4-methylphenol	205, 220
2- <i>tert</i> -butyl-4,6-dimethylphenol	135, 163, 178
2,6-di- <i>tert</i> -butylphenol	191, 206, 192
2,4,6-tri- <i>tert</i> -butylphenol	161, 247, 262
2-fluorobiphenyl (internal standard)	83, 141, 169

2.4. MDGC analysis of antioxidants

Heart-cut analyses were carried out on an Agilent 7890A GC with 5975C single quadrupole mass spectrometer (Agilent Technologies, Santa Clara, USA) equipped with a Deans switch assembly. The GC oven was programmed as follows; 60 °C for 1 min, 8 °C/min to 130 °C for 3 min, 10 °C/min to 168 °C for 10 min, then 30 °C/min to 250 °C for 5 min. The multimode inlet was operated in split mode at 50:1 and heated to 250 °C. Helium carrier gas was supplied at constant pressure of 39.51 psi to the primary column, and 26.27 psi to the Deans switch. Separations of 0.2 μL of sample were completed through a HP-5 ms (30 m × 0.25 mm × 0.25 μm) capillary column in the first dimension. The deactivated fused silica restrictor column was 0.64 m × 0.1 mm and the second dimension column was a BPX-90 (30 m × 0.25 mm × 0.25 μm). Mass spectral data were collected in scan/SIM mode, scanning over the range *m/z* = 50–350, and SIM on the ions specified in the previous section.

2.5. GCMS analysis of naphthalene, tetralin and decalin

GCMS was used to determine the concentration of naphthalene, tetralin and decalin in the samples. The experimental conditions were as per Section 2.3 using external calibration with tetralin as a standard. Results were calculated on selected ions for naphthalene, *m/z* 128, tetralin, *m/z* 104 and decalin *m/z* 138.

3. Results and discussion

All fuels were examined for initial antioxidant content and of the four antioxidants examined, only two were observed,

Table 4
Hydroprocessed fuels PetroOxy results with re-addition of antioxidant.

Description of hydrotreated fuel	Age (years in ambient storage)	Sample	Antioxidant (ppm)	Sulfur (ppm)	PetroOxy (time in minutes to 10% loss of oxygen)
Jet A1 fresh refinery 100% HT no AO	0	AO-24	0.0	10.0	361
F-44	2	AO-32	13.5	3.7	346
F-34	7	AO-33	16.8	19.1	349
F-34	1	AO-34	13.1	296.0	294
Jet A1 fresh refinery 100% HT + 20 ppm BHT	0	AO-24-BHT	20	10.0	437
F-44 + 20 ppm BHT	2	AO-32 + BHT	33.5	3.7	407
F-34 + 20 ppm BHT	7	AO-33 + BHT	36.8	19.1	397
F-34 + 20 ppm BHT	1	AO-34 + BHT	33.1	296.0	377
F-44 + 100 ppm BHT	2	AO-32 + 100 BHT	113.5	3.7	649
F-34 + 100 ppm BHT	7	AO-33 + 100 BHT	116.8	19.1	755
F-34 + 100 ppm BHT	1	AO-34 + 100 BHT	113.1	296.0	552
F-44 HMAS Stirling	2	AO-18	6.5	9.2	320

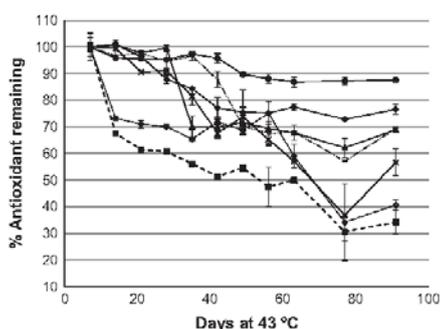


Fig. 1. Antioxidant depletion after re-addition for MEROX fuels. Samples Aging 2 and 3 contained residual antioxidant as per Table 1.

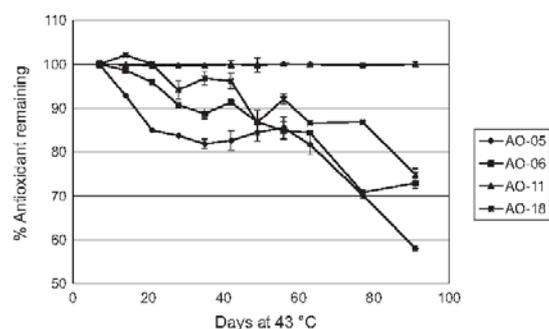


Fig. 2. Antioxidant depletion after re-addition for hydroprocessed F-44 fuels.

2,6-di-*tert*-butylphenol and 2,4,6-tri-*tert*-butylphenol. Re-addition of antioxidant to aged and fresh fuels was examined in three distinct groupings, MEROX, hydroprocessed and F-44. The F-44 samples were examined as a sub-set of the hydroprocessed samples as it was believed they had undergone more severe hydroprocessing.

3.1. MEROX

No peroxides were observed in any of the MEROX fuels prior to aging at 43 °C, as shown in Table 1. It is known that the presence of sulfur compounds can act to reduce peroxide formation by a decomposition process [27,28]. All but one MEROX fuel produced peroxides after 26 weeks storage at 43 °C. The Aging 7 fuel was approximately 6 months old and did not produce measurable peroxides. There was insufficient sample to track peroxide formation at regular time intervals for all of the samples.

The fuels were examined via the PetroOxy test without further addition of antioxidant, with the results in Table 2. There is no current limit set for rating of jet fuel stability by this method; however the long induction times observed for the MEROX fuels are all significantly greater than those for hydroprocessed fuels, Table 4. Thus the rate of oxygen consumption in stressed MEROX fuels is lower than that for hydroprocessed fuels. This result infers that the MEROX fuels still contain significant natural antioxidant capacity even after time in storage. The PetroOxy results for Aging 1 and 3 samples show that the antioxidant package after 17 years still

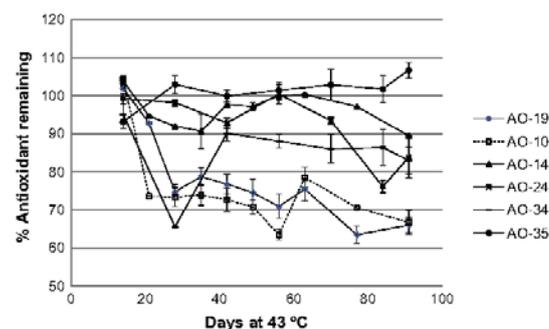


Fig. 3. Antioxidant depletion after re-addition for hydroprocessed F-34 and F-35 fuels.

provides longer induction times, and is more resistant to oxidation than the Aging 1 sample that does not have the military additive package.

The rate of depletion of the synthetic antioxidant was in general greater for MEROX fuels which suggests the synthetic antioxidant is consumed in preference to naturally occurring antioxidant species, Fig. 1. The addition of antioxidant to the aged MEROX fuels has not inhibited the formation of peroxides using 43 °C storage stressing conditions.

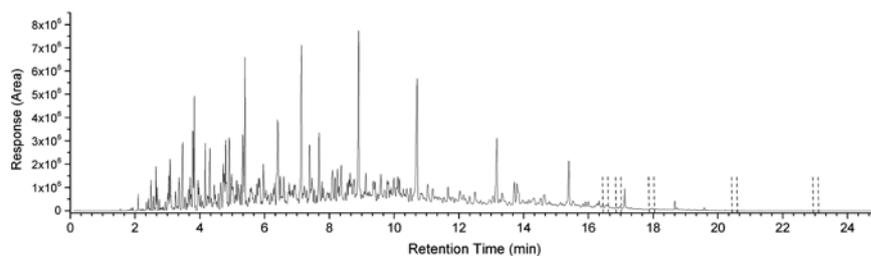


Fig. 5a. First dimension chromatogram of MEROX fuel. Vertical dashed lines indicate heart cut regions corresponding with the retention time of antioxidants.

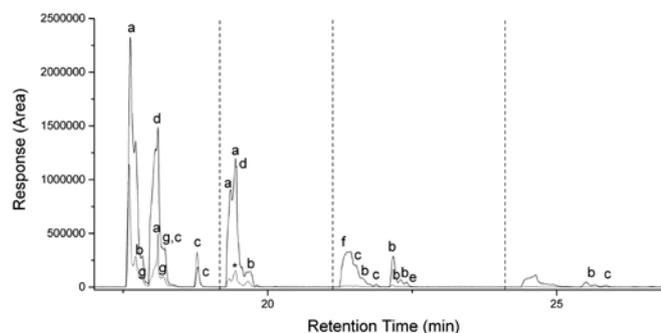


Fig. 5b. Heart cut chromatogram of a MEROX (solid line) and hydrotreated (dotted line) fuel. Vertical dashed lines indicate elution space of four separate heart cut regions. Letters above peaks indicate the class of compound identified; (a) normal or branched alkane, (b) alkyl naphthalene or hydroaromatic, (c) biphenyls, (d) alkyl cycloalkanes, (e) alkyl azulene, (f) alkyl alcohol and (g) alkyl benzenes. Asterisk indicates an antioxidant compound.

and baseline resolution of the compounds of interest is rarely achieved. There is little advantage to be gained by exploiting the polarity of synthetic antioxidant additives, particularly in MEROX or fuels which have been only slightly hydroprocessed and still retain a significant portion of polyaromatic and other polar species that coelute with the compounds of interest under the conditions explored in this study (see Figs. 5a and 5b).

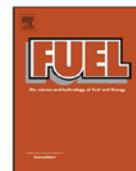
4. Conclusion

The re-addition of antioxidant to a range of MEROX and hydroprocessed fuels subsequently aged at 43 °C was found in general to have little effect on the formation of peroxides. There is little benefit in adding a synthetic antioxidant to a MEROX fuel as they are sufficiently stable as produced. Hydroprocessed fuels all produced measurable peroxides after storage for 13 and 26 weeks at 43 °C, while still having remaining antioxidant, indicating the antioxidant is not effective in inhibiting peroxide formation under these conditions. Stability performance based on oxygen induction times showed that all fuels were improved with re-addition of antioxidant. An unknown fuel's level of hydroprocessing may be best estimated by comparison of its sulfur and decalin contents.

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The oxidative stability of synthetic fuels and fuel blends with monoaromatic blending components



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ABSTRACT

Alternative jet fuels and blends are required to meet a minimum aromatic concentration of 8%. It has been proposed that some monoaromatic compounds may make suitable single component aromatics to meet this minimum. One monoaromatic of interest is *p*-cymene which can be efficiently produced from eucalyptus oil. The oxidative stability of *p*-cymene and a range of monoaromatics blended with a range of alternative fuels are examined. Their oxygen induction times and peroxide formation under accelerated storage conditions are reported. It was found that some monoaromatics can impact final blend stability and that *p*-cymene produces very high levels of peroxides with all fuels examined. It was also observed that the choice of conventional fuel used for blending also influenced the blend stability.

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1. Introduction

With the increasing acceptance of alternative fuel blends by both commercial and military users there has been increased effort to understand the stability characteristics of synthetic fuels and blends made with fuels from conventional crude feedstocks. One mandated property of alternative fuels blends is a minimum aromatic content of the final blend of 8% by volume.

Aromatics are required in jet fuel to ensure compatibility with fuel seals to enable sufficient swelling characteristics [1]. Most conventional jet fuels used for blending are expected to have sufficient aromatic content to ensure a final conventional and synthetic blend will meet the 8% minimum. In situations where this is not the case and for potential future 100% synthetic fuels, an option for ensuring minimum aromatic content is the blending of aromatic compounds into the alternative fuel [2].

One proposed aromatic is *p*-cymene (1-Methyl-4-(1-methylthyl)benzene) which can be produced by a pyrolytic conversion process using cineole extracted from eucalyptus oil as a feedstock. A process for this conversion is reported by Leita et al. [3]. This is an attractive option for indigenous Australian production due to

the availability of eucalyptus feedstock and high yield of the conversion process.

As the current generation of alternative fuels are expected to be blended with conventional fuels up to 50% by volume, the low temperature (140 °C) oxidative stability of a range of blends with and without the addition of *p*-cymene and a range of alkyl monoaromatic compounds was examined. No diaromatics were chosen as they are currently limited to a maximum of 3% in jet fuel and are unlikely to be used in their pure form as aromatic blending components. Also the inclusion of diaromatics to synthetic fuels (synfuels) has been reported to negatively impact synfuel blend's thermal stability [4]. The synfuels available at the time of this study were experimental synfuels and not all met the requirements of ASTM D7566 standard specification for aviation turbine fuel containing synthesized hydrocarbons.

Fuel storage stability may be assessed by a range of techniques including induction times, peroxide formation and sediment formation [5–9]. Those chosen for this study were oxidation induction time and peroxide formation. The influence of aromatic blends on synfuel blend's thermal stability and sediment formation has been examined in detail by DeWitt et al. [4] using a range of aromatic distillate fractions as blending components and deposit formation as an indicator of stability.

It is expected that the influence of aromatic compounds on stability is based on their degree, relative position of alkyl substitutions and the presence of benzylic hydrogens. A range of

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monoaromatics were chosen to examine this influence and to specifically examine *p*-cymene's influence on stability.

Synfuels do not contain natural antioxidant capacity, which is normally derived from trace levels of compounds such as phenols and sulfur heteroatoms and their resistance to oxidative stress as measured by oxygen uptake rates is expected to be lower than conventional fuels [10,11]. It was expected that the naturally occurring antioxidant species in conventional fuels and the synthetic phenolic antioxidants added to hydroprocessed fuels may assist in stabilising the final blends. It has also been previously established that blending of stable and non-stable fuels may improve the final blend stability [12,13].

The distribution of individual aromatics is not normally characterised in jet fuel [14]. Aromatic content is reported only as a total percentage by volume or less often as a total aromatic broken down into mono, di and poly aromatic fractions.

This study examines the impact of individual mono-aromatic compounds on the stability of conventional and synfuel blends and the stability of synfuels blended with conventional fuels without further addition of an aromatic component.

2. Experimental

The following experiments were undertaken to examine synfuel blend stability and the influence of single monoaromatics on stability.

- Blending of *p*-cymene at 0%, 8%, 16% and 24% v/v with a range of conventional and synthetic fuels with PetroOxy stability testing.
- Blending of a range of individual mono-aromatics at 16% v/v with a range of conventional and synthetic fuels with PetroOxy stability testing.
- Blending of conventional fuels with synthetic fuels without further addition of aromatics with subsequent PetroOxy and low pressure reactor stressing with peroxide testing.

To assist in understanding the impact of inclusion of high concentrations of a single component mono-aromatic, the natural abundance of the test aromatic compounds was measured for a set of jet fuels taken from in-service bulk tankage. All of the single component aromatics used in this study were found to occur naturally in the fuels examined.

2.1. Synthetic fuel samples

Synthetic fuels were received from a range of sources and are described in Table 1.

Samples of current generation alternative fuels were procured and where not available were generated. The butene oligomer and FT-GTL products were synthesized by local university research groups.

The FT-GTL synfuel was un-hydrotreated and contained approximately 75% *n*-paraffins, 5% iso-paraffins and 20% *n*-olefins of which 10% were 1-olefins. It was included to examine the impact of an un-hydroprocessed FT-GTL and what may be expected of its stability characteristics. All other synfuels samples were experimental fuels and not production batches. The synfuels synthetic phenolic antioxidant content was measured before blending. The results are reported using a gas chromatographic triple quadrupole mass spectrometry method [15]. A chromatogram of the synfuels is given in Fig. 1 to compare profiles which are each consistent with distillation characteristics of the respective fuels.

The two conventional jet fuels used for blending with the synthetic components were taken from known sources. The first from an in-service military base that was delivered from a refinery known to hydrotreat (JP-8-HT) and the second a Jet A-1 from a local refiner known to use a Merox finishing process (Jet A-1 – Merox).

Iso-par M and dodecane were included in the trial to examine the response of the synthetic components to known *n*-paraffin and iso-paraffins that contained no antioxidant.

2.2. Monoaromatics

The single component aromatic compounds were obtained from Sigma-Aldrich (Castle Hill, NSW, Australia). Aromatics chosen where, *p*-cymene, *o*-xylene, ethylbenzene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene.

2.3. Experimental methods

Two methods were used to assess the fuel's storage stability. Induction time testing was undertaken by ASTM D7545 using a PetroOxy (Anton-Paar) instrument which determines a fuel's oxidation stability by heating 5 mL of fuel at 140 °C under an oxygen atmosphere. The stability result is the time taken for a 10% drop in the oxygen pressure. The PetroOxy is normally used for diesel fuels, however, when used for a range of jet fuels it has been found to have good repeatability for jet fuel induction period assessment at ±6%. This repeatability is based on our laboratory experience with repeated samples.

Blends were stressed and peroxide content measured based on a process described by Pande et al. using a low pressure reactor (LPR) at 100 °C with 500 kPa air overpressure for 16 h with subsequent peroxide measurement [16,17]. Peroxide testing was

Table 1
Summary of jet fuel samples used in this study.

Sample	Feedstock	Processing/refining method	Dominant component(s)	Total synthetic phenolic antioxidant, (mg/L)
Bioderived SPK	Camelina	Hydroprocessed esters of fatty acids	Mixed <i>n</i> /iso - paraffins from C8–C16	14.8
HT-IPK	Coal/syngas	High temperature Fischer–Tropsch	Mixed normal/iso paraffins C8–C16	12.3
HRJ	Algae	Hydroprocessed esters of fatty acids	Mixed normal/iso paraffins C9–C17	10.1
A2J	Biogenic isobutanol	Alcohol to jet	C12 and C16 iso-paraffins	NIL
FT-GTL	Natural gas	Un-hydrotreated Fischer–Tropsch	<i>n</i> -alkane + alkene mix C8–C17	NIL
Butene oligomer	Butene	Hydroprocessed oligomer	C12, C16, C20 iso-paraffins	NIL
Algae JP5	Algae	Hydroprocessed esters of fatty acids JP-5	C15–C18 <i>n</i> -paraffins plus iso-paraffins	NIL
DSH	Algae	Direct sugar to hydrocarbon	2,6,10-trimethyldodecane	NIL
Jet A-1 – Merox	Fossil	Merox	Conventional jet fuel	NIL
JP-8 – HT	Fossil	Hydroprocessed with military additives	Conventional jet fuel	14.2
Iso-par M	Fossil	Purified synthetic iso-paraffins	Iso-paraffins	NIL
Dodecane	Fossil	Sigma-Aldrich	C12	NIL

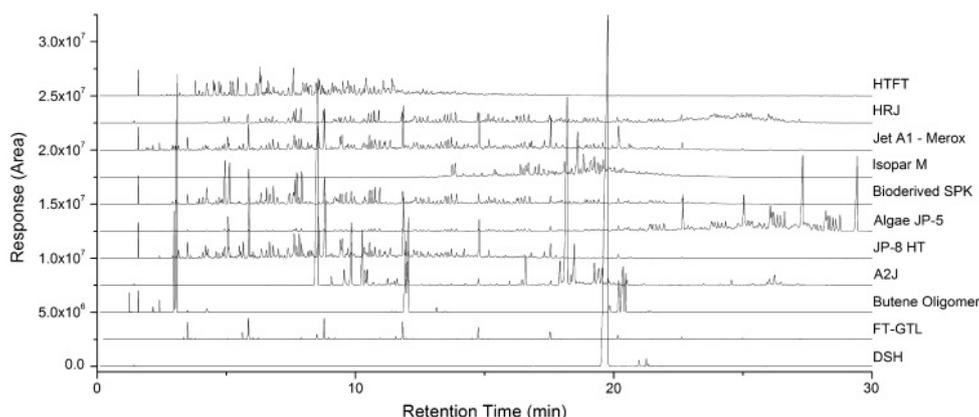


Fig. 1. Overlaid chromatograms of synfuels and conventional fuels.

performed using ASTM D3703 standard test method for hydroperoxide number of aviation turbine fuels, gasoline and diesel fuels applied to a Mettler Toledo T50 titrator (Mettler-Toledo International, Columbus, Switzerland).

Samples of neat aromatics were stressed in the PetroOxy and were examined by GCMS to determine the range of oxidation products formed during the stressing process.

2.3.1. Gas chromatography–Mass spectrometry

The aromatic components of interest were analysed by gas chromatography with mass spectrometry (GC–MS). Analyses were carried out on an Agilent 7890A-5975C (Agilent Technologies, Santa Clara, CA, USA) gas chromatograph-mass spectrometer. Operating parameters of the GC–MS system are given in Table 2. The mass spectrometer was operated in selected ion monitoring (SIM) and scan mode, with quantitation on the SIM ions for each analyte of interest. The concentration of the aromatic compounds was determined in both neat and thermally oxidised fuel samples via a multi-point external standard calibration. Each sample was run on a slightly polar 5% phenyl column as well as a polar wax column, in order to conduct a thorough investigation of the oxygenated compounds generated. MSD Chemstation version E.02.00 was used for data collection and MassHunter version B.07.00 for data processing.

3. Results and discussion

The aromatic compounds were tested in the PetroOxy to establish a baseline for their stability prior to blending with the synthetic and conventional fuels, Fig. 2. The *p*-cymene was found to have a very short induction time of 32 min. The lower stability of the *p*-cymene can be explained due to the tertiary carbon adjacent

to its aromatic ring. This tertiary carbon is much more susceptible to oxidation than primary carbons under similar conditions. Secondary carbons, such as for the ethylbenzene also show this susceptibility [18].

The differences between the stability of the 1,2,4- and 1,3,5-trimethylbenzenes was significant. The oxidation rate of trimethylbenzenes has been observed to follow the order 1,2,3 > 1,2,4 > 1,3,5-trimethylbenzene [19,20]. This supports our observations of lower stability of 1,2,4 vs 1,3,5-trimethylbenzene based on oxygen induction times [21]. This appears to be related to the number of adjacent methyl pairs versus unreactive isolated methyl pairs as discussed by Silva [22]. Silva observed that reactivity was greatly enhanced as shown by a decrease in RON from 1,2,3 < 1,2,4 < 1,3,5-trimethylbenzene. Similar results were observed from toluene, *o*-xylene showing the effect of substitution and the location of substituents on the ring. Morley and Westbrook also describe the relationship between RON and ease of oxidation [23,24].

The stability of alkyl aromatics to oxidation initiated by a hydroperoxide pathway has been examined by Zabarnick et al. Formation of the initial hydroperoxide is dependent on the ease of abstraction of the compound's benzylic hydrogen. Ethylbenzene was found to produce hydroperoxides at lower temperatures than dodecane highlighting that benzylic hydrogens on alkyl aromatics are more reactive than paraffinic hydrogens. Zabarnick's work found that in jet fuels the oxidation pathways are mainly due to

Table 2
GC–MS conditions and operating parameters.

Columns	HP-5, Innowax
Length/ID/ <i>d_f</i>	30 m/0.25 mm/0.25 μm
Oven	50 °C ↑ 200 °C (5 °C/min)
Injector	280 °C
Inj. vol./split ratio	0.1 μL/100:1
Carrier gas	He
Flow; velocity	1.2 mL/min; 39.92 cm/s
Transfer line	280 °C
Ionisation	EI, 70 eV
Quadrupole; source T	150 °C; 230 °C

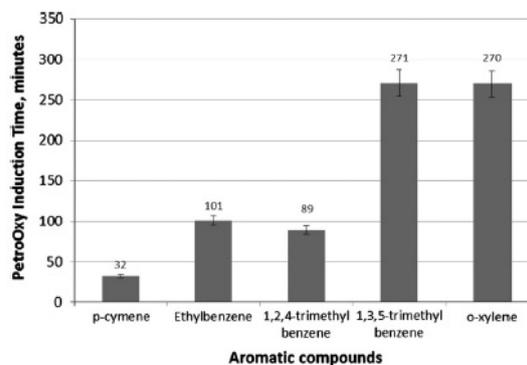


Fig. 2. Induction times for single component aromatics.

alkyl aromatic oxidation and that the normal approximate 80% concentration of paraffins in jet fuel can be considered unreactive with respect to peroxy radical reactions [21,25]. Zabarnick's work highlights the importance of understanding oxidation of potential single component aromatic blending components.

The main products of oxidation of di- and poly-alkylbenzenes are generated via a hydroperoxide pathway which goes on to produce aryl alcohols and aryl aldehydes and ketones. These can go on to be oxidised to the corresponding aryl acid [26]. Detailed GCMS analysis of the aromatics post oxidation in the PetroOxy supports at least the first part of this proposal, however no acids were found in any of the post PetroOxy samples. Under the stress conditions examined and without the presence of a catalyst to promote hydroperoxide decomposition the autoxidation reactions do not go on to form acidic degradation products.

No substitution of the aromatic ring was observed with only formation of aldehydes and alcohols on single alkyl groups observed. There was also evidence of a competing reaction to the ongoing hydroperoxide propagation process where a number of diaryl compounds were observed. These may be due to terminating chain reactions during the hydroperoxide propagation phase.

3.1. *p*-cymene blending – induction times

As *p*-cymene was the main aromatic examined in this study its impact on stability was measured over three concentrations being 8%, 16% and 24% v/v (Fig. 3). The changes in induction times due to the addition of *p*-cymene varied across the synfuels and conventional fuels. The synfuel showing the most impact was the FT-GTL which contained un-hydroprocessed olefins in the final blend. Olefins have long been known to have a significant negative impact on fuel stability especially in the presence of peroxides [27–30].

No general trend can be noted based on distributions of iso to normal-paraffinic compounds in the synfuels. The addition at 24% *p*-cymene has in most cases decreased the blend stability based on oxygen consumption rates.

The reactivity of the *p*-cymene is due to the ease of abstraction of its benzylic hydrogens. It has been shown that the isopropyl group of *p*-cymene is oxidised in preference to the methyl group and that oxidation of an alkyl benzene normally produces the corresponding carbonyl compound via a hydroperoxide formed at the alpha position on the aromatic ring [26,31]. The reactivity of the alpha-methylnic hydrogen for cymene has been compared to that of toluene at ratio of 4.1:1 at 85 °C [32], albeit metal-catalysed.

An increase in the number of similar substituent groups on the benzene ring typically considerably increases the ease of oxidation of aryl-aliphatic hydrocarbons but the introduction of a methyl group in the para position to a substituent with a tertiary alpha carbon atom apparently diminishes the oxidisability of the hydrocarbon [33].

GCMS analysis of the oxidation products of *p*-cymene found the following compounds, *p*-cymene-8-ol, *p*-cymene-7-ol, *p*-isopropylbenzaldehyde, 4-methylacetophenone and 4-methyl- α -methylstyrene as degradation products. The 4-methylacetophenone can be explained by a degradation mechanism proposed by Mushrush et al. for cumene hydroperoxide where the hydroperoxide initially undergoes homolytic cleavage then a subsequent beta-scission during the propagation phase [34].

3.2. Monoaromatic blends with fuels

The individual mono-aromatics were blended at 16% with the conventional and synfuels, Fig. 4. The Isopar M and dodecane stabilities were improved by addition of the aromatics. The degree of branching of the alkane had some impact on the stability as the dodecane blends all had longer induction times when compared with the iso-paraffinic Isopar M. This is true also for the iso-paraffinic butene oligomer. The DSH synthetic is comprised of mostly a single component farnesane (2,6,10-trimethyldodecane) and shows little response to most aromatics other than the 1,3,5-trimethylbenzene. There was a general trend for improved stability across all of the synfuels when blended with 1,3,5-trimethylbenzene. Blending aromatics into conventional fuels has decreased final stability in all cases except for 1,2,4-trimethylbenzene.

The general trend is that the addition of single component aromatics to the synthetic fuels has improved stability with 1,3,5-trimethylbenzene offering the largest stability increase and *p*-cymene the lowest. It was observed that this is not the case for conventional fuels JP-8-HT and Jet A-1 – Merox, where there was a general decrease in stability. These fuels already contained naturally occurring level of aromatics at 17.6% and 19.2% v/v respectively thus bringing the totals to 33.6% and 35.2% v/v for the test blends which is above the 25% v/v maximum. An aromatic blend of 16% v/v was chosen as it lies midway between the synfuel 8% minimum and the 25% maximum allowable in most jet fuel specifications.

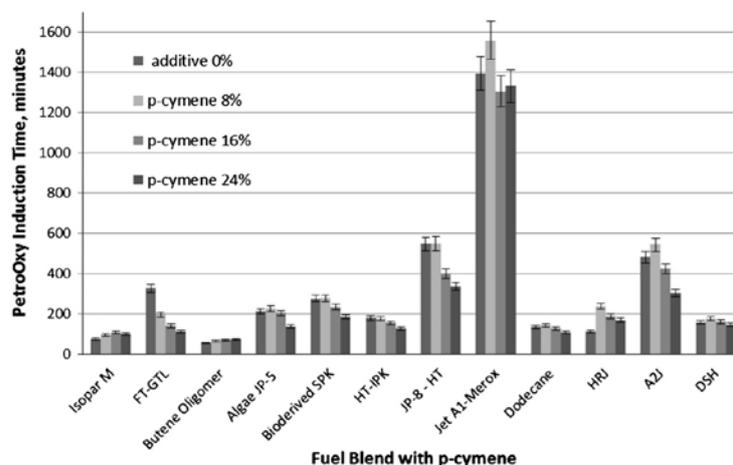


Fig. 3. Induction times for fuels blended with *p*-cymene at 0%, 8%, 16% and 24%.

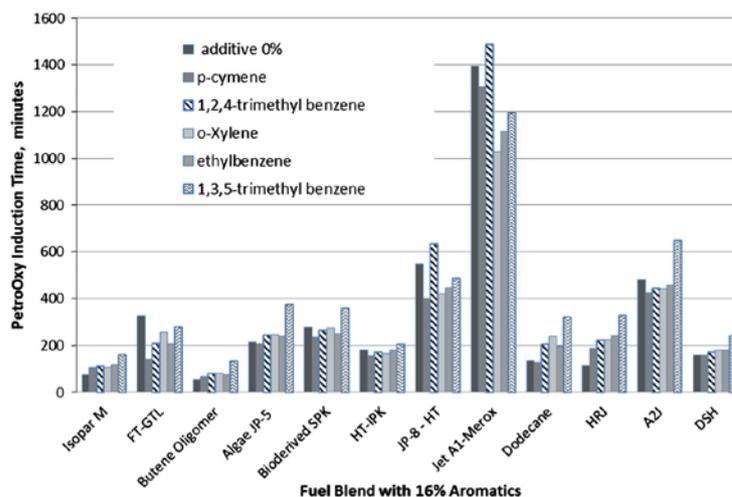


Fig. 4. Induction times for fuels blended with a range of single component aromatics at 16%.

Whilst deposit formation was not examined as a measure of storage stability in this study, Taylor observed that for thermal stressing temperatures of 93–177 °C the addition of 10% aromatics to paraffinic fuels tends to inhibit deposit formation [35,36]. Stability improvement was related to the number of benzylic hydrogen atoms in the aromatic compound. The type and number of alkyl additions to the benzene ring in monoaromatics influences the alkyl aromatics stability characteristic with respect to hydroperoxide formation and propagation. This is influenced by the stronger inductive effect that longer alkyl groups have versus methyl groups. Howard and Ingold reported a range of alkyl aromatic compound reactivities of the alpha hydrogen atoms toward abstraction by three different radicals and reported increased reactivities for ethylbenzene and cymene over toluene [37].

3.3. Conventional fuel blends with synfuels and p-cymene

As both of the conventional fuels used in this study (JP-8-HT and Jet A-1 – Mercox) contained sufficient aromatics to meet the minimum 8% at 50:50 blending ratios the stability of these fuels

blended at 50% with the synfuels was examined without further addition of aromatics (Figs. 5 and 6).

Blending with 50% synfuel has little impact on induction times of the Mercox fuel. This suggests that fuels containing a normal distribution of naturally occurring antioxidants may have sufficient antioxidant capacity to ensure good stability of blended finished fuels.

The JP-8-HT has shown a decreased stability of the blends except for the A2J blend. This fuel contains low level of naturally occurring phenolic antioxidants and has a total sulfur content of only 9.9 mg/L, consisting of benzothiophenes and dibenzothiophenes. For comparison the Jet A-1 – Mercox has a total sulfur content of 1175 mg/L. The natural phenolic content of the JP-8-HT was measured as per a method described by Abdallah et al. [38] at 44 ppm total phenolics. The main stabilisation of this fuel is provided by its synthetic phenolic antioxidant. The rapid autoxidation of hydroprocessed fuels with low concentrations of natural antioxidants has been described by Jones [39].

The Jet A-1 – Mercox: synfuel blends were found to remain relatively stable with only the A2J and HT-IPK generating measurable

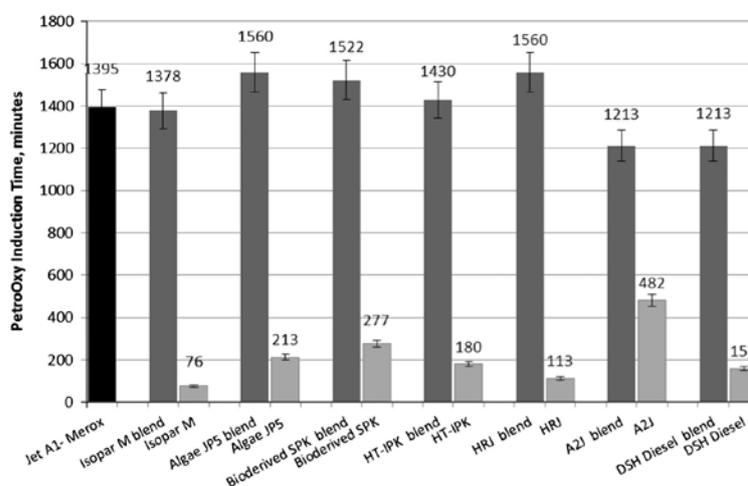


Fig. 5. Induction times for synfuels blended at 50% with Jet A1-Mercox conventional fuel.

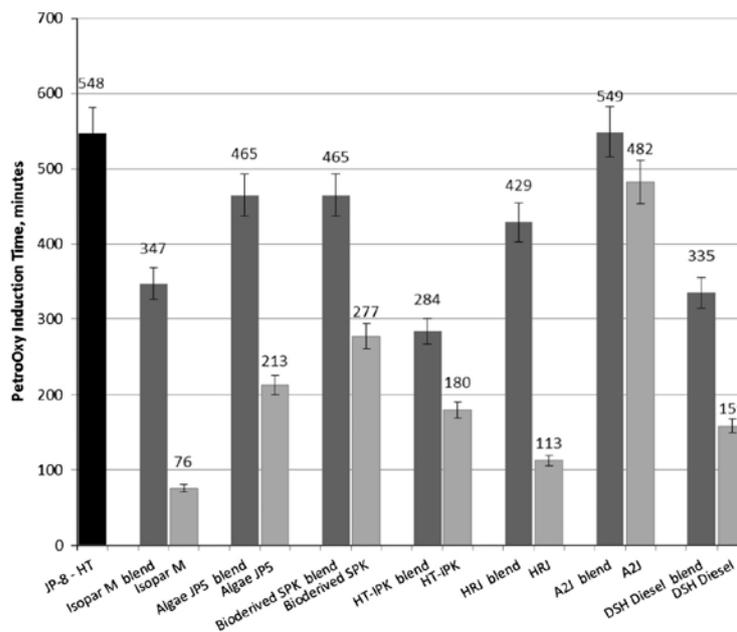


Fig. 6. Induction times for synfuels blended at 50% with JP-8-HT conventional fuel.

peroxides. The JP-8-HT: synfuel blends produced measurable levels of peroxides for all of the synfuel blends, this suggests a possible reduced capacity for blending of less stable synfuels with conventional fuels that are stabilised by only a synthetic phenolic antioxidant.

As the influence of *p*-cymene on final fuel blends was of specific interest in this study a second experiment was conducted using the conventional fuels with the addition of *p*-cymene. It was added to the two conventional fuels at 16% knowing this would increase the total aromatic content of the blends. The 16% *p*-cymene addition has given a total aromatic content of 25.6% and 24.8% for the Jet A1 Mercox and the JP-8-HT respectively.

When 16% *p*-cymene was blended with the conventional: synfuel mixtures there was a dramatic increase in peroxide concentration (Figs. 7 and 8). These very high levels of peroxides generated in both conventional fuel series is due to the ease of formation of the peroxide at the tertiary carbon on the *p*-cymene molecule. The peroxide concentration is well above the previous limit of 7 mg/kg which was controlled in USN JP-5 specification MIL-DTL-5624U [40]. The peroxide concentration was higher for all blends

with the JP-8-HT fuel. The Mercox fuel is normally stable due to its natural antioxidant phenolic and residual peroxide-decomposing sulfur compound contents. Even so, blending with reactive *p*-cymene and synfuel overcomes this stability [41,42]. The Mercox fuel has also been able to inhibit peroxide formation in all blends except for the HT-IPK. Its strong antioxidant potential is apparent for the A2J fuel which had an initial peroxide content of 31.1 mg/kg and was lowered to 1.5 mg/kg after stressing, Fig. 8.

While peroxide content is no longer controlled in aviation fuels their formation is well established in the pathway for oxidative degradation of hydrocarbon fuels [10,11,43–48]. These concentrations of peroxides would be highly damaging to aircraft fuel systems and fuel handling systems [49]. The *p*-cymene addition at 16% is significant and lower concentrations added only to meet the required 8% minimum for the final blends may be less prone to peroxide formation. This is an area for further investigation if *p*-cymene is to advance as a proposed single component blending aromatic. The impact of blending synthetic fuels and *p*-cymene at 16% was examined, Figs. 7 and 8.

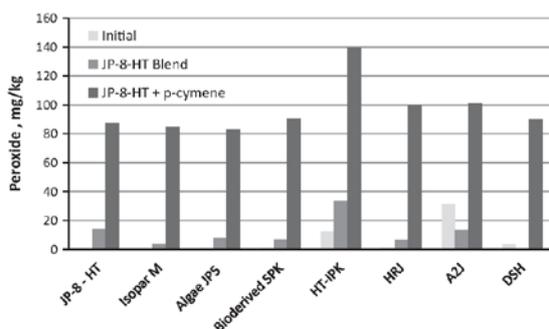


Fig. 7. Peroxide content of fuels post-low pressure reactor stressing for JP-8-HT fuel blends.

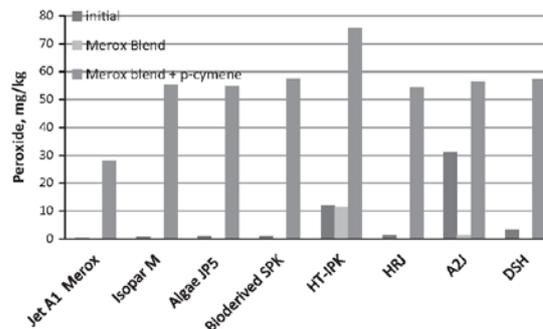


Fig. 8. Peroxide content of fuels post-low pressure reactor stressing for Jet A1 Mercox fuel blends.

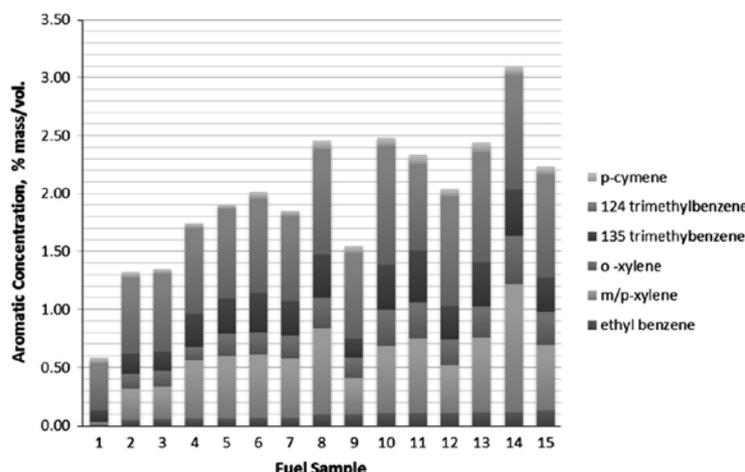


Fig. 9. Natural abundance of the single component aromatic compounds used in this study measured in a range of in-service jet fuels. Note the relative standard deviations ranged between 7.4% and 9% for individual aromatics.

3.4. Natural abundance of selected aromatics in conventional fuels

The aromatic blending components examined were found to be all naturally occurring in a range of 15 in-service jet fuels (Fig. 9). The fuels were found to contain a wide distribution of the aromatics with the abundance following the series 1,2,4-trimethylbenzene > *m/p*-xylene > 1,3,5-trimethylbenzene > *o*-xylene > ethyl benzene > *p*-cymene in most cases. Sample 9 in Fig. 7 in the series was known to have undergone hydroprocessing which may have impacted the concentration of some of the alkylbenzenes. The meta and para xylenes co-eluted for the GC method used and are reported as a combined concentration. The single aromatic compounds quantified for these fuels cover the range 0.058–2.232%, Fig. 9 which corresponds to a significant quantity of the maximum allowed 25% total aromatics in jet fuel. Given the influence of aromatic compounds to a jet fuels stability further examination of the distribution of monoaromatic compounds in middle distillates may be warranted.

4. Conclusions

When considering blending monoaromatic compounds into synthetic fuels, all aromatics examined, and especially *p*-cymene, impact the final blend stability after subsequent blending with hydroprocessed fuels. The severity of the impact depends on the concentration of the addition and the normal to iso-paraffinic ratio of the synfuel. The formation of hydroperoxides in synfuel blends with *p*-cymene was significant and blending of lower concentrations of *p*-cymene should be examined in more detail. The trialkyl aromatic 1,3,5-trimethylbenzene tended to have the most beneficial effect on final blend stability with respect to induction times. Conventional fuel, be it Mercox versus hydroprocessed, can impact the final blend stability. Mercox fuels were found to be the more stable and hydroprocessed blends less stable, in terms of the rate of initial oxidation as measured by the PetroOxy induction times.

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