The pre-separation of oxygen containing compounds in oxidised heavy paraffinic fractions and their identification by GC-MS with Supersonic Molecular Beams.

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Abstract

The heavy petroleum fractions produced during refining processes need to be upgraded to useable products to increase their value. Hydrogenated heavy paraffinic fractions can be oxidised to produce high value products that contain a variety of oxygenates. These heavy oxygenated paraffinic fractions need to be characterised to enable the control of oxidation processes and to understand product properties. The accurate identification of the oxygenates present in these fractions by electron ionisation (EI) mass spectrometry is challenging due to the complexity of these heavy fractions. Adding to this challenge is the limited applicability of EI mass spectral libraries due to the absence of molecular ions from the EI mass spectra of many oxygenates. The separation of oxygenates from the complex hydrocarbon matrix prior to high temperature GC-MS (HT-GC-MS) analysis reduces the complexity of these fractions and assists in the accurate identification of these oxygenates. Solid Phase Extraction (SPE) and Supercritical Fluid Chromatography (SFC) were employed as pre-fractionation techniques. GC-MS with Supersonic Molecular Beams (also named GC-MS with Cold-EI) utilises a supersonic molecular beam (SMB) interface with which electron ionisation is done with vibrationally cold sample compounds in a fly-through ion source (Cold-EI) resulting in a substantial increase in the molecular ion signal intensity in the mass spectrum. This greatly enhances the accurate identification of the oxygenates in these fractions. This study investigated the ionisation behaviour of oxygenated compounds using Cold-EI. The pre-fractionation by SPE and SFC and the subsequent analysis with GC-MS with Cold-EI was applied to an oxygenated heavy paraffinic fraction.

Keywords: Mass Spectrometry with Supersonic Molecular Beam, Solid Phase Extraction, Supercritical Fluid Chromatography, oxygen-containing compounds, heavy paraffinic fractions.

1 Introduction

To increase the value of heavy petroleum fractions produced during crude and synthetic crude oil refining processes, these fractions need to be upgraded to useable products. Usually these heavy fractions are upgraded into fuel products by hydrocracking, hydroisomerisation and hydrogenation processes. These fractions are also used to produce other high value commercial products like lubricant oils and waxes by distillation, hydrogenation, oxidation and blending [1 - 5]. Oxidation of hydrogenated heavy paraffinic fractions produces high value products that contain a variety of oxygenates and heavy paraffinic fractions that are used in various applications like plastics, rubber, leather, paper, inks and textiles [5]. The characterisation of these heavy oxygenated paraffinic fractions is very important for the control of oxidation processes and to understand the properties of the products, but presents a difficult analytical challenge. The first challenge in the characterisation of these fractions is that only a limited carbon number range of these oxygenates can be analysed directly by gas chromatography (GC) and this challenge is further compounded by the complexity of these samples. The number of hydrocarbon isomers significantly increases with increasing carbon number, adding to the complexity of these heavy oxidised paraffinic fractions [6]. The high number of compounds as well as the reduced chromatographic separation at high-temperature conditions results in inevitable co-elution of peaks [7].

The second challenge is the accurate identification of the oxygenates present in these heavy oxidised paraffinic fractions by electron ionisation (EI) mass spectrometry. The use of EI mass spectral libraries for identification are of limited applicability since the mass spectra of most of these heavy oxygenates are not available. Furthermore, the absence of the molecular ions (M^+) from the EI mass spectra and the similarity of the prominent smaller fragment ions of most of these oxygenates within a specific oxygenate class complicate their identification via classical mass spectral interpretation rules. The presence of molecular ions or characteristic high mass fragments in the mass spectra of these heavy oxygenates are essential for their identification [8 - 9].

Many attempts have been made to address the challenge of extending the range of heavy molecules that can be analysed by GC with high-temperature gas chromatography (HT-GC). In HT-GC, heavy molecules are not derivatised prior to GC analysis but their elution is improved by the extension of the conventional separation temperature and the adaptation of chromatographic conditions [6, 10]. Although the difference between GC and HT-GC is not well defined, various authors agree that HT-GC refers to separations with final temperatures higher than 340°C [6, 10]. The use of HT-GC instrumentation, column and stationary phase technologies are critical for analysis at these high temperatures. Metal columns or fused silica columns with a special protective coating are required to withstand these high temperatures [11]. Alternatively, the use of short columns with high column flow rates and Cold-EI can serve to extend the range of compounds amenable for GC-MS analysis [12] and hydrocarbons up to $C_{86}H_{174}$ were analysed by Cold-EI with abundant or dominant molecular ions [13]. The extension of the molecular weight range that can be analysed by HT-GC also involves the adaptation of chromatographic conditions that includes the use of short wide bore columns with a reduced film thickness, the latter to achieve lower elution temperatures due to the high phase ratio. HT-GC is already an established technique and allows for the analysis of a wide molecular weight range (~100 to >1400 Da, equivalent to alkanes from C7 to >C100) [10, 14].

Multidimensional chromatographic systems have been used to address the complexity of heavy oxidised paraffinic samples and the peak co-elution observed when analysed by GC. High temperature comprehensive two-dimensional gas chromatography (HT-GC×GC) was used to increase peak capacity and analyse complex heavy petroleum samples [6, 15 - 22].

Another way of reducing the sample complexity prior to HT-GC analysis is to apply a fractionation step prior to the analysis by GC [23 - 27]. Solid-phase extraction (SPE) is one of the most widely used methods for extraction, sample clean-up, analyte concentration, and fractionation of organic compounds from a number of sample matrices [28 - 30]. HPLC fractionation has also been used extensively [18, 25 - 26] and various methods utilising supercritical fluid chromatography (SFC) as an on-line fractionation step were published [27, 31 - 32]. Venter et al. [33] reported the group-type analysis of oxygenated compounds with a silica gel porous layer open tubular (PLOT) column combined with comprehensive two-dimensional SFC and GC (SFC×GC) as a means of oxygenate separation and identification. The separation of oxygenates from the complex hydrocarbon matrix prior to HT-GC-MS analysis reduces the complexity of oxygenated heavy paraffinic fractions and will assist in the accurate identification of these oxygenates. Hence SPE and SFC were employed in this study for the pre-fractionation of oxygenates.

The GC-MS with Cold-EI (GC-SMB-MS) was developed by Amirav and co-workers [9, 34 - 35] and utilises a supersonic molecular beam (SMB) interface between the GC and the MS and a fly-through EI ion source [36] for the electron ionisation of vibrationally cold molecules in the SMB (Cold-EI). This results in a substantial increase in the molecular ion intensity in the mass spectrum [8 - 9, 34]. GC-MS with Cold-EI has many beneficial features with the enhanced molecular ion that is observed in the mass spectra [8 - 9, 13], even for very large hydrocarbons [9, 13, 34], being the most significant for this study. Given the lack of molecular ion information in conventional EI the enhanced molecular ion obtained with the use of Cold-EI allows the accurate identification of the oxygenates present in heavy oxidised paraffinic fractions. Research groups have also reported the use of pulsed flow modulation GC×GC-MS with SMB for the analysis of complex petrochemical samples [37 - 38].

In this study the ionisation behaviour of various oxygenated compound classes were investigated using Cold-EI. Using pre-fractionation of the oxygenates by SPE and SFC and subsequent analysis on GC-MS with Cold-EI, the characterisation of oxygenates in oxidised heavy paraffinic fractions was investigated.

2 Materials and methods

2.1 Chemicals

Analytical gases for the SFC and GC-MS with Cold-EI were obtained from Afrox (South Africa). A standard mixture consisting of the components listed in Table 1 was prepared in cyclohexane at a concentration of 0.5 % (w/w) of each compound. This standard mixture was utilised to investigate the ionisation behaviour of these compounds on the GC-MS with Cold-EI. This standard was also utilised for the optimisation of the pre-fractionation procedures. The standards and cyclohexane were obtained from Sigma Aldrich (St Louis, MO, USA). A hydrogenated heavy paraffinic fraction was oxidised in the laboratory and used in the pre-fractionation experiments.

Table 1. Standards used to determine the Cold-EI mass spectra and for the optimisation of the pre-fractionation procedures.

Alkanes	*Ester*	*Carbonyls*	*Alcohols*
(a) n-Eicosane ($C_{20}H_{42}$) MW: 282	(e) Hexadecyl Dodecanoate ($C_{28}H_{56}O_2$) MW: 424	(i) 2-Octadecanone ($C_{18}H_{36}O$) MW: 268	(n) 1-Tridecanol ($C_{13}H_{28}O$) MW: 200
(b) n-Docosane ($C_{22}H_{46}$) MW: 310		(j) 8-Pentadecanone ($C_{15}H_{30}O$) MW: 226	(o) 1-Tetradecanol ($C_{14}H_{30}O$) MW: 214
		(k) 16-Hentriacontanone ($C_{31}H_{62}O$) MW: 450	(p) 1-Hexadecanol ($C_{16}H_{34}O$) MW: 242
Alkene	*Acids*	(l) n-Docosanal ($C_{22}H_{44}O$) MW: 324	(q) 1-Heptadecanol ($C_{17}H_{36}O$) MW: 256
(c) 1-Eicosene ($C_{20}H_{40}$) MW: 280	(f) Undecanoic Acid ($C_{11}H_{22}O_2$) MW: 186		(r) 1-Octadecanol ($C_{18}H_{38}O$) MW: 270
	(g) Tetradecanoic Acid ($C_{14}H_{28}O_2$) MW: 228	*Diol*	(s) 1-Eicosanol ($C_{20}H_{42}O$) MW: 298
Ether	(h) Arachidic Acid ($C_{20}H_{40}O_2$) MW: 312	(m) 1,12-Octadecandiol ($C_{18}H_{38}O_2$) MW: 286	(t) 1-Tetracosanol ($C_{24}H_{50}O$) MW: 354
(d) Didecyl-Ether ($C_{20}H_{42}O$) MW: 282			(u) 1-Docosanol ($C_{22}H_{46}O$) MW: 308
			(v) 2-Octyl-1-dodecanol ($C_{20}H_{42}O$) MW: 298

2.2 Heavy paraffinic fraction oxidation

The oxidised heavy paraffinic fraction sample was prepared according to the procedure described in a previous study [15] whereby a bubble column type reactor was used to oxidise a heavy paraffinic fraction with air containing 21.2 % oxygen. The hydrogenated heavy paraffinic fraction sample (800 g) was loaded into the reactor and air was passed through the system at a low flow rate until the required oxidation temperature was reached (160 ºC). The air flow rate was then adjusted to 1.8 L/min for the remainder of the experiment (300 min). The reaction product was used in the pre-fractionation experiments.

2.3 GC-MS with Cold-EI method

The GC-MS with Cold-EI instrument was a 7890A gas chromatograph (GC) coupled to an Agilent 5975 mass selective detector (MSD), (Agilent Technologies, Santa Clara, USA) that was converted into GC-MS with Cold-EI with an Aviv Analytical (Tel Aviv, Israel) 5975 SMB Supersonic Molecular Beam interface (SMB) and its Cold-EI fly-through ion source. A Multimode injector (Agilent Technologies, Santa Clara, USA) was used on this system and was programmed from 40 °C (0 min) to 400 °C at 100 °C/min and kept at this temperature for 30 min. Helium was used as the carrier gas at 4 mL/min for 23 min after which it was increased at 3 mL/min^2 to 28 mL/min for faster elution of heavy compounds and kept at this flow rate for 5 min. A split ratio of 10:1 and injection volume of 0.5 µL was used for the analysis of the fractions collected from the SPE experiments whilst the liners from the SFC experiments were desorbed in splitless mode. Samples were introduced manually onto a MXT-1 column (15 m x 0.28 mm, 0.15 µm) from Restek (Bellefonte, USA). The oven was programmed from 40 °C held for 2.0 min to 400 °C at 2 °C/min and kept at the final temperature for 12 min. The Cold-EI transfer line temperature was 300 °C (23 min) and was subsequently increased at 10 °C/min to 350 °C and kept at this temperature for 22 min. Samples were analysed using an electron energy of 70 eV. The SMB helium make-up flow was 90 mL/min. The MS scan range was 45 – 1050 Da at 1.5 scans/sec. Samples and standards were also analysed with conventional EI for comparative purposes, especially in cases where National Institute of Standards and Technology (NIST) library mass spectra were not available for the compounds studied.

2.4 SPE pre-fractionation.

The standard from Table 1 was diluted further to a concentration of 100 µg/g per component and 1 mL of this standard solution was applied to the SPE cartridge. The oxidised heavy paraffinic fraction sample (0.1 g) was dissolved in cyclohexane (10 mL) and 2 mL of this sample was applied to the SPE cartridge. A Sep-Pak silica plus long cartridge from Waters (Massachusetts, USA) with 690 mg sorbent per 5 mL cartridge and 55-105 µm particle size was used. The SPE protocol consisted of the following steps:

1. Conditioning: 4 x 4 mL of acetone followed by 4 x 4 mL of hexane.
2. Loading: 1 mL of the standard solution or 2 mL of the oxidised heavy paraffinic fraction sample solution.
3. Washing: 5 x 4 mL hexane.
4. Elution: 4 mL acetone.

The recovered fraction was evaporated at room temperature and re-dissolved in 0.2 mL cyclohexane before injecting into GC-MS with Cold-EI system.

2.5 SFC pre-fractionation

A Selerity Series 4000 SFC system equipped with SFC pump, SFC oven, a pneumatically actuated rotary injection valve and a flame ionisation detector operated at a temperature of 400 °C was used for the pre-separation and detection of the oxygenates (Selerity Technologies, Utah, USA). In order to achieve the pre-separation, a Petrosil column (10 cm × 1.0 mm, 5 µm d_p) from Selerity Technologies (Utah, USA) was used to separate the oxygenates from the paraffins. The SFC oven is also equipped with a six-port two-position switching valve to allow backflushing of the analytical column. The SFC mobile phase (carbon dioxide) was delivered at a constant pressure of 20 MPa. The injection volume was 0.5 µL and the analysis temperature of 70 °C was used throughout. After separation on the analytical column, the column eluent was split through a flow splitter to the FID detector and to a capillary restrictor that vented to atmosphere. After the elution of the paraffins and olefins (8 min) the column was backflushed to elute the retained oxygenates. The CO_2 eluting from the column through a capillary restrictor (9-19 min) was vented into a GC liner containing glass wool (Restek, Bellefonte, USA) to trap the oxygenates after expansion of the CO_2. The trapping procedure was repeated several times to increase the concentration of oxygenates. The liner was then inserted into the GC-MS with Cold-EI for analysis. The oxidised paraffinic fraction sample for the SFC separation was more dilute, compared to the sample used for SPE separation, to prevent blockages in the SFC lines and 0.02 g of the oxidised heavy paraffinic sample was diluted with cyclohexane (10 mL) before injecting 0.5 µL onto the SFC.

3 Results and Discussion

3.1 Cold-EI Results

The standards in Table 1 were analysed by GC-MS with Cold-EI to investigate the ionisation behaviour of the various oxygenated compounds when using Cold-EI. Similar to the work published by Fialkov et. al. [8], abundant molecular ions are observed for alkanes with Cold-EI compared to the significantly smaller molecular ions in the NIST mass spectra of these compounds. Fialkov et. al. [8] stated that molecular ions are not present with conventional electron ionisation GC-MS for alkanes larger than $C_{28}H_{58}$ using typical ion source temperatures. An abundant molecular ion was also observed in the Cold-EI mass spectrum of 1-eicosene with the molecular ion being significantly smaller in the NIST mass spectrum. The mass spectra for these components are included as supplementary material.

3.1.1 Ethers:

Didecyl ether ($C_{20}H_{42}O$) was used as representative of this group. Figure 1 shows the NIST mass spectrum (bottom) as well as the Cold-EI mass spectrum (top) of this compound. In the NIST mass spectrum the highest observed mass with a relative abundance of greater than 10 % at m/z 141 ($C_{10}H_{21}^+$) corresponds to the fragment of the molecule after the loss of a $C_{10}H_{21}O$ group and the molecular ion is absent from the mass spectrum. In the Cold-EI mass spectrum an abundant molecular ion at m/z = 298 is observed. The high mass fragment at 141 ($C_{10}H_{21}^+$) after inductive cleavage and the fragment at m/z 159 ($C_{10}H_{23}O^+$) after rearrangement was also observed.

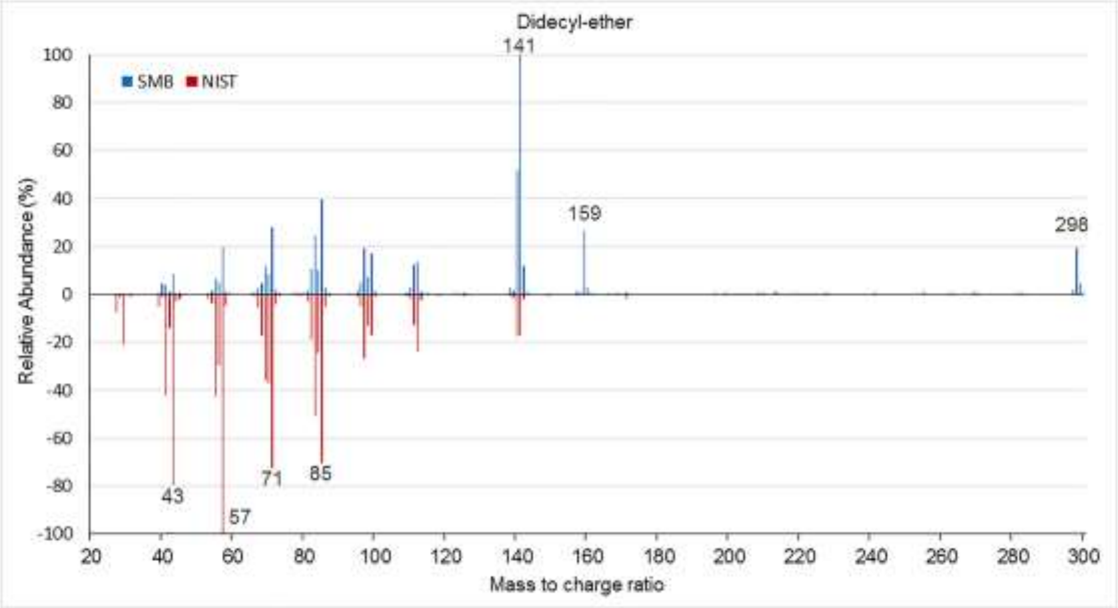

Figure 1: Mass spectra of didecyl ether ($C_{20}H_{42}O$) with conventional EI (bottom) and Cold-EI (top).

3.1.2 Esters:

The NIST mass spectrum of the selected representative ester, hexadecyl dodecanoate ($C_{28}H_{56}O_2$), is presented in Figure 2 (bottom). The base peak at m/z 201 corresponds to the acid fragment of the molecule ($C_{12}H_{25}O_2$) after the loss of a $C_{16}H_{31}$ group by 2H rearrangement. The molecular ion at m/z 424 is also observed in the mass spectrum with a relative abundance of approximately 5 %. In the Cold-EI mass spectrum for this compound (Figure 2, top), the molecular ion is observed as the base peak. With Cold-EI the relative abundance of the characteristic high mass fragments at m/z 224 and m/z 269 ($C_{16}H_{32}$ and $C_{17}H_{33}O_2$, respectively) also increased substantially relative to the low mass ions.

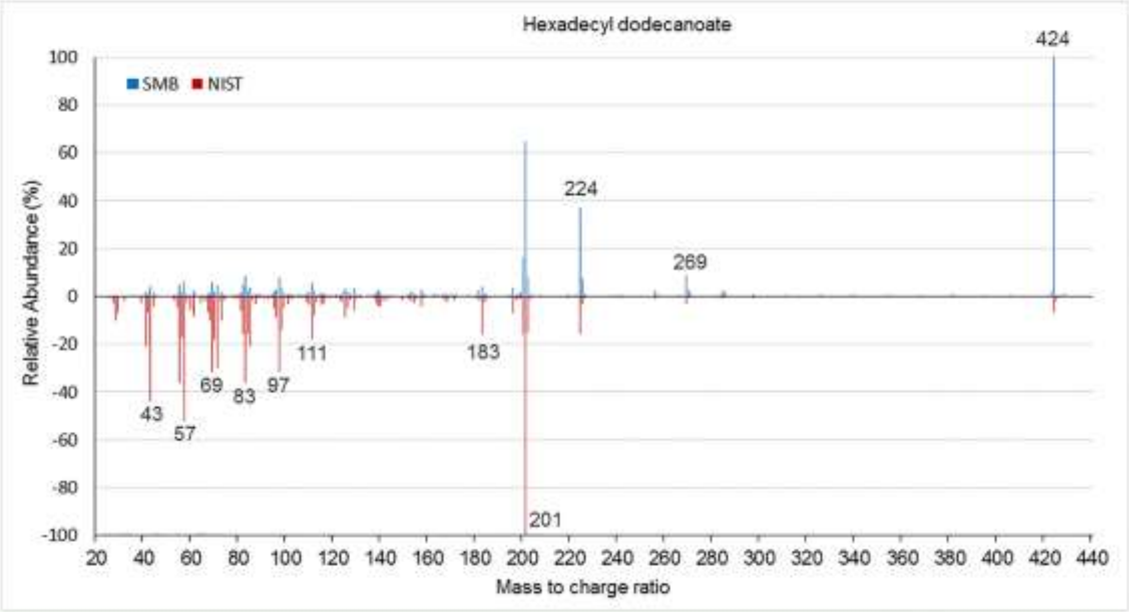

Figure 2: Mass spectra of hexadecyl dodecanoate ($C_{28}H_{56}O_2$) with conventional EI (bottom) and Cold-EI (top).

3.1.3 Organic acids:

The NIST library mass spectrum and the Cold-EI mass spectrum for arachidic acid ($C_{20}H_{40}O_2$) is presented in Figure 3. The mass spectra for undecanoic acid ($C_{11}H_{22}O_2$) and tetradecanoic acid ($C_{14}H_{28}O_2$) are included as supplementary material. It can be seen that molecular ions are observed for all three these acids in the NIST mass spectra with relative abundances below 20 %. The characteristic acid fragment at m/z 60 ($C_2H_4O_2$) is prominent in the NIST mass spectra of all three the evaluated acids with relative abundances between 50 and 100 %. In the Cold-EI mass spectra for these compounds, the molecular ions at m/z 186, m/z 228 and m/z 312 are observed as the base peak in the mass spectra of undecanoic acid, tetradecanoic acid and arachidic acid, respectively. The characteristic acid fragment at m/z 60 decreased substantially with the use of

Cold-EI; a relative abundance of 20 % was observed in the mass spectrum of undecanoic acid. For tetradecanoic acid and arachidic acid the relative abundance of this fragment decreased to 10 % and <5 %, respectively. The use of this characteristic acid fragment for identification purposes is therefore limited when using GC-MS with Cold-EI, but is more than compensated for by the intense molecular ions obtained. An additional benefit of Cold-EI in the analysis of underivatised free fatty acids is that their response is linear without intra-ion source degradation, which prevails with standard EI [39].

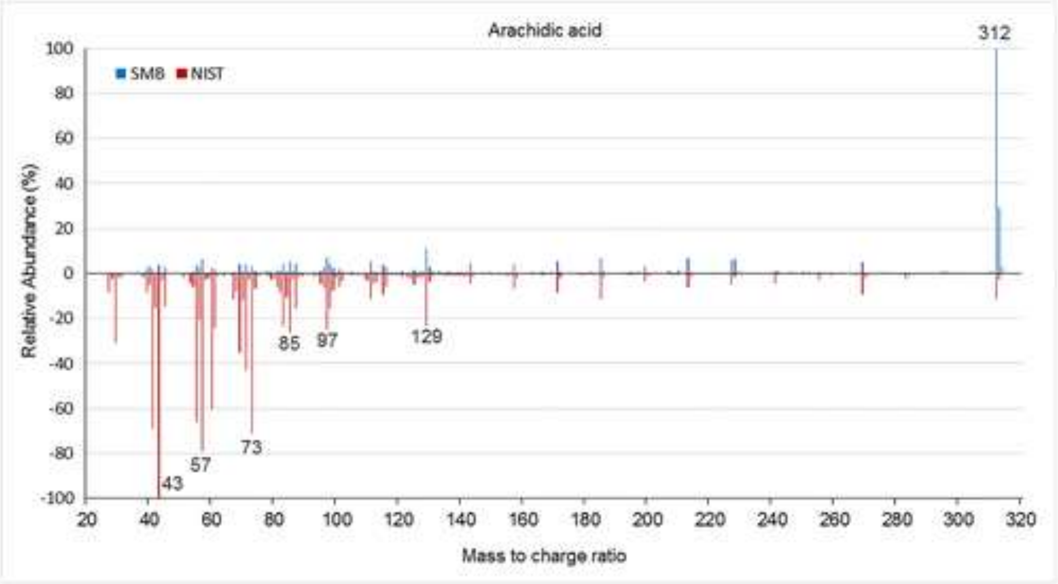

Figure 3: Mass spectra of arachidic acid ($C_{20}H_{40}O_2$) with conventional EI (bottom) and Cold-EI (top).

3.1.4 Carbonyls:

The molecular ion at m/z 324 is not observed for n-docosanal ($C_{22}H_{44}O$) in the mass spectrum using conventional EI (Figure 4A, bottom). The highest observed mass peak in this spectrum was m/z 306, with a relative abundance of ±10 %, which corresponds to the fragment of the molecule after the loss of H_2O. In the Cold-EI mass spectrum (Figure 4A, top) for this compound, the fragment after the loss of H_2O was the base peak. The molecular ion at m/z 324 was observed in the Cold-EI mass spectrum at a relative abundance of ±10 %. The availability of a small molecular ion and large $[M-18]^+$ fragment ion serves as an indication for the presence of an alcohol or aldehyde. The NIST mass spectra of 8-pentadecanone ($C_{15}H_{30}O$), 2-octadecanone ($C_{18}H_{36}O$) and 16-hentriacontanone ($C_{31}H_{62}O$) are presented in Figure 4B, C and D (bottom). Molecular ions were observed for all these ketones in the conventional EI mass spectra with relative abundances between 5 % and 20 %. As expected, characteristic heavy fragments were observed for the carbonyls containing the carbonyl functionality in the middle of the hydrocarbon

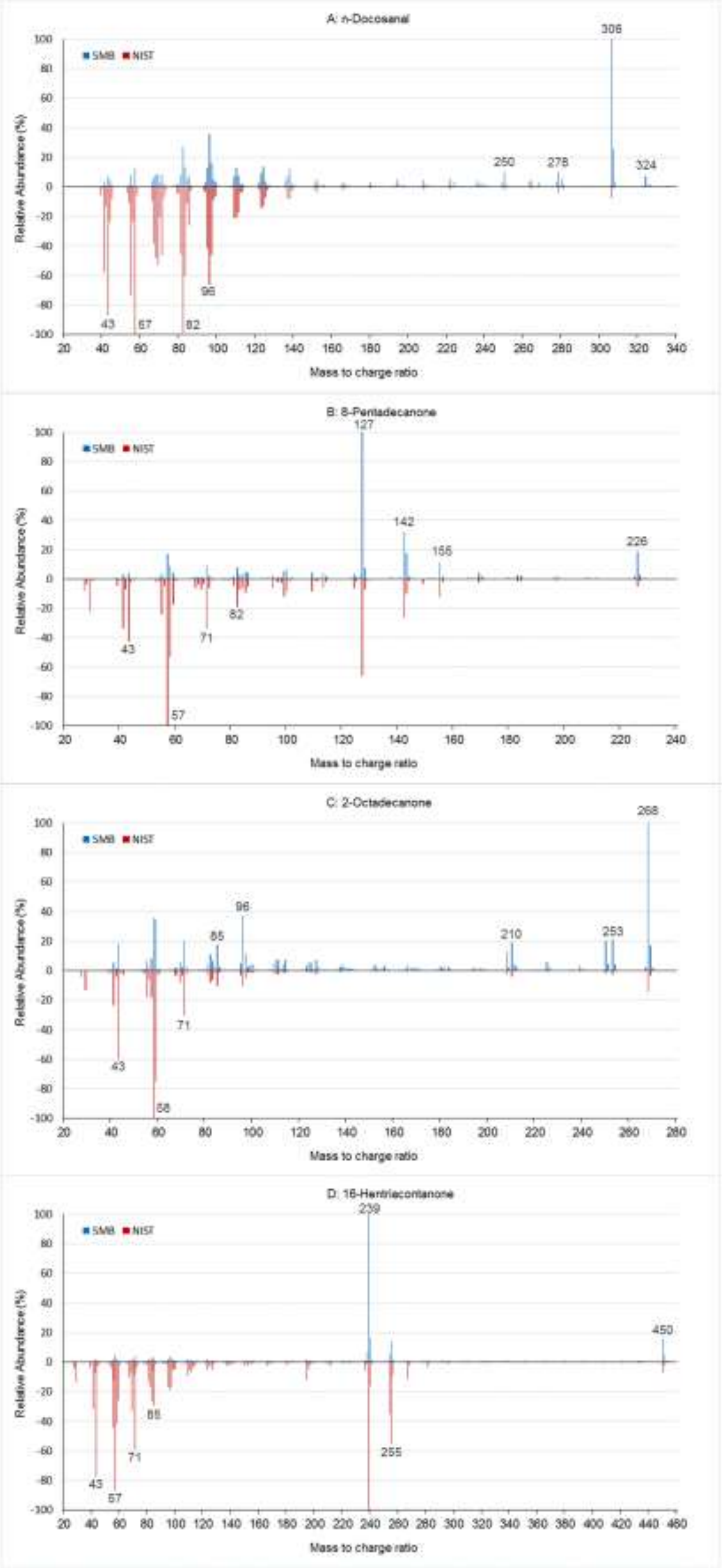

Figure 4: Mass spectra of A) n-docosanal ($C_{22}H_{44}O$), B) 8-pentadecanone ($C_{15}H_{30}O$), C) 2-octadecanone ($C_{18}H_{36}O$) and D) 16-hentriacontanone ($C_{31}H_{62}O$) with conventional EI (bottom) and Cold-EI (top).

chain. For the NIST spectrum of 8-pentadecanone, the fragment at m/z 127 with an abundance of 70 % corresponds to the fragment ($C_8H_{15}O$) after the loss of a C_7H_{15} group. Similarly, for 16-hentriacontanone (Figure 4D, bottom) the fragment at m/z 239, that corresponds to the $C_{16}H_{31}O$ fragment after the loss of a $C_{15}H_{31}$ group, was observed as the base peak in the NIST spectrum. In the Cold-EI mass spectrum for 8-pentadecanone (Figure 4B, top) the fragment at m/z 127 was observed as the base peak and the molecular ion at m/z 226 increased to an abundance of ±20 %, compared to < 10 % in the NIST spectrum. In the Cold-EI mass spectrum of 2-octadecanone (Figure 4C, top) the molecular ion at m/z 268 substantially increased and was observed as the base peak with the heavy mass fragments ($[M-CH_3]^+$ and $[M-H_2O]^+$) also increasing in abundance to ±20 %. For 16-hentriacontanone the fragment at m/z 239 is also observed as the base peak in the Cold-EI mass spectrum whilst the abundance of the molecular ion at m/z 450 doubled in abundance compared to the NIST spectrum.

3.1.5 Alcohols:

A series of linear 1-alcohols was investigated. The NIST mass spectra and the Cold-EI mass spectra of the lightest alcohol, 1-tridecanol ($C_{13}H_{28}O$), and the heaviest alcohol, 1-tetracosanol ($C_{24}H_{50}O$) are presented in Figure 5A and 5B. The conventional and Cold-EI mass spectra for 1-tetradecanol ($C_{14}H_{30}O$), 1-hexadecanol ($C_{16}H_{34}O$), 1-heptadecanol ($C_{17}H_{36}O$), 1-octadecanol ($C_{18}H_{38}O$), 1-eicosanol ($C_{20}H_{42}O$) and 1-docosanol ($C_{22}H_{46}O$) are included as supplementary material. No molecular ions were observed in the conventional EI mass spectra for any of these alcohols and the highest observed mass fragment in each spectrum corresponded to the fragment of the molecule after the loss of H_2O. The abundance of this peak in all cases was below 20 %. In the Cold-EI mass spectra of the linear alcohols (Figure 5, top) the fragment after loss of H_2O substantially increased and was the base peak for all the linear alcohols. It was also observed that as the hydrocarbon chain length of the alcohol increases the abundance of the molecular ion increases to an abundance of ±20 % for 1-tetracosanol (Figure 5B, bottom). This is consistent with Dagan and Amirav [34] who reported the effects of alkane chain length on the Cold-EI mass spectra and concluded that the amount of vibrational energy per atom is reduced linearly with the chain length, which makes the dissociation to small fragments less likely.

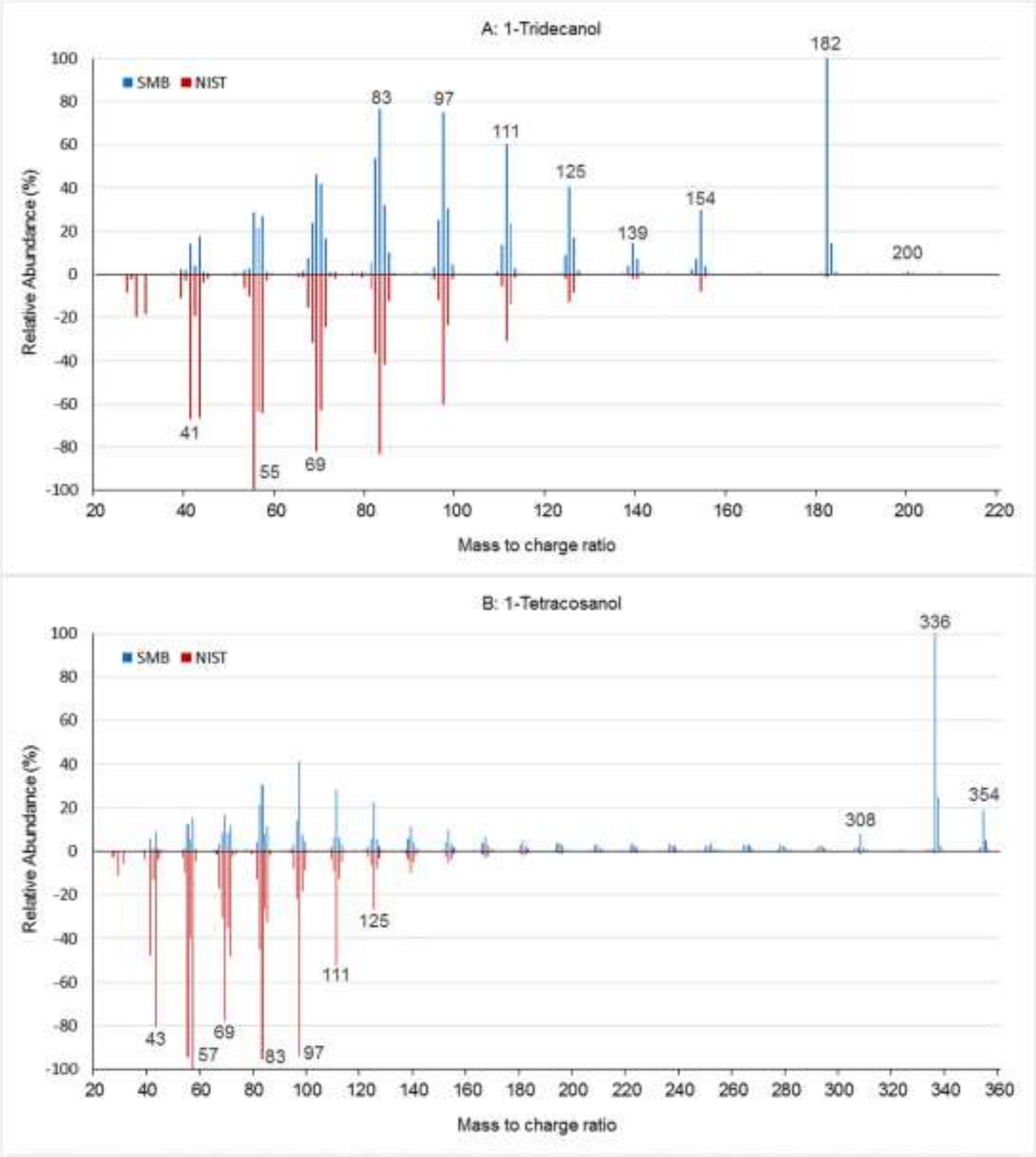

Figure 5: Mass spectra of A) 1-tridecanol ($C_{13}H_{28}O$) and B) 1-tetracosanol ($C_{24}H_{50}O$) with conventional EI (bottom) and Cold-EI (top).

Figure 6A (bottom) shows the NIST mass spectra of a branched alcohol, 2-octyl-1-dodecanol ($C_{20}H_{42}O$). This mass spectrum is dominated by small fragments and the molecular ion is not observed. The fragment of the molecule after the loss of H_2O has an abundance of <5 %. In the Cold-EI mass spectrum of 2-octyl-1-dodecanol (Figure 6A, top) it was observed that, similar to the linear alcohols, the fragment of the molecule after the loss of H_2O substantially increased and was present as the base peak. The molecular ion at m/z 298 was also observed in the Cold-EI mass spectrum at a relative abundance of 5 %. Figure 6B (bottom) shows the mass spectrum obtained from the conventional EI analysis of 1,12-octadecandiol ($C_{18}H_{38}O_2$). This mass spectrum was also dominated by small fragments and no molecular ion was observed. The fragment of the molecule after the loss of H_2O observed in the mass spectra of linear alcohols was not observed for this diol. In the Cold-EI mass spectrum of 1,12-octadecandiol (Figure 6B, top) the base peak was at $[M - 85]^+$, indicating the loss of a C_6H_{13} group due to alpha cleavage. Contrary to the Cold-EI spectra of the other alcohols analysed in this study, the loss of H_2O did not produce the base peak; this fragment had a very low abundance, whilst the fragment after the loss of two water molecules was more abundant. The molecular ion at m/z 286 was observed at a very low abundance in the Cold-EI mass spectrum.

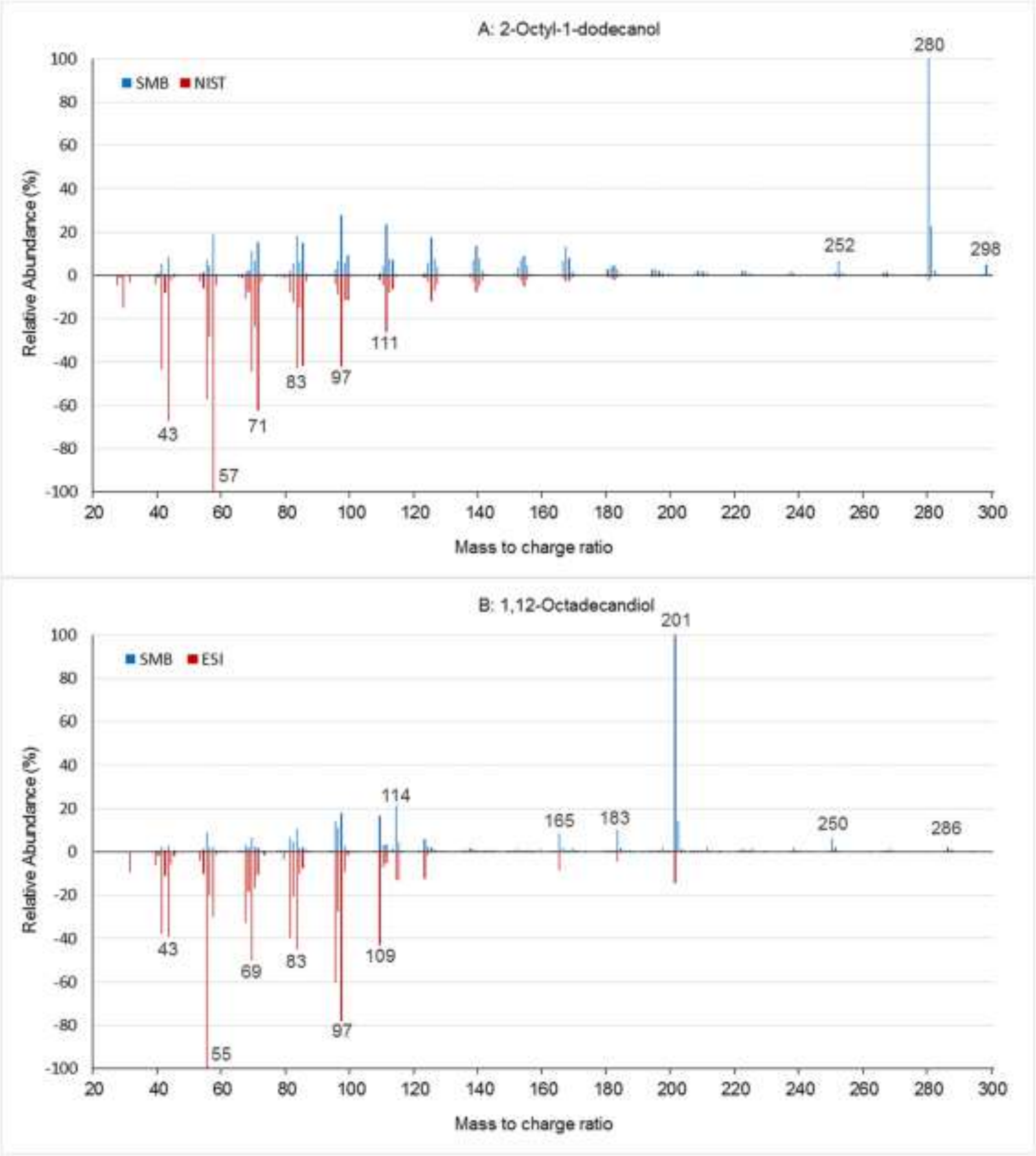

Figure 6: Mass spectra of A) 2-octyl-1-dodecanol ($C_{20}H_{42}O$) and B) 1,12-octadecandiol ($C_{18}H_{38}O_2$) with conventional EI (bottom) and Cold-EI (top).

3.2 SPE Fractionation

Solid phase extraction (SPE) using silica gel was tested for the pre-fractionation of oxygenates. Strong hydrogen bonding is present between silica gel and highly polar carboxylic acids and alcohols that act as proton donors and acceptors in these interactions and these compound classes have high retentions on silica gel. The less polar ethers, esters and carbonyls that only act as proton acceptors in hydrogen bonding interactions are less retained on silica gel. The retained oxygenates can be removed from the silica by competitive interaction, in this case by the introduction of a polar solvent such as methanol or acetone.

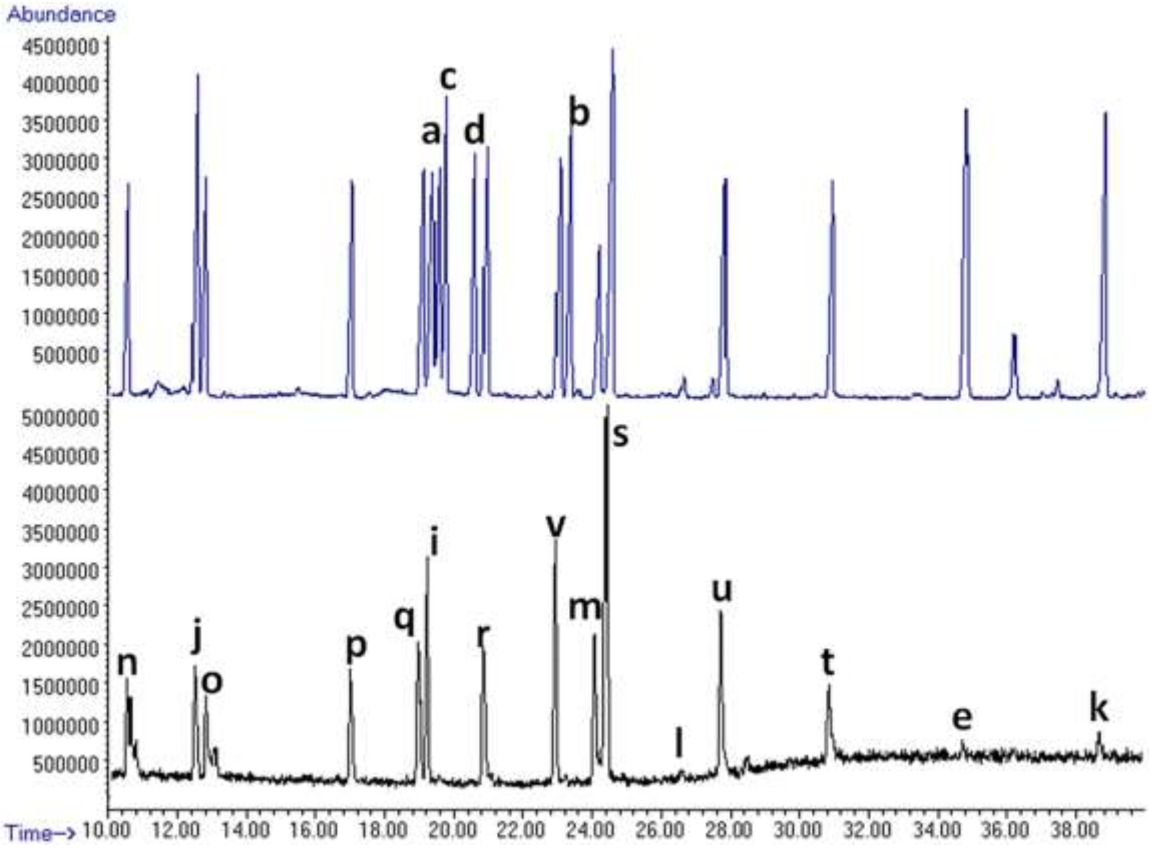

Figure 7: GC-MS with Cold-EI total ion chromatograms of the standard before (top) and after (bottom) fractionation by SPE using silica gel. (Peak labels as defined in Table 1).

Initially 2 mL of a standard containing 2000 µg/g of each of the components listed in Table 1 was separated by SPE according to the procedure described in the experimental section. Subsequent GC-MS with Cold-EI analysis showed that the paraffins (n-alkanes) and olefins (alkenes) passed through the SPE cartridge and could be successfully separated from the oxygenate fraction. It was also observed that not all the oxygenate classes were retained on the silica gel. The diol, acids and alcohols were successfully retained but the ether, ester and carbonyls passed through the cartridge. This could conceivably be due to the saturation of the SPE cartridge. Saturation is not only affected by the sorbent characteristics, but also by the concentrations of the analytes in solution [40]. The standard was subsequently diluted to contain 100 µg/g of each of the components listed in Table 1, and 1 mL of this standard was separated by the SPE procedure. Figure 7 shows stacked GC-MS with Cold-EI mass chromatograms of the standard before and after fractionation by SPE.

The diol and alcohols were successfully retained. Because of the non-polar GC column used, the organic acids are not visible in Figure 7, however, when molecular masses of these acids are extracted they are observed as flat broad peaks both before and after fractionation by SPE. Additionally, with the dilute standard, low concentrations of the ester and carbonyl compounds were also retained, however, the ether passed through the cartridge. The ether has the lowest polarity of all the oxygenates tested and the polarity of this long chain ether is further reduced due to the effect of the long aliphatic chains on both sides of the polar oxygen, reducing the proton acceptor interaction with the silica gel and resulting in the ether being unretained.

3.3 SFC Fractionation

The second procedure tested for the fractionation of the oxygenates was supercritical fluid chromatography (SFC) using a silica column. The same interactions between silica gel and the various oxygenates are responsible for their retention. The oxygenates can also be removed from the silica by introducing a polar modifier to the SFC mobile phase. Unfortunately a modifier could not be used with the SFC instrument used in this study. The SFC used in this study was equipped with an FID detector which prevented the use of an organic modifier in the mobile phase. In the SFC separation, the oxygenates were backflused from the SFC column with the aid of an electrically actuated 6-port valve that was controlled from the SFC software. The standard (0.5 µL) containing 2000 µg/g of each of the components listed in Table 1 was separated by SFC according to the procedure described in the previous section. The trapping procedure was repeated three times to concentrate the oxygenates in the standard mixture on the liner. Figure 8 shows stacked GC-MS with Cold-EI mass chromatograms of the standard before and after fractionation by SFC.

Analysis by GC-MS with Cold-EI showed that the paraffins and olefins, labelled a, b and c in Figure 8, passed through the SFC column, successfully separating them from the oxygenate fraction. Similar to the separation by SPE, the diol, acids, alcohols, ester and carbonyl compounds were successfully retained. In the case of SFC separation, a peak for the ether was also observed, indicating that the least polar ether was also successfully retained on the SFC column. Peak fronting is observed for the oxygenates after fractionation by SFC (Figure 8 bottom) due to the high concentration of these oxygenates trapped in the liner that lead to column overload.

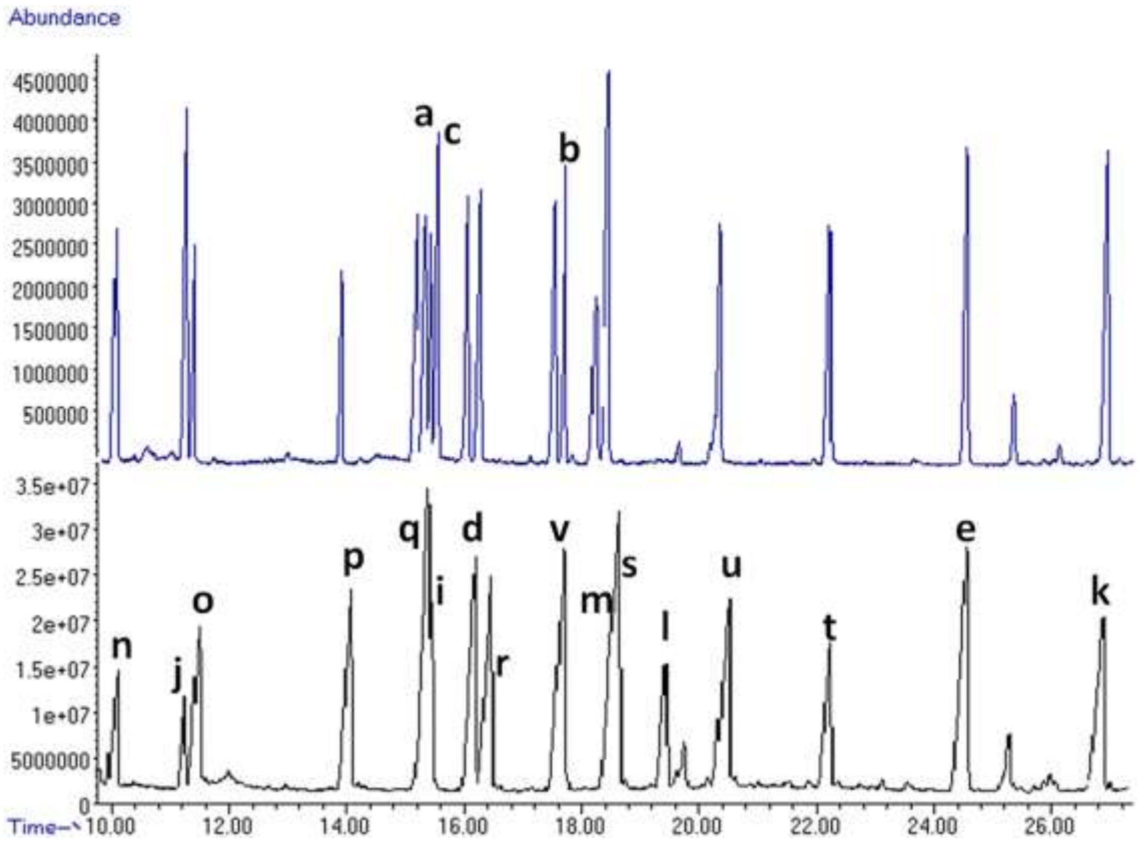

Figure 8: GC-MS with Cold-EI total ion chromatograms of the standard before (top) and after (bottom) fractionation by SFC using a silica column. (Peak labels as defined in Table 1).

3.4 Separation of an oxidised heavy paraffinic sample.

Both separation procedures were applied to an oxidised heavy paraffinic sample with the aim of accurately identifying the oxygenates present in the sample. Figure 9 shows the GC-MS with Cold-EI mass chromatograms of the oxidised heavy paraffinic sample before (top) and after (bottom) fractionation by SPE.

Figure 9 clearly shows that the n-alkanes that dominated the oxidised heavy paraffinic fraction were completely removed by the SPE fractionation procedure. After the selective retention of the oxygenates by SPE and elution of the overlapping n-alkanes, only the retained oxygenates were observed in the total ion chromatogram as shown in the insert in Figure 9. The oxygenates with molecular masses m/z 504 and 518 remained with the C38 and C39 alkanes completely removed.

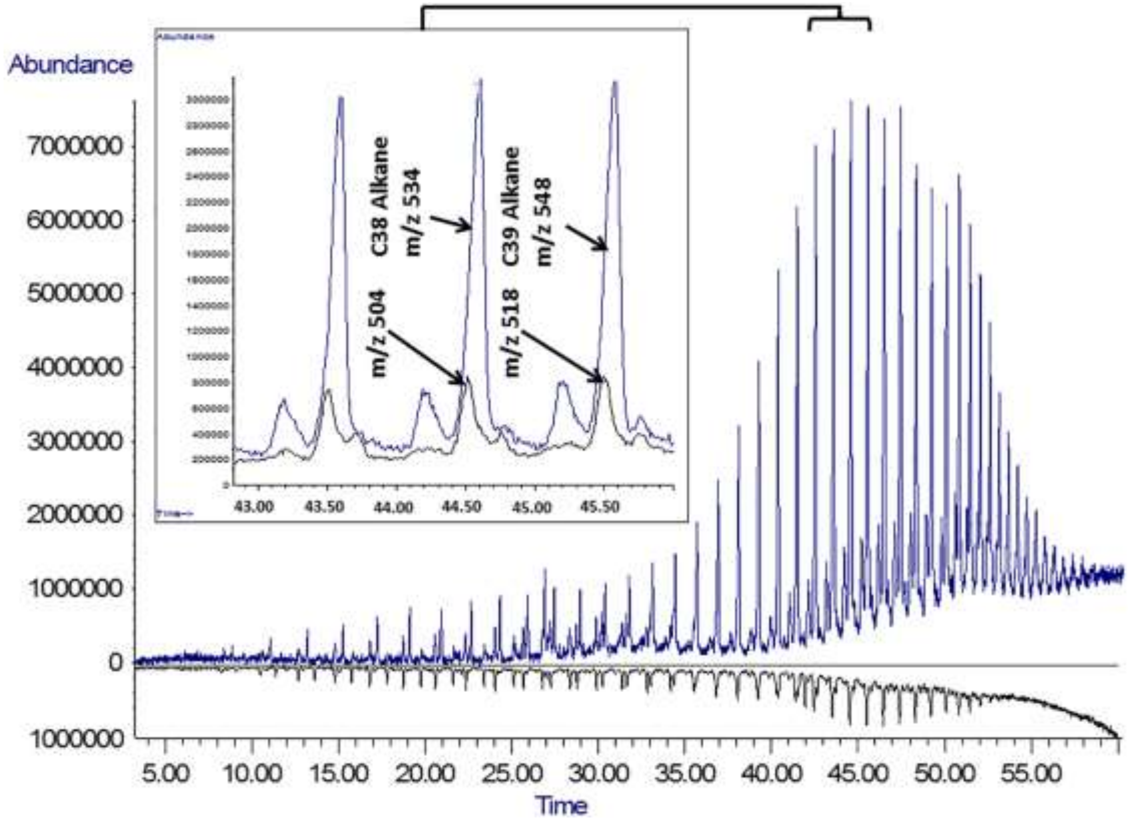

Figure 9: GC-MS with Cold-EI total ion chromatograms of the oxidised heavy paraffinic sample before (top) and after (bottom) fractionation by SPE. The insert shows the C37 to C39 alkane region of the chromatogram before (blue) and after (black) fractionation.

The SFC fractionation and subsequent trapping in GC injection liners was repeated several times to increase the concentration of oxygenates in the liner. In the case of the oxidised heavy paraffinic fraction, the trapping procedure was repeated fifteen times to concentrate the oxygenates on the liner for subsequent GC-MS with Cold-EI analysis. The oxygenate fraction separated using SFC contained a series of heavy n-alkanes (C20 - C46) that once again dominated the chromatogram (results not shown). This might be due to the low temperatures of the SFC oven and the restrictor outside the oven, causing the heavy n-alkanes to solidify in the lines, column and restrictor and resulting in breakthrough into the oxygenate fraction. The oxygenates in this fraction could only be observed when selected masses were extracted. Additionally, the concentrations of the oxygenates were a lot lower compared to the SPE separation procedure due to the SFC instrument requiring more dilute samples and smaller injection volumes. For this reason only the results from the oxidised heavy paraffinic sample after fractionation by SPE is discussed.

The GC-MS with Cold-EI mass chromatogram of the oxidised heavy paraffinic sample after fractionation by SPE is shown in Figure 10. The two oxygenate distributions (homologous series) at the start and the third distribution at the end of the chromatogram is also indicated. The Cold-EI mass spectrum for the peak at 14.8 min in the oxygenate distribution labelled 1 is shown in Figure 11 (top) as well as the NIST library mass spectrum (bottom).

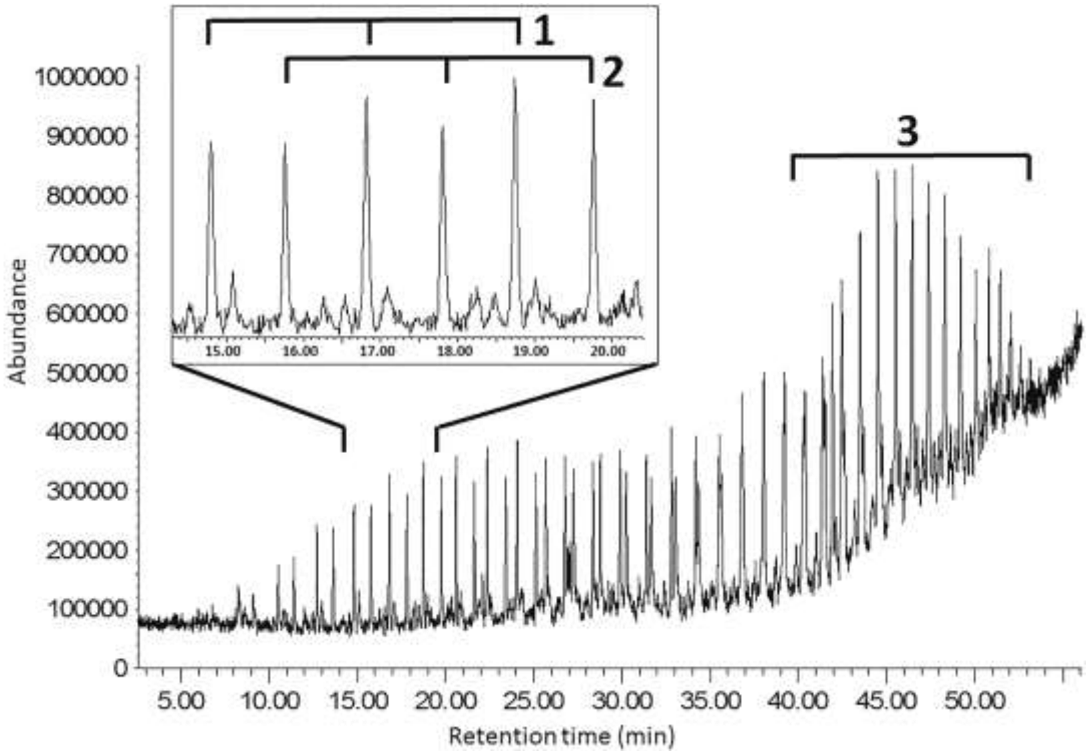

Figure 10: GC-MS with Cold-EI total ion chromatogram of the oxidised heavy paraffinic sample after fractionation by SPE.

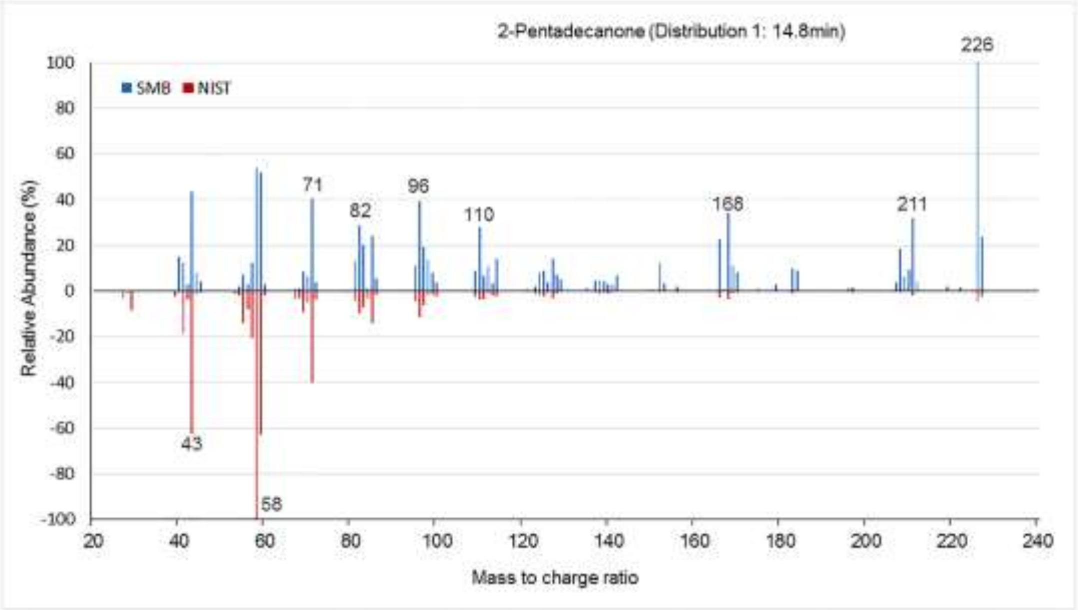

Figure 11: Mass spectra of the oxygenate eluting at 14.8 min (labelled 1 in Figure 10).

The oxygenates in the first distribution in Figure 10 were identified as 2-ketones with the peaks eluting at 14.8, 16.8 and 18.8 min identified as 2-pentadecanone ($C_{15}H_{30}O$), 2-hexadecanone ($C_{16}H_{32}O$) and 2-heptadecanone ($C_{17}H_{34}O$), respectively. The conventional and Cold-EI mass spectra for 2-hexadecanone ($C_{16}H_{32}O$) and 2-heptadecanone ($C_{17}H_{34}O$) are included as supplementary material. The Cold-EI behaviour of these 2-ketones is consistent with that of 2-octadecanone (Figure 4A, top), where the substantially increased molecular ion is observed as the base peak and the abundance of the heavy mass fragments ($[M\text{-}CH_3]^+$ and $[M\text{-}H_2O]^+$) are increased when compared to the NIST library mass spectra. Extracting the molecular ions of the 2-ketone homologous series showed that all the 2-ketones from C12 to C42 were present in the oxidised heavy paraffinic sample [41].

The Cold-EI mass spectrum for the oxygenate eluting at 13.6 min, that forms part of the second distribution, is shown in Figure 12 (top) together with the NIST library mass spectrum (bottom).

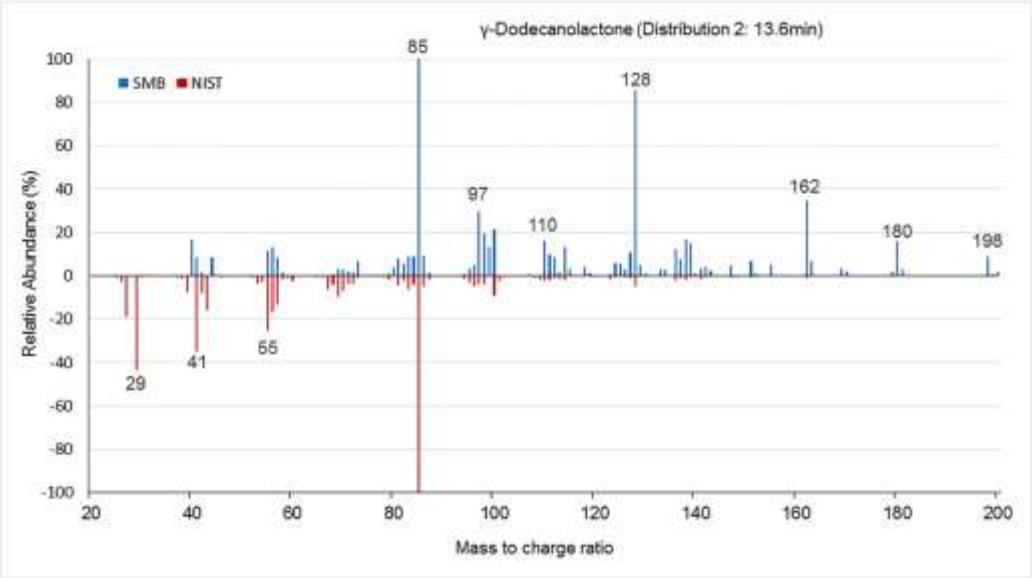

Figure 12: Mass spectra of the oxygenate eluting at 13.6 min that form part of the second distribution (labelled 2 in Figure 10).

The peaks eluting at 13.6 and 25.1 min as part of the second distribution in Figure 10 were identified by NIST library matching as γ-dodecanolactone ($C_{12}H_{22}O_2$) and γ-stearolactone ($C_{18}H_{34}O_2$), respectively (the NIST library spectra for peaks eluting from 15 - 20 min in Figure 10 are not available). The conventional EI and Cold-EI mass spectra for γ-stearolactone ($C_{18}H_{34}O_2$) is included as supplementary material. Very weak (<5 %) or no molecular ions were observed for the γ-lactones in the NIST library mass spectra (Figure 12, bottom). The base peak observed for both these γ-lactones was at m/z 85, corresponding to the γ-butyrolactone fragment

($C_4H_5O_2$). In the Cold-EI mass spectrum of γ-dodecanolactone there was a substantial increase in the heavy mass fragments ([M-H_2O^+] and [M-36]$^+$) and an increased molecular ion at m/z 198 with a relative abundance of ±10 %. For the γ-stearolactone the Cold-EI mass spectrum also showed a substantial increase in the heavy mass fragments ([M-H_2O]$^+$ and [M-36]$^+$) and an increased molecular ion at m/z 282 with a relative abundance of 20 %. Clearly the abundance of the molecular ion increases with increased chain length of these γ-lactones when using Cold-EI. Similar mass spectra were obtained for the other peaks that form part of the second distribution and these oxygenates could all be identified as γ-lactones. The formation of γ-lactones as the major ester product during the autoxidation of hydrocarbons is consistent with the observations from other studies [41 - 42], where an intramolecular pathway from alkyl hydroperoxides for the formation of these γ-lactones was presented. Extracting the molecular ions of the γ-lactone homologous series showed that all the γ-lactones from C10 to C41 were present in the oxidised heavy paraffinic sample.

A third oxygenate distribution eluted towards the end of the GC-MS (Cold-EI) mass chromatogram and is labelled 3 in Figure 10. The Cold-EI mass spectrum (top) as well as the conventional EI mass spectrum (bottom) of the peak eluting at 44.5 min as part of this distribution is presented in Figure 13.

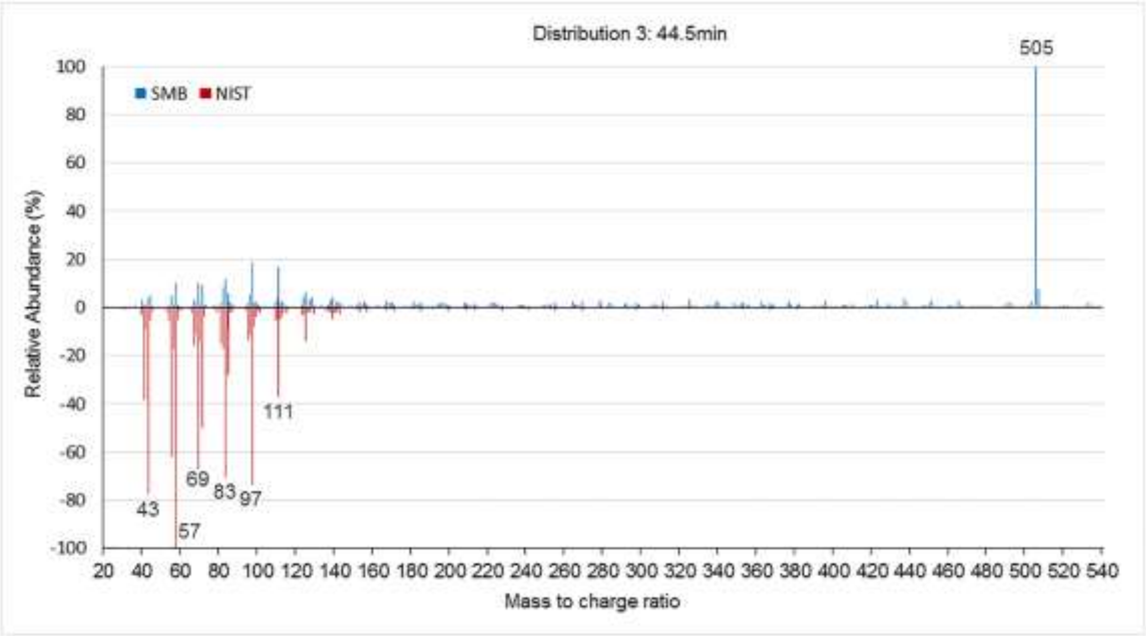

Figure 13: Mass spectra of the oxygenate eluting at 44.5 min that form part of the third distribution (labelled 3 in Figure 10).

The ion measured at m/z 504.6 is displayed in this spectrum to the nearest integer of 505 and represents the even nominal mass 504. Not to be confused with the presence of a nitrogen atom in the normal odd molecular ion rule for molecular ions of organic molecules.

The conventional EI and Cold-EI mass spectra for the peaks eluting at 45.5 min and 46.5 min that form part of the third distribution are included as supplementary material. No molecular ions were seen in the conventional EI mass spectra for these late eluting compounds. In the Cold-EI mass spectra of these compounds molecular ions at nominal mass 504, 518 and 532 were the base peaks with no heavy mass fragments. In each case these molecular ions were two mass units lower than the molecular ions expected for 2-ketones as seen in the first oxygenate distribution, labelled 1 in Figure 10. It is therefore possible that these compounds could be carbonyls containing a cyclic or a double bond functionality, however, more work is needed to confirm the identity of these compounds. Based on the assumption that that these compounds are carbonyls containing a cyclic or a double bond functionality, a homologous series from C14 to C51 was observed to be present in the oxidised heavy paraffinic sample when the expected molecular ions of these compounds were extracted.

The availability of molecular ions enables the use of the Tal Aviv molecule identifier (TAMI) software that inverts the molecular ion group of isotopomers into elemental formulae [43]. Consequently, the TAMI software based on isotope abundance analysis can further confirm or reject NIST library identification of the oxygenates and provide elemental formula information in case they are not included in the NIST library. Peaks in this distribution were also analysed by TAMI software to confirm the identity of these compounds. TAMI is an improved compound identification method that utilises a combination of Isotope Abundance Analysis (IAA), unit resolution mass accuracy and library search for identification [43]. Co-elution is inevitable for late eluting compounds in complex samples such as these and co-elution with low concentration oxygenates that have the same molecular masses as the $[M+1]^+$ and $[M+2]^+$ isotopes of the third oxygenate distribution could result in these isotopes being higher than expected, which complicated the application of the TAMI software. The molecular ion of the peak eluting at 44.5 min suggests that this peak is an alkene or cycloalkane ($C_{36}H_{72}$) or an oxygenate ($C_{35}H_{68}O$). The molecular ion at m/z = 504.6 is due to the effect of the large number of hydrogen atoms with isotopic mass 1.008 amu on the measured m/z, also in the supplementary figures O and P. The C36 alkenes or cycloalkanes do not elute at 44.5 min (based on GC-MS results before SPE fractionation), which supports the previous suggestion that the unknown peak is an oxygenate containing a cyclic or a double bond functionality. While not all the peaks in this distribution were analysed using TAMI, it is reasonable to assume that they contain the same functional group.

Characteristic molecular and fragment ions for the other oxygenates present in the standard in Table 1 were also extracted to check for the presence of these components in the oxidised heavy paraffin sample. Low concentrations of linear acids from C8 to C21 and traces of alcohols were found.

These results show that oxygenates in an oxidised heavy paraffinic sample were successfully separated from the hydrocarbon matrix allowing the subsequent characterisation by GC-MS with Cold-EI. The identified oxygenates (2-ketones and γ-lactones) are also consistent with the typical oxygenates that are formed during the autoxidation of saturated hydrocarbons reported in other studies [41 - 42, 44 - 45]. It is clear that the enhanced molecular ion abundance as well as the enhanced intensity of the characteristic high mass fragments obtained with GC-MS with Cold-EI aids in the identification of heavy oxygenated compounds for which molecular ions are not observed in their conventional EI mass spectra. The use of pulsed flow modulation two-dimensional comprehensive gas chromatography in combination with mass spectrometry (MS) with an SMB interface [37 - 38] can be investigated in the future to improve the GC separation of oxidised heavy paraffinic samples to allow identification of oxygenated compounds without the use of offline pre-separation techniques, such as SPE. The use of pulsed flow modulation in combination with Cold-EI is also preferred to cryogenic modulation and standard EI to reduce peak tailing of high boiling compounds [46]. The column sets for the optimum HT-GC×GC separation of oxygenates in oxidised heavy paraffinic fractions was reported previously [15] and hydrocarbons up to a carbon number of C60 could be eluted with a reversed column configuration.

4 Conclusions

The ionisation of various oxygenated compound classes was investigated using GC-MS with Cold-EI. The Cold-EI mass spectra of the oxygenate standards evaluated are characterised by substantially increased relative abundances of the molecular ions as well as the characteristic high mass fragments and in most cases the molecular ion was the base peak in the mass spectra. While one can also use low electron energy Cold-EI to further increase of the relative abundance of the molecular ion in Cold-EI as reported in [47], 70 eV Cold-EI combines the availability of molecular ions together with fragment ions that enables NIST library identification with good signal strength as shown throughout this study. The data format of the Cold-EI mass spectra are fully compatible with NIST library identification and while the matching factors are reduced the identification probabilities are often increased [48]. We note, as shown above, that the larger the compound, the greater the gain in molecular ion enhancement with the molecular cooling in Cold-EI. The oxygenates were also successfully separated from the oxidised paraffinic matrix by SPE which allowed the subsequent identification by GC-MS with Cold-EI. This would not be possible using conventional EI. Alkane breakthrough into the oxygenate fraction was observed when using SFC for the separation of oxygenates in an oxidised heavy paraffinic sample. The SFC trapping procedure is labour intensive since it requires several repeats because of the limited capacity of the SFC column, and the SPE separation procedure is favoured in this study. Pulsed flow modulation two-dimensional comprehensive gas chromatography combined with supersonic molecular beam mass spectrometry could conceivably allow the direct separation and positive identification of oxygenated compounds in oxidised heavy paraffinic matrices without the use of prior separation.

REFERENCES

[1] A. Elkilani, M.A. Fahim, T.A. Al-Sahhaf, Fundamentals of Petroleum Refining, **2010**.

[2] S. Parkash, Refining Processes Handbook, **2003**.

[3] A. Steynberg, M.E. Dry, Introduction to Fischer-Tropsch Technology, Stud. Surf. Sci. Catal. **2007**, *152*, 406.

[4] A. de Klerk, Fischer-Tropsch Refining, Ph.D. Thesis, University of Pretoria, **2008**.

[5] G.V. Webber, The origin of multiple DSC melting peaks of Fischer-Tropsch hard waxes, Ph.D. Thesis, University of Cape Town, **2009**.

[6] T. Dutriez, M. Courtiadea, D. Thiébaut, H. Dulot, F. Bertoncinia, J. Vial, M. Hennion, High-temperature two-dimensional gas chromatography of hydrocarbons up to nC60 for analysis of vacuum gas oils, J. Chromatogr. A **2009**, *1216*, 2905.

[7] T. Dutriez, M. Courtiade, D. Thiébaut, H. Dulot, F. Bertoncini, M. Hennion. Extended characterization of a vacuum gas oil by offline LC-high-temperature comprehensive two-dimensional gas chromatography, J. Sep. Sci. **2010**, *33*, 1787.

[8] A.B. Fialkov, A. Gordin, A. Amirav, Hydrocarbons and fuels analyses with the supersonic gas chromatography mass spectrometry - The novel concept of isomer abundance analysis, J. Chromatogr. A **2008**, *1195*, 127.

[9] A. Amirav, A. Gordin, M. Poliak, A.B. Fialkov, Gas Chromatography Mass Spectrometry with Supersonic Molecular Beams, J. Mass Spectrom. **2008**, *43*, 141.

[10] E. Kaal, H.G. Janssen, Extending the molecular application range of gas chromatography, J. Chromatogr. A **2008**, *1184*, 43.

[11] K. Grob, G. Grob, Capiliary columns with immobilized stationary phases. Part 5: Determination of column bleeding; re-silylation, J. High Resolut. Chromatogr. **1982**, *5*, 349.

[12] A.B. Fialkov, A. Gordin, A. Amirav, Extending the range of compounds amenable for gas chromatography-mass spectrometric analysis, J. Chromatogr. A **2003**, *991*, 217.

[13] A.B. Fialkov, U. Steiner, L. Jones, A. Amirav, A New Type of GC-MS with Advanced Capabilities, Int. J. Mass. Spectrom. **2006**, *251*, 47.

[14] D 6352. Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174°C to 700°C by Gas Chromatography, ASTM International. West Conshohocken. USA.

[15] H. Potgieter, R. Bekker, J. Beigley, E. Rohwer, Analysis of oxidised heavy paraffininc products by high temperature comprehensive two-dimensional gas chromatography, J. Chromatogr. A **2017**, *1509*, 123.

[16] F. Adam, F. Bertoncini, N. Brodusch, E. Durand, D. Thiébaut, D. Espinat, M. Hennion. New benchmark for basic and neutral nitrogen compounds speciation in middle distillates using comprehensive two-dimensional gas chromatography, J. Chromatogr. A **2007**, *1148*, 55.

[17] T. Dutriez, M. Courtiade, D. Thiébaut, H. Dulot, M. Hennion, Improved hydrocarbons analysis of heavy petroleum fractions by high temperature comprehensive two-dimensional gas chromatography, Fuel **2010**, *89*, 2338.

[18] T. Dutriez, M. Courtiade, D. Thiébaut, H. Dulot, F. Bertoncini, M. Hennion. Extended characterization of a vacuum gas oil by offline LC-high-temperature comprehensive two-dimensional gas chromatography, J. Sep. Sci. **2010**, *33*, 1787.

[19] T. Dutriez, J. Borras, M. Courtiade, D. Thiébaut, H. Dulot, F. Bertoncini, M. Hennion. Challenge in the speciation of nitrogen-containing compounds in heavy petroleum fractions by high temperature comprehensive two-dimensional gas chromatography, J. Chromatogr. A **2011**, *1218*, 3190.

[20] L. Mahé, T. Dutriez, M. Courtiade, D. Thiébaut, H. Dulot, F. Bertoncini. Global approach for the selection of high temperature comprehensive two-dimensional gas chromatography experimental conditions and quantitative analysis in regards to sulfur-containing compounds in heavy petroleum cuts, J. Chromatogr. A **2011**, *1218*, 534.

[21] B.M.F. Ávila, R. Pereira, A.O. Gomes, D.A. Azevedo. Chemical characterization of aromatic compounds in extra heavy gas oil by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry, J. Chromatogr. A **2011**, *1218*, 3208.

[22] L. Mahé, M. Courtiade, C. Dartiguelongue, J. Ponthus, V. Souchon, D. Thiébaut, Overcoming the high-temperature two-dimensional gas chromatography limits to elute heavy compounds, J. Chromatogr. A **2012**, *1229*, 298.

[23] G. S. Frysinger, R. B. Gaines, L. Xu, C. M. Reddy, Resolving the unresolved complex mixture in petroleum-contaminated sediments, Environ. Sci. Technol. **2003**, *37*, 1653.

[24] R. Edam, J. Blomberg, H.-G Janssen, P. J. Schoenmakers, Comprehensive multi-dimensional chromatographic studies on the separation of saturated hydrocarbon ring structures in petrochemical samples, J. Chromatogr. A. **2005**, *1086*, 12.

[25] D. Mao, H. v.d. Weghe, L. Diels, N. De Brucker, R. Lookman, G. Vanermen, High-performance liquid chromatography fractionation using a silver-modified column followed by two-dimensional comprehensive gas chromatography for detailed group-type characterization of oils and oil pollutions, J.Chromatogr. A, **2008**, *1179*, 33.

[26] R. Van der Westhuizen, H. Potgieter, N. Prinsloo, A. de Villiers, P. Sandra, Fractionation by liquid chromatography combined with comprehensive two-dimensional gas chromatography-mass spectrometry for analysis of cyclics in oligomerisation products of Fischer-Tropsch derived light alkenes, J. Chromatogr. A **2011**, *1218*, 3173.

[27] H. Potgieter, R. van der Westhuizen, E. Rohwer, D. Malan, Hyphenation of supercritical fluid chromatography and two-dimensional gas chromatography-mass spectrometry for group type separations, J. Chromatogr. A **2013**, *1294*, 137.

[28] A. Andrade-Eiroa, M. Canle, V. Leroy-Cancellieri, V. Cerdà, Solid-phase extraction of organic compounds: A critical review (Part I), Trends in Anal. Chem. **2016**, *80*, 641.

[29] A. Andrade-Eiroa, M. Canle, V. Leroy-Cancellieri, V. Cerdà, Solid-phase extraction of organic compounds: A critical review. part ii, Trends in Anal. Chem. **2016**, *80*, 655.

[30] C. Adelhelm, R. Niessner, U. Pöschl, T. Letzel, Analysis of large oxygenated and nitrated polycyclic aromatic hydrocarbons formed under simulated diesel engine exhaust conditions (by compound fingerprints with SPE/LC-API-MS), Anal. Bioanal. Chem. **2008**, *391*, 2599.

[31] F. Adam, D. Thiebaut, F. Bertoncini, M. Courtiade, M.-C. Hennion, Supercritical fluid chromatography hyphenated with twin comprehensive two-dimensional gas chromatography for ultimate analysis of middle distillates, J. Chromatogr. A **2010**, *1217*, 1386.

[32] T. Dutriez, D. Thiébaut, M. Courtiade, H. Dulot, F. Bertoncini, M.-C. Hennion, Application to SFC-GC×GC to heavy petroleum fractions analysis, Fuel **2013**, *104*, 583.

[33] A. Venter, P.R. Makgwane, E.R. Rohwer, Group-Type analysis of oxygenated compounds with a silica gel porous layer open tubular column and comprehensive two-dimensional supercritical fluid and gas chromatography, Anal. Chem. **2006**, *78*, 2051.

[34] S. Dagan, A. Amirav, Electron impact mass spectrometry of alkanes in supersonic molecular beams, J. Am. Soc. Mass Spectrom. **1995**, *6*, 120.

[35] A. Amirav, A. Gordin, N. Tzanani, Supersonic Gas Chromatography - Mass Spectrometry, Rapid. Com. Mass Spectrom. **2001**, *15*, 811.

[36] A. Amirav, A.B. Fialkov, A. Gordin, Improved Electron Ionization Ion Source for the Detection of Supersonic Molecular Beams, Rev. Sci. Instrum. **2002**, *73*, 2872.

[37] M. Poliak, A.B. Fialkov, A. Amirav, Pulsed flow modulation two-dimensional comprehensive gas chromatography-tandem mass spectrometry with supersonic molecular beams, J. Chromatogr. A, **2008**, *1210*, 108.

[38] U. Keshet, A.B. Fialkov, T. Alon, A. Amirav, A New Pulsed Flow Modulation GC×GC-MS with Cold EI System and its Application for Jet Fuel Analysis, Chromatographia, **2016**, *79*, 741.

[39] A. Amirav, D. Benanou, Free Fatty Acids Analysis by GC-MS - Cold EI Versus Standard EI, blog.avivanalytical.com, **2013**, 05

[40] S.N. Semenov, J.A. Koziel, J. Pawliszyn, Kinetics of solid-phase extraction and solid-phase microextraction in thin adsorbent layer with saturation sorption isotherm, J. Chromatogr. A, **2000**, *873*, 39.

[41] A. Goosen, D. H. Morgan, Autoxidation of Nonane and Decane: A Product Study, J. Chem. Soc. Perkin Trans. **1994**, *2*, 557.

[42] A. Goosen, S. Kindermans, Decane autoxidation: Precursors of gamma lactones and other minor products, S. Afr. Chem. **1997**, *50*, 9.

[43] T. Alon, A. Amirav, Isotope Abundance Analysis Method and Software for Improved Sample Identification with the Supersonic GC-MS, Rapid Commun. Mass Spectrom. **2006**, *20*, 2579.

[44] E.L.J. Breet, A.S. Luyt, Oxidation kinetics of a Fischer-Tropsch wax. Part 2. Induction period as first macroscopic process stage, S. Afr. J. Chem. **1991**, *44 (4)*, 101.

[45] A. de Klerk, Continuous-Mode Thermal Oxidation of Fischer-Tropsch Waxes, Ind. Eng. Chem. Res. **2003**, *42*, 6545.

[46] C. Duhamel, P. Cardinael, V. Peulon-Agasse, R. Firor, L. Pascaud, G. Semard-Jousset, P. Giusti, V. Livadaris, Comparison of cryogenic and differential flow (forward and reverse fill/flush) modulators and applications to the analysis of heavy petroleum cuts by high-temperature comprehensive gas chromatography, J. Chromatogr. A, **2015**, *1387*, 95.

[47] A. Amirav, U. Keshet, A. Danon, Soft Cold EI - Approaching Molecular Ion Only with Electron Ionization, Rapid. Commun. Mass. Spectrom. **2015**, *29*, 1954.

[48] T. Alon, A. Amirav, How Enhanced Molecular Ions in Cold EI Improve Compound Identification by the NIST Library, Rapid. Commun. Mass. Spectrom. **2015**, *29*, 2287.