

# **Developments towards the comprehensive analysis of petrochemical streams**

by

**Johannes H W Potgieter**

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Department of Chemistry

University of Pretoria

Pretoria, South Africa

Supervisor: Professor E.R. Rohwer

Co-supervisor: Doctor R. Bekker

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# Declaration

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I, Johannes H W Potgieter, declare that the dissertation, which I hereby submit for the degree Philosophiae Doctor (Chemistry) at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Contributions by co-workers are acknowledged in the separate chapters.

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Signature

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Date

# Acknowledgements

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# Summary

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Petrochemical products derived from crude oil and Fischer-Tropsch (FT) processes contain a variety of compounds over a wide carbon number range and a large number of fuels and chemicals are produced during product workup. The characterisation of these fuels and chemicals as well as intermediate process streams is very important to control conversion processes. The analysis of any one of these phases is very challenging. Typical oil phase samples may contain thousands of compounds.

In many cases, complete characterisation of these complex samples is possible with comprehensive two-dimensional gas chromatography (GC×GC), but even with the increase in separation power obtained by comprehensive GC, peak co-elution still occurs when complex samples are analysed. In this work chromatographic techniques were investigated and the hyphenation of these techniques was evaluated, addressing some of the remaining analytical challenges in petrochemical analysis.

The on-line hyphenation of supercritical fluid chromatography (SFC) to a GC×GC system as a pre-separation technique was successfully developed to address the challenge of the separation between cyclic and non-cyclic alkenes and alkanes. The developed SFC pre-separation method also pre-separated the sample of interest into other chemical groups (saturates, unsaturates, oxygenates and aromatics) for further characterisation by GC×GC. On-line hydrogenation after GC×GC separation was successfully developed to address the challenge of distinguishing between isomeric cyclic and double bond containing compounds with the same (two or more) double bond equivalents. The number of rings and alkene double bonds in specific compounds could be determined from the mass spectra of the compounds before and after hydrogenation in a complex petrochemical sample requiring GC×GC separation.

A high temperature (HT)-GC×GC method was developed to replace titrimetric procedures traditionally used for the control of oxidation processes of heavy paraffinic fractions. The advantages of the developed HT-GC×GC method include the selective quantification of



oxygenate classes and obtaining the concentration for each oxygenate class by carbon number. This allows the optimisation of conditions used to oxidise heavy paraffinic fractions. The challenge of the identification of oxygenates in these oxidised heavy paraffinic fractions was also addressed with the development of a method that pre-separates the oxygenates before subsequent analysis by gas chromatography mass spectrometry, with the use of a supersonic molecular beam (GC-SMB-MS). The EI spectra with enhanced molecular ions obtained by GC-SMB-MS aided tremendously in the identification of oxygenates and the advantage of this procedure was illustrated, whereby the heavy oxygenates in an oxidised heavy paraffinic sample could be better identified.

This study successfully addressed various analytical challenges in the field of petrochemical analysis and the developed techniques may be useful for the comprehensive characterisation of various streams in other areas of petrochemical analysis.

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# Abbreviations

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## **Analytical techniques**

1D-GC	Conventional one-dimensional gas chromatography
Cold-EI	GC-MS with supersonic molecular beams
EI	Electron ionisation
ESI	Electrospray ionisation
FID	Flame ionisation detector
FT-ICR-MS	Fourier transform ion cyclotron resonance mass spectrometry
GC	Gas chromatography
GC-MS	Gas chromatography mass spectrometry
GC×GC	Comprehensive two-dimensional gas chromatography
GPC	Gel permeation chromatography
O-FID	Oxygen selective detector
HT-GC	High-temperature gas chromatography
HPLC	High performance liquid chromatography
HRT	High resolution time-of-flight detector
IAA	Isotope abundance analysis
MSD	Mass selective detector
PTV	Programmed temperature vaporisation injector
RFF	Reverse a fill/flush differential flow modulator
SEM-EDS	Scanning electron microscope and energy dispersive X-ray spectrometer
SFC	Supercritical fluid chromatography
SFC×GC	Comprehensive two-dimensional SFC and GC
SFC×SFC	Comprehensive two-dimensional supercritical fluid chromatography
SIMDIS	Simulated distillation
SMB	Supersonic molecular beam
SPE	Solid phase extraction
TAMI	Tal Aviv molecule identifier
TOF-MS	Time-of-flight mass spectrometry

## Hyphenated techniques

GC×GC-TOF-MS

GC×GC-FID

SFC-GC×GC-TOF-MS

HT-GC×GC-TOF-MS

HT-GC×GC-FID

SFC-FID

GC-SMB-MS

## Other

RS <sub>2D</sub>	2D resolution (not resolution in the second dimension ( <sup>2</sup> R <sub>s</sub> ))
ω	Peak width at 10% peak height
AEBP	Atmospheric equivalent boiling point
ATRs	Autothermal reformers
CTL	Coal-to-liquids
DAH	Di aromatic hydrocarbons
FAME	Fatty acid methyl esters
FBP	Final boiling point
FT	Fischer-Tropsch
FT syncrude	Synthetic crude oil obtained from Fischer-Tropsch technology
GTL	Gas-to-liquids
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulphurisation
HTFT	High temperature Fischer-Tropsch
ID	Internal diameter
LAB	Linear alkyl benzene
LTFT	Low temperature Fischer-Tropsch
m/z	Mass to charge ratio
M <sup>+</sup>	Molecular ion
MAH	Mono aromatic hydrocarbons

MEK	Methyl ethyl ketone
NIST	National Institute of Standards and Technology
NMP	N-methylpyrrolidone
PLOT	Porous layer open tubular
PAH	Poly aromatic hydrocarbons
PVA	Poly(vinyl alcohol)
SAS™	Advanced Synthol™
Sasol SPD™	Sasol Slurry Phase Distillate™
TIC	Total ion chromatogram
VDU	Vacuum distillation unit
VGO	Vacuum gas oil
VR	Vacuum residue



# Chapter 1

## Introduction

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## 1. Preface

The demand for petrochemical products has grown steadily over the past ten years and more growth is forecast since the key drivers (increased population, standard of living and urbanisation) will continue to increase. Accelerated growth is also expected in the petrochemical product segments that will play an important role in the global efforts to cut carbon emissions (improved manufacturing materials, insulation materials, improved packaging etc.). To ensure long term growth and sustainability, the petrochemical refining industry will need to reduce its carbon footprint and become more integrated and efficient [1 - 2].

The petrochemical products derived from crude oil and Fischer-Tropsch (FT) refining processes are very complex and contain many chemical compound classes over a wide carbon number range. During product workup, refineries transform the primary cuts obtained from these sources into valuable end products that meet market demands. These refining processes further increase the complexity of these petrochemical streams [3 - 4].

The characterisation of these refinery streams is very important for the monitoring, control and optimisation of refining processes. However, the complexity poses various challenges from an analytical perspective. Complete characterisation of complex petrochemical streams is sometimes achieved with comprehensive two-dimensional gas chromatography (GC×GC) [5 - 10] and this technique is used in many petrochemical laboratories around the world. This technique has been one of the substantial developments in analytical chemistry for the analysis of volatile organic chemicals in highly complex petrochemical matrices. However, even with the huge increase in separation power obtained by GC×GC, peak co-elution still occurs in various samples, and many analytical challenges still remain in the petrochemical industry.

The continuous quest of the refinery industry to become more efficient will also continuously add to the analytical challenges. Refinery efforts, such as the expansion into cleaner sources, utilisation of lower value heavy petroleum fractions and production of heavy speciality

chemicals will require continuous development of new analytical techniques to characterise these samples. There have been many developments to extend the capabilities of GC×GC [11 - 13], the hyphenation of GC×GC with other selective separations [14 - 16] and the comprehensive coupling of techniques to combine unique selectivities [17 - 18]. This work forms part of the continuous quest to develop new methods addressing the analytical challenges that remain in the petrochemical industry and thereby contribute toward the comprehensive analysis of petrochemical process streams.

## 2. Objective

The separation of cyclic paraffins and olefins is one of the remaining analytical challenges in the field of petrochemical analysis. This separation is especially difficult since these compounds have similar retention time characteristics in the GC×GC separation plane. Although time-of-flight mass spectrometry (TOF-MS) is very powerful in the identification of different chemical groups, it is also not able to distinguish between the cyclic alkane and alkene component classes because of their identical molecular masses and similar fragmentation patterns. Other compounds that also elute in similar areas of the GC×GC chromatogram with identical molecular masses and similar fragmentation patterns are compounds with a similar level of unsaturation (e.g. dienes and cyclic olefins). The separation of these compounds before analysis by GC×GC will aid in the comprehensive characterisation of these petrochemical streams.

The use of high performance liquid chromatography (HPLC) as a pre-fractionation procedure to separate cyclic alkanes and olefins by means of silver ion chromatography with the subsequent GC×GC analysis of the separated fractions has been previously published by our group [15]. Although this approach worked well, there were several disadvantages associated with this method. The use of supercritical fluid chromatography (SFC) for group-type separation has been published before and the separation achieved with SFC proved to be very similar to that obtained by HPLC [19 - 21]. The hyphenation of SFC with GC is also less complicated than the hyphenation with HPLC and has been achieved by other groups by decompression of the supercritical fluid through a restrictor into the GC injection port

[22 - 24]. In this study, the use of SFC as a pre-separation method will be investigated with the aim of separating a sample into different chemical groups (saturates, unsaturates, oxygenates and aromatics) in order to subsequently characterise these separated groups by GC×GC by means of on-line hyphenation.

The SFC-GC×GC approach using a silver modified column cannot distinguish between classes like dienes and cyclic olefins, since both these classes contain alkene double bonds that will form adducts with the silver ions of the analytical column. On-line hydrogenation after GC×GC separation is a possible way to distinguish between these compounds since the number of rings and alkene double bonds in the compound structure can be determined from the mass spectra of the compounds before and after hydrogenation. On-line hydrogenation was used by other groups to achieve hydrogenation in a capillary column after 1D-GC separation [25 - 28] as well as between GC×GC columns of the same phase in order to obtain orthogonal dimensions [29]. In this study, the development of a GC×GC method with post column hydrogenation, in which the analytes undergo hydrogenation after the second dimension separation, will be investigated.

Heavy petroleum fractions are produced during crude and synthetic crude oil refining processes. To increase the value of these heavy petroleum fractions, they require upgrading to marketable products. Oxidation of heavy paraffinic fractions produces high value products that contain a variety of oxygenates. The characterisation of these oxidised heavy paraffinic fractions by GC×GC is complicated due to their complexity and the high boiling points of these fractions [11, 30]. The challenge of the characterisation of oxidised heavy paraffinic fractions needs to be addressed, and analytical techniques need to be developed to enable accurate control of oxidation processes. Other groups have investigated the use of mid-polarity column combinations to extend the carbon number range attainable by GC×GC and have optimised these column combinations for the separation of aromatics, nitrogen-containing compounds as well as sulphur-containing compounds in heavy petroleum fractions [11 - 14, 31 - 34]. In this study the use of high temperature (HT)-GC×GC will be investigated to enable the optimum separation of oxygenates in these oxidised heavy paraffinic fractions.

The accurate identification of the oxygenates present in the oxidised heavy paraffinic 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. GC-MS with a supersonic molecular beam (SMB) interface provides EI spectra with enhanced molecular ion intensity, making it easier to identify these oxygenates [35 - 37]. As part of this study the feasibility of pre-separation of the oxygenates present in oxidised heavy paraffinic samples, as well as the hyphenation of this pre-separation procedure with GC-SMB-MS will be investigated.

To summarise: The aim of this project is therefore to develop chromatographic techniques (pre-separation by SFC, on-line hydrogenation, high temperature GC×GC and supersonic molecular beam MS) and to investigate the hyphenation of these techniques to comprehensively characterise compounds and compound classes of interest in petrochemical streams to enable the monitoring, control and optimisation of refining processes.

### **3. Organisation**

Chapter 2 provides a literature review of crude oil and FT syncrude (synthetic crude oil obtained from Fischer-Tropsch technology), as well as the processing of crude oil and FT syncrude produced in different FT processes. The characterisation of petrochemical process streams and the different analytical techniques used is also reviewed. Some of the remaining analytical challenges in the characterisation of petrochemical process streams are also discussed at the end of the chapter. The analytical techniques developed to address these remaining analytical challenges are discussed in-depth in Chapters 3, 4, 5 and 6.

Chapter 3 is concerned with the separation between cyclic paraffins and olefins in complex petrochemical samples. The on-line hyphenation of SFC to a GC×GC system to comprehensively characterise the chemical groups (saturates, unsaturates, oxygenates and aromatics) in a FT sample is discussed. In Chapter 4 the challenge of determining the backbone of cyclic/olefinic isomers is addressed and the development of a GC×GC method

with post column hydrogenation, in which the analytes undergo hydrogenation after the second dimension separation, is discussed.

Chapter 5 addresses the challenge of the characterisation and monitoring of oxygenates in oxidised heavy paraffinic fractions. The investigation of HT-GC×GC parameters for the optimum separation of oxygenates in oxidised heavy paraffinic fractions is discussed and the advantage of using the developed method in the monitoring oxidation reactions is illustrated. In Chapter 6, the pre-separation of oxygen containing compounds in oxidised heavy paraffinic fractions for the identification by supersonic molecular beam mass spectrometry is discussed. The use of this method for the improved characterisation of oxygenates is also illustrated.

The final conclusions, remaining challenges and recommendations for future work are given in Chapter 7.

Appendix A contains additional mass spectra referred to in the text.

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# Chapter 2

## Literature

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## 1. Crude oil

Fossil fuels are defined as hydrocarbon deposits which occur naturally throughout the world. These fossil fuels are formed from the decomposed remains of organic matter, and the three major fossil fuels present in the world are coal, crude oil and natural gas [1].

Crude oil is the main source of transportation fuels and is mainly made up of alkanes, cycloalkanes and aromatics. The alkanes present in crude oil are mostly linear, while the cycloalkanes are mainly 5- or 6-membered rings. Mono-, di- and polynuclear aromatics (MAH's, DAH's and PAH's) are found in high concentrations in most crude oils, whilst very little or no alkenes are present. The heteroatom most commonly encountered in crude oil is sulphur with total sulphur concentrations ranging from 0.1% to 5%. Sulphur can be present in either organic or inorganic forms, with sulphides, thiols and thiophenes being the most encountered organic classes. Nitrogen containing compounds are mostly found in heavy crude oil fractions (bp. > 250°C) with nitrogen concentrations ranging from 0.5% to 2%. Basic, neutral and acidic nitrogen compounds are present in these heavy fractions with amines, amides, pyrroles and pyridines being the most prominent organic classes. Oxygenates are present in the lowest concentrations of the heteroatomic species and the most prominent oxygenates encountered in crude oils are furanes, phenols, esters and carboxylic acids [2].

Fossil fuels are non-renewable energy sources and are subject to strategic availability and price fluctuations. Since crude oil is the main source of transportation fuel, there is motivation to develop and commercialise technologies that would enable the use of gas or coal as alternative transportation fuels for energy security. In the transportation fuels business, the alternative technology that had the most commercial success thus far, is Fischer-Tropsch synthesis, where synthesis gas (or syngas) from coal gasification or natural gas is converted into liquid fuels and chemicals. Fischer-Tropsch technology, as well as the processing of both crude oil and Fischer-Tropsch synthetic crude products are discussed in the following paragraphs.

## 2. Fischer-Tropsch Technology

Sasol is an international integrated energy and chemicals company that builds and operates world-scale facilities and develops and commercialises technologies. Sasol produces a range of high-value products, including liquid fuels and chemicals, from coal and natural gas. Sasol also produces low-carbon electricity from natural gas. Sasol was established in 1950 in South Africa and remains one of the country's largest investors in capital projects, skills development and technology research and development. Although Sasol was established in South Africa, it is an international company with 32000 employees working in 37 countries. Sasol also has international gas-to-liquids (GTL) ventures in Qatar (Oryx GTL), Nigeria (Escravos GTL) and Uzbekistan. Sasol is also actively capitalising on growth opportunities in Southern Africa and North America [1, 3].

Sasol produces synthesis gas from the gasification of coal or from natural gas and converts the synthesis gas into liquid fuels and chemicals through FT synthesis. Sasol's main coal-to-liquids (CTL) process at Secunda (South Africa) utilises a multi-unit gasification plant where coal is converted into crude synthesis gas with the aid of heat, pressure, steam and oxygen, while natural gas is reformed at high temperature with steam and oxygen in autothermal reformers (ATRs) to produce synthesis gas for the gas-to-liquids (GTL) processes. Coal conversion to synthesis gas is much more expensive than converting natural gas to synthesis gas. Sasol utilises two distinct types of FT processes for syngas conversion, namely high temperature (HTFT) and low temperature (LTFT). For the HTFT process in Secunda, purified syngas is processed in the Advanced Synthol™ (SAS™) reactors, whereby the syngas is converted to fuels and chemicals with the aid of an iron-based catalyst at temperatures of about 350°C. For the LTFT process in Sasolburg, purified syngas is processed in iron catalyst-based fixed-bed tubular and Sasol Slurry Phase Distillate™ (Sasol SPD™) reactors at a lower temperature than the SAS™ reactors to produce linear hydrocarbon waxes and paraffins. In another LTFT process, an advanced cobalt catalyst is used in the Sasol SPD™ FT reactor. This Co-LTFT process is used in Sasol's three-step gas-to-liquids (GTL) process that includes syngas generation, FT synthesis and product upgrading. This three-step process is currently used in the ORYX GTL (Qatar) and Escravos GTL (Nigeria) plants.

Sasol produces a wide range of chemical products that are distributed across the world. Sasol's base chemicals include polymers, solvents, explosives and fertiliser products, whilst the performance chemical business includes surfactants, fatty alcohols, linear alkyl benzene (LAB), short-chain linear alpha olefins, ethylene, petrolatum, paraffin waxes, synthetic waxes, cresylic acids, high-quality carbon solutions as well as alumina products [1, 3, 4].

Steynberg et al. [4] defined Fischer-Tropsch technology as a means to convert synthesis gas containing hydrogen and carbon monoxide to hydrocarbon products. FT is a surface polymerisation reaction that is initiated by adsorption of carbon monoxide (CO) on the catalyst surface, followed by chain propagation and chain termination. The main products are paraffins, olefins and oxygenates. De Klerk et al. [2] showed that paraffins, olefins, aromatics, primary alcohols, carboxylic acids and aldehydes are all primary Fischer-Tropsch products whilst ketones, esters and secondary alcohols seem to be secondary products. The four metals that are sufficiently active for FT synthesis include iron, cobalt, nickel and ruthenium. Ruthenium is the most active. However, it is too expensive and scarce to be used commercially. Nickel is also very active but it produces much more methane than Co or Fe catalysts, which is unwanted in FT processes. Additionally, nickel is easily converted to volatile carbonyls at FT plant temperatures and pressures, resulting in continuous metal losses. Only cobalt and iron based catalysts can therefore be considered as practical FT catalysts. Since cobalt is much more active than iron, cobalt catalysts will probably be used in future plants mainly aimed at the production of diesel, whilst iron catalysts operated at high temperatures will remain the choice for high value linear alkene production. Iron catalysts are also preferred when coal derived synthesis gas is used. This is because synthesis gas from coal gasification is prone to contain coal derived catalyst poisons. These catalyst poisons are difficult to remove from the synthesis gas and would quickly poison the more expensive cobalt FT catalyst. FT catalyst poisons are easily removed from the natural gas-derived synthesis gas. The poisons are removed prior to the reforming step and therefore cobalt catalysts are preferably used with natural gas-derived synthesis gas.

There are three broad classes of commercial FT catalysts and each of these classes has an appropriate area of application [4]. These classes are:

1. Fused iron catalysts (HTFT),
2. Precipitated iron catalysts (LTFT),
3. Supported cobalt catalysts (LTFT).

The liquid products obtained with fused iron catalysts are highly olefinic, making this catalyst highly desirable for olefin production. Alkali promoters are added to these catalysts to enhance catalyst activity, while structural promoters are added to enhance the surface area of the catalysts. High alkali levels are desirable to decrease methane selectivity. However, if the methane selectivity is too low, several operational problems can be encountered, including heavy hydrocarbons in the liquid phase, increased carbon formation on the catalyst and high levels of organic acids in the products.

The precipitated iron catalysts can achieve methane selectivities as low as 3%. This requires the use of FT reactors containing hydrocarbons in the liquid phase (liquid phase synthesis), entailing operation at lower temperatures than those used for the fused iron catalysts. Higher catalyst surface areas are therefore used to compensate for the lower operating temperature and hence, lower reaction rate. Higher surface area catalyst particles are weaker and therefore the applied structural promoters and procedures are very important aspects of the catalyst preparation process.

Supported cobalt catalysts are prepared by depositing cobalt on a support material like silica, alumina, titania or zinc oxide. Since it appears that promoters are not essential to produce a good supported cobalt catalyst, but rather to effectively reduce cobalt to its metallic form, cobalt is impregnated with promoter metals that are known to enhance the subsequent reduction step. These metals include lanthanum, platinum, palladium, rhenium and ruthenium. In contrast with the iron catalysts where olefins are the predominant product, the hydrocarbon products from supported cobalt catalysts comprise predominantly of paraffins. The primary hydrocarbon products obtained from the supported cobalt catalysts are also highly linear. The methane selectivity of the supported cobalt catalysts is slightly higher than

for the LTFT precipitated iron catalysts. However, the selectivity towards oxygenated hydrocarbons in the aqueous phase is lower.

### **3. Crude oil Product Processing**

Crude oil produced in the oil field is a very complex hydrocarbon mixture ranging from methane to asphalt, with each boiling point fraction varying in paraffin, naphthene and aromatic compositions [5]. In a typical crude oil refinery the primary cuts include gases, naphtha, kerosene, gas oil and heavy residue. The purpose of a typical crude oil refinery is to transform these primary cuts into valuable end products that meet market demands. Since market demands are constantly changing, crude oil refineries also need to change to meet these demands and although some broad cuts can be marketed and sold directly, others require further processing and upgrading in refinery units. In modern crude oil refineries the refining processes can be mainly divided into physical separation processes and chemical conversion processes [2, 6].

The physical separation processes include distillation, solvent deasphalting, solvent extraction and solvent dewaxing. Crude oils are first desalted and then introduced to an atmospheric distillation column which is the main separation step in a crude oil refinery. In this column the crude oil is fractionated into straight run naphtha, kerosene, distillate and atmospheric residue. These fractions are then routed to other conversion units. The residue from the atmospheric distillation column is further processed in the vacuum distillation unit (VDU). The products from the VDU include vacuum gas oil (VGO) and vacuum residue (VR). The vacuum residue is a heavy product (boiling point above 550°C) and contains most of the crude oil contaminants. The vacuum residue is then fed to another physical separation process called deasphalting. Deasphalting is a liquid-liquid extraction whereby propane is used to dissolve the last molecules that can be refined to white products (liquefied petroleum gas, gasoline, kerosene and diesel), leaving asphaltene to precipitate. The deasphalted oil is used as feedstock for the lubrication oil plant. Solvent extraction is a process whereby lubrication oil stock is treated by a solvent, such as N-methylpyrrolidone (NMP), to dissolve the aromatic components to separate them from the rest of the oil (raffinate). After the solvent is removed,

the raffinate is dewaxed. Dewaxing involves the gradual cooling of the raffinate after it was dissolved in a solvent like MEK (methyl ethyl ketone). The high molecular weight paraffins are crystallised during the cooling process and removed to produce lubrication oil.

Conversion processes are required to convert the products from the separation units into desirable products, and these conversion processes were placed into four categories by de Klerk et al. [2]. The first category are conversion processes that increase the molecular mass of the molecules, like oligomerisation processes, and these processes are referred to as carbon number growth processes. Conversion processes like cracking that decrease the molecular mass of the molecules are referred to as carbon number reduction processes. Functionalisation processes are processes that change the functional group of a molecule (hydrodesulphurisation, reforming and etherification). Processes that can modify the molecular structure without changing the functional group or carbon number (hydroisomerisation and double bond isomerisation) are referred to as rearrangement processes.

The atmospheric and vacuum residues produced during distillation need to be further refined. The first option in the refining of these residues is focused on reducing the average carbon number for transforming the residue to fuels by utilising processes like fluid catalytic cracking, visbreaking, coking and hydrocracking. These residues can also be modified for non-fuel applications like lubricants, white oils, waxes, bitumen and coke.

Kerosene and distillate produced during distillation usually meet carbon number fuel specifications and only requires refining in terms of sulphur and aromatic content to meet the remaining fuel specifications. These specifications are usually achieved by hydrotreating processes. Hydroisomerisation and dewaxing is also used in the kerosene and distillate fractions to modify or remove the linear paraffins in order to improve cold flow properties.

In order to meet fuel specifications, the naphtha and gas fractions need to be refined. The required changes include the reduction of the sulphur content, increase in the octane number and carbon number adjustments. Removing the sulphur is achieved by hydrotreating, whilst the octane number specification is increased by catalytic reforming or etherification units.



Carbon number adjustments when dealing with the gas can be achieved by carbon number growth refining processes.

## **4. Fischer-Tropsch Product Processing**

The product produced during FT synthesis is called synthetic crude (or “syncrude”), which needs to be refined to produce final fuel and chemical products. Although synthetic crude is very different from crude oil in terms of composition, the same technologies used for crude oil refining have been adapted for synthetic crude refining. Valuable products, like linear alpha-olefins, can be extracted from the FT synthetic crude and therefore the refining focus is very different from crude oil refining. The synthetic crude obtained from the different FT processes described above differs in terms of composition and therefore the preferred refining processes used are also different [4].

### **4.1. HTFT Processing**

The synthetic crude obtained from the HTFT process is very rich in olefins and contain percentage levels of oxygenates. The Schultz-Flory distribution [4] for the HTFT syncrude is heavily weighted towards light hydrocarbons and the products are highly linear with a low degree of branching. FT synthetic crude is essentially sulphur free and low in nitrogen content and therefore no hydrodesulphurisation or other sulphur reduction technologies are needed to meet fuel sulphur specifications. Most of the light oxygenated products are dissolved in the FT process reaction water and therefore the FT products lighter than C5 are oxygenate free or has oxygenates present in very low concentrations. The oxygenates in the reaction water are separated from the water by distillation and valuable commodity chemicals are produced by the further purification of these oxygenates. However, the high levels of oxygenates in HTFT products heavier than C5 creates refining challenges. The presence of carboxylic acids can be of great concern since these acids can restrict the metallurgy of processing equipment and cause metal leaching of some catalysts. These acids are difficult to remove by hydrotreating, and unlike hydrodesulphurisation (HDS) and hydrodenitrogenation

(HDN) that produce hydrogen sulphide and ammonia, respectively, hydrodeoxygenation (HDO) produces water, which creates catalysis issues and complicates product work-up.

As mentioned before, the carbon number distribution of HTFT syncrude is heavily weighted towards lighter products. Due to the highly olefinic nature of these light products, oligomerisation can be used to shift the carbon number distribution to heavier hydrocarbons. The carbon number distribution of heavier material in HTFT syncrude can also be shifted to lighter products by means of hydrocracking. Since this heavier material contains no sulphur and low concentrations of polynuclear aromatics, standard commercial hydrocracking catalysts can be utilised.

From a petrol production perspective, unrefined HTFT product has a low octane number with a high olefin content and the refining strategy for HTFT product is therefore focused on the utilisation of the high olefin content to deal with the low degree of branching and the low aromatic content. Firstly, olefins have a low octane number and the extraction of alpha-olefins as chemicals is therefore desirable from both a chemicals and a fuels perspective. Secondly, the low degree of branching and low aromatic content can be addressed by skeletal isomerisation of the olefins and paraffins, selective aromatisation or reforming.

From a diesel production perspective, the low aromatic content and low degree of branching in HTFT primary product contribute to a good cetane number. However, the low degree of branching results in poor cold flow properties, while the low aromatic content results in an undesirable low density of the synthetic diesel fuel. These issues are usually addressed by a slight hydroisomerisation of the primary diesel to improve the quality. Because of the high cetane number obtained in FT diesel, these diesels are used as a blending component to enhance the properties of crude derived diesel.

From the discussion above it can be seen that the refining processes utilised for HTFT primary product upgrading includes oligomerisation, hydrocracking, hydrogenation, aromatisation and isomerisation [2, 4].

## 4.2. LTFT Processing

The iron and cobalt LTFT primary products can be upgraded to middle distillates with naphtha ( $\pm C5$  to 200°C BP) as a by-product. Diesel is the middle distillate of highest value and can be produced from the primary LTFT product by hydrocracking and oligomerisation processes. Hydrocracking of the heavy paraffinic fraction reduces the boiling range to middle distillates and also improves the cold flow properties of the middle distillate product as mostly branched products are produced during hydrocracking. Hydrocracking of wax is the largest contributor to the diesel fuel pool and therefore the FT slurry reactors are operated for maximum wax production. In contrast to crude derived hydrocracking feeds, the feed obtained from the LTFT process is highly paraffinic, free from sulphur and metals containing only small amounts of aromatics, ideal for hydrocracking, and can be processed under much milder conditions than the typical crude oil derived feeds. The LTFT feed also contains low levels of oxygenates, however, these are easily hydrodeoxygenated under hydrocracking conditions. Another advantage of the clean nature of the LTFT derived feed is that non-sulphided hydrocracking catalysts containing a noble metal component like platinum or palladium, either alone or in combination, can be considered. As previously mentioned, diesel produced from hydrocracking contains slightly more branched paraffins than the primary diesel obtained from the LTFT process and therefore has a slightly lower cetane number. However, the final diesel pool still has a cetane number of above 70 (measured on a test engine in accordance with ASTM D613). The high cetane number gives the synthetic LTFT diesel superior combustion characteristics compared to crude derived diesel, whilst the low aromatic content and the absence of sulphur gives it an important environmental advantage. However, the low levels of aromatics and naphthenes (cycloalkane hydrocarbons) result in a lower fuel density.

The primary naphtha produced from the FT process as well as the naphtha produced during hydrocracking have very low octane numbers, since both these naphtha streams consists predominantly of linear alkanes. The naphtha streams would require considerable octane number upgrading to be used as gasoline and are therefore more suited for the production of ethylene by steam cracking. The product obtained from the steam cracking of the naphtha streams yield a much higher concentration of ethylene than would be obtained from the steam cracking of crude oil naphtha.

High value lubricant oils can also be produced from fractions of the LTFT wax. These oils are produced by catalytic dewaxing followed by a hydrofinishing step to hydrogenate polynuclear aromatics that may have formed during catalytic dewaxing which stabilises the base oils. Hydrotreating is often used to improve the quality of the primary FT products. The primary objective of the hydrotreatment of primary products is to saturate olefins and oxygenates to produce paraffins which increases the long term storage stability of these products and also improves the colour and stability of wax products.

From the discussion above it can be seen that the refining processes utilised for LTFT primary product upgrading includes hydrocracking, oligomerisation, catalytic dewaxing and hydrogenation [2, 4].

## **5. Characterisation of Petrochemical Process Streams (Analytical Techniques)**

From the previous paragraphs it can be seen that the FT process produces a variety of hydrocarbons which are distributed across a wide carbon number range. Blomberg et al. [7] estimated a crude-oil derived middle distillate can contain more than  $10^6$  compounds and although FT product streams are less complex, they can still contain tens-of-thousands of compounds. It was also mentioned that, contrary to crude-derived streams, FT streams do not contain S- and N-containing compounds, however, they do contain oxygenates and olefins. During the processing of these FT products a large variety of synthetic fuels and chemicals are produced and these processing steps add to the complexity of the fuels and chemicals [8]. The FT processes, as well as the subsequent refining processes, need to be optimised in order to produce the desired fuel and chemical products. Selectivity models have often been used to describe the product distribution obtained from these processes [4].

Characterisation of crude and FT process streams is essential in the optimisation of the FT and subsequent refining processes. However, the wide carbon number range as well as the variety of products produced creates many challenges in their characterisation. Until recently, one-dimensional GC (1D-GC) was exclusively used in the characterisation of these process streams.

However, it became apparent that single-column separations do not provide enough separation efficiency to resolve every compound in these complex streams, even when using high efficiency capillary columns that provide a peak capacity in the order of ~500 - 600 [9]. The co-elution observed in 1D-GC is not only as a result of the limited peak capacity of the column, but also because of the shared physical properties of the compounds being analysed [8]. As an example, consider two compounds with similar volatilities and different polarities. These compounds may co-elute on a column in which separation is based on volatility only, despite the fact that the total number of peaks in the sample is lower than the peak capacity of the column. Van der Westhuizen et al. [8] showed an example of co-elution for the C10 fraction of an HTFT oil on a non-polar column where the 1-alkene elutes before the n-alkane, followed by the cis-internal alkene and the trans-internal alkene. The authors showed that the cis-2-internal alkene peak elutes closer to the n-alkane peak with increasing carbon number until it eventually co-elutes with the corresponding n-alkane. This results in an overestimation of the alkanes and an underestimation of the internal alkenes. Another concern is that branched paraffin isomers, olefins and oxygenates also co-elute on the non-polar column. These authors also showed that when the same sample is analysed on a polar column, a greater extent of peak co-elution is observed.

### **5.1. Multidimensional gas chromatography (GC×GC)**

Multidimensional gas chromatography is a method for increasing peak capacity or increasing selectivity in GC systems, and was already developed in the 1960's with the heart-cut technique as one of the most frequently used multidimensional systems [10]. The heart-cut technique is still in use today and is based on the practice where a narrow fraction from the first column is re-injected on a second column with a different selectivity for further separation [11]. Another example of multidimensional gas chromatography is the PIONA-analyser, which has been employed to separate paraffins, iso-paraffins, olefins, naphthenes and aromatics [12 - 14]. The PIONA analyser uses four packed columns, three sample traps and six switching valves to achieve the group-type separation per carbon number. However, this analyser system is not able to separate oxygenates from the hydrocarbon matrix. A system called the Reformulyzer was subsequently developed which overcame this

shortcoming [15]. The Reformulyzer utilises packed as well as capillary columns and is still in use in many refinery laboratories today.

In 1991 John Phillips and his co-workers demonstrated a new two-dimensional GC technique [16], and since then this technique has been adapted by several research groups. The technique involves the coupling of two capillary columns of different selectivities through a modulator. The modulator collects small fractions of eluent from the first dimension column and sends them to the second column for further separation. The first dimension separation is preserved and separation on the second dimension column is completed before the next fraction of eluent is received. Using this technique, all compounds in the sample are subjected to both separation dimensions. There are several advantages with the use comprehensive two-dimensional gas chromatography (GC×GC) for the analysis of complex petrochemical samples. The main advantage is the large increase in peak capacity [17], which is in the order of tens-of-thousands (in the order of a few hundred for 1D-GC). Another advantage is that peaks are arranged in highly structured two dimensional plots, where peaks belonging to a homologous series are positioned along straight lines on the retention plane. A roof-tile effect is also obtained where groups of structurally related compounds are piled upon each other, forming a roof-tile pattern in the separation plane. The different compounds in a single roof-tile pattern in the separation plane have the same carbon number but different structural arrangements and this ordered separation aids in group-type classification and identification [18 - 19]. The increase in sensitivity (up to 10 fold, compared to 1D-GC) is another advantage of GC×GC. This sensitivity increase is due to the re-concentration of peaks in the modulator and the very fast separation achieved in the second dimension column. This minimises peak broadening and effectively increases the signal-to-noise ratio [20 - 21]. This increase in sensitivity is especially important in the petrochemical industry, since several components that are critical in the optimisation of refining processes are only present at trace levels. A number of authors have applied GC×GC for the analysis of highly complex petrochemical mixtures [8, 16, 21 - 24]. Profiling of fuels is usually performed by GC×GC in normal configuration, where a non-polar column is used in the first dimension with a polar column in the second dimension. Vendevre et al. [25] used GC×GC in the reversed configuration, with a polar column in the first dimension and a non-polar column in the second dimension, for better characterisation of the aromatics in crude-derived middle-distillates. Van der

Westhuizen et al. [26] showed that the highest orthogonality for FT products is obtained with GC×GC in the reversed configuration with complete utilisation of the two dimensional separation space and superior class separation of alkenes, aromatics and oxygenates. Despite the increase in separation power obtained with GC×GC, this technique also has its limitations when highly complex petrochemical mixtures are analysed. Some of the remaining analytical challenges are discussed in the following sections.

## 5.2. Supercritical fluid chromatography (SFC)

Supercritical fluid chromatography (SFC) is a form of chromatography where the mobile phase is at pressures and temperatures near or above the critical point. The purpose of employing a mobile phase above the critical point is to enhance the solvating power of the mobile phase [27]. The first experiments using supercritical fluids as mobile phase were already performed in 1962 [28].

Because of the nature of supercritical fluids, the mobile phase can easily be varied comprise of characteristics between gas and liquid, which leads to a several advantages of SFC compared to other separation techniques. For instance, fluids with low critical temperatures permit separations at low temperatures to prevent decomposition of thermally labile compounds. The solvating ability of supercritical fluids (similar to those of liquids) also allows for the analysis of high molecular mass compounds that do not elute easily in gas chromatography (even at elevated temperatures) since they have low vapour pressures. SFC is also compatible with most detectors used in GC and HPLC. SFC allows for the use of both open tubular capillary and packed columns. [27].

Several SFC parameters can be controlled to change the retention of compounds. These SFC parameters include; mobile phase pressure, density, temperature and composition. The column stationary phase can also be used as a way to effect the retention of compounds [27]. Gases, supercritical fluids, and liquids have been compared as chromatographic mobile phases [29]. CO<sub>2</sub> is the most commonly used SFC mobile phase, while miscible organic modifiers are commonly added to enhance the solvating power of the mobile phase [27].

SFC with CO<sub>2</sub> as the mobile phase combines many advantages of GC and HPLC, enabling its use for the separation of hydrocarbons. The application of SFC to the petroleum industry has thus already started in the 1980's and since then several application areas have been identified [30].

One routine GC application in the petroleum industry is GC simulated distillation (SIMDIS). The final boiling point (FBP) that can be reached by this technique is in excess of 538°C [31]. In another application, atmospheric equivalent boiling points (AEBP's) of around 700°C can be determined by HT-GC with oven temperatures up to 450°C [32 - 34]. Hydrocarbons containing more than 80 - 100 atoms are difficult to elute in GC without the thermal cracking of these hydrocarbons [35]. Due to the solvent strength of a supercritical fluid and the polarity of supercritical CO<sub>2</sub>, the elution of these hydrocarbons can be obtained in SFC at much lower temperatures than in HT-GC. Many research groups showed that hydrocarbons containing more than 80 - 100 atoms can be eluted using either packed or open tubular capillary columns; the elution of hydrocarbons of up to C<sub>136</sub> has been reported [35 - 38]. Since hydrocarbons from a carbon number of C<sub>20</sub> to more than C<sub>130</sub> can be eluted in SFC without the risk of cracking at high temperatures, it is an attractive alternative to HT-GC.

Another routine application in the petroleum industry is hydrocarbon group-type analysis and this is the most studied HPLC application. In HPLC the refractive index detector is commonly used for group-type analysis. The refractive index detector requires calibration for hydrocarbon type, which can be very inaccurate. When using FID, on the other hand, only a minor or no correction is needed for hydrocarbon type analysis. The flame ionisation detection (FID) can be used with SFC, provided pure CO<sub>2</sub> is used as mobile phase, which makes it very appealing for group-type separations. Group-type analysis with SFC was also improved by the use of different stationary phases, in series or in a multidimensional mode. Other groups reported SFC group-type separations for the determination of non-aromatic, mono and polyaromatic hydrocarbon groups in light fuel fractions (gasoline, gas oil, jet fuel) [39] and the resolution between these groups was improved by the implementation of two different columns connected in series [40]. Multidetector has also been used to further improve group-type analysis and the improved aromatic group determination by detection with both UV and FID was reported [30].



SFC group-type separations are also used in the determination of olefins using Ag modified columns. The multidimensional ASTM method D6550 [41] utilises a switching valve connected to a silica column employed for aromatic and oxygenated compound retention. The olefins are retained on a silver modified column connected in series to the first silica column via a second switching valve. The valves are then switched in such a way that the different hydrocarbon groups elute in the order of saturates, aromatics, oxygenates and olefins. This method was modified to include a third column packed with polyvinyl alcohol-bonded silica for the separation of olefins in denatured ethanol [42]. Other SFC group-type separations include application to heavy samples [43 - 45], middle distillates [45] and vacuum distillate [46].

Using CO<sub>2</sub> as mobile phase also has the advantage of the ease of hyphenation with GC and comprehensive two-dimensional GC (GC×GC). These techniques can be hyphenated by the decompression of the dense CO<sub>2</sub> in the gas state into the GC or GC×GC injector and no dedicated interface is needed [47 - 49]. A comprehensive SFC×GC instrument was also developed for the separation of polar compounds in commercial gasoline [50] using a porous layer open tubular silica gel column with subcritical CO<sub>2</sub> as the mobile phase in the first dimension for group-type separation of polar oxygenates. In the second dimension a GC column was resistively heated to perform fast GC separations and comprehensive two-dimensional analysis was carried out in stop-flow mode. Because of the unique separation power obtained with this technique, further developments in the field of SFC×GC instrumentation is expected.

The development of comprehensive two dimensional SFC (SFC×SFC) by means of a computer-controlled ten-port valve and subsequently by means of an on-line comprehensive 2D HPLC interface was also reported [46, 51]. Recently the first SFC×SFC-FID chromatogram was published on coal tar vacuum distillate [30]. These authors also predicted that the chromatograms could be improved to be very similar to those obtained by GC×GC with optimisation of the fraction transfer between the two columns.

Recently Malan et al. [52] reported the development of a comprehensive two dimensional SFC×GC instrument with FID detection and the application of this technique to biodiesel, demonstrating the utilisation of complementary selectivity achieved on SFC.

### 5.3. Supersonic molecular beams (GC-Cold-EI-MS)

In the last decade Fialkov et al. [53 - 55] developed a new type of ionisation source for GC-MS, based on the use of a supersonic molecular beam (SMB), named Supersonic GC-MS. Supersonic GC-MS is based on the use of a SMB in the interface between the GC and the MS. SMB's are formed by the expansion of gas through a small shaped nozzle into a vacuum chamber. In this expansion, the GC carrier gas is combined with helium make-up gas added to the system. The heavier sample molecules are all accelerated to the velocity of the helium. This uniform velocity results in slow intra-beam relative motion and collisions during the supersonic expansion which results in vibrational cooling of the compounds. In a SMB, the molecules are therefore vibrationally supercooled before entering the ion source, reducing the amount of internal energy available for fragmentation of the molecular ion [53, 55 - 57]. This leads to a substantial increase in the molecular ion peak height in the mass spectrum. The single passage of molecules through the fly-through EI ion source results in the low molecular vibrational temperature to be independent of the source temperature, avoiding molecular thermal decomposition and adsorption-desorption on the ion-source walls [53]. SMB's are characterised by intra-molecular vibrational super-cooling, unidirectional molecular motion with controlled hyperthermal kinetic energy (1 - 20 eV), mass focusing similar to that of a jet separator and the capability to handle a very broad range of column flow rates from standard 1 mL/min up to 90 mL/min [54, 58].

Supersonic GC-MS has many beneficial features, with the enhanced molecular ion in the mass spectra [55 - 56, 58] being most significant, even for very large hydrocarbons [53, 55, 58]. The presence of molecular ions aid tremendously in the mass spectral identification of compounds. The enhanced signal for the molecular ion also decreases the chance of peak overlap since matrix interference is exponentially reduced with mass increase [59]. Other groups have also used fast GC-MS with supersonic molecular beams to extend the range of compounds amenable for GC-MS analysis [60 - 61]. Thermally labile pesticides, that are difficult or impossible to analyse in standard GC-MS, were analysed with increased sensitivity and fast analysis times.

Because of the advantages of Supersonic GC-MS, it has been widely applied in petroleum industry research. The analysis of straight chain alkanes by Supersonic GC-MS was studied by Dagan et al. [53], while Fialkov et al. [56] published a paper on hydrocarbons and fuels analyses with Supersonic GC-MS and demonstrated that it can be used in a variety of hydrocarbon analyses applications. The application of flow modulation GC×GC-MS with a supersonic molecular beam to complex matrices (diesel and jet fuels) was also published [62 - 64] and the method was applied to complex matrices such as diesel fuel and jet fuel. A study on the use of fast GC-MS with SMB for the analysis of fatty acid methyl esters (FAME) in jet fuel was reported [60] and Supersonic GC-MS was also used for the analysis of free fatty acids in a hydrocarbon based antifoam [65].

## **6. Characterisation of Petrochemical Process Streams (Analytical Challenges)**

### **6.1. Cyclic alkane and alkene differentiation**

Even in GC×GC, peak co-elution can still occur when samples containing isomeric compounds are analysed. To separate cyclic paraffins and olefins is difficult since these compounds elute in similar positions on the GC×GC chromatogram. Group-type identification can be achieved to a large extent when using time-of-flight mass spectrometry (TOF-MS) in combination with GC×GC, however, this technique is also not able to distinguish between the cyclic paraffins and olefins since these compounds have identical molecular masses and similar fragmentation patterns.

A fractionation step can be applied prior to GC×GC analysis to address this challenge [66 - 68]. An HPLC fractionation procedure prior to GC×GC-TOF-MS analysis was previously published by our group, to distinguish between cyclic paraffins and olefins [69]. The separation of the alkenes and alkanes was achieved on a silver-modified HPLC column where the silver ions interact with the alkene double bond by complex formation [68]. The TOF-MS was used to then distinguish between the linear and cyclic alkanes un-retained by the silver modified column and the linear and cyclic alkenes retained by this column. Co-elution of the HPLC

solvents and the volatile sample components, as well as dilution of the samples were the major drawbacks of this fractionation procedure [69]. Since off-line hyphenated techniques are susceptible to sample loss and contamination during collection and re-concentration [70], this method still needs improvement to eliminate the mentioned drawbacks.

Silver column chromatography cannot be used to distinguish between classes with varying degrees of unsaturation when both rings and double bonds are present (eg. dienes and cyclic olefins) since both these classes contain alkene double bonds that will form strong adducts with silver ions and separation will not be achieved. An alternative method for the positive identification of these compounds needs investigation. On-line hydrogenation after GC separation is a possible way to distinguish between these compounds, since the number of rings and alkene double bonds in the compound structure can be determined from the mass spectra of the compounds before and after hydrogenation [71 - 73]. However, the application of capillary hydrogenation after separation by gas chromatography is not suitable for highly complex petrochemical samples, and the use of capillary hydrogenation after GC×GC separation for the analysis of complex samples needs to be developed.

## 6.2. Characterisation of heavy oxidised paraffinic fractions

The characterisation of heavy petrochemical fractions is a difficult analytical challenge. Not only does the number of hydrocarbon isomers increase with increasing carbon number, but only a limited range of relatively small and non-polar molecules can be analysed directly by GC [74 - 75]. Various attempts have been made to extend the range of GC for the analysis of heavy compounds. Derivatisation reactions [76] involve the transformation of non-volatile compounds into elutable species, whilst pyrolysis GC [77] involves the destruction of the samples into smaller fragments prior to GC analysis. Another important method to extend the molecular range analysable by GC is high-temperature gas chromatography (HT-GC). Importantly, compounds are not altered prior to analysis and their elution is improved only by the extension of the conventional temperature of separation and the adaptation of chromatographic conditions. Although HT-GC is not well defined, various authors have stated that it concerns GC separations with final temperatures higher than 340°C [74 - 75].

HT-GC is an established technique and allows for the resolution of a wide molecular weight range (~100 to >1400 Da, equivalent to n-alkanes from C7 to >C100) within a single analysis [78 - 79]. The use of HT-GC instrumentation is critical for the analysis of heavy fractions. Discrimination towards high-boiling compounds can be observed during the injection step and needs to be eliminated by the use of cold on-column or programmed temperature vaporization (PTV) injectors [78 - 79]. Column and stationary phase technology also need careful consideration in HT-GC. Regular polyimide coated columns need to be replaced with metal columns or columns with a special protective coating. To reduce bleeding (thermal degradation of the stationary phase) in HT-GC applications, end-capping as well as the quality of surface chemistry of the underlying fused silica are very important [80 - 81]. As mentioned before, due to the temperature limitation of polar columns, HT-GC is mostly limited to non-polar stationary phases. The extension of the molecular range amenable for HT-GC analysis also involves adapted chromatographic conditions. Short columns with thin film thicknesses are used to decrease the retention time of heavy compounds and the low column outlet pressure achieved when using mass spectrometry detection enables further lowering of the elution temperature of these heavy compounds due to higher optimum linear flow rates achievable [81].

Despite HT-GC being an established technique, peak overlap still occurs to a great extent when complex heavy petrochemical fractions are analysed. As discussed in the preceding paragraphs, GC×GC is a powerful tool to analyse complex samples where the peak capacity [17] is increased by combining two chromatographic columns with different separation mechanisms. During a single GC×GC analysis, the entire sample composition is subjected to two independent GC separations and the entire paraffinic fraction is separated into thousands of different components. The resulting GC×GC separation can therefore provide a great deal of information on molecular composition and the presence of different hydrocarbon types in a sample [82].

Until quite recently the use of GC×GC was limited to petrochemical samples in the middle distillate range (boiling point of <450°C). The extension of GC×GC to heavier petrochemical fractions would be of great value as it would enable the determination of the molecular composition of heavy fractions. However, the applicability of GC×GC to heavy fractions is

limited by the temperature limitation of polar columns as well as modulation problems during the desorption step of the heavy compounds. The following adaptive conditions were developed to address these limitations. Firstly, previous groups [82 - 83] showed that flow programming, whereby the liquid-nitrogen cooled gas flow rate of a cryogenic nitrogen modulator was reduced during analysis, improves desorption of heavier compounds and provides better peak shapes. The GC×GC separation up to C47 of a partial vacuum gas oil (VGO) was reported [82] nitrogen gas flow programming of the cold jet. Secondly, Dutriez et al. [74] reported on the impact of the various abovementioned high-temperature conditions on GC×GC, and showed that column dimensions are the most critical parameters to optimise. Dutriez selected an experimental set of capillary columns based on the following factors: stationary phase chemistry, column diameter, film thickness and column length. The results showed that compounds can elute quicker from the first dimension column to reach the second column at a lower temperature. With the correctly adapted parameters and with the developed method, Dutriez could elute hydrocarbons of up to C60, as well as tetra-aromatic compounds in vacuum gas oil (VGO). This is still significantly lower than the C100 elution achievable with HT-GC.

Many groups have used HT-GC×GC to extend the carbon number range attainable by GC×GC and have optimised the HT-GC×GC parameters for the separation of aromatics, nitrogen-containing compounds as well as sulphur containing compounds in heavy petroleum fractions [74, 84 - 90]. Oxidation of heavy paraffinic fractions produces high value products that contain a variety of oxygenates. The characterisation of these heavy oxygenates is very important for the control of oxidation processes and the optimisation of HT-GC×GC parameters for the optimum separation of oxygenates in heavy oxidised paraffinic fractions needs to be investigated.

### **6.3. Improved identification of oxygenates**

As mentioned in the previous paragraphs, the characterisation of heavy petrochemical fractions is a difficult analytical challenge and techniques like HT-GC×GC are needed to characterise these streams. The accurate identification of the oxygenates present in the

oxidised heavy paraffinic fractions by electron ionisation (EI) mass spectrometry is challenging due to the complexity of these heavy fractions and because oxygenates are present in low concentrations. Most of these heavy oxygenates are not included in the mass spectral library, which limits the use of electron ionisation (EI) libraries and the absence of the molecular ion ( $M^+$ ) from the mass spectra of most of these oxygenates make their identification even more difficult [56].

The use of Supersonic GC-MS for the identification of oxygenates present in oxidised heavy paraffinic fractions needs to be studied. This technique has been applied to various hydrocarbon mixtures [53, 56] and work has been published on the improved identification of n-alkanes from heavy petrochemical fractions. To aid in the identification of these heavy oxygenates, pre-fractionation procedures for the pre-separation of oxygenates prior to Supersonic beam GC-MS analysis will also be investigated.

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## Chapter 3

# Hyphenation of supercritical fluid chromatography and two-dimensional gas chromatography-mass spectrometry for group-type separations

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E. Rohwer provided assistance with the optimisation of hyphenation experiments.

D. Malan provided assistance with the preparation of integral restrictors.

**Abstract**

The Fischer-Tropsch (FT) process produces a variety of compounds over a wide carbon number range and the synthetic crude oil produced by this process is rich in highly valuable olefins and oxygenates, which crude oil only contains at trace levels. The characterisation of these products is very challenging even when using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOF-MS). The separation between cyclic paraffins and olefins is especially difficult since they elute in similar positions on the GC×GC chromatogram and since they have identical molecular masses with indistinguishable fragmentation patterns. Previously, a high performance liquid chromatography (HPLC) fractionation procedure was used prior to GC×GC-TOF-MS analysis to distinguish between alkenes and alkanes, both cyclic and non-cyclic, however, there was co-elution of the solvents used in the HPLC fractionation procedure, and the volatile components in the gasoline sample and the dilution introduced by the off-line fractionation procedure made it very difficult to investigate components present at very low concentrations. The hyphenation of supercritical fluid chromatography (SFC) to GC×GC is less complicated and the removal of the supercritical CO<sub>2</sub> can be easily achieved without any loss of the volatile sample components, eliminating the introduction of co-eluting solvents as well as the dilution effect. This paper describes the on-line hyphenation of SFC to a GC×GC system in order to comprehensively characterise the chemical groups (saturates, unsaturates, oxygenates and aromatics) in an FT sample.



## 1. Introduction

The Fischer-Tropsch (FT) process produces a variety of compounds over a wide carbon number range and involves a series of catalysed reactions of carbon monoxide and hydrogen. A large variety of synthetic fuels and chemicals are produced during product workup [1] that are practically free of sulphur- and nitrogen-containing compounds, alleviating environmental concerns when compared to crude-derived products. The high temperature FT (HTFT) products are rich in highly valuable olefins and oxygenates, which crude oil only contains at trace levels. For the HTFT processes products are spread over gas, oil and water phases with only a small amount of wax being formed. The analysis of any one of these phases is very challenging and typical oil phase samples may contain thousands of compounds. The characterisation of these phases is very important for the study of FT selectivity models and their deviations [2]. Previously one-dimensional separation techniques were used for the study of the selectivity models [2 - 9], however these techniques cannot separate all compounds, even when using high efficiency capillary columns providing peak capacities in the order of  $\pm 500 - 600$  [10].

The introduction of comprehensive two-dimensional gas chromatography (GC $\times$ GC) provides several advantages for the analysis of these complex oil phase samples. The peak capacities are in the order of tens of thousands and peaks are arranged in highly structured plots where peaks belonging to a homologous series are positioned along straight lines on a retention plane. Another advantage of GC $\times$ GC is the increase in sensitivity (up to 10 fold) compared to 1D-GC because of the re-concentration of peaks in the modulator and the very fast separation achieved in the second dimension column that minimises peak broadening and effectively increases the signal-to-noise ratio [11, 12]. The application of GC $\times$ GC to the analysis of highly complex petrochemical mixtures has been described by a number of authors [12 - 17].

Even with the huge increase in separation power obtained by comprehensive GC, peak co-elution still occurs when very complex mixtures are analysed. The separation between cyclic paraffins and olefins is especially difficult since they elute in similar positions on the GC $\times$ GC chromatogram. Time-of-flight mass spectrometry (TOF-MS) is very powerful in group-type

identification but is also not able to distinguish between the cyclic alkane and alkene component classes because of their identical molecular masses and similar fragmentation patterns. One way of improving the GC×GC separation is to apply a fractionation step prior to GC×GC analysis [18 - 20]. Previously, an HPLC fractionation procedure using a silver-modified column was used prior to GC×GC-TOF-MS analysis to distinguish between alkenes and alkanes, both cyclic and non-cyclic [21, 22]. This robust fractionation step before GC×GC was used to separate saturated from unsaturated hydrocarbons since it is known that the silver ions interact with the alkene double bond by formation of a complex. It was shown by Mao et al. [21] that the complexation of silver ions with alkene double bonds occurs with both aromatic and non-aromatic compounds. It was observed that the saturated hydrocarbons were not retained on the silver-modified column and eluted with the non-polar mobile phase, n-hexane, whilst the unsaturated hydrocarbons were retained on the column. The unsaturated hydrocarbons were subsequently released from the column by changing the mobile phase to the more polar acetone. The GC×GC-TOF-MS was then utilised to distinguish between the non-cyclic and cyclic alkanes eluted by the hexane solvent and the non-cyclic and cyclic alkenes eluted by the acetone solvent. Although this approach worked well, there was co-elution of the solvents used in the HPLC fractionation procedure and the volatile components of the gasoline sample [22]. Another drawback of this procedure is that the solvents used in the HPLC method diluted the sample and large amounts of the collected fractions had to be injected in order to detect the smaller peaks by GC×GC. Direct transfer of large volumes of collected fractions requires instrument modifications [24]. Low level components can go undetected without reconcentration of the collected fraction, a process that can lead to severe discrimination against the volatile compounds in the sample. The susceptibility of off-line hyphenated techniques to sample loss and contamination during collection and reconcentration has been described by other groups [23], emphasising the need for an on-line pre-fractionation step.

Supercritical fluid chromatography (SFC) utilises supercritical CO<sub>2</sub> as mobile phase. The use of SFC for group-type separation has been published before and the separation achieved with SFC has proved to be very similar to that obtained by HPLC [25 - 27]. The hyphenation of SFC to GC×GC is less complicated and has been achieved by other groups merely by decompression of the supercritical fluid through a restrictor into the GC injection port [28 -

30]. This allows the transfer of an eluting fraction from the supercritical phase to the gas phase with simultaneous loss of only the highly volatile CO<sub>2</sub>. Utilising SFC as pre-fractionation method would eliminate the introduction of co-eluting solvents as well as the dilution stemming from the HPLC fractionation procedure [22]. In order to comprehensively characterise the chemical groups (saturates, unsaturates, oxygenates and aromatics) in a sample, the on-line hyphenation of SFC to a GC×GC system is described.

The first part of this paper addresses the development and optimisation of the SFC chromatographic conditions to achieve the group-type separation whilst the second part deals with the GC×GC method. Subsequently the on-line hyphenation of SFC to the GC×GC and the results obtained from the analysis of an oil sample are also discussed. Some applications are also mentioned at the end of this chapter.

## **2. Experimental**

### **2.1. Chemicals**

Analytical gases for both the SFC and the GC×GC were obtained from Afrox (South Africa). The HTFT Light oil, kerosene and narrow distillation cut samples were obtained from Sasol Synfuels, Secunda, South Africa. Standards of the various chemical groups were obtained from Sigma Aldrich (St Louis, MO, USA).

### **2.2. SFC group-type separation**

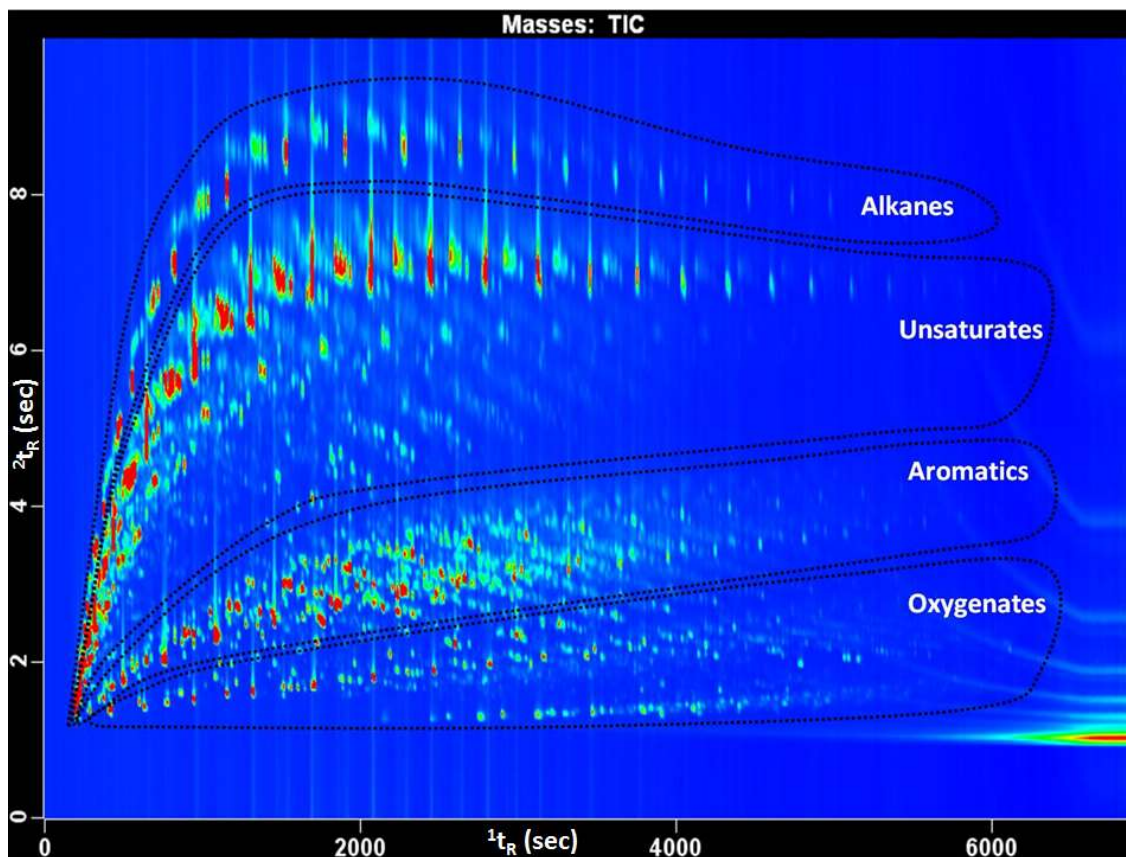
A Selerity Series 4000 SFC system equipped with SFC pump, autosampler, SFC oven, a pneumatically actuated rotary injection valve and a flame ionisation detector operated at a temperature of 400°C was used for the group-type separations (Selerity Technologies, Utah, USA). The optimisation of the group-type separation (saturates, unsaturates, aromatics and oxygenates) utilising SFC was performed using a variety of standards typically found in a HTFT light oil sample. In order to achieve the group-type separation, three analytical columns were used in series, namely a PVA-silica column (50 mm L × 1.0 mm ID, 5 μm d<sub>p</sub> from Selerity

Technologies, Utah, USA) that was used to retain the oxygenates whilst the Petrosil column (50 cm L  $\times$  1.0 mm ID, 5  $\mu$ m  $d_p$  from Selerity Technologies, Utah, USA) was used to separate the aromatics from the unsaturates. A PetroAG silver-loaded cation exchange column (50 mm L  $\times$  1.0 mm ID, 5  $\mu$ m  $d_p$  from Selerity Technologies, Utah, USA) was used to retain all the unsaturates. The SFC oven was also equipped with two six-port two-position switching valves to allow forward and backflushing of the analytical columns. The silver loaded column was operated in a secondary oven at a temperature of 140°C throughout to allow faster clearance of the olefins and other unsaturates through the column. The SFC mobile phase (carbon dioxide) was delivered at a constant pressure of 200 atm. The injection volume was 0.1  $\mu$ L and the analysis temperature of 40°C for the primary oven was used throughout. An external six-port, two-position switching valve was used to direct the SFC effluent to either the FID on the SFC instrument or the GC $\times$ GC instrument. A split connector (Restek, Bellefonte, USA) was installed on the capillary going to the GC $\times$ GC in order to control the amount of effluent that is sent to the GC $\times$ GC and this amount could be varied using different restrictor combinations. The SFC eluent was introduced into the PTV injector by an integral restrictor [31] inserted through the septum. The combined flow sent through the restrictor and vented by the split matched the flow to the SFC's FID. The SFC columns were set up similar to the method described for the determination of olefin content in denatured ethanol by SFC [32] and once the retention times for each group was determined using the FID, the external valve could be switched on at these respective times to transfer the appropriate SFC fractions to the GC $\times$ GC.

### 2.3. GC $\times$ GC method

The GC $\times$ GC instrument used was a Pegasus 4D from Leco Corporation (St. Joseph, USA) equipped with a time-of-flight mass spectrometer and a 7683B auto injector system (Agilent Technologies, Little Falls, USA). A programmed temperature vaporization (PTV) injector (Gerstel, Mulheim an der Ruhr, Germany) was used on this system. In previous studies the advantages of a polar  $\times$  non-polar column set (in contrast to the more common non-polar  $\times$  polar column set) for the analysis of Fischer-Tropsch oil products were described [16, 17]. Hence, in the first dimension a 60 m  $\times$  0.25 mm ID, 0.25  $\mu$ m  $d_f$  StabilWax (Restek, Bellefonte, USA) and in the second dimension a 2 m  $\times$  0.1 mm ID, 0.1  $\mu$ m  $d_f$  RTX $\text{i}$ -5 column (Restek,

Bellefonte, USA) was used in this study. Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min. A split ratio of 400:1 and injection volume of 0.5  $\mu\text{L}$  was used for the analysis of the light oil sample whilst for the hyphenation experiments the injector was operated in splitless mode. The first oven was programmed from 40°C (2.0 min) to 255°C at 2°C/min. The secondary oven and modulator followed the first temperature programme but started at 60 and 70°C, respectively. A modulation period of 10s was used. TOF-MS spectra were collected between 30 and 500  $m/z$  at 100 spectra/s. A GC $\times$ GC chromatogram (without SFC pre-separation) of a typical HTFT light oil sample indicating the different chemical groups is shown in Fig. 3.1.



**Figure 3.1** Contour plot obtained for the GC $\times$ GC-TOF-MS analysis of the HTFT light oil sample used to develop this method with the polar  $\times$  non-polar column configuration.

## 2.4. Hyphenation of SFC and GC×GC

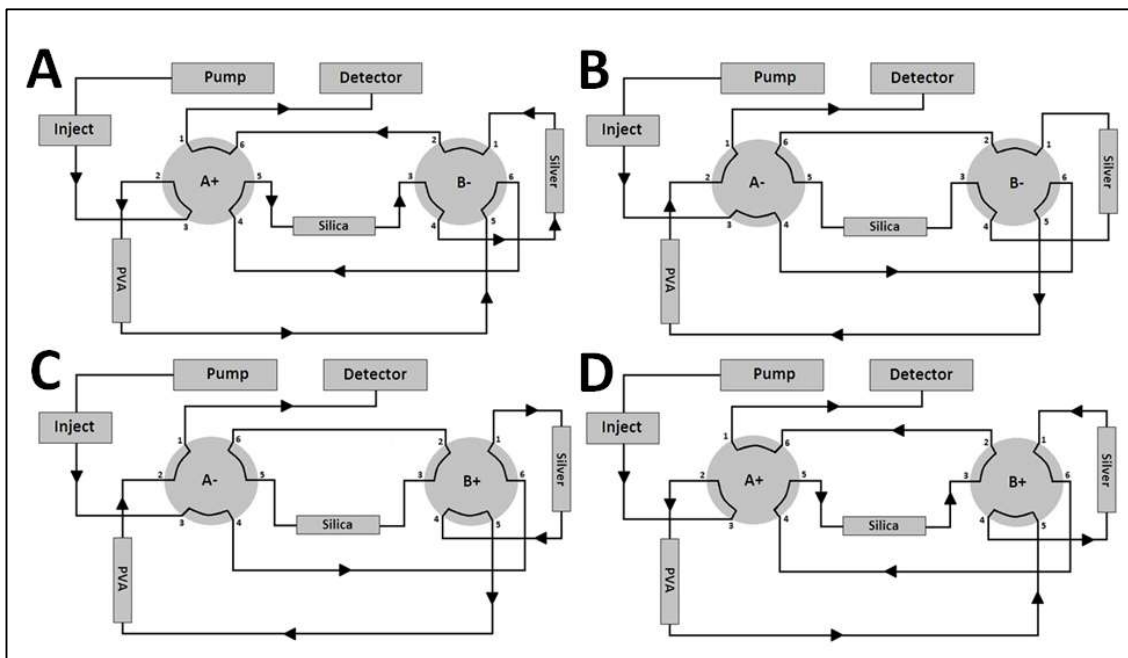
The experimental set-up involved the insertion of the end restrictor from the 'on' position of the external six-port switching valve into the septum of a PTV injector. Previous studies [30] indicated that the length of restrictor that is introduced into the injector does not affect yields of recoveries and therefore 5 cm of the restrictor was introduced into the injector. In order to transfer the SFC peak of interest to the GC×GC, the external six-port valve was switched to the 'on' position at the start of the peak of interest. The analytes were cryogenically focussed at the head of a thick phase (0.05 m × 0.25 mm ID, 1.0 μm d<sub>f</sub>) HP-1MS column (Agilent Technologies, Little Falls, USA) inside the injector by dispensing liquid nitrogen to the injector via a nitrogen cryogenic valve (Agilent Technologies, Little Falls, USA). The first dimension column (Section 2.3) was connected to this HP-1MS column inside the column oven. The injector temperature was maintained at -50°C during the transfer of the SFC effluent. The normal oven starting temperature of 40°C was maintained throughout the effluent transfer. Once the whole peak of interest was transferred to the GC×GC, the external six-port valve was once again switched to the 'off' position sending the SFC effluent to the FID detector, allowing the SFC chromatographic run to finish normally. Once all the CO<sub>2</sub> passed through the GC×GC columns (inlet depressurised), the normal GC×GC analysis (Section 2.3) was started by heating the PTV injector to 260°C at a rate of 720°C/min. The sample was injected four times onto the SFC with a different peak of interest transferred from each SFC run for subsequent GC×GC analysis.

### 3. Results and Discussion

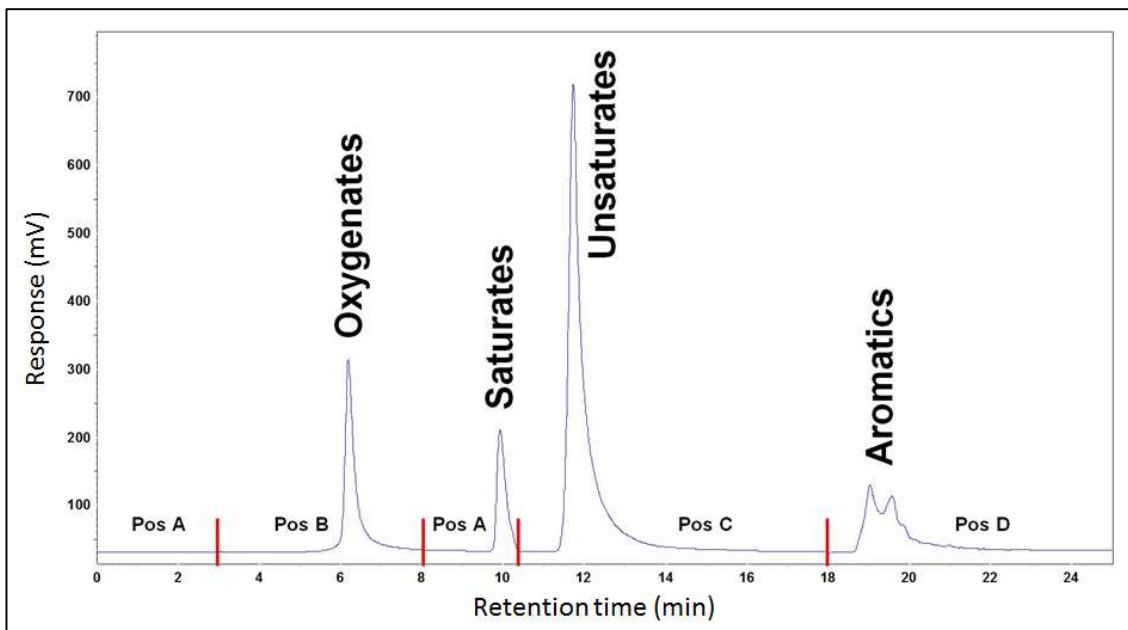
#### 3.1. Optimisation of SFC fractionation

A variety of standards typically found in a HTFT light oil sample was used in order to optimise the valve switching times. These standards included alkanes, cyclic alkanes, olefins, cyclic olefins, dienes, cyclic dienes, alkylbenzenes, alcohols, carbonyls, and acids in the C5 - C25 carbon range. These compounds are tabled in Appendix A.

In order to separate oxygenates from the other compounds, the PVA column, silica column and silver column were operated in forward flush mode connected in series (Fig. 3.2A). In this position the oxygenates were retained on the PVA column whilst all the other groups eluted from the column within 3.0 min to be collected on the silica column. At this time valve A is switched to the negative position in order to operate the PVA column in backflush mode whilst the silica and silver columns are in stop-flow mode (Fig. 3.2B). All the oxygenates retained on the PVA column were backflushed from the PVA column within 8.0 min and valve A was once again switched on (Fig. 3.2A) in order to elute the saturates, retain the aromatics on the silica column and to load all the olefins on the silver column. All the saturates eluted from the silver column at 10.0 min and at this time valve A was switched off whilst valve B was switched on removing the silica column from the flow path (Fig. 3.2C), operating both the PVA column and silver columns in backflush mode in order to elute all the unsaturate species from the silver column. All the olefin species were eluted at 18.0 min and at this time both valves were switched on to include all the columns in forward flush mode (Fig. 3.2D), with the silica column last in the series, to elute all the aromatics to the detector. At 25.0 min all the aromatics were eluted and the run was ended. The SFC-FID chromatogram obtained for the analysis of a light oil sample (Fig. 3.3) shows the group-type separation obtained.



**Figure 3.2** The SFC column configurations for the elution of oxygenates (A (0 - 3 min); B (3 - 8 min)), saturates (A; 8 - 10 min), unsaturates (C; 10 - 18 min) and aromatics (D; 18 - 25 min) (For detail see text.).



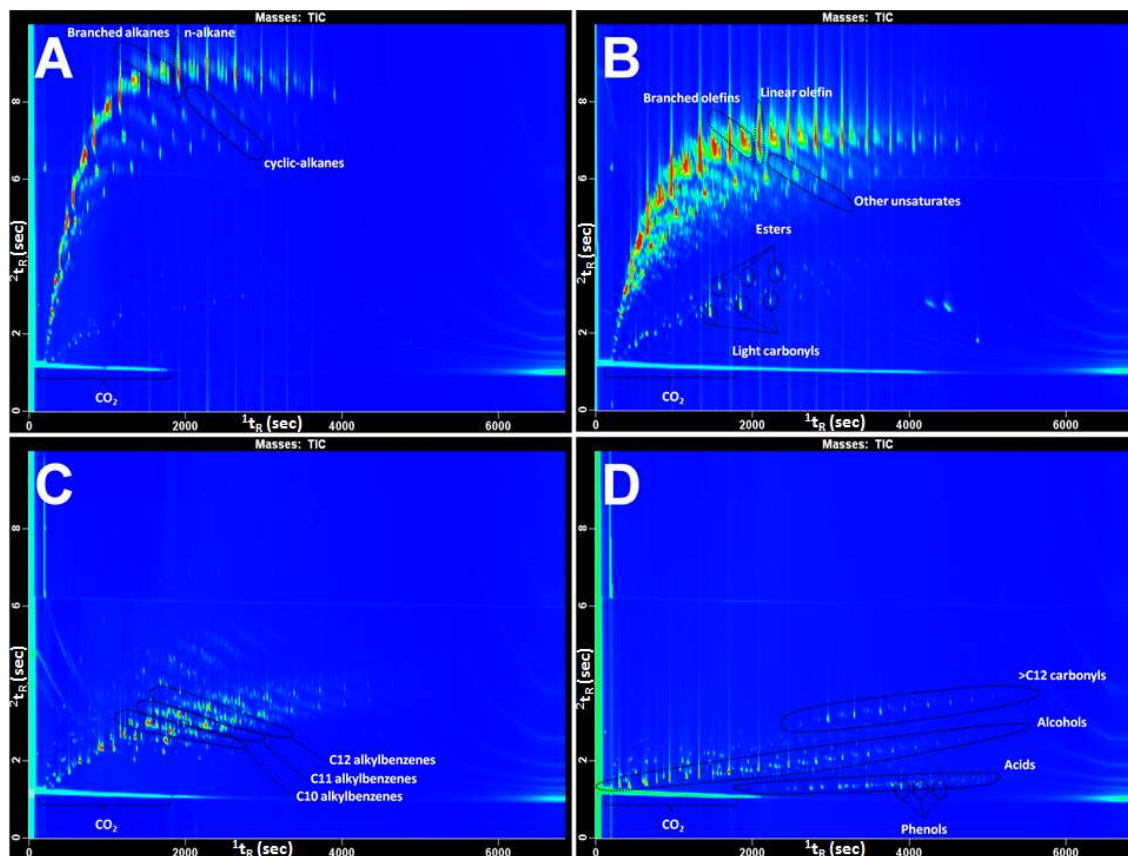
**Figure 3.3** SFC-FID analysis of the HTFT light oil. Valve switching times as well as the valve positions between switching times are indicated on the chromatogram.



### 3.2. Hyphenation of SFC and GC×GC

As suggested by Adam et al. [30] cryofocussing of solutes was used in order to continuously trap analytes transferred from the SFC at the head of the GC×GC primary column. The integral restrictor was inserted into a split/splitless inlet in splitless mode through the septum. The oven of the primary column was cooled using the cryogenic cooling function of the chromatograph. The eluent of the SFC would therefore pass into the cold column and be trapped at the head of the cold column. Initial attempts to trap solutes using this experimental set-up remained unsuccessful, resulting in the insufficient trapping of the volatile components in the light oil sample even at oven temperatures of  $-50^{\circ}\text{C}$ . This was mostly due to the fact that at this low trapping temperature the primary GC×GC column was operated out of its recommended operating conditions (the minimum operating temperature of the stationary phase is  $40^{\circ}\text{C}$ ) and this resulted in a liquid-solid phase transition of the column stationary phase. Furthermore, upon subsequent heating of the column, the solid-liquid phase transition is not immediate. This results in loss of efficiency, reduced sample capacity as well as poor retention time reproducibility. It was subsequently decided to replace the split/splitless inlet with a programmed temperature vaporization (PTV) injector and to cryofocus the solutes on a thick phase column inside the PTV injector as described in Section 2.4.

It can be seen in Fig. 3.4A that in the case of the saturated group of the light oil sample, the volatile compounds were trapped sufficiently and the resolution was similar to that obtained from the direct GC×GC analysis (see Fig. 3.1). It can be seen from this contour plot that the saturates were isolated successfully and that none of the other groups of interest eluted in this fraction. The n-alkanes, branched alkanes and cyclic alkanes are easily distinguishable. The GC×GC results achieved without SFC fractionation (Fig. 3.1) can readily be imagined by superimposing A and B. Looking at the retention times of the cyclic alkanes on the contour plot, it can be seen that they would elute in the same area as the olefins and since the olefins are present in high concentrations in the original light oil sample, the cyclic paraffins would co-elute severely with the olefins as in Fig. 3.1, preventing classification and even detection. With SFC fractionation, however, no olefins were observed in the saturate fraction and the complexity of this area on the chromatogram was drastically reduced.



**Figure 3.4** Contour plots obtained for the SFC-GC×GC-TOF-MS analysis of the (A) saturate, (B) unsaturate, (C) aromatic and (D) oxygenate fractions of HTFT light oil.

The GC×GC-TOF-MS contour plot of the unsaturate fraction (Fig. 3.4B) shows no traces of saturates, allowing clear separation of linear and branched olefins. Other unsaturates (cyclic olefins, dienes, cyclic dienes) also elute in this fraction whilst the aromatics were completely absent from this fraction. A distribution of light carbonyls (<C12) and esters is also observed in the unsaturate fraction. It is possible that the light carbonyls and esters remained on the PVA column when the heavier carbonyls and esters were backflushed from the PVA column (Fig. 3.2B). Once the unsaturates were backflushed from the silver column, the eluent also flowed through the PVA column in backflush mode (Fig. 3.2C) and these light carbonyls and esters were removed from the PVA column and eluted with the unsaturate fraction. This was not a major concern since these carbonyls elute in a different chromatographic region than the olefins and other unsaturates on the contour plot. The aromatics that usually co-elute with the carbonyls and esters in this region were completely removed from this fraction. The selectivity of the PVA column can be further investigated to explain why the light carbonyls and esters elute with the unsaturate fraction.

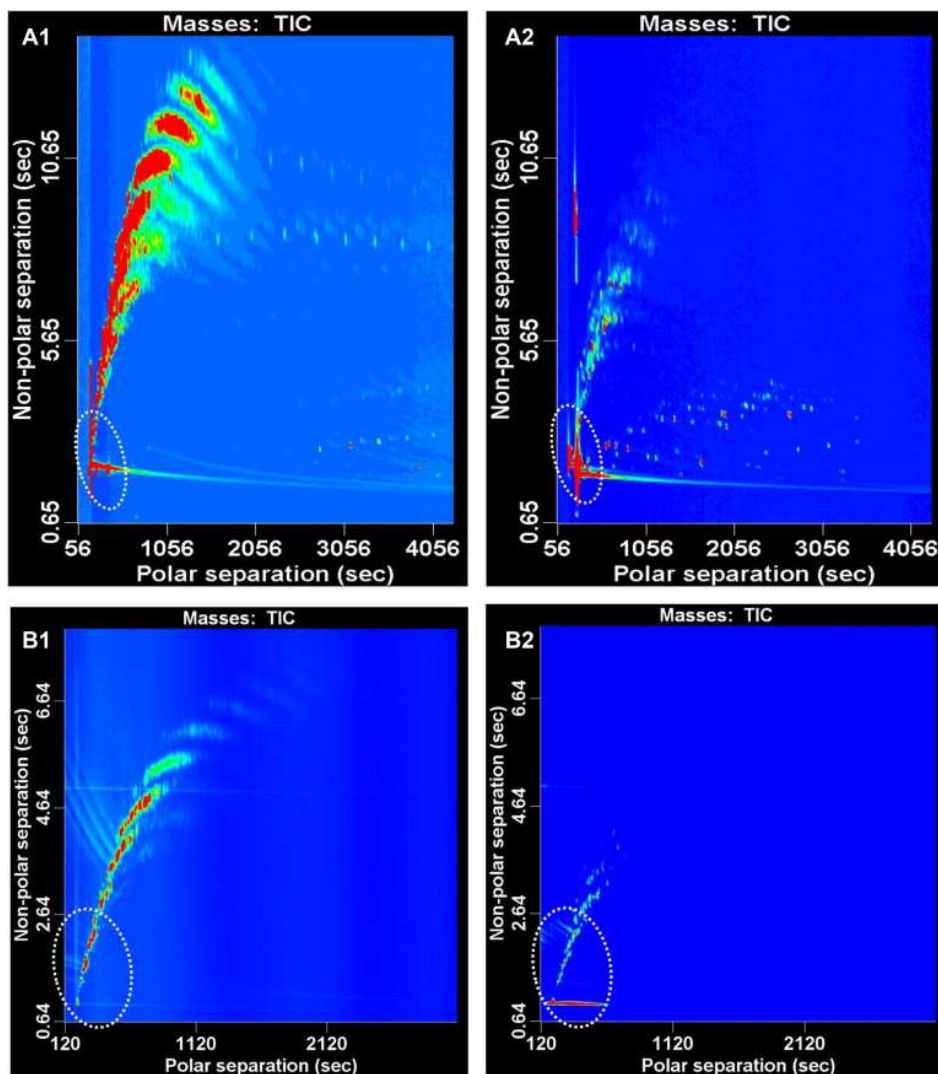
The aromatic fraction (Fig. 3.4C) is also well separated from the other groups of interest and the branched carbonyls that elute in the same contour plot area were completely removed from this fraction. This enables the investigation of the aromatics in the light oil fraction without the added complexity of co-elution with other nonaromatic and oxygen-containing compounds. It was also observed that not only monocyclic aromatic hydrocarbons elute in this aromatic group, but also bicyclic and polycyclic aromatic hydrocarbons. Highly unsaturated hydrocarbons were also retained on the silica column and eluted with the aromatic fraction and these compounds eluted just above the alkylbenzenes (Fig. 3.4C). This was not a concern since these compounds eluted in a different chromatographic region than the aromatics.

The oxygenate fraction (Fig. 3.4D) shows the full distribution of alcohols and carboxylic acids and phenols. Only a partial distribution (>C12) of the carbonyls were observed and the light carbonyls eluted with the unsaturate fraction as previously discussed. Remaining CO<sub>2</sub> can be observed in all the fractions indicating that small amounts of CO<sub>2</sub> were bleeding from dead-volumes of the multitude of connections, however, CO<sub>2</sub> is well separated from the rest of the compounds and does not interfere with the analysis.

The GC×GC contour plots of the saturate, unsaturate, aromatics and oxygenate fractions confirm that the SFC fractionation procedure was highly successful in reducing the complexity of oil samples. The oil sample used for the development of the SFC separation method in this study has a wide carbon number range which shows that the SFC group separation is robust (except for carbonyls and esters) and could be applied to different distillation cuts within this carbon number range. The SFC-FID method in itself can also be used as a screening tool to monitor how different process conditions can influence the relative concentrations of these different groups, since these groups have now been well-characterised by GC×GC-TOF-MS.

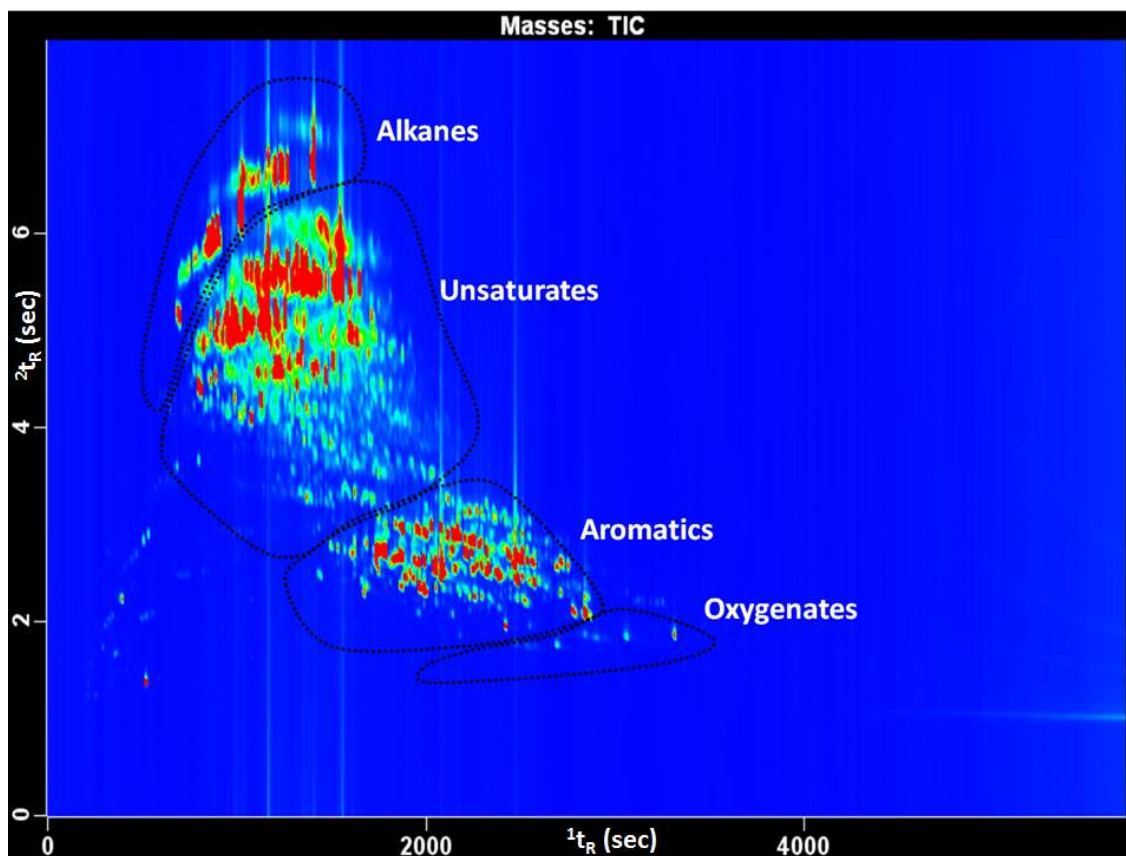
### 3.3. Application of SFC-GC×GC-TOF-MS

In order to compare the initial results obtained by the HPLC fractionation procedure with off-line GC×GC-TOF-MS analysis [22] and the results obtained from the method developed in this study, the same kerosene sample analysed in the previous HPLC study was analysed by means of the SFC-GC×GC-TOF-MS method, and the saturate and unsaturated fractions were compared (Fig. 3.5). It was observed that the areas where the HPLC mobile phases previously eluted on the contour plot (circle in Fig. 3.5) is now free of any interferences, even though there is some CO<sub>2</sub> in this region, it does not overlap with the analytes. The peaks in this area were trapped sufficiently with SFC injection, resulting in a contour plot resolution similar to that of the direct GC×GC-TOF-MS analysis (Fig. 3.1). Since the HPLC fractionation utilise only a silver column, oxygenates and aromatics also elute in the unsaturated fraction and therefore some additional peaks are observed in this fraction (Fig. 3.5A2). The chromatograms from the previous HPLC study (Fig. 3.5A1 and A2) and the current SFC-GC×GC-TOF-MS analysis (Fig. 3.5B1 and B2) were obtained with slightly different GC×GC-TOF-MS methods resulting in different elution times. However, besides concentration differences, similar contour plots to the HPLC fractionation for the saturated and unsaturated hydrocarbons are observed and this shows that the separation on the SFC was just as effective as the separation obtained using the HPLC.



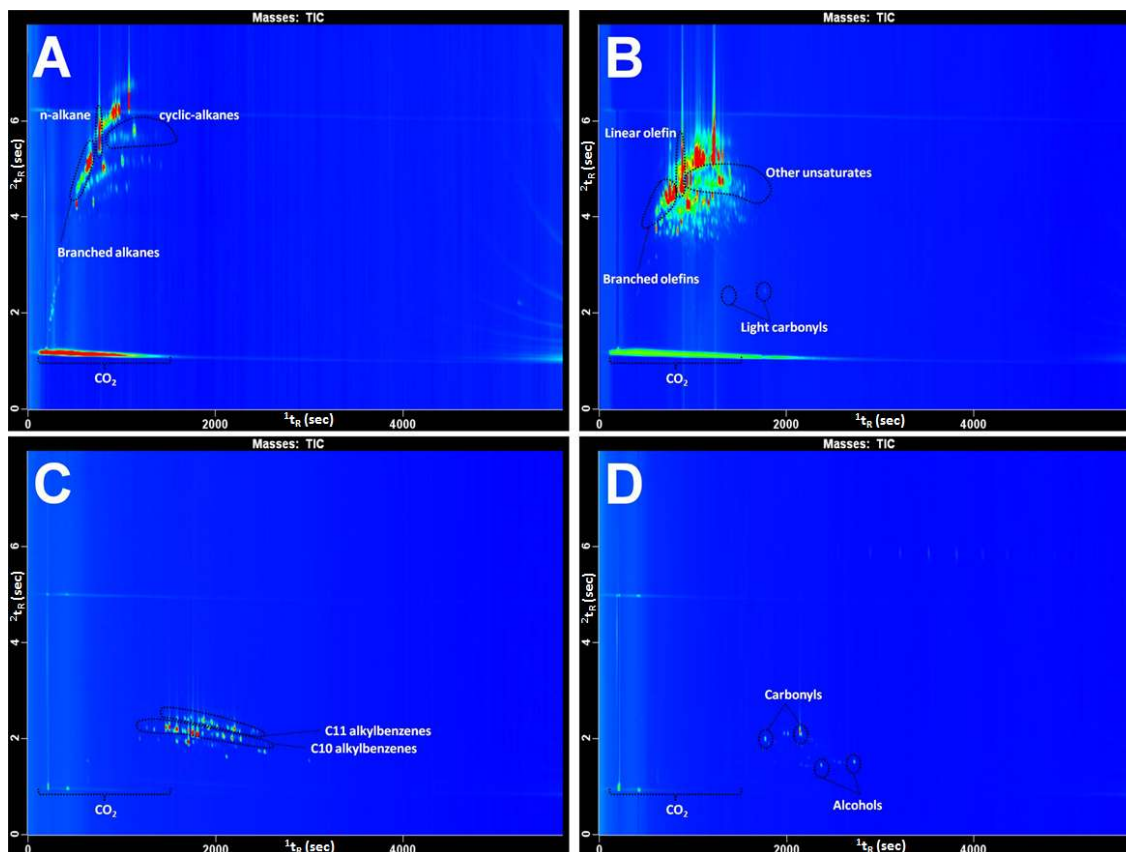
**Figure 3.5** Comparison between the contour plots obtained from the HPLC GC×GC-TOF-MS analysis of the (A1) saturate and (A2) unsaturate fractions of a kerosene sample [22] and the SFC-GC×GC-TOF-MS analysis of the (B1) saturate and (B2) unsaturate fractions of the same kerosene sample. (The circle indicates the area of concern where HPLC mobile phase elutes).

In order to evaluate the application of the SFC group-type separation to a section within the broad carbon number range of the light oil sample, a narrow distillation cut was analysed. From the conventional GC×GC contour plot of the unfractionated sample it can be seen that this sample is highly unsaturated whilst saturates, aromatics as well as oxygenates are also observed (Fig. 3.6).



**Figure 3.6** Contour plot obtained for the GCxGC separation of the highly unsaturate narrow distillation fraction with the polar  $\times$  non-polar column configuration.

The SFC-GCxGC-TOF-MS contour plot of the saturate fraction (Fig. 3.7A) once again shows linear, branched and cyclic paraffins without any interference from the unsaturated compounds in the sample. Most of the cyclic paraffins could not be identified without SFC pre-fractionation. The unsaturated fraction (Fig. 3.7B) confirms a high degree of unsaturation (large amounts of dienes, cyclic olefins, cyclic dienes, bicyclic olefins etc.) whilst the aromatics were also completely removed. A distribution of light carbonyls (<C12) is once again observed in the olefin fraction. The aromatic fraction (Fig. 3.7C) is well separated from the other groups and none of the highly unsaturated compounds eluted in this fraction. Only narrow distributions of alcohols and carboxylic acids at low concentrations were observed in the oxygenate fraction (Fig. 3.7D).



**Figure 3.7** Contour plots obtained for the SFC-GC×GC-TOF-MS analysis of the (A) saturate, (B) unsaturate, (C) aromatic and (D) oxygenate fractions of the highly unsaturated narrow distillation fraction.

By applying the developed fractionation procedure to the narrow distillation cut sample, the complexity thereof could also be drastically reduced enabling its comprehensive characterisation. This illustrates the applicability of the SFC separation to distillation cuts within the carbon number range of the light oil sample (<C25) without additional method modification.

#### 4. Conclusions

A SFC method for the fractionation of (linear and cyclic) saturates, (linear and cyclic) unsaturates, aromatics and oxygenates of a light oil sample was developed. These fractions were transferred to the GC×GC-TOF-MS in an on-line mode and the successful further separation of these groups of interest was obtained. Application of this procedure to the same

sample previously analysed by the HPLC fractionation procedure showed that the mobile phase interferences prevalent in the HPLC procedure was eliminated whilst volatile components were trapped sufficiently. The developed procedure can be applied without additional method modification to distillation cuts within the carbon number range of the light oil sample to reduce sample complexity. Further GC×GC method optimisation for better utilisation of the 2D separation space for the analysis for each group of interest will increase our capability to comprehensively characterise these groups.



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# Chapter 4

## Two-dimensional gas chromatography-online hydrogenation for improved characterisation of petrochemical samples

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R. Bekker provided assistance with scope of the study.

A. Govender performed the SEM-EDS experiments.

E. Rohwer provided assistance with the optimisation of capillary reactors.

**Abstract**

The Fischer-Tropsch (FT) process produces a variety of hydrocarbons over a wide carbon number range and during subsequent product workup a large variety of synthetic fuels and chemicals are produced. The complexity of the product slate obtained from this process is well documented and the high temperature FT (HTFT) process products are spread over gas, oil and water phases. The characterisation of these phases is very challenging even when using comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOF-MS). Despite the increase in separation power, peak co-elution still occurs when samples containing isomeric compounds are analysed by comprehensive two dimensional GC. The separation of isomeric compounds with the same double bond equivalents is especially difficult since these compounds elute in a similar position on the GC×GC chromatogram and have identical molecular masses and similar fragmentation patterns in their electron ionisation (EI) mass spectra. On-line hydrogenation after GC×GC separation is a possible way to distinguish between these isomeric compounds since the number of rings and alkene double bonds can be determined from the mass spectra of the compounds before and after hydrogenation. This paper describes development of a GC×GC method with post column hydrogenation for the determination of the backbone of cyclic/olefinic structures enabling us to differentiate between classes like dienes and cyclic olefins in complex petrochemical streams.

## 1. Introduction

The complexity of the product slate obtained from the Fischer-Tropsch (FT) process is well documented in literature [1]. A series of catalysed reactions of carbon monoxide and hydrogen produces a variety of hydrocarbons over a wide carbon number range and during subsequent product workup a large variety of synthetic fuels and chemicals are produced. Contrary to crude-derived products, these FT products are practically free of sulphur- and nitrogen-containing compounds making them more environmentally friendly. The high temperature FT (HTFT) process products are spread over gas, oil and water phases with only a small amount of wax being formed. These products are rich in highly valuable olefins and oxygenates, which crude oil only contains at trace levels.

The characterisation of these phases is very important for better understanding, control and optimisation of conversion processes. The characterisation of any one of these phases is very challenging and a typical oil phase sample may contain thousands of compounds. All these components cannot be separated by one-dimensional separation techniques, even when high efficiency capillary columns are used [2]. The introduction of comprehensive two-dimensional gas chromatography (GC×GC) provides several advantages for the analysis of these complex oil samples. The peak capacities are in the order of tens of thousands and peaks are arranged in highly structured contour plots where peaks of a homologous series are positioned along lines on a retention plane. Increased sensitivity of up to 10 fold is also obtained by GC×GC when compared to 1D-GC. This is due to the re-concentration of peaks in the modulator as well as the very fast separation achieved in the second dimension that minimises peak broadening and effectively increases the signal-to-noise ratio [3, 4].

The application of GC×GC to the analysis of highly complex petrochemical mixtures has been described by a number of authors [3 - 9]. However, despite the increase in separation power, peak co-elution still occurs when samples containing isomeric compounds are analysed by comprehensive two dimensional GC. The separation of isomeric compounds with the same double bond equivalents is especially difficult since these compounds elute in a similar position on the GC×GC chromatogram [10]. By using time-of-flight mass spectrometry (TOF-

MS), group-type identification can be achieved to a large extent, but this technique is also not able to distinguish between isomeric compounds with the same double bond equivalents since these compounds have identical molecular masses and in many cases, similar fragmentation patterns in their electron ionisation (EI) mass spectra e.g. distinguishing between cyclic alkanes and alkenes, and between dienes and cyclic alkenes. One way of addressing this problem is to apply a fractionation step to separate these isomers prior to GC×GC analysis [10 - 13].

Pre-separation of alkenes and cyclic alkanes with high performance liquid chromatography (HPLC) prior to the GC×GC-TOF-MS analysis was used to distinguish between these cyclic and non-cyclic isomers containing one double bond equivalent [11, 14]. The separation of cyclic paraffins and olefins by HPLC was achieved using a silver-modified column whereby the silver ions interact with the alkene double bond by formation of a complex. Although this approach worked well, the large dilution of the sample as well as the co-elution of the HPLC solvents with the volatile components in the gasoline sample were disadvantages associated with this method [14]. Subsequently, methods utilising supercritical fluid chromatography (SFC) as an on-line pre-fractionation step were developed [15, 16] (see Chapter 3).

The hyphenation of SFC to GC×GC is less complicated and the removal of the supercritical CO<sub>2</sub> can be easily achieved without any loss of the volatile sample components or the introduction of co-eluting solvents and their dilution effect. The SFC method [16] separates the sample into four groups, namely (cyclic and non-cyclic) alkanes, (cyclic and non-cyclic) alkenes, aromatics and oxygenates. These groups were transferred separately to the GC×GC-TOF-MS in an on-line mode. As in the case of the HPLC fractionation, the separation of cyclic paraffins and olefins was also achieved using a silver-modified column. This approach cannot be used to distinguish between classes like dienes and cyclic olefins since these isomeric compounds both contain alkene double bonds that will form adducts with silver ions and therefore both will be retained on the silver modified column.

On-line hydrogenation after GC×GC separation is a possible way to distinguish between these isomeric compounds since the number of rings and alkene double bonds in the compound structure can be determined by comparing the mass spectra of these compounds before and

after hydrogenation. Hydrogenation of compounds after their chromatographic separation, but before their entry into the mass spectrometer was proposed Lindeman in 1962 [17]. Other groups have also used hydrogenation after one dimensional gas chromatographic separation to characterise complex samples [18 - 21] where hydrogenation was achieved using a capillary fused silica tube coated with either platinum or palladium using hydrogen as carrier gas. Delmonte et al. [22] developed a GC×GC method utilising columns of the same polarity in the first and second dimensions and used on-line capillary hydrogenation between the first and second dimension columns to change the chemical structure of the analytes before separation on the second dimension column as a means of introducing orthogonality to the separation in the two dimensional space.

The aim of this study was the development of a GC×GC method with post column hydrogenation by which the analytes undergo hydrogenation after the second dimension separation, before their entry into the mass spectrometer. Capillary hydrogenation after GC×GC separation allows for the mass spectra of these isomeric compounds to be obtained after hydrogenation. Comparing the mass spectra of these compounds before and after hydrogenation will aid in the determination of the backbone of these cyclic/olefinic isomers and hence enable us to differentiate between classes like dienes and cyclic olefins in complex petrochemical streams.

## 2. Experimental

### 2.1. Chemicals

Analytical gases for the GC×GC were obtained from Afrox (South Africa). Standards of the various chemical groups were obtained from Sigma Aldrich (St Louis, MO, USA), Fluka (Steinheim, Germany) and ChemSampCo (Dallas, TX, USA). A standard mixture was prepared in hexane to optimise the GC×GC-TOF-MS method with post column hydrogenation. This standard mixture consisted of 1% (v/v) of 1-butanol; 1-octene; 1-octanol; 3-octyne; toluene; cyclooctane; 1,7-octadiene; 1,3-cyclooctadiene and 1,3-octadiene. Platinum(II) acetylacetonate and dichloromethane used in the preparation of capillary reactors were



obtained from Sigma Aldrich (St Louis, MO, USA). An HTFT light oil sample was obtained from Sasol Synfuels (Secunda, South Africa).

## 2.2. Capillary reactor preparation

The coated capillaries were prepared by static coating according to the procedure described by Schomburg [19] whereby Pt or Pd acetyl-acetonate salt is loaded on a capillary tube and dried on the inner surface of the tube before decomposition into metallic Pt or Pd. Precious metals are highly active hydrogenation catalysts [23 - 24] and platinum was selected as the catalyst in this application. One hundred milligrams of Pt acetyl acetate was weighed into a 10 mL volumetric flask and dissolved in dichloromethane. A deactivated fused silica capillary column (3 m) was filled with the solution using a 1 mL syringe. After filling the column, one end was plugged and the other end evacuated to enable static coating of the capillary for 24 h before subsequent decomposition of the Pt acetyl-acetonate salt under a constant hydrogen flow of  $\pm 2$  mL/min for 2 h at 340°C. The coating procedure was repeated 5 times to increase the amount and dispersion of Pt metal inside the capillary and hence to increase the hydrogenation efficiency of the reactor.

## 2.3. GC×GC method

The GC×GC instrument used was a Pegasus 4D from Leco Corporation (St. Joseph, USA) equipped with a time-of-flight mass spectrometer. A split/splitless injector and 7683B auto injector (Agilent Technologies, Little Falls, USA) was used on this system. The first dimension column was a 30 m × 0.25 mm ID, 0.25  $\mu\text{m}$   $d_f$  StabilWax column (Restek, Bellefonte, USA) and in the second dimension a 1.5 m × 0.1 mm ID, 0.1  $\mu\text{m}$   $d_f$  RTX-5 column (Restek, Bellefonte, USA) was used with a deactivated fused silica capillary (21 cm × 0.18 mm ID) installed in the transfer line. Helium was used as a carrier gas at a constant flow rate of 1.5 mL/min. A split ratio of 200:1 and injection volume of 0.5  $\mu\text{L}$  was used for all analysis. The first oven was programmed from 40°C (2.0 min) to 255°C at 2°C/min. The secondary oven and modulator followed the first temperature program but started at 60°C and 70°C, respectively. A modulation period of 6s was used. TOF-MS spectra were collected between 35 and 500 m/z

at 100 spectra/s. For the hydrogenation experiments the same instrument and column combination was used. Hydrogen was used as a carrier gas at a constant flow rate of 1.5 mL/min and the deactivated fused silica capillary installed in the transfer line was replaced with a capillary reactor (21 cm × 0.18 mm ID).

#### **2.4. Installation of hydrogenation reactor**

The capillary hydrogenation reactors used in previous studies [18, 19, 22] were typically between 30 and 60 cm in length and ranged from 0.15 to 0.35 mm in diameter. All of these reactors were heated inside the GC oven along with the analytical column or by means of a separate oven. For this study, the aim was to install a capillary reactor in the transfer line to the TOF-MS. This would allow for independent heating of the capillary reactor without the installation of an additional oven or any other instrument modifications. However, installing the capillary reactor in the transfer line only allows for a reactor length of 21 cm and therefore high efficiency capillary reactors are required to ensure complete hydrogenation. For the hydrogenation experiments, a capillary reactor (21 cm) was installed in the TOF-MS transfer line and operated at 250°C. The capillary was connected to the 2<sup>nd</sup> dimension column by means of a universal presstight connector (Restek, Bellefonte, USA) and hydrogen was used as a carrier gas at a constant flow rate of 1.5 mL/min.

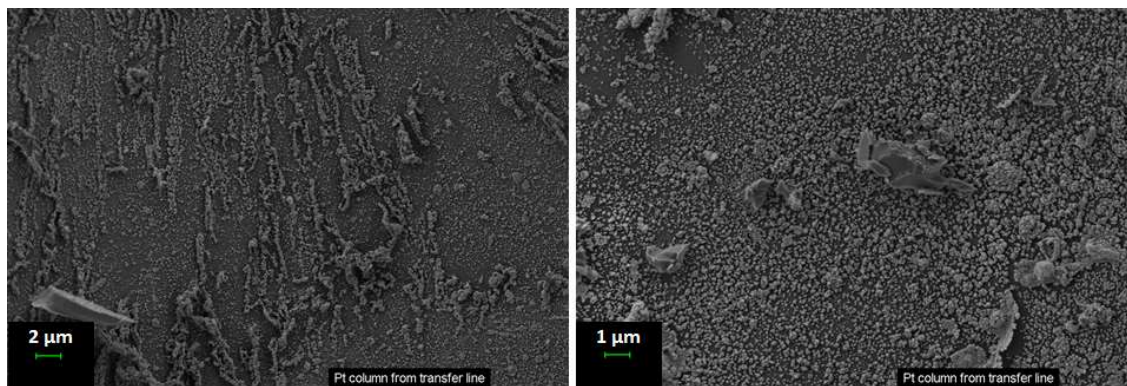
Hydrogen is potentially explosive and care must be taken when it is used as a GC carrier gas in a GC-MS system. Hydrogen is combustible over a wide range of concentrations at atmospheric pressure (4 - 74% by volume). Some of the dangers associated with the use of hydrogen as GC carrier gas includes the combustion of leaking hydrogen, combustion due to rapid expansion of hydrogen from a high pressure cylinder, accumulation of hydrogen in the GC oven and subsequent combustion as well as accumulation of hydrogen in the mass spectrometer and subsequent combustion when the vacuum pumps are not operational. To eliminate these dangers the source of hydrogen must always be turned off in case of a system shutdown or loss of vacuum.

### 3. Results and Discussion

#### 3.1. Optimisation of the coating procedure

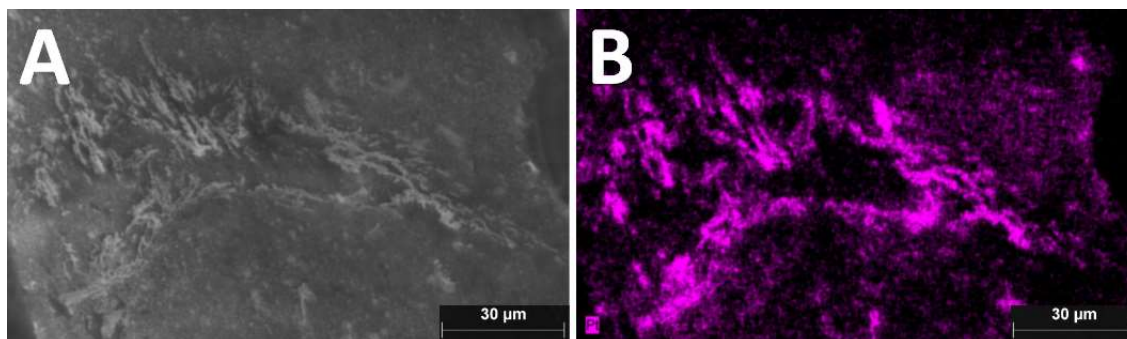
After coating with Pt acetyl-acetonate salt, the capillary was inspected under a light microscope to investigate the salt dispersion within the capillary. Inconsistent deposition was observed with large crystals of Pt acetyl-acetonate salt randomly distributed throughout the capillary. The influence of vacuum as well as temperature control on the coating efficiency was therefore investigated in order to optimise the coating procedure. For the purpose of investigating the influence of vacuum on the coating efficiency, the same capillary was coated at pressures between 40 and 70 kPa below atmosphere and inspected under the light microscope after each coating. The influence of temperature control on the coating efficiency was also investigated and a capillary was again coated at different pressures whilst dispersed in water at 20°C. Dispersion of the capillary in water maintained a constant temperature throughout the evaporation process and prevented the formation of cold spots within the capillary due to solvent evaporation. The capillary was again inspected after each coating. A pressure of 66 kPa below atmosphere combined with constant column temperature (20°C) were found to yield the most uniform coating throughout the column. The Pt acetyl-acetonate salt was subsequently decomposed under a mild hydrogen flow for 2 h at 340°C to deposit platinum inside the column [23]. Small uncoated areas were still observed throughout the capillary after coating and therefore the coating procedure was repeated an additional 4 times to increase the amount of Pt metal inside the capillary. After the capillary was coated five times, no uncoated areas could be observed through the light microscope and the capillary appeared grey and non-transparent throughout.

The metal dispersion within the capillary reactor was investigated by means of a scanning electron microscope and energy dispersive X-ray spectrometer (SEM-EDS) to ensure that high efficiency reactors were prepared successfully. Fig. 4.1 shows two SEM images of the inside of the capillary.



**Figure 4.1** SEM images of the inside of the Pt coated capillary.

Fig. 4.1 indicates that high dispersion of particles was obtained within the capillary. The presence of platinum was confirmed with EDS mapping of the SEM images. Fig. 4.2A shows a SEM image of the inside wall of the capillary whilst Fig. 4.2B shows the EDS platinum map of Fig. 4.2A.



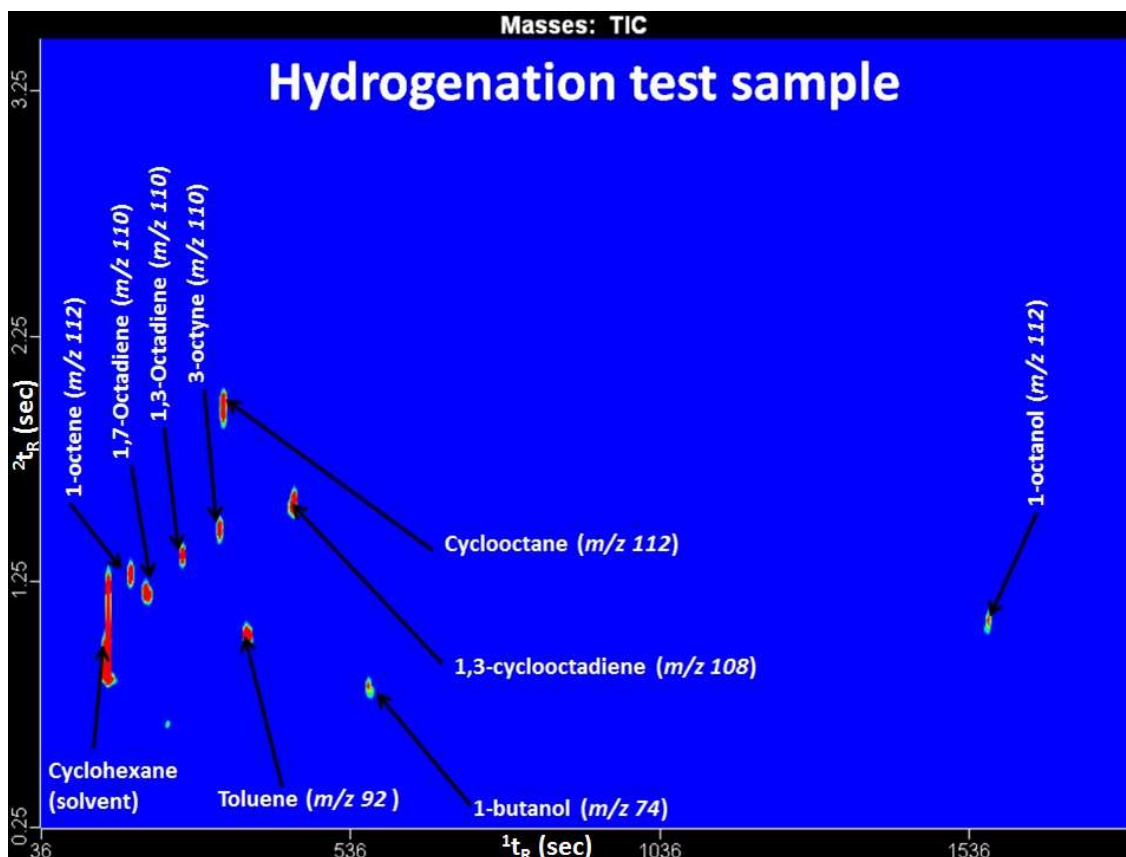
**Figure 4.2** A) SEM image of the inside wall of the capillary. B) EDS platinum map of the same area in A.

The observed platinum matches the pattern of observed particles exactly (Fig. 4.2) and therefore confirms the high dispersion of platinum within the capillary.

### 3.2. Optimisation of capillary reactor diameter

A standard mixture consisting of hydrocarbons with varying combinations of rings and double bonds were used to optimise the GC×GC-TOF-MS method with post column hydrogenation. An alkylbenzene and two alcohols were also included in this standard to investigate the hydrogenation severity. Fig. 4.3 shows the GC×GC-TOF-MS contour plot of the standard

mixture without a capillary reactor installed and the observed molecular masses of all the compounds are indicated on the chromatogram.

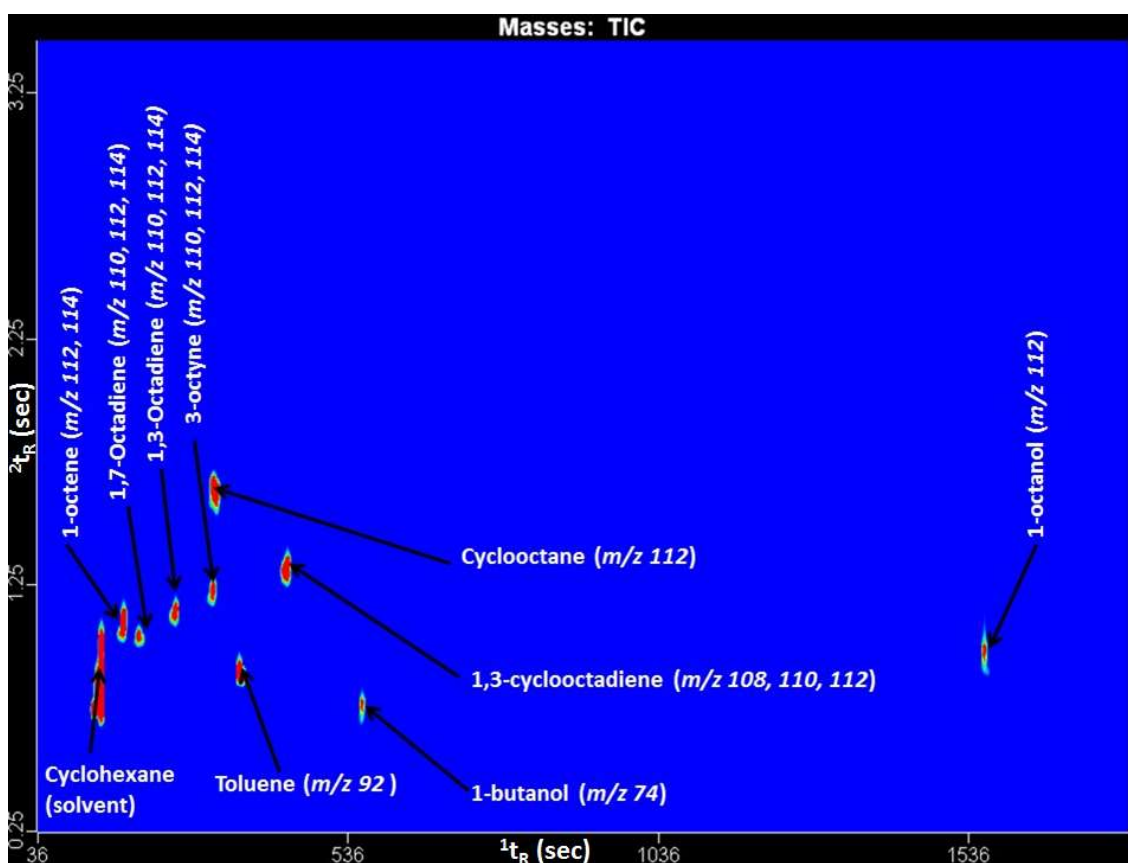


**Figure 4.3** GCxGC-TOF-MS contour plot of the standard mixture without a capillary reactor installed.

All the compounds within the mixture are well separated and good peak shapes were obtained throughout. Molecular masses for all the compounds were observed in the mass spectra except for 1-octanol where the molecular ion with a loss of water was observed ( $m/z$  112).

Temperature, pressure, residence time and catalyst loading influence the rate of hydrogenation [24]. In order to optimise the residence time of compounds within the hydrogenation reactor, the flow through the reactor was optimised. In GCxGC, the carrier gas flow rate is set to the optimum flow rate of the 1<sup>st</sup> dimension column. Since the 1<sup>st</sup> and 2<sup>nd</sup> dimension columns are connected in series, but have different internal diameters, the carrier gas linear flow rate through the 2<sup>nd</sup> dimension column is dependent on the diameter of that

column. The same is also true for the capillary reactor since it is installed in series after the 2<sup>nd</sup> dimension. The optimum residence time of compounds within the hydrogenation reactor was optimised by evaluating the extent of hydrogenation achieved using capillary reactors with different diameters. For the purpose of this study, capillary reactors with diameters of 0.10, 0.15 and 0.18 mm were evaluated. Fig. 4.4 shows the GC×GC-hydrogenation-TOF-MS chromatogram utilising a 0.10 mm diameter capillary reactor in series after the 0.10 mm 2<sup>nd</sup> dimension column. Once again the observed molecular masses of all the compounds are indicated on the chromatogram.

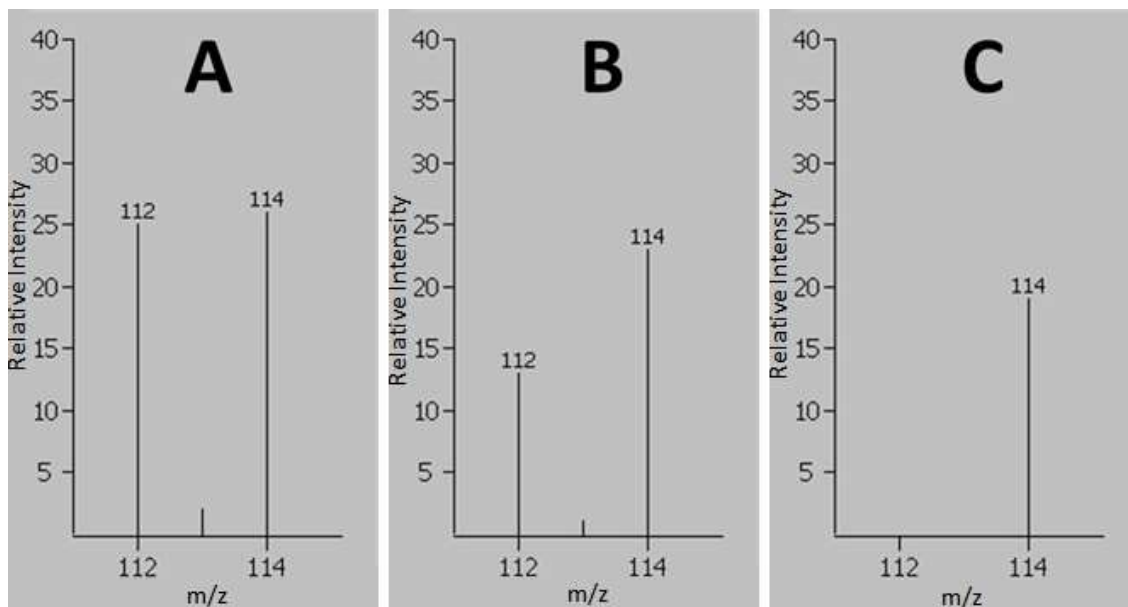


**Figure 4.4** GC×GC-hydrogenation-TOF-MS chromatogram utilising the 0.10 mm capillary reactor in combination with a 0.10 mm 2<sup>nd</sup> dimension column showing that the capillary reactor did not influence the separation or the peak shapes previously achieved without a capillary reactor.

The use of a capillary reactor after the 2<sup>nd</sup> dimension column did not influence the separation or the peak shapes previously achieved without a capillary reactor (compare Figs. 4.3 and 4.4). However, inspection of the mass spectra of all the compounds showed that only partial

hydrogenation was achieved with the 0.10 mm capillary reactor and the molecular masses of the un-hydrogenated compounds were still observed in the mass spectrum. No hydrogenation was achieved for butanol, octanol and toluene.

Fig. 4.5A-C shows the molecular ion region of the 1-octene mass spectrum obtained with 0.10, 0.15 and 0.18 mm capillary reactors, respectively.



**Figure 4.5** The molecular ion region of the 1-octene mass spectrum observed with the A) 0.10 mm, B) 0.15 mm and C) 0.18 mm capillary reactors showing that hydrogenation improves with an increase in the diameter of the capillary reactor.

It is clear that hydrogenation improves with an increase in the diameter of the capillary reactor and that complete hydrogenation of 1-octene was achieved with the 0.18 mm capillary reactor. This was also true for the other olefinic compounds. Heptane was the primary product obtained after hydrogenation of 1-octanol with the 0.18 mm capillary reactor whilst propane was the primary product obtained after hydrogenation of 1-butanol. Other studies [26, 27] on Pt catalysts with C3 alcohols have shown that these undergo an initial dehydrogenation to form an aldehyde, which can then undergo decarbonylation to produce ethane and CO. No hydrogenation was achieved for toluene with the use of these capillary reactors. This is expected since hydrogenation of these compounds is generally more difficult to achieve compared to olefinic compounds [26].

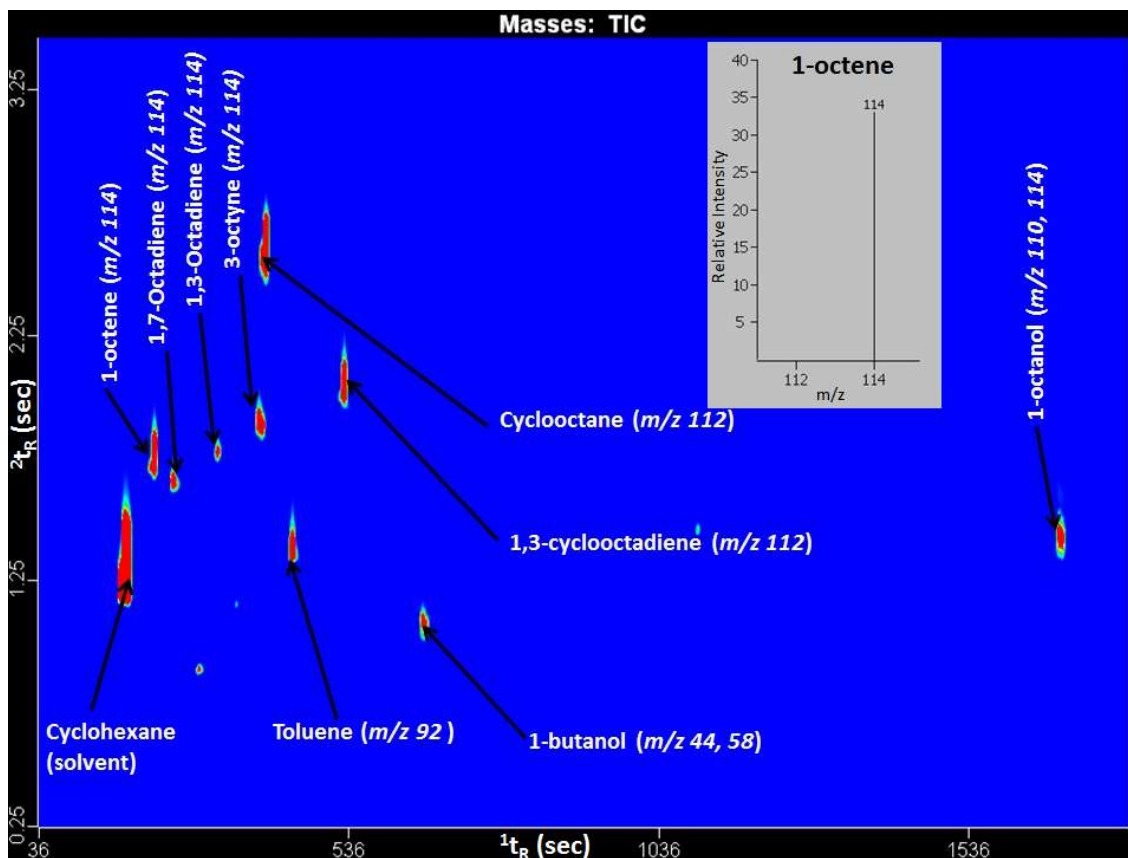
The low degree of hydrogenation with the 0.10 and 0.15 mm reactors might be ascribed to two factors. Firstly, the higher linear flow rates achieved with the smaller diameter reactors results in insufficient residence times and subsequently, incomplete hydrogenation. Secondly, the lack of hydrogenation might be due to the difference in the mass of platinum present in the different reactors. The coating procedure requires that a column is coated 5 times using a 1% platinum salt solution. The volume of solution present in these reactors before evaporation is higher for the 0.18 mm reactor than for the other two reactors, resulting in higher masses of platinum deposited within this reactor. In order to investigate the possibility of the different platinum loadings in these reactors being responsible for incomplete hydrogenation, a 0.18 mm reactor with only two coatings was prepared. This resulted in the 0.18 mm reactor containing a mass of platinum close to the 0.10 mm reactor. The different platinum loadings in the different reactors is illustrated in Table 4.1.

**Table 4.1** Mass of platinum deposited in each reactor.

Reactor Diameter (mm)	Reactor Volume (mm <sup>3</sup> )	Number of coats	Mass Platinum (µg)
0.10	1.649	5	56
0.15	3.711	5	125
0.18	5.344	5	181
0.18	5.344	2	72

Fig. 4.6 shows the GC×GC-hydrogenation-TOF-MS chromatogram utilising the 0.18 mm capillary reactor coated only two times. The molecular ion region of the 1-octene mass spectrum is shown in the chromatogram, while the observed molecular masses of all the other standards are also indicated on the chromatogram.





**Figure 4.6** GCxGC-hydrogenation-TOF-MS chromatogram utilizing the 0.18 mm capillary reactor coated only two times in combination with a 0.10 mm 2<sup>nd</sup> dimension column. The molecular ion region of the mass spectrum of 1-octene is also inserted.

The mass spectra of all the alkenes show that complete hydrogenation was achieved using the 0.18 mm column containing 72  $\mu\text{g}$  platinum. The molecular ion region of the 1-octene mass spectrum also shows that all the 1-octene was hydrogenated to octane with no 1-octene remaining after hydrogenation. The successful hydrogenation confirms that the incomplete hydrogenation observed with the 0.10 and 0.15 mm reactors is as a result of the reactor diameter (contact time) and that a sufficient amount of platinum for complete hydrogenation was present in the 0.15 mm reactor. These results show that the linear flow rates achieved through the capillary reactors with reactor diameters smaller than 0.18 mm are too high for complete hydrogenation within a reactor with limited length (210 mm) installed in the TOF-MS transfer line.

Only slight peak tailing was observed in the second dimension with the use of the 0.18 mm capillary reactor. This was also observed by other authors [18 - 20, 22] and is credited to the adsorption of the compounds on the surface of the catalyst. This peak tailing did not significantly influence the GC×GC separation and was considered acceptable.

A general signal intensity decrease was observed when hydrogen was used as carrier gas but no changes in the fragmentation behaviour of the unhydrogenated compounds (cyclooctane and toluene) were observed. The signal to noise ratio decrease (due to the presence of more background) and slight changes in the fragmentation was also observed by Munoz-Guerra et al. [25]. A higher vacuum due to the higher diffusivity of hydrogen was observed in this study but a stable vacuum was obtained for all hydrogenation experiments.

### **3.3. Optimisation of transfer line temperature**

As mentioned in the previous section, the rate of hydrogenation is influenced by the temperature, pressure, residence time and catalyst loading. The reaction temperature can be optimised by controlling the temperature of the transfer line. Normally the TOF-MS transfer line is operated at 250°C with no capillary reactor installed. In order to optimise the hydrogenation reaction temperature, the 0.15 mm reactor was installed in the TOF-MS transfer line since only partial hydrogenation was obtained with this reactor and molecular masses of both unhydrogenated and hydrogenated species were observed. The ratio of the un-, partially and fully hydrogenated molecular masses was determined at various temperatures from 150 to 340°C. Table 4.2 shows the calculated ratios for 1-octene at various TOF-MS transfer line temperatures.

**Table 4.2** Calculated ratios of the un- and fully hydrogenated molecular masses for 1-octene.

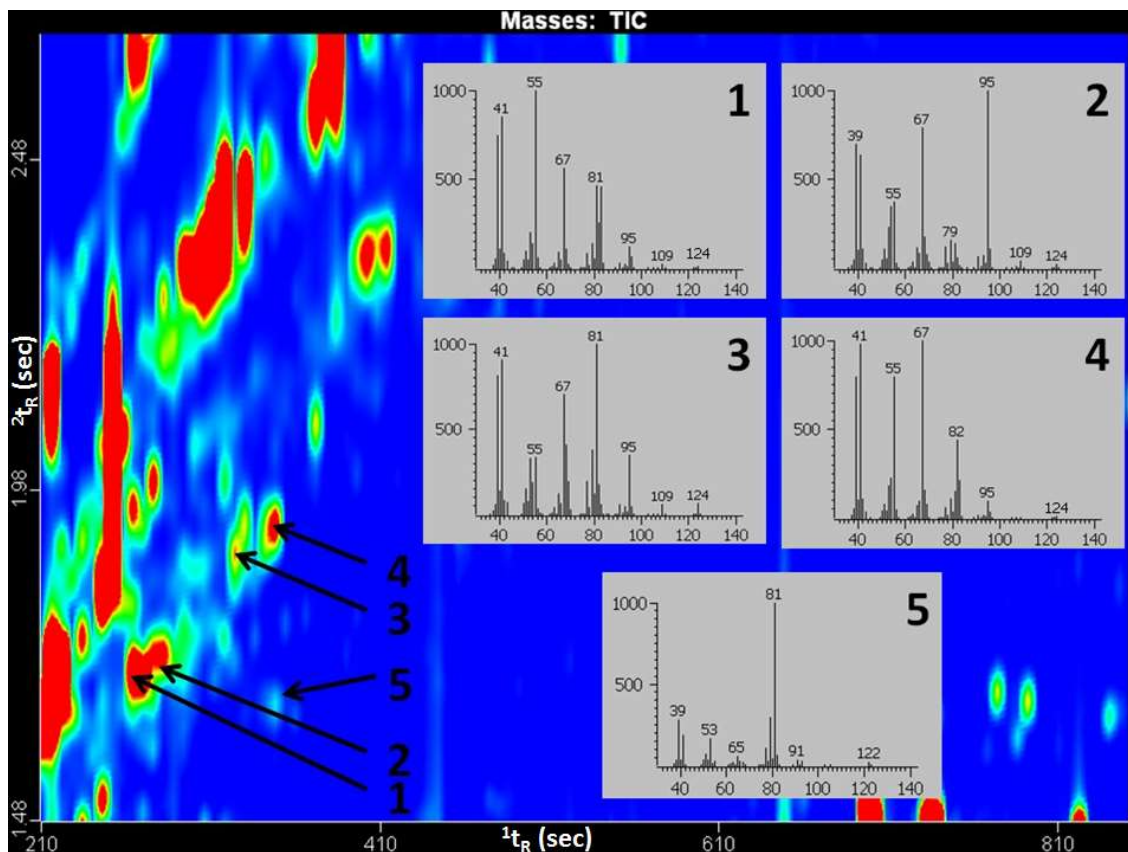
Temperature (°C)	Molecular Mass Ratio
	1-Octene 112:114 ( <i>m/z</i> )
150	1 : 0.95
200	1 : 0.42
250	1 : 0.31
300	1 : 0.27
340	1 : 0.23

It is observed in Table 4.2 that the degree of hydrogenation decreases with increasing temperature. Henneberg et al. [18] also reported a lower degree of hydrogenation at higher temperatures and ascribed it to the lower residence times of the molecules on the metal. Another possible reason for the observed decrease in the degree of hydrogenation with increasing temperature is the possibility that the hydrogenation reaction has reached equilibrium. Hydrogenation is a strongly exothermic reaction and an increase in temperature will shift the reaction equilibrium towards reactants, according to the Le Chatelier principle. The free energy was calculated for the hydrogenation of 1-octene and 1,3-octadiene at the investigated temperatures (Table 4.2) at pressures of 50, 100 and 500 kPa to determine if the reaction was at equilibrium conditions. It was determined that the hydrogenation reaction is not at equilibrium at 340°C. This is also shown in the equilibrium conversion of the dehydrogenation of C2 - C15 alkenes described in Ullmann's Encyclopaedia of Industrial Chemistry [24]. The decreased hydrogenation observed at 340°C is therefore due to lower residence times of the molecules within the column (higher volume flow rates for the same mass flow, hence higher linear flow rates and lower residence times). In order to support the findings, the influence of temperature on the degree of hydrogenation achieved with the 0.18 mm reactor was also investigated. Complete hydrogenation was obtained at all the investigated temperatures and no unreacted reagent was observed at 340°C. This also shows that the hydrogenation reaction is not at equilibrium conditions at these temperatures.

Because the degree of hydrogenation achieved with the 0.18 mm capillary reactor was not influenced by the transfer line temperature, the transfer line temperature was kept at 250°C for both the GC×GC separation with and without post column hydrogenation.

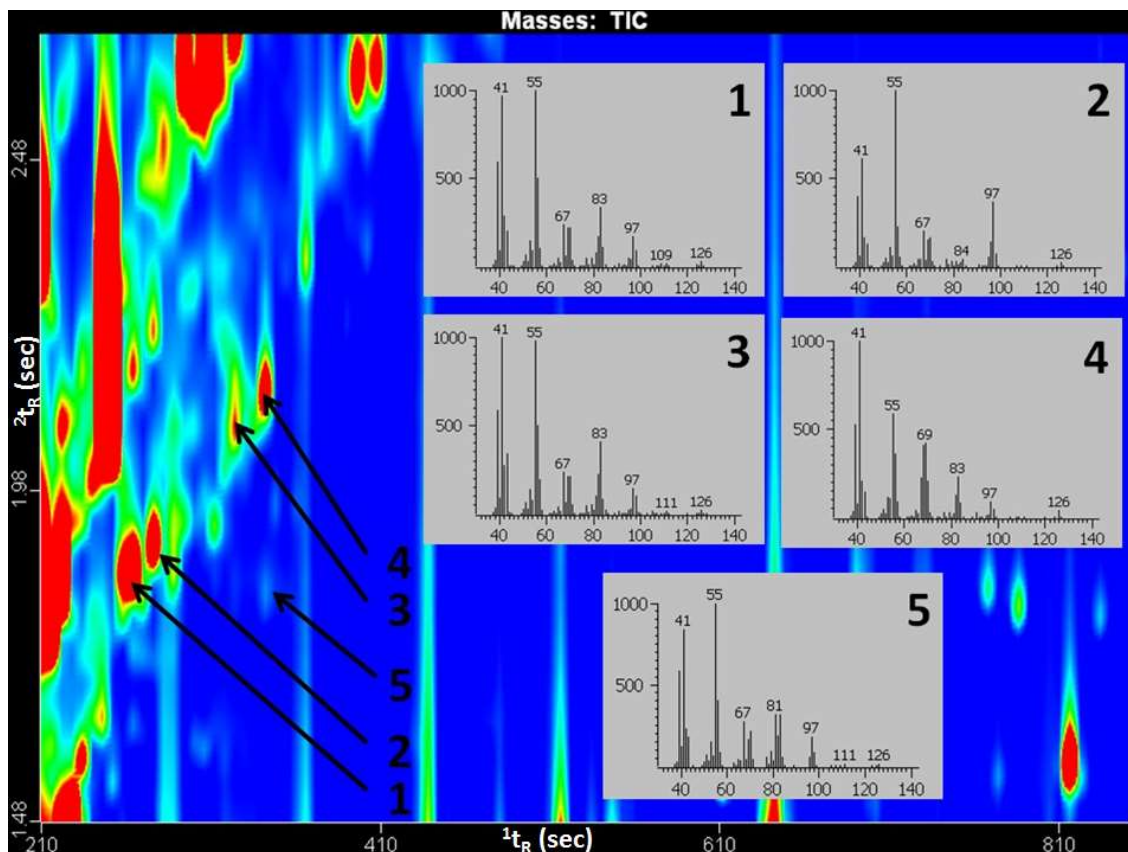
### **3.4. Application to petrochemical sample**

The potential of the developed technique was demonstrated by applying it to a complex HTFT light oil sample. The sample contains low concentrations of compounds with different degrees of unsaturation attributed to a combination of rings and double bonds. GC×GC-TOF-MS analysis of the sample revealed the presence of isomeric compounds with the same double bond equivalents and it is of great importance to distinguish between them since they will behave differently in downstream processing units. Diolefins are gum precursors [28] and may deactivate certain catalysts whilst the same behaviour is not true for cyclic olefins and/or bicyclic components. The accurate identification of these compounds is therefore very important for the control and optimisation of conversion processes. Fig. 4.7 shows the C9 aliphatic region of the GC×GC-TOF-MS chromatogram of the HTFT light oil sample. The mass spectra of five selected C9 compounds are also included in the chromatogram.



**Figure 4.7** GCxGC-TOF-MS chromatogram of the HTFT light oil sample without the capillary reactor together with mass spectra for selected species.

Compounds 1 - 4 have molecular masses of  $m/z$  124 which corresponds to C9 compounds with two double bond equivalents whilst compound 5 has a molecular mass of  $m/z$  122 that corresponds to a C9 compound with three double bond equivalents. For all the compounds library matches can be obtained for more than one component class. The sample was therefore analysed by means of GCxGC-TOF-MS with capillary hydrogenation (Fig. 4.8).



**Figure 4.8** GCxGC-hydrogenation-TOF-MS chromatogram of the HTFT light oil sample.

Almost identical separation was observed in the initial GCxGC-TOF-MS analysis and during hydrogenation GCxGC-TOF-MS analysis and the compounds of interest are easily recognised in Fig. 4.8. Compounds 1 - 4 all have a molecular mass of  $m/z$  126 (C9 cyclic alkane) after hydrogenation. This confirms that compounds 1 - 4 were C9 cyclic olefins before hydrogenation. After hydrogenation, compound 5 also has a molecular mass of  $m/z$  126 (C9 cyclic alkane) which confirms that compound 5 was a C9 cyclic diene before hydrogenation. Compounds 1 and 3 have identical mass spectra after hydrogenation, indicating that they have a similar cyclic backbone. Further structural interpretation was not required since the aim of this study was the differentiation of compound classes and not the identification of individual compounds.

These results clearly demonstrate the ability of this method to determine the backbone of cyclic/olefinic structures in complex petrochemical samples which enables differentiation between classes like dienes and cyclic olefins. It is also possible with this method to distinguish

between n-alkenes and cyclic paraffins where an increase of 2 mass units will be observed in the molecular ion of n-alkenes whilst the molecular ions of cyclic paraffins will remain unchanged after hydrogenation.

#### **4. Conclusions**

A two dimensional gas chromatographic method with post column hydrogenation, by which the analytes undergo hydrogenation after the second dimension separation, was developed. Installing a capillary reactor in the TOF-MS transfer line enables complete hydrogenation of alkene double bonds at convenient transfer line temperatures without instrument modifications. The catalytic hydrogenation step is fast enough to prevent significant distortion of the narrow second dimension peaks. The number of rings and alkene double bonds in the compound structure can be determined from two GC×GC-MS injections and comparison of the mass spectra from identical chromatographic peaks with and without hydrogenation. The influence of capillary reactor diameter and temperature on the degree of hydrogenation was also extensively investigated to achieve complete hydrogenation of olefinic compounds. The developed method makes it possible, for the first time, to identify the level of unsaturation in isomeric hydrocarbon molecules with the same double bond equivalents (eg. dienes and cyclic olefins) in complex petrochemical streams previously separated by GC×GC without post column hydrogenation.

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# Chapter 5

## Analysis of oxidised heavy paraffinic products by high temperature comprehensive two-dimensional gas chromatography

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### Contributions by co-workers:

R. Bekker provided assistance with scope of the study.

J. Beigley provided assistance with oxidation experiments.

E. Rohwer provided assistance with scope of the study.

## Abstract

Heavy petroleum fractions are produced during crude and synthetic crude oil refining processes and they need to be upgraded to useable products to increase their market value. Usually these fractions are upgraded to fuel products by hydrocracking, hydroisomerisation and hydrogenation processes. These fractions are also upgraded to other high value commercial products like lubricant oils and waxes by distillation, hydrogenation, and oxidation and/or blending. Oxidation of hydrogenated heavy paraffinic fractions produces high value products that contain a variety of oxygenates and the characterisation of these heavy oxygenates is very important for the control of oxidation processes. Traditionally titrimetric procedures are used to monitor oxygenate formation, however, these titrimetric procedures are tedious and lack selectivity toward specific oxygenate classes in complex matrices. Comprehensive two-dimensional gas chromatography (GC×GC) is a way of increasing peak capacity for the comprehensive analysis of complex samples. Other groups have used HT-GC×GC to extend the carbon number range attainable by GC×GC and have optimised HT-GC×GC parameters for the separation of aromatics, nitrogen-containing compounds as well as sulphur-containing compounds in heavy petroleum fractions. HT-GC×GC column combinations for the separation of oxygenates in oxidised heavy paraffinic fractions are optimised in this study. The advantages of the HT-GC×GC method in the monitoring of the oxidation reactions of heavy paraffinic fraction samples are illustrated.

## 1. Introduction

Heavy petroleum fractions are produced during crude and synthetic crude oil refining processes. To increase the value of these heavy petroleum fractions, they need upgrading to various marketable products. Usually these fractions are upgraded into fuel products to address the increasing fuel demand using hydrocracking, hydroisomerisation and hydrogenation processes [1, 2]. Hydrocracking processes are used to reduce the boiling range of these fractions whilst hydroisomerisation processes are used to improve the cold flow properties of fuel. Hydrotreatment processes are used to improve the quality of upgraded products. These heavy petroleum fractions are not only used for the production of fuel but other high value commercial products like lubricant oils and waxes can also be produced by distillation, hydrogenation, and oxidation and/or blending [3]. Oxidation of hydrogenated heavy paraffinic fractions produces high value products that contain a variety of oxygenates. The characterisation and monitoring of these heavy oxygenates is very important for the control of oxidation processes.

Traditionally titrimetric procedures [4 - 6] are used to determine the acid, alcohol and ester concentrations in an attempt to monitor oxygenate formation and the use of these methods for the control of oxidation processes are reported in previous studies [7 - 9]. These titrimetric procedures are tedious and lack selectivity toward specific oxygenate classes in complex matrices. It is stated in the standard test method for acid number [4] that the compounds considered to have acidic characteristics include organic acids, esters, phenolic compounds and lactones whilst the standard test method for hydroxyl groups [6] is not suitable for determination of hydroxyl groups attached to tertiary carbon atoms. Another shortcoming of these procedures is that only total concentrations for these oxygenate classes are determined and values are not reported per carbon number. The selective monitoring of oxygenates during the oxidation of heavy paraffinic fractions will be a great advantage in the control of these processes.

Gas chromatography with an oxygen selective detector (GC-O-FID) has been used by other groups to determine the oxygenates in a complex hydrocarbon matrix [10] and the use of

electrospray ionisation Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR-MS) and gas chromatography mass spectrometry (GC-MS) for the identification of oxygen compounds in shale oil and coal tar was reported by Geng et al. [11]. The applicability of these techniques to oxidised heavy paraffinic fractions is yet to be investigated and the characterisation of these samples remains a difficult analytical challenge. Firstly, as a rule only a limited range of relatively small and non-polar molecules can be analysed directly by gas chromatography (GC) and secondly, the number of hydrocarbon isomers increase with increasing carbon number [12, 13].

Many attempts have been made to address the first challenge of extending the range of heavy molecules that can be analysed by GC. One way to address the first challenge involves the transformation of the heavy molecules present in these fractions to species that can be analysed directly by GC by the addition of a pre-treatment step. These include derivatisation reactions [14] that involve the transformation of non-volatile heteroatomic molecules into elutable species and pyrolysis [15] that involves the destruction of the samples into smaller fragment-molecules prior to GC analysis. Another important method regularly employed to extend the range of heavy molecules analysable by GC is high-temperature gas chromatography (HT-GC). In HT-GC, heavy molecules are not transformed prior to GC analysis but their elution is improved by the extension of the conventional separation temperature and the adaptation of chromatographic conditions [12]. The difference between GC and HT-GC is not well defined; however, various authors have stated that GC separations with final temperatures higher than 340°C [12, 13] can be defined as HT-GC.

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) [16, 17]. The use of HT-GC instrumentation is critical for analysis at temperatures higher than 340°C and column and stationary phase technologies need careful consideration. HT-GC analysis requires metal columns or fused silica columns with a special protective coating to withstand these high temperatures. Stationary phase end-capping and the quality of the surface chemistry of the underlying fused silica are also very important aspects to reduce column bleeding in HT-GC [18, 19]. Due to the lower temperature limits of polar polymer stationary phases compared to non-polar stationary phases, HT-GC is mostly limited to non-polar

stationary phases. The use of cool on-column or programmed temperature vaporizing (PTV) injectors in HT-GC is also critical to eliminate discrimination towards high-boiling compounds observed during the injection step when split/splitless injectors are used [16, 17].

The extension of the molecular range that can be analysed by HT-GC is not only reliant on the higher temperatures achievable but also involves the adaptation of chromatographic conditions. These adaptive conditions include the use of short columns with a reduced film thickness, the latter to achieve lower elution temperatures due to the high gas phase ratio. Despite HT-GC being an established technique, chromatographic resolution is often compromised and peak overlap is a major concern when complex samples are analysed. Comprehensive two-dimensional gas chromatography is a way of increasing peak capacity and GC×GC is a powerful tool to analyse complex petrochemical samples. In GC×GC the peak capacity is increased by combining two chromatographic columns with different separation mechanisms [20] and during a single GC×GC analysis the entire sample is subjected to two independent GC separations. The resulting GC×GC chromatogram provides a great deal of information on molecular composition of these samples and also on the presence of different hydrocarbon classes [21]. Until quite recently, the use of GC×GC was limited to the analysis of the molecular range attainable by normal GC analysis.

The extension of GC×GC into the HT-GC realm would be of great value as it would reduce the extent of peak overlap observed when analysing oxidised heavy paraffinic fractions. Unfortunately, the extension of GC×GC to HT-GC temperatures is limited by the thermal stability of polar columns. Additionally, heavy compounds are often not re-volatilised effectively during the modulation step. These limitations were addressed by other research groups [21, 22] showing that flow programming in a cryogenic nitrogen modulator improved the desorption of heavy compounds whilst Dutriez et al. [12] reported on the evaluation of various column sets utilising mid polarity columns with higher temperature stabilities to do GC×GC at HT-GC temperatures. Dutriez selected an experimental set of capillary columns based on stationary phase chemistry, column diameter, film thickness and column lengths. The results showed that with the correctly adapted parameters, compounds can elute earlier from the first dimension column to reach the second dimension column at lower temperatures. It was concluded that column dimensions are one of the most critical

parameters to optimise in HT-GC×GC. With the developed method, hydrocarbons of up to C60 as well as tetra-aromatic compounds in vacuum gas oil (VGO) could be eluted. Many groups have used HT-GC×GC to extend the carbon number range attainable by GC×GC and have optimised HT-GC×GC parameters for the separation of aromatics, nitrogen-containing compounds as well as sulphur-containing compounds in heavy petroleum fractions [12, 23 - 29].

In this study, the optimised HT-GC×GC column combinations for the separation of oxygenates in oxidised heavy paraffinic fractions are reported for the first time. The method is also applied to monitor the oxidation reaction of a hydrogenated heavy paraffinic fraction to illustrate the advantage of using HT-GC×GC, as compared to traditional titrimetric methods.

## **2. Experimental**

### **2.1. Chemicals**

Analytical gases for the HT-GC×GC were obtained from Afrox (South Africa). Cyclohexane was obtained from Sigma Aldrich (St Louis, MO, USA) and a hydrogenated heavy paraffinic fraction was obtained from Sasol Wax (Sasolburg, South Africa) for the oxidation experiments.

### **2.2. Oxidation of a heavy paraffinic fraction**

The oxidised heavy paraffinic fraction sample was prepared according to the procedure described by Breet et al. [30]. A bubble column type reactor that consists of a Pyrex glass column was used to oxidise the heavy paraffinic fraction with air containing 21.2% oxygen. The air entered the reactor through a frit to ensure proper sparging and improved oxidation. The temperature within the reactor was regulated with a contact thermometer. The reactor was loaded with 800 g of the hydrogenated heavy paraffinic fraction sample and air was passed through the system at a low flow rate until the required oxidation temperature was reached (160°C). The air flow rate was then adjusted with a rotameter to 1.8 L/min for the



remainder of the experiment. The reactor was kept at this temperature for 300 min. The reaction product was used to evaluate different column combinations.

In addition, an oxidation reaction was monitored at different times during the reaction. The start of the experiment ( $t_0$ ) was defined as the time when the desired temperature was reached and the air flow was increased. Samples ( $\pm 5$  g) were then taken with a glass tube from the reactor at 30, 60, 120, 180 and 210 min intervals during a single oxidation reaction.

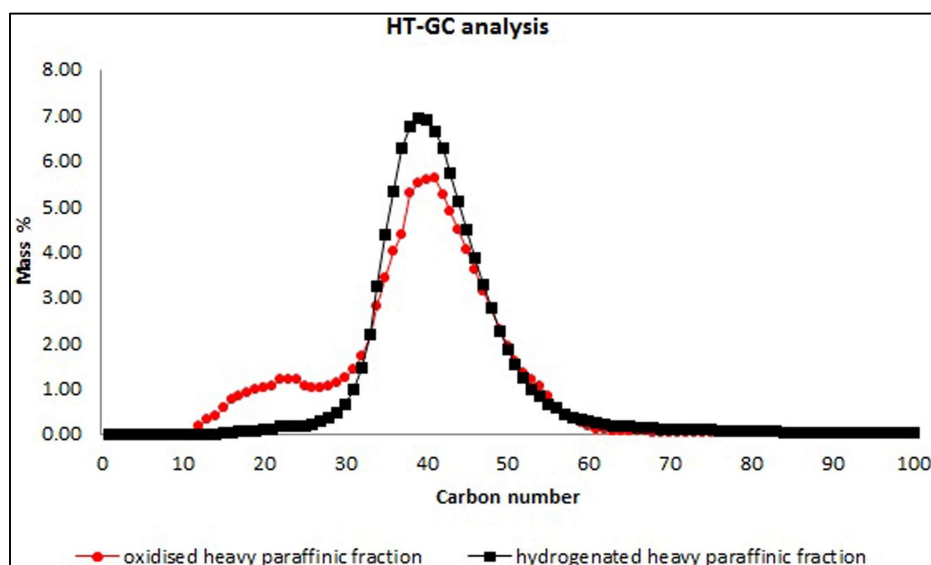
### 2.3. GC×GC method

A Pegasus 4D GC×GC from Leco Corporation (St. Joseph, USA) equipped with a cryogenic N<sub>2</sub> dual jet modulator and time-of-flight mass spectrometer (TOF-MS) was used for all column set evaluation experiments and TOF-MS spectra were collected between 35 and 1000 m/z at 100 spectra/s. A cool-on-column injector (Agilent Technologies, Little Falls, USA) was used on this system. The oxidised heavy paraffinic fraction samples (20 mg) were diluted in cyclohexane (10 mL) prior to injection and 0.5  $\mu$ L of this solution was injected for all experiments. Data analysis was performed using ChromaTOF software (Leco, v4.50.8.0). Different combinations of non-polar and medium polarity columns were evaluated and these are presented in Table 5.1. All the experiments were carried out using helium as a carrier gas at a constant flow rate close to the optimum velocity of the first dimension column [31]. The HT-GC×GC oven was operated at programmed temperatures starting in all cases at 100°C and increasing at 3°C/min to the maximum temperature of the column set (370°C for all the column sets) and kept constant at the final temperature for 5 min (Table 5.1). The liquid 2 L N<sub>2</sub> dewar supplying the cryogenic modulator was filled only once at the start of the analysis. This resulted in the gradual evaporation of the liquid nitrogen from the dewar from start of the analysis until 60 min, after which the cooling jets continued at room temperature. The modulation period was set to 6 s in all cases.

**Table 5.1** Combinations of non-polar and medium polarity columns were evaluated.

Set	Configuration	First Column	Second Column	Max
1	Reversed	Trb50ht (30m×0.32mm, 0.1µm)	BPX-1 (1.0m×0.1mm, 0.1µm)	370°C
2	Reversed	Trb50ht (30m×0.25mm, 0.1µm)	BPX-1 (1.0m×0.1mm, 0.1µm)	370°C
3	Reversed	Trb50ht (10m×0.32mm, 0.1µm)	BPX-1 (0.5m×0.1mm, 0.1µm)	370°C
4	Reversed	Trb50ht (10m×0.25mm, 0.1µm)	BPX-1 (0.5m×0.1mm, 0.1µm)	370°C
5	Normal	DB1HT (30m×0.32mm, 0.1µm)	Trb50ht (1.5m×0.1mm, 0.1µm)	370°C
6	Normal	DB1HT (10m×0.32mm, 0.1µm)	Trb50ht (0.5m×0.1mm, 0.1µm)	370°C
7	Normal	DB1HT (10m×0.53mm, 0.15µm)	Trb50ht (0.5m×0.1mm, 0.1µm)	370°C

Column set 2 was selected for the analysis of the samples taken at different times during the oxidation reaction. A flame ionisation detector (FID) was used to perform quantitative HT-GC×GC analyses of these oxidised samples. A standard HT-GC method [32] was used to confirm that more than 99% of the oxidised heavy paraffinic fraction sample and 97% of the hydrogenated heavy paraffinic fraction sample eluted within the carbon number range attainable by HT-GC×GC (<C60) [12]. The carbon number distributions as determined by HT-GC is presented in Fig. 5.1. Relative quantification was performed by normalisation of peak areas obtained from the FID detector and relative response factors were used for the compounds in the sample as determined from the analysis of structurally related standards (Appendix A).

**Figure 5.1** Carbon number distributions for the oxidised heavy paraffinic fraction and the hydrogenated heavy paraffinic fraction as determined by HT-GC.

### 3. Results and Discussion

#### 3.1. Selection of 2D configurations

Of all the chromatographic conditions described above, the selected combination of GC columns is probably the most critical for the analysis of heavy paraffinic fractions. GC×GC and HT-GC×GC analysis of fuels and heavy petroleum fractions is commonly reported using a normal configuration [12, 26, 29, 33, 34], with a non-polar column in the 1<sup>st</sup> dimension. Polydimethylsiloxane phases are commonly used in one-dimensional high temperature applications [35] since they have very good thermal stability and easily elute hydrocarbons. Agilent DB1HT (Little Falls, USA) and SGE BPX-1 (Ringwood, Australia) columns were therefore selected to as the non-polar phases for the different column sets (Table 5.1).

Several groups [33, 36 - 39] showed that the highest orthogonality in GC×GC for products containing alkanes, alkenes, aromatics and oxygenates is obtained in the reversed column configuration with a polar column in the 1<sup>st</sup> dimension. The columns used by these authors cannot be applied to the HT-GC×GC analysis of heavy oxidised paraffinic fractions due to the reduced upper temperature limits of polar columns. As reported in previous HT-GC×GC column set evaluations [12, 23 - 29], a mid polarity column with a higher temperature stability was used in this study. Dutriez et al. [12] used a (50% Phenyl)polysilphenylene-siloxane column from SGE (Victoria, Australia) with a 370°C maximum programmable temperature. However, after a performance review by SGE, the maximum programmable temperature of this column was lowered to 350°C. The TRB-50 column with (50%) Diphenyl-(50%)dimethyl polysiloxane phase from Teknokroma (Barcelona, Spain) with a 370°C maximum programmable temperature was therefore selected as the mid polar stationary phase for the different column sets (Table 5.1). As in other studies [12, 26, 27] the selection of the column sets focused on columns of different lengths with a reduced film thickness and also on different normal and reversed configuration column combinations.

Gaines et al. [22] investigated the temperature requirements for the trapping and releasing of compounds in a cryogenic gas loop-type modulator and showed that excessive cold temperatures cause peak distortions for heavy compounds (>C<sub>26</sub>). To avoid these excessive

cold temperatures during the analysis of heavy hydrocarbons with a liquid N<sub>2</sub> cryogenic modulator, the liquid N<sub>2</sub> nitrogen dewar attached to the instrument was only filled at the start of the analysis. The gradual evaporation of the liquid N<sub>2</sub> from the dewar resulted in the gradual increase in modulation temperature from start of the analysis until approx. 60 min of the analysis after which modulation continued at room temperature. No significant peak broadening along the first dimension was observed for heavy molecules as published by Gaines et al. [22] and the modulation produced very narrow peaks which indicated that the procedure of gradual evaporation was successful in limiting first dimension peak broadening due to cold modulator temperatures.

### 3.2. Evaluation of 2D configurations

The selectivity of the 2D column sets in Table 5.1 was compared to one another to determine which set provides the optimum separation of oxygenates in oxidised heavy paraffinic fractions. Similar to previous studies [26, 27] where the optimum separation of sulphur- and nitrogen-containing compounds was investigated, the 2D selectivity was estimated by calculating the 2D resolutions ( $RS_{2D}$ ) for selected peaks. The 2D resolution method introduced by Giddings [20] was used where the 2D resolution,  $RS_{2D}$ , between solutes A and B is defined as the Euclidean norm of the resolution over the two axes (Eq. (1)),

$$RS_{2D} = \sqrt{{}^1RS^2 + {}^2RS^2} \quad (1)$$

where  ${}^1R_s$  and  ${}^2R_s$  are the respective resolutions between two compounds of interest along the first and the second dimensions. The 2D resolution can also be given as

$$RS_{2D} = \sqrt{\frac{4 * (\Delta^1 t_R)^2}{({}^1\omega_A + {}^1\omega_B)^2} + \frac{4 * (\Delta^2 t_R)^2}{({}^2\omega_A + {}^2\omega_B)^2}} \quad (2)$$

where,  ${}^1\omega$  and  ${}^2\omega$  are the peak widths along each dimension at 10% peak height for compounds A and B. The difference in retention times between the apices of the two

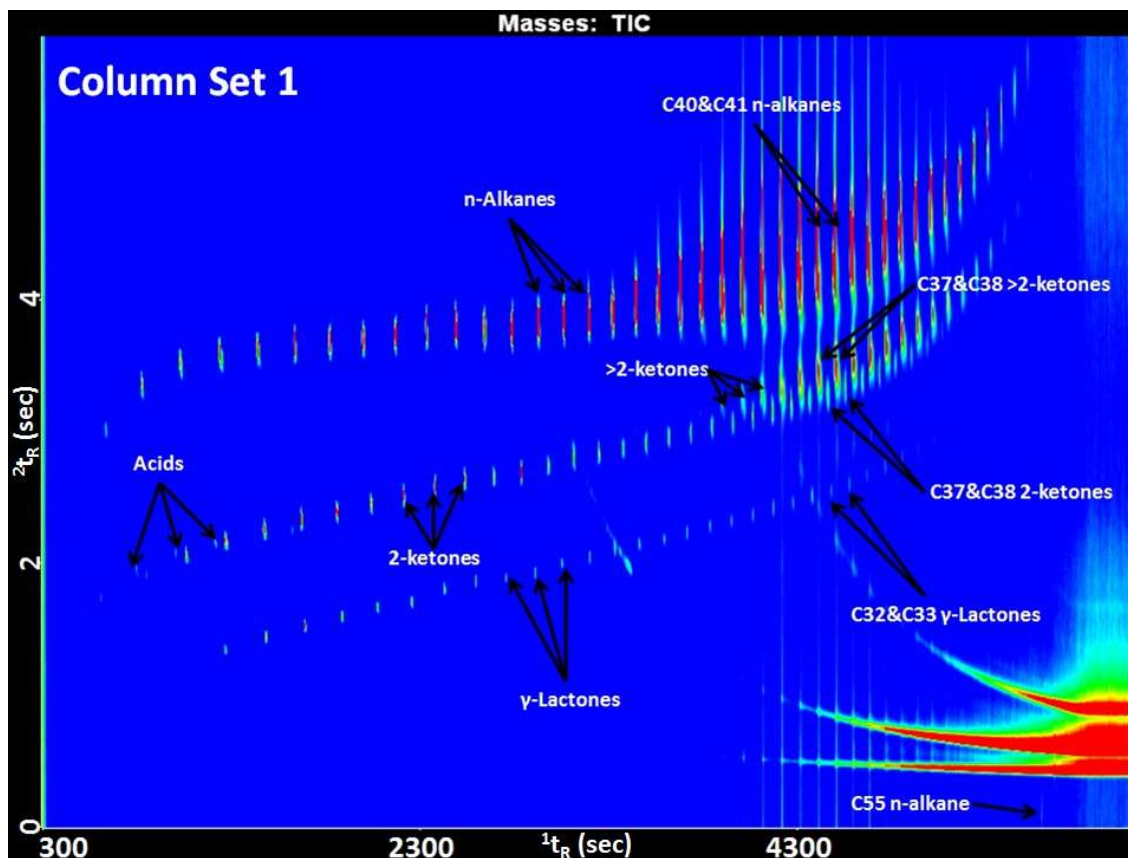
compounds are depicted as  $\Delta^1t_R$  and  $\Delta^2t_R$ . The first dimension peak widths ( ${}^1\omega$ ) are considered equal to the sum of the amount of time of the number of modulations for the compound of interest providing that the modulated peaks are higher than 10% of the peak height of the largest modulated peak. The second dimension peak widths ( ${}^2\omega$ ) at 10% peak height were measured on the chromatogram.

2D occupation was also used as criteria to determine which column set provides the optimum separation of oxygenates and was calculated to quantify the spreading of peaks on each 2D contour plot [27, 40]. To calculate the 2D occupation, the first and last eluted peaks in each dimension was considered and the occupation was calculated according to Eq. (3).

$$\text{2D Occupation} = \frac{{}^1t_R(a) - {}^1t_R(b)}{{}^1t_R(\text{total})} \times \frac{{}^2t_R(c) - {}^2t_R(d)}{P_M} \quad (3)$$

where,  ${}^1t_R(a)$  is the first dimension retention time of the peak that eluted last in the first dimension,  ${}^1t_R(b)$  is the first dimension retention time of the peak that eluted first in the first dimension,  ${}^2t_R(c)$  is the second dimension retention time of peak that eluted last in the second dimension,  ${}^2t_R(d)$  is the second dimension retention time of the peak that eluted first in the second dimension,  ${}^1t_R(\text{total})$  is the total run time or total first dimension analysis time and  $P_M$  is the 2D modulation period.

The sample prepared for the column set evaluation was analysed with the column sets presented in Table 5.1. The 2D contour plots for the reversed column configurations and the 2D contour plots for the normal column configurations were very similar and therefore only the 2D contour plots of the first column set of each configuration is presented. The 2D contour plot obtained with Column Set 1 is shown in Fig. 5.2.



**Figure 5.2** 2D contour plot of the oxidised heavy paraffinic fraction corresponding to Column Set 1.

A highly ordered 2D chromatogram was obtained and the two-dimensional separation space was well utilised. The separation in the two-dimensional separation plane occurs according to polarity differences as well as boiling point and n-alkanes up to a carbon number of C60 (b.p. 615°C) are eluted with the paraffins from C55 eluting in “wrap-around”, i.e. with more than one period of modulation. Some of these peaks overlapped with the column bleed and were integrated, where possible, with the rising baseline. Separation is also observed between n-alkanes and different classes of oxygenates in the second dimension. These prominent oxygenates were identified by mass spectra library [41] matching as carboxylic acids, 2-ketones and  $\gamma$ -lactones. Ketones with the carbonyl functionality further along the hydrocarbon chain than position 2 were also identified and since these ketones could not be accurately identified from the mass spectra, they were named >2-ketones. In GC $\times$ GC peaks are often arranged in highly ordered and structured plots, where peaks belonging to homologous series are positioned along straight lines on the retention plane and one can

clearly distinguish the different classes of oxygenates eluting below the paraffins (see Fig. 5.2) with the more polar oxygenate classes having the shortest second dimension retention times [33]. When using the reversed GC×GC configuration, the separation of oxygenates in the second dimension is very much a function of the polarity of the first dimension column since the more polar oxygenates have longer first dimension retention times compared to the non-polar alkanes. These oxygenates therefore elute from the first dimension column together with slightly higher boiling alkanes and due to differences in their volatilities, these compounds are then separated very well in the second dimension [42].

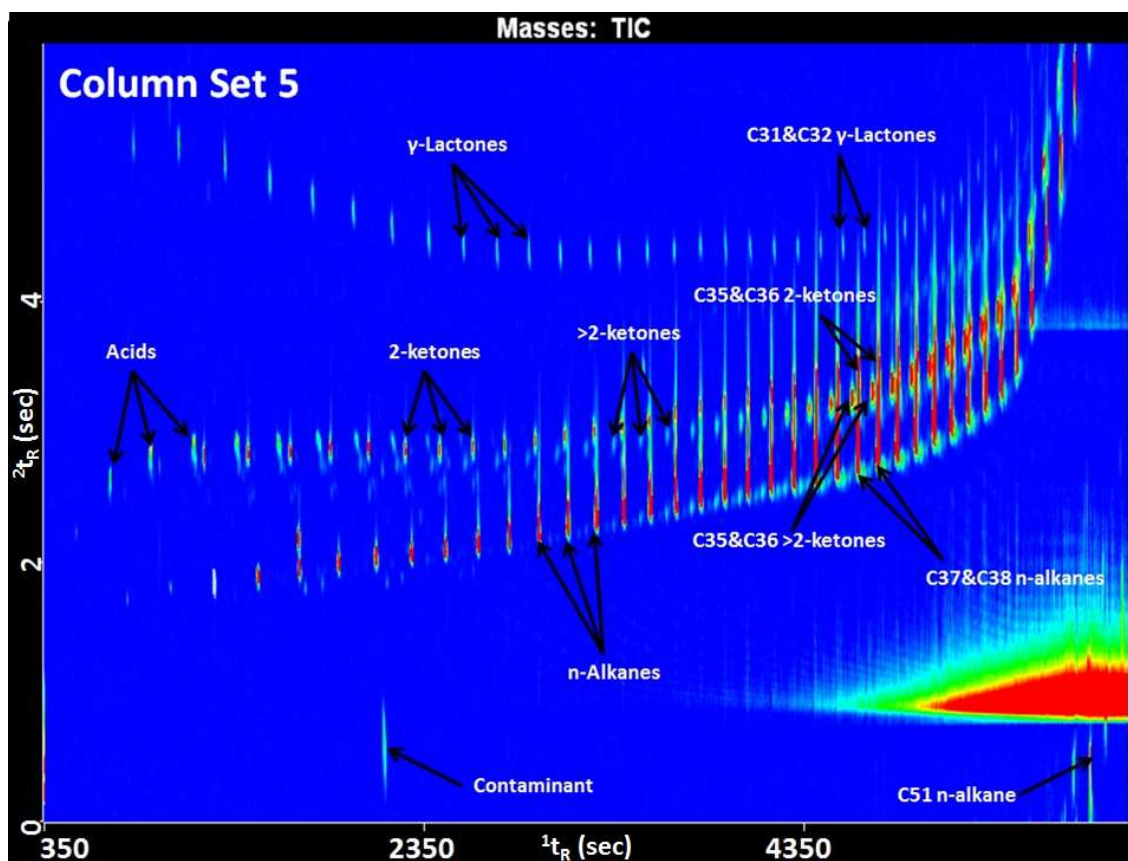
The identified oxygenates are consistent with the typical oxygenates that are formed during the autoxidation of saturated hydrocarbons with molecular oxygen which is a free radical chain process. Goosen et al. [7] have shown that the autoxidation of nonane and decane occurs in three stages with the initial stage leading to alkyl hydroperoxide formation. The alkyl hydroperoxide decomposes during the second stage to produce alcohols and ketones as major products. In the third stage the products are oxidised in competition with the alkanes. With the applied conditions of their autoxidation study, the alkanes produced  $\gamma$ -lactones as the major ester components and carboxylic acids were formed in the latter stages of oxidation. Other studies have also reported the formation of these species [7 - 9].

In this study the intra-family resolutions for all the reversed configuration column sets were obtained by calculating the 2D resolutions between C40 and C41 alkanes, C37 and C38 2-ketones, C37 and C38 > 2-ketones and C32 and C33  $\gamma$ -lactones.

In order to calculate the inter-family resolutions the concept of neighbouring peaks needs to be established since it is very different for two-dimensional chromatography compared to one-dimensional chromatography. According to the work by Pieters et al. [43], one peak in a two dimensional chromatogram may be surrounded by more than two neighbouring peaks and a method was proposed to determine actual neighbouring peaks. The method involves the connection of lines between all the 1D peak maxima of two peaks of interest (peak A and peak B). If all the connecting lines between peak A and peak B cross the peak region of a peak eluting between peak A and peak B, they are not considered neighbours. In the case where not all or none of the connecting lines between the peak A and peak B cross the peak region

of a peak eluting between peak A and peak B, they are considered neighbours. Based on this description, the C40 alkane and C37 > 2-ketone, C37 > 2-ketone and C37 2-ketone, C40 alkane and C37 2-ketone and the C37 2-ketone and C32  $\gamma$ -lactone were selected to calculate the inter-family resolutions for all reversed configuration column sets (Table 5.1). These selected compounds were close to the middle of the carbon distribution of the oxidised heavy paraffinic fraction and therefore in the region of the chromatogram where peak overlap is most likely to occur and where optimum resolution between compounds is critical.

The 2D contour plot of the sample prepared for the column evaluations obtained with the normal column configuration set 5 (Table 5.1) is shown in Fig. 5.3.

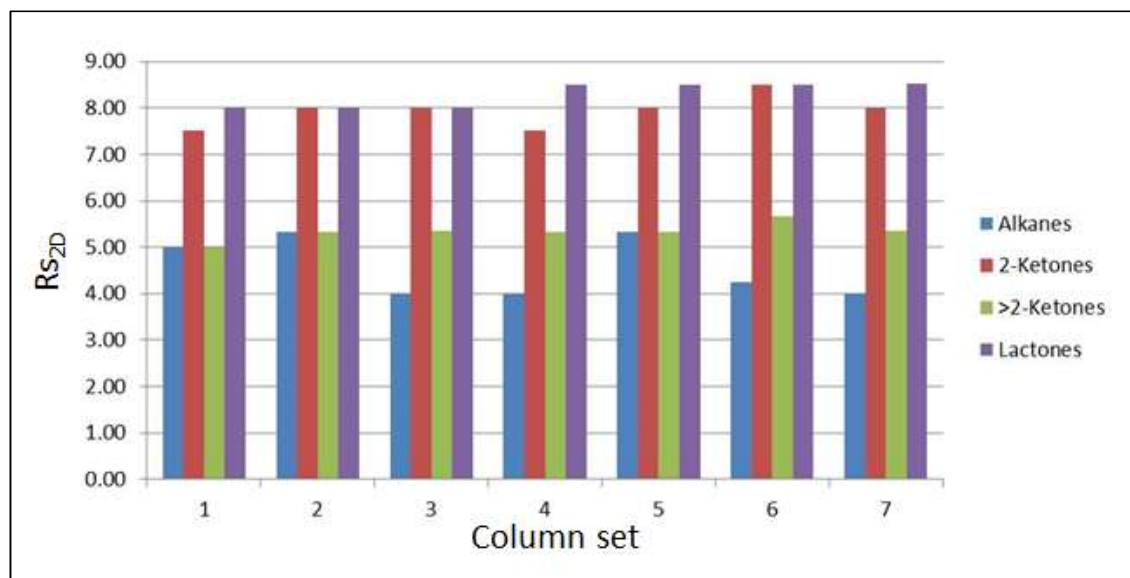


**Figure 5.3** 2D contour plot of the oxidised heavy paraffinic fraction corresponding to column Set 5.



The intra-family resolutions for all the normal configuration column sets were obtained by the calculation of the 2D resolutions between C37 and C38 alkanes, C35 and C36 2-ketones, C35 and C36 > 2-ketones and C31 and C32  $\gamma$ -lactones. Based on the description of neighbouring peaks by Pieters et al. [43], the inter-family resolutions for all the normal configuration column sets (Table 5.1) were calculated between the C37 alkane and C35 > 2-ketone, C35 > 2-ketone and C35 2-ketone, C37 alkane and C35 2-ketone and between the C35 2-ketone and C32  $\gamma$ -lactone. Once again, these compounds were close to the middle of the carbon distribution of the oxidised heavy paraffinic fraction and the region of the chromatogram where peak overlap will most likely occur.

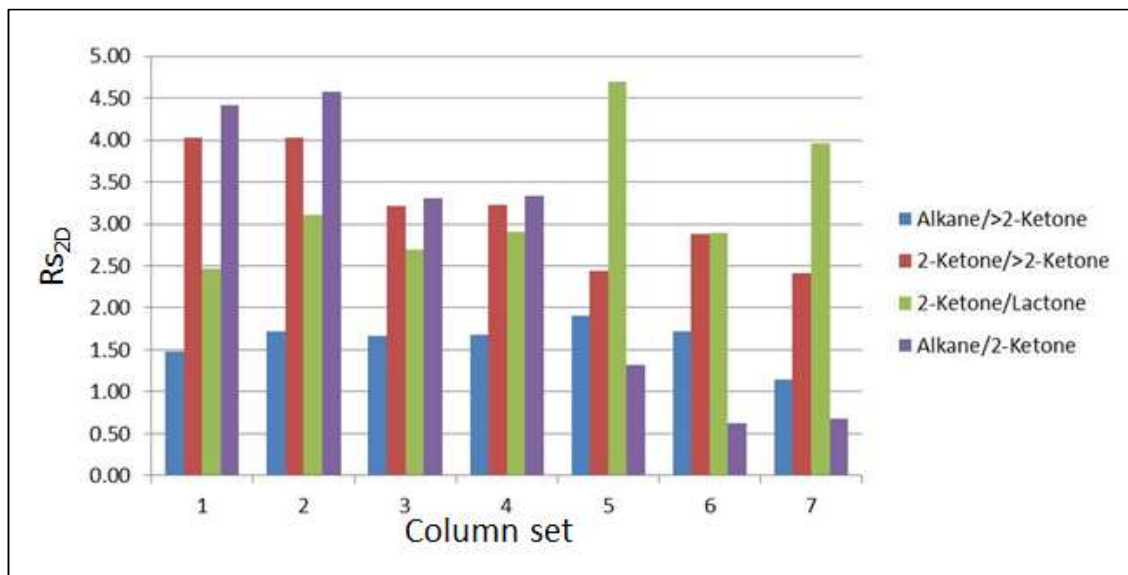
The intra-resolutions for the column sets (Table 5.1) are presented in Fig. 5.4.



**Figure 5.4** Intra-family resolutions for the evaluated column sets.

Based on 1D-GC convention,  $Rs_{2D}$  is sufficient when it is higher than 1.5 [27]. Fig. 5.4 indicated that intra-family resolutions were very similar for all column sets and in all cases the resolutions were higher than 1.5 and therefore the intra-family resolutions were deemed sufficient for all the investigated column sets.

The inter-family resolutions for the column sets (Table 5.1) are presented in Fig. 5.5.

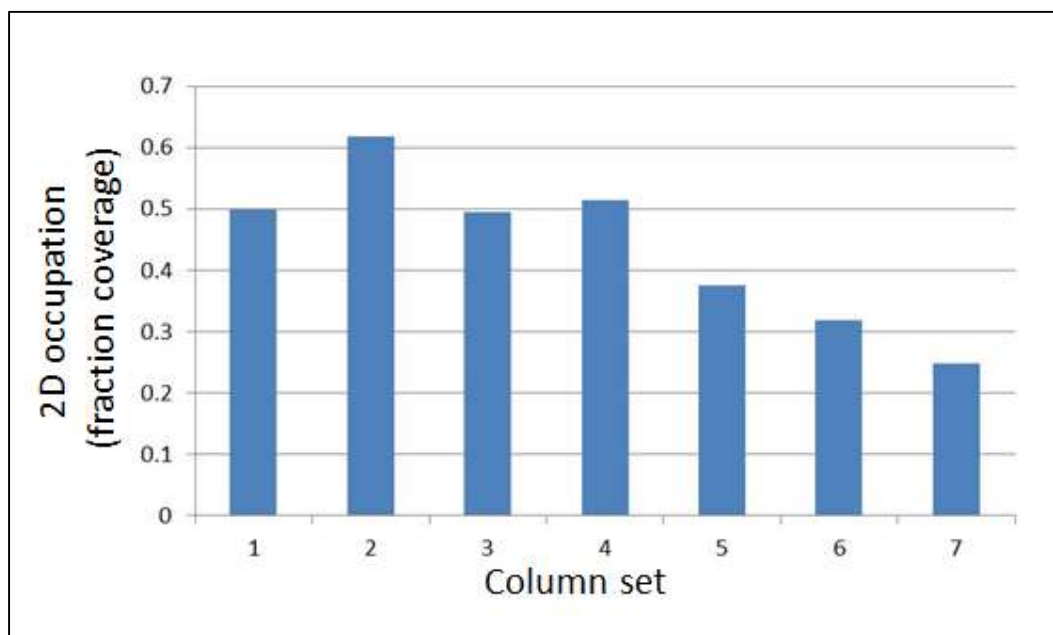


**Figure 5.5** Inter-family resolutions for the evaluated column sets.

Fig. 5.5 indicates that inter-family resolutions between the alkane and the >2-ketone were close to the required 1.5 for all the evaluated column sets with column set 1 and set 7 having resolutions below the required 1.5. Slightly better resolutions between the alkane and the >2-ketones were obtained by column sets 2 - 6. The resolutions between the 2-ketone and >2-ketone as well as the resolutions between the 2-ketone and  $\gamma$ -lactone were sufficient for all the column sets. Insufficient resolutions were obtained between the alkane and 2-ketone for all the normal configuration column sets (Sets 5 - 7) whilst all the reversed column configurations (Sets 1 - 4) showed sufficient resolutions with column set 2 having the highest resolution between these two compounds. The resolution between the alkane and 2-ketone was more than 2 times higher with the reversed column configuration column sets than that achieved with the normal column configuration column sets. In the case of the reversed column configuration, the n-alkanes eluted at the top of the separation plane and the large 2<sup>nd</sup> dimension peak widths of the n-alkanes, due to their high concentrations, caused fractions of these n-alkane peaks to elute at the bottom of the separation plane (wrap-around). No other oxygenates have 2<sup>nd</sup> dimension retention times in the same region and therefore the overlap between the alkanes and 2-ketones in normal configuration were not observed in the reversed column configurations. The resolution between these compounds classes was

therefore viewed as critical in this evaluation and weighed heavily in the choice of a column set that provides optimal separation of the compounds present.

The 2D occupations for the different column sets are presented in Fig. 5.6.



**Figure 5.6** Comparison of 2D occupation for the different column sets.

In Fig. 5.6 it is clear that the reversed configuration column sets (sets 1 - 4) provide the best 2D occupations with the normal configuration column sets providing lower 2D occupations in each case. Previous groups that focussed on the optimal separation of FT-products that contained mostly alkanes, alkenes, aromatics and oxygenates also showed that the highest orthogonality for these products is obtained in the reversed column configuration [33, 36 - 39]. Based on the above discussion, column set 2 was chosen as the optimum column set for the separation of oxygenates in oxidised heavy paraffinic fractions.

### 3.3. Oxidation reaction monitoring

As mentioned previously, the characterisation and monitoring of heavy oxygenate formation is very important for the control of oxidation processes. In order to illustrate the use of HT-GC×GC in oxidation reaction monitoring, the hydrogenated heavy paraffinic fraction sample

prior to oxidation as well as samples taken from the oxidation reactor during oxidation were analysed using column set 2 (Table 5.1).

The 2D contour plots of the hydrogenated heavy paraffinic fraction, prior to oxidation, as well as the oxidised products after 30, 60, 120, 180 and 210 min of oxidation are presented in Fig. 5.7.

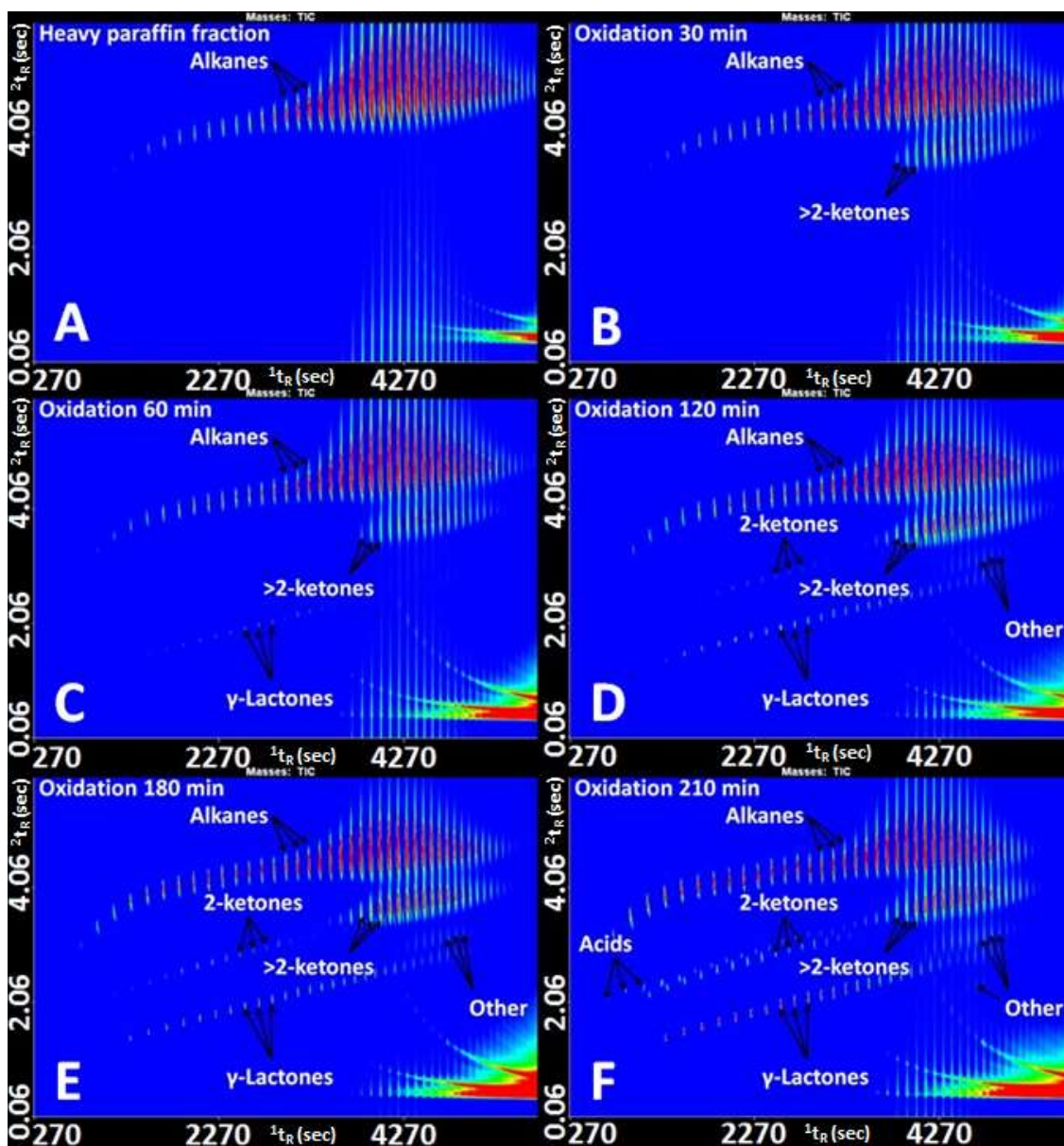
The increase in oxygenates with the increasing time intervals is clearly observed in Fig. 5.7. In addition, the major classes of oxygenates are distinguishable in the chromatograms. The major classes of oxygenates were quantified (HT-GC×GC-FID) and the weight % of the compounds present in the samples are presented in Table 5.2.

**Table 5.2** Quantification results (HT-GC×GC-FID) of the heavy paraffinic fraction sample as well as the oxidised products.

Sample	Paraffins (mass %)	2-ketones (mass %)	>2-ketones (mass %)	$\gamma$ -lactones (mass %)	Acids (mass %)	Other (mass %)
Heavy paraffinic fraction	100.00	0.00	0.00	0.00	0.00	0.00
30 min	89.97	3.02	5.71	0.96	0.02	0.32
60 min	83.88	4.28	8.23	2.72	0.15	0.74
120 min	69.76	7.43	14.99	4.77	0.41	2.64
180 min	61.38	9.21	17.91	6.70	0.73	4.07
210 min (Final Product)	51.87	9.37	18.17	9.78	3.97	6.84

It can be seen from Table 5.2 that there is a steady increase in the oxygenate concentration with the final product after 210 min of oxidation containing 48.13 mass % of oxygenates. The >2-ketones were observed to be the oxygenate class with the highest concentration. Cyclic esters ( $\gamma$ -Lactones) were also observed in high concentrations and carboxylic acids were only formed in the latter stages of the oxidation reaction. This is consistent with the observations by Goosen et al. [7] in their study of the autoxidation of nonane and decane. Other minor oxidation products were grouped together and the concentration of these oxygenates were 6.84 mass %. The minor oxidation products were not identified as part of this study and more work is needed to identify these minor oxygenates. Contrary to previous studies [7 - 9], alcohols were only identified as a minor component in the oxidation products.

The advantage of using HT-GC×GC over the use of titrimetric procedures in oxidation reaction monitoring is clearly illustrated in this example where the concentrations of different oxygenate classes could be determined selectively with the added advantage that the concentrations for each oxygenate class can be reported by carbon number. It is for example clear from the chromatograms (see Fig. 5.7) that the carbon number distribution of the alkanes changes with time and that each oxygenate class has a different carbon number distribution. Another advantage is that the separate titrimetric procedures can be replaced by a single HT-GC×GC analysis to monitor oxidation reactions. The developed HT-GC×GC method can only be used for heavy paraffinic fractions with a carbon number distribution up to C60 (b.p. 615°C) which is similar to the carbon number distribution eluted in other studies [12] where column sets with similar geometries were used. Peak tailing in the second dimension is still observed for the alkanes present in high concentrations (Fig. 5.7). The use of a reverse fill/flush (RFF) differential flow modulator [44] can be investigated in future to reduce the observed tailing which will also improve quantification.



**Figure 5.7** 2D contour plots of the heavy petroleum fraction A) prior to oxidation B) After 30 min C) 60 min D) 120 min, E) 180 min and F) 210 min of oxidation.

#### 4. Conclusions

The evaluation of HT-GC×GC column sets for the optimum separation of oxygenates in oxidised heavy paraffinic fractions is reported for the first time. HT-GC×GC in the reversed configuration provides the optimum separation for oxygenates in oxidised heavy paraffinic fraction samples and hydrocarbons up to a carbon number of C60 could be eluted. The

advantages of using the developed HT-GC×GC method in the monitoring of the oxidation reactions of heavy paraffinic fraction samples were clearly illustrated by the selective quantification of oxygenate classes. It is also possible to obtain the concentration for each oxygenate class by carbon number (not shown). Replacing separate titrimetric procedures by a single HT-GC×GC analysis also reduces the time and effort of analysis. HT-GC×GC analysis therefore allows for the optimisation of oxidation conditions to produce higher value heavy paraffinic fractions. Future work may include the pre-separation and identification of the minor oxygenates classes. The use of a reverse fill/flush (RFF) differential flow modulator can also be investigated to reduce the observed tailing and to improve quantification. The repeatability of the quantitative analysis and the use of an internal standard quantification method could be further investigated in future.

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## Chapter 6

# 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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E. Rohwer provided technical guidance in the field of study.

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## **Abstract**

To increase the value of the heavy petroleum fractions produced during refining processes, these fractions need to be upgraded to useable products. Oxidation of hydrogenated heavy paraffinic fractions produces high value products that contain a variety of oxygenates. 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. 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 assist in the accurate identification of these oxygenates. Solid phase extraction (SPE) and supercritical fluid chromatography (SFC) were employed in this study as pre-fractionation techniques. GC-MS with supersonic molecular beams (also named GC-MS with Cold-EI) utilises a supersonic molecular beam (SMB) interface between the GC and the MS 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 in the mass spectrum. The increased molecular ion greatly enhances the accurate identification of the oxygenates present in these fractions. In this study we investigated the ionisation behaviour of various 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.

## 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]. 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, 12]. 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 [13] and hydrocarbons up to C<sub>86</sub>H<sub>174</sub> were analysed by Cold-EI with abundant or dominant molecular ions [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 1D-GC. High temperature comprehensive two-dimensional gas chromatography (HT-GC×GC) was used to increase peak capacity and analyse complex heavy petroleum samples (see Chapter 5) [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 (see Chapter 3) [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, 14, 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 [37 - 38] for the analysis of complex petrochemical samples.

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 were investigated.

## **2. Experimental**

### **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 6.1 was prepared in cyclohexane at a concentration of 0.5 mass % of each compound. This standard 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 (see Chapter 5) was oxidised in the laboratory and used in the pre-fractionation experiments.

**Table 6.1** Standards used to investigate the ionisation behaviour and for the optimisation of the pre-fractionation procedures.

<i>Alkanes</i>	<i>Ester</i>	<i>Carbonyls</i>	<i>Alcohols</i>
(a) n-Eicosane	(e) Hexadecyl Dodecanoate	(i) 2-Octadecanone	(n) 1-Tridecanol
(b) n-Docosane		(j) 8-Pentadecanone	(o) 1-Tetradecanol
		(k) 16-Hentriacontanone	(p) 1-Hexadecanol
<i>Alkene</i>	<i>Acids</i>	(l) n-Docosanal	(q) 1-Heptadecanol
(c) 1-Eicosene	(f) Undecanoic Acid		(r) 1-Octadecanol
	(g) Tetradecanoic Acid	<i>Diol</i>	(s) 1-Eicosanol
<i>Ether</i>	(h) Arachidic Acid	(m) 1,12-Octadecandiol	(t) 1-Tetracosanol
(d) Didecyl-Ether			(u) 1-Docosanol
			(v) 2-Octyl-1-dodecanol

## 2.2. Heavy paraffinic fraction oxidation

The oxidised heavy paraffinic fraction sample was prepared according to the procedure described in a previous study (see Chapter 5) [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°C). 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. SPE pre-fractionation

A Sep-Pak silica plus long cartridge from Waters (Massachusetts, USA) with 690 mg sorbent per 5 mL cartridge and 55 - 105  $\mu\text{m}$  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 standard (Table 6.1) was diluted further to a concentration of 100  $\mu\text{g/g}$  per component and 1 mL of the diluted 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.

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.

### 2.4. 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 oxygenates (Selerity Technologies, Utah, USA). In order to achieve the pre-separation a Petrosil column (10 cm  $\times$  1.0 mm, 5  $\mu\text{m}$   $d_p$ ) 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  $\mu\text{L}$  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<sub>2</sub> 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<sub>2</sub>. The trapping procedure was repeated fifteen times to increase the concentration of oxygenates. The liner was then inserted into the GC-MS with Cold-EI for analysis. The sample dilution for the SFC separation was more dilute 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.

## 2.5. GC-SMB 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 supersonic molecular beam (SMB) interface 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<sup>2</sup> 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 (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 of interest.

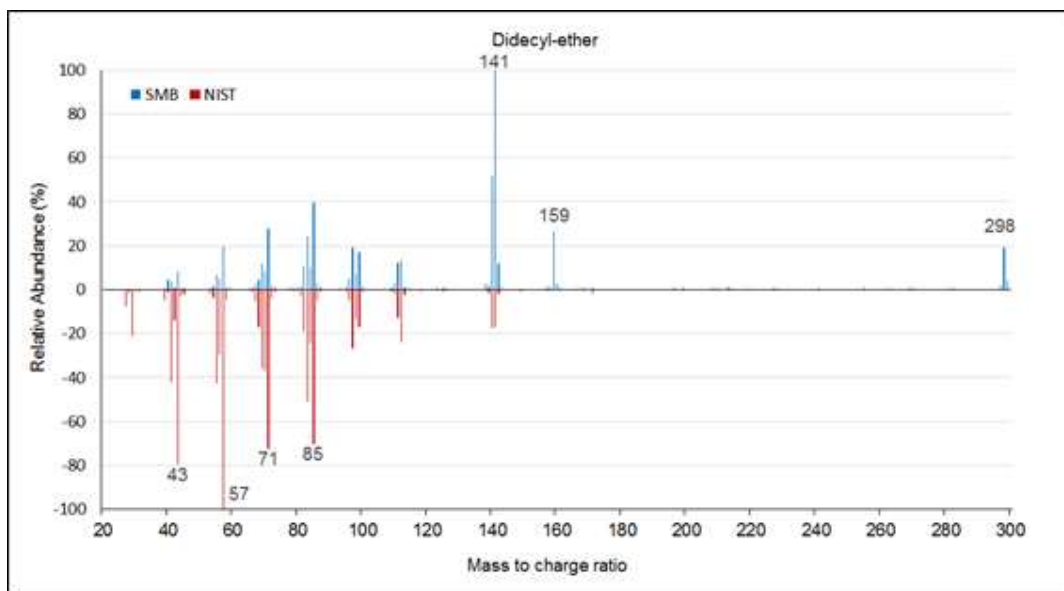
### 3. Results and Discussion

#### 3.1. GC-MS with Cold-EI of standard oxygenates

The standards in Table 6.1 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 in this study compared to the significantly lower intensity 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 in Appendix A.

##### Ethers:

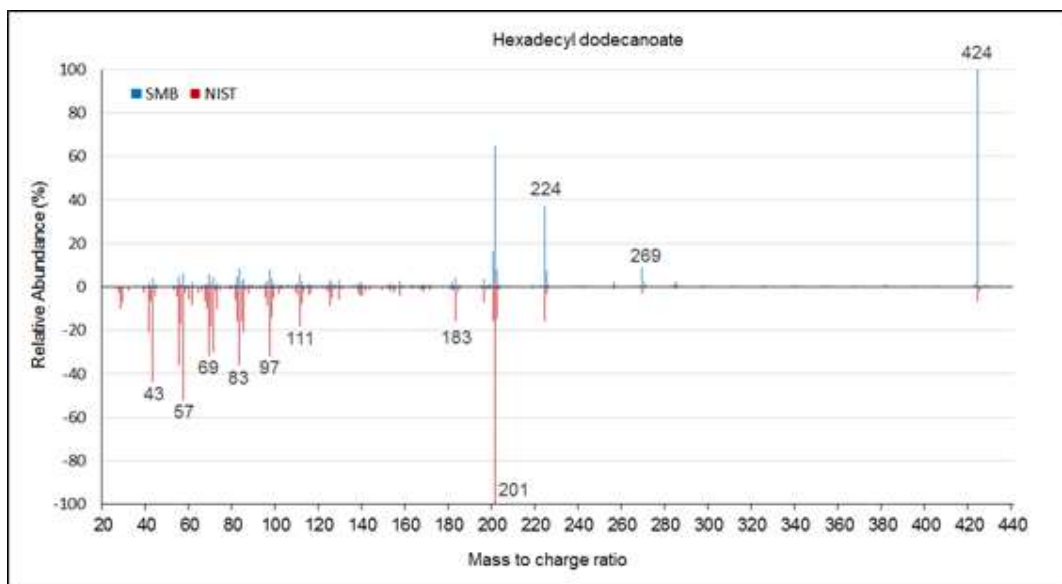
Didecyl ether ( $C_{20}H_{42}O$ ) was used as representative of this group. Fig. 6.1 shows the NIST mass spectrum (bottom) as well as the Cold-EI mass spectrum (top) of this compound. In the NIST mass spectrum the highest observed mass with a relative abundance of greater than 10% at  $m/z$  141 ( $C_{10}H_{21}^+$ ) 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 6.1** Mass spectra of didecyl ether with conventional EI (bottom) and Cold-EI (top).

#### Esters:

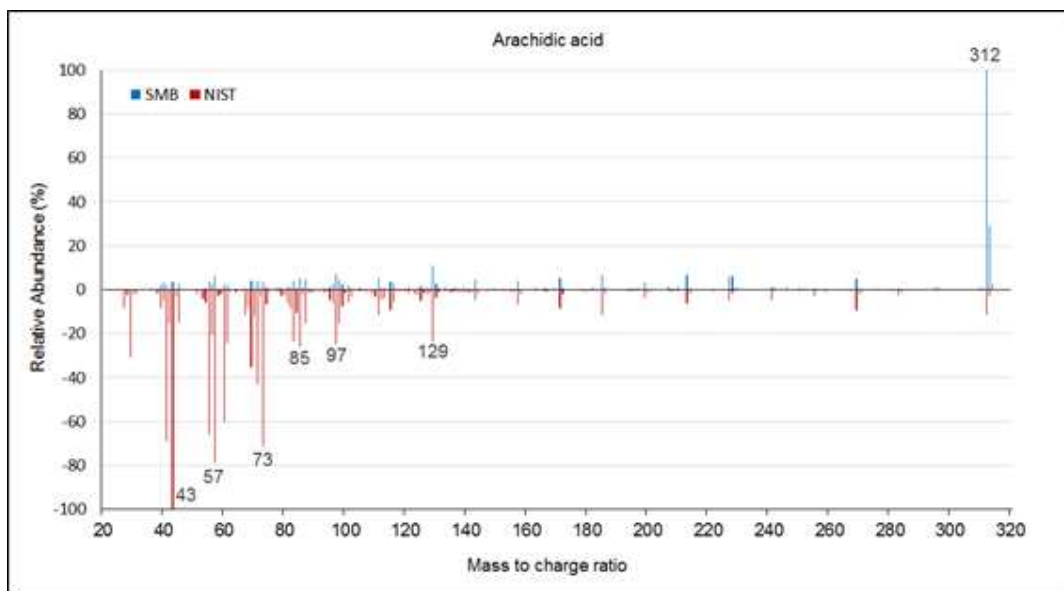
The NIST mass spectrum of the selected representative hexadecyl dodecanoate ester ( $C_{28}H_{56}O_2$ ), is presented in Fig. 6.2 (bottom). The base peak at  $m/z$  201 corresponds to the acid fragment of the molecule ( $C_{12}H_{25}O_2$ ) after the loss of a  $C_{16}H_{31}$  group by 2H rearrangement. 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 (Fig. 6.2, 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 6.2** Mass spectra of hexadecyl dodecanoate with conventional EI (bottom) and Cold-EI (top).

#### 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 Fig. 6.3. The mass spectra for undecanoic acid ( $C_{11}H_{22}O_2$ ) and tetradecanoic acid ( $C_{14}H_{28}O_2$ ) are included in Appendix A 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 of 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 each mass spectrum for 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 underivatized free fatty acids is that their response is linear without intra-ion source degradation, which prevails with standard EI [39].



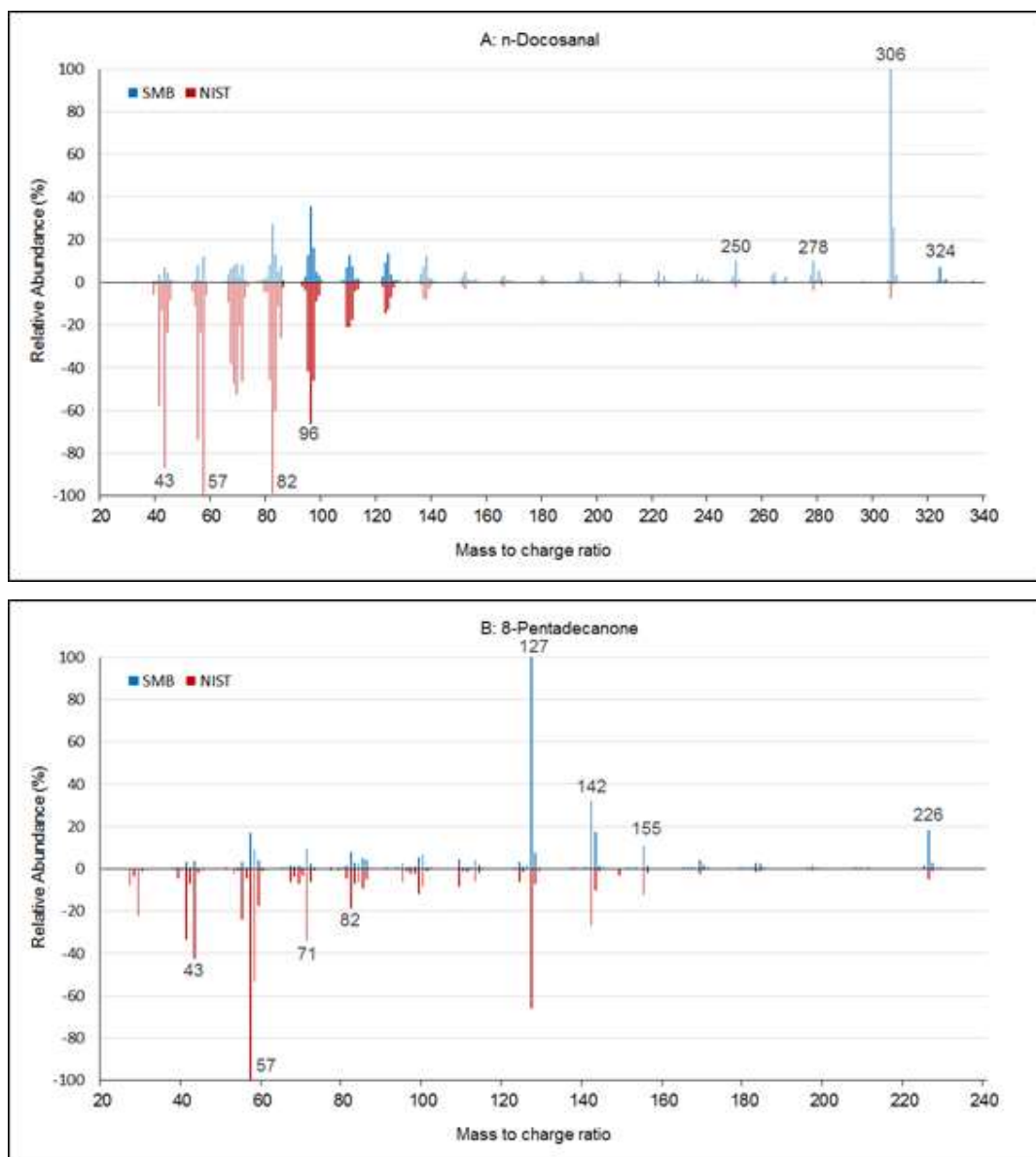
**Figure 6.3** Mass spectra of arachidic acid ( $C_{20}H_{40}O_2$ ) with conventional EI (bottom) and Cold-EI (top).

#### Carbonyls:

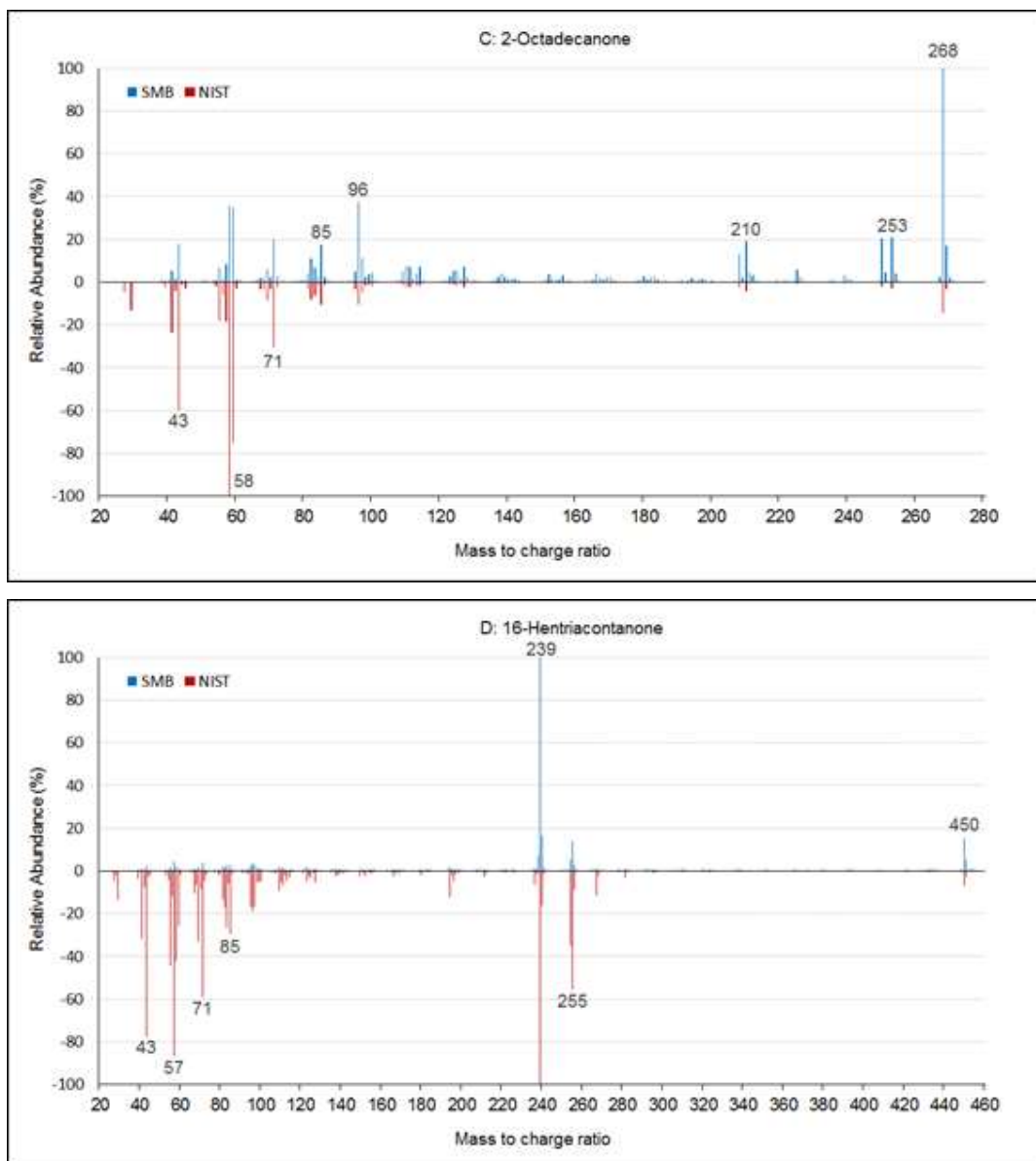
The molecular ion at  $m/z$  324 is not observed for *n*-docosanal ( $C_{22}H_{44}O$ ) in the mass spectrum using conventional EI (Fig. 6.4A, bottom). The highest observed mass peak in this spectrum was  $m/z$  306, with a relative abundance of  $\pm 10\%$ , which corresponds to the fragment of the molecule after the loss of  $H_2O$ . In the Cold-EI mass spectrum (Fig. 6.4A, 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  $\pm 10\%$ . The availability of small molecular ion and large  $[M - 18]^+$  fragment ion MS peaks 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 Fig. 6.4B, C and D (bottom). Molecular ions were observed for all these ketones in the conventional EI mass spectra with relative abundances of between 5% and 20%.

As expected, characteristic heavy fragments were observed for the carbonyls containing the carbonyl functionality in the middle of the hydrocarbon 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 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 (Fig. 6.4B, 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  $\pm 20\%$  (compared to  $< 10\%$  in the NIST spectrum). In the Cold-EI mass spectrum of 2-octadecanone (Fig. 6.4C, top) the molecular ion at  $m/z$  268 substantially increased and was observed as the base peak with the heavy mass fragments ( $[M - \text{CH}_3]^+$  and  $[M - \text{H}_2\text{O}]^+$ ) also increasing in abundance to  $\pm 20\%$ . 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.





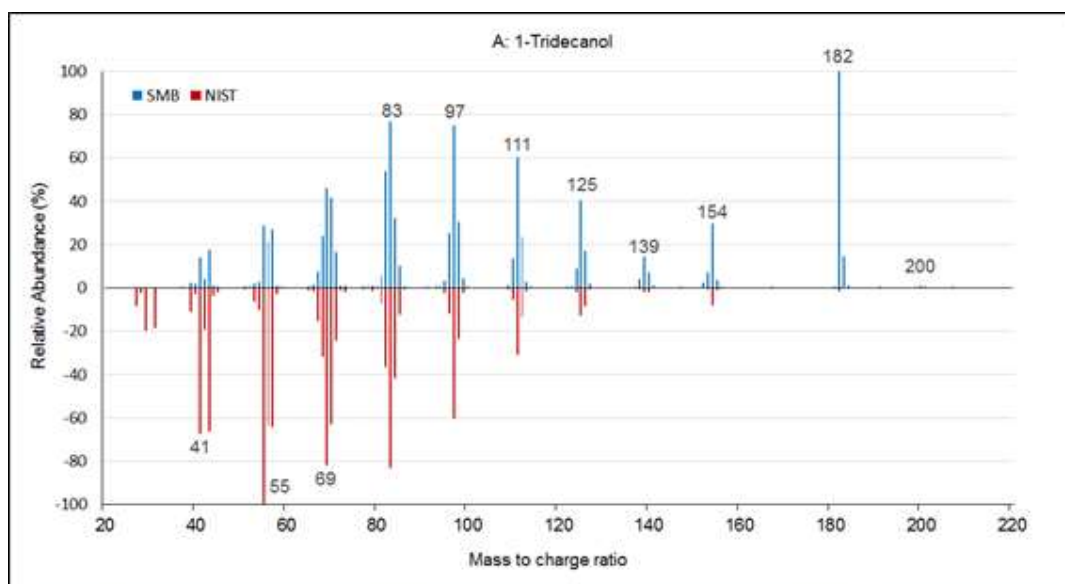


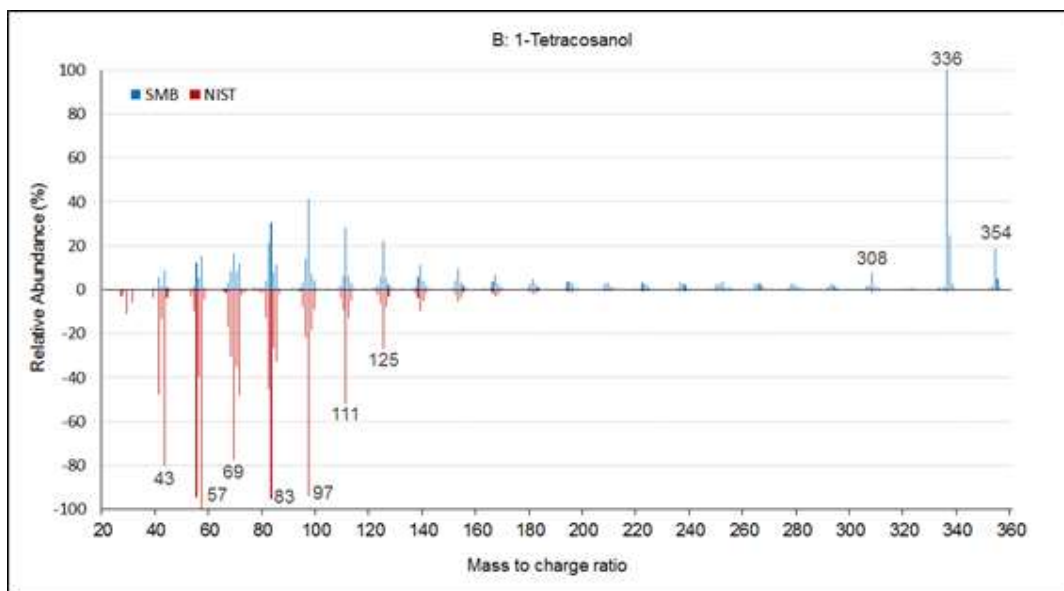
**Figure 6.4** Mass spectra of A) n-docosanal ( $C_{22}H_{44}O$ ), B) 8-pentadecanone ( $C_{15}H_{30}O$ ), C) 2-octadecanone ( $C_{18}H_{36}O$ ) and D) 16-hentriacontanone ( $C_{31}H_{62}O$ ) with conventional EI (bottom) and Cold-EI (top).

### 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 Fig. 6.5A and 6.5B. 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 in Appendix A as supplementary material. No molecular ions were observed in the conventional

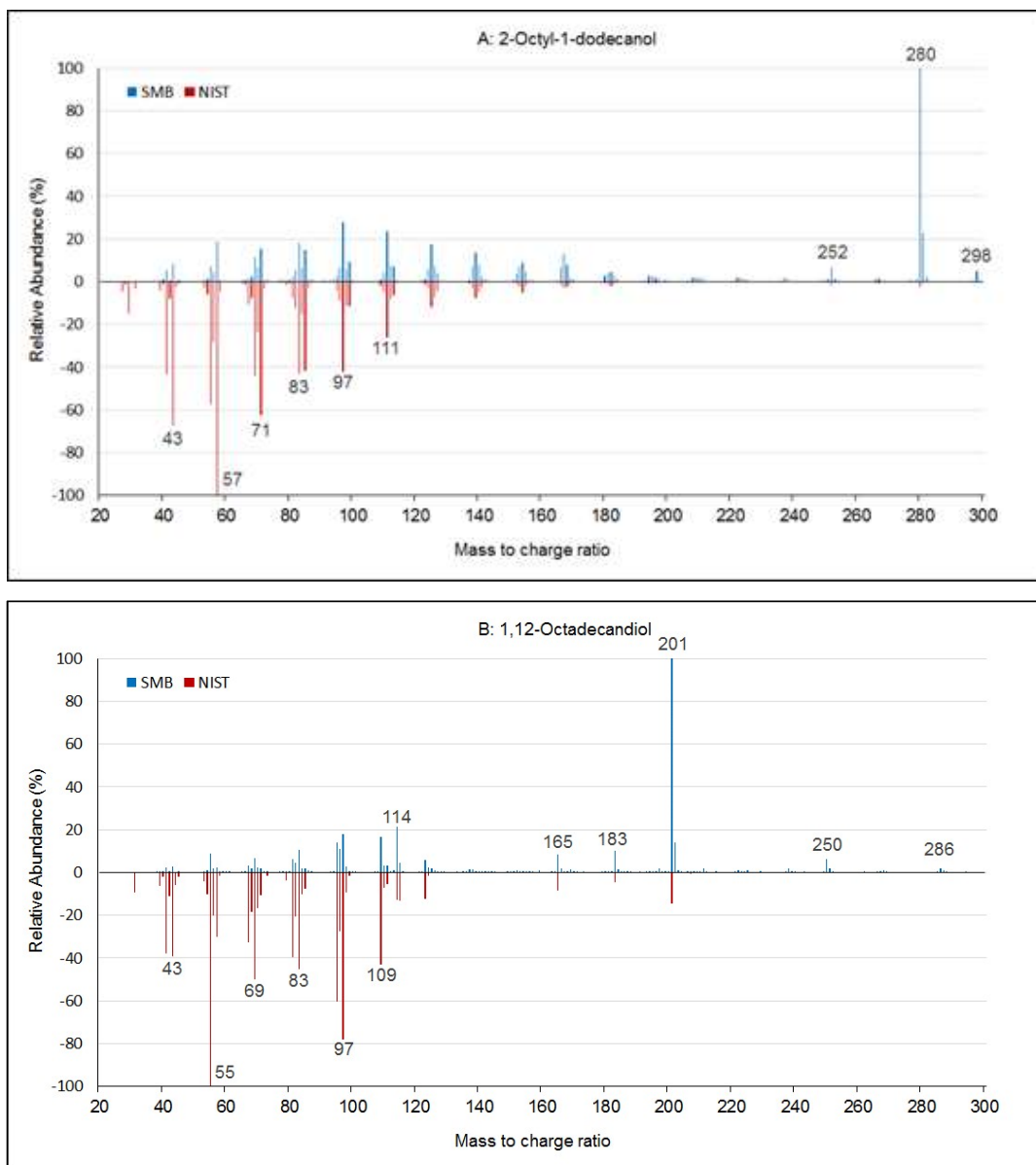
EI mass spectra for any of these alcohols and the highest observed mass fragment in each spectrum corresponded to the fragment of the molecule after the loss of H<sub>2</sub>O. The abundance of this peak in all cases was below 20%. In the Cold-EI mass spectra of the linear alcohols (Fig. 6.5, top) the fragment after loss of H<sub>2</sub>O substantially increased and was the base peak in 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  $\pm 20\%$  for 1-tetracosanol (Fig. 6.5B, top). This is consistent with Dagan and Amirav [34] that reported the effects of alkane chain length on the Cold-EI mass spectra, where it was 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 6.5** 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).

Fig. 6.6A (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 (Fig. 6.6A, top) it was observed that, similar to the linear alcohols, the abundance of 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%. Fig. 6.6B (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 (Fig. 6.6B, top) the base peak was at  $[M - 85]^+$  that was obtained after 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.



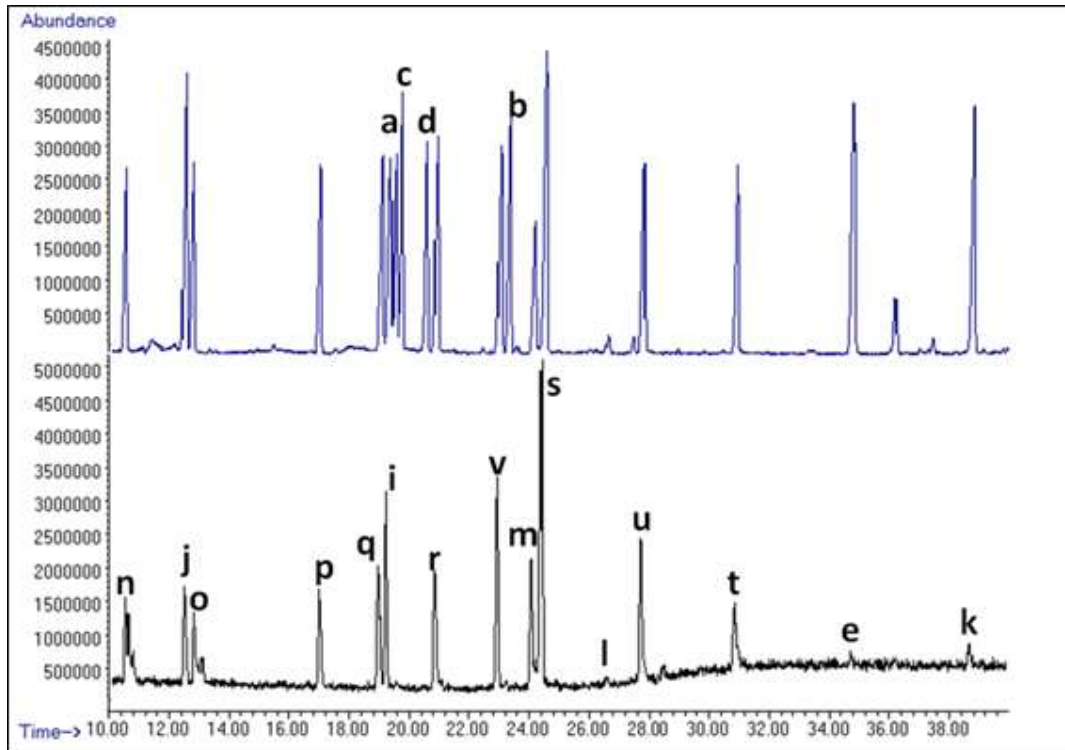
**Figure 6.6** Mass spectra of A) 2-octyl-1-dodecanol and B) 1,12-octadecandiol with conventional EI (bottom) and Cold-EI (top).

### 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. These

retained oxygenates can then be removed from the silica gel by competitive interaction, in this case by the introduction of a polar solvent such as methanol or acetone.

Initially 2 mL of a standard containing 2000  $\mu\text{g/g}$  of each of the components listed in Table 6.1 was separated by SPE according to the procedure described in the experimental section. Subsequent GC-MS with Cold-EI analysis showed that the paraffins and olefins 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 only 100  $\mu\text{g/g}$  of each of the components listed in Table 6.1, and 1 mL of this standard was separated by the SPE procedure. Fig. 6.7 shows stacked GC-MS with Cold-EI mass chromatograms of the standard before and after fractionation by SPE.



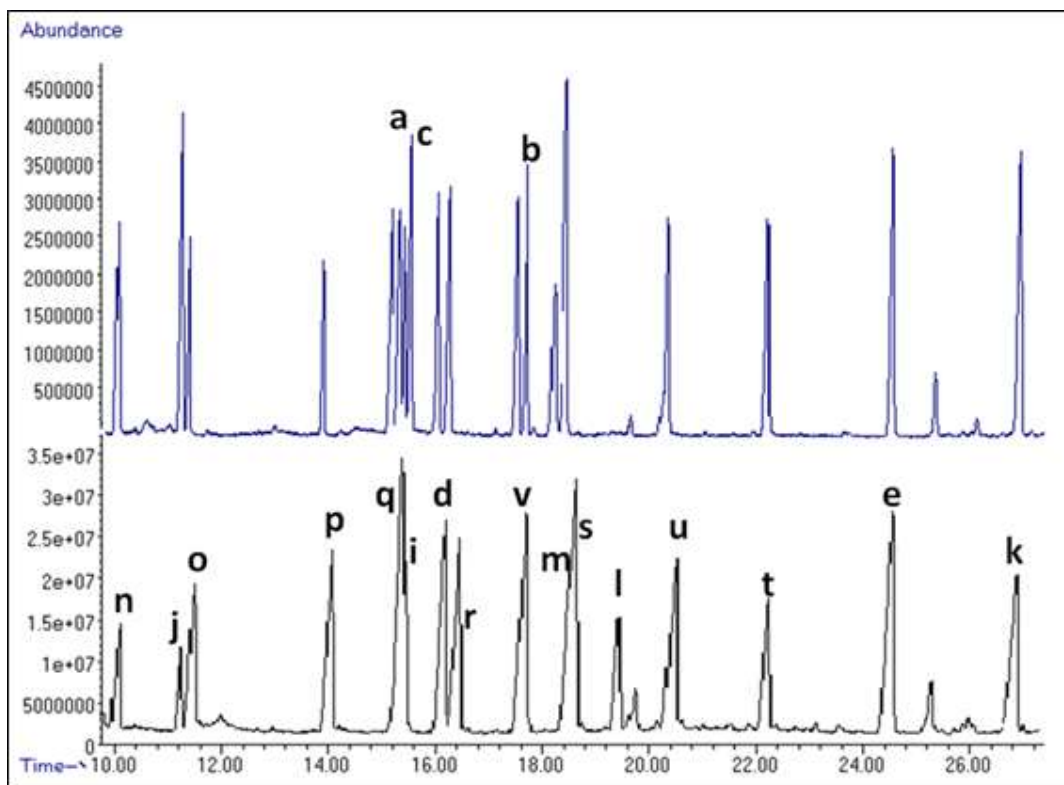
**Figure 6.7** GC-MS with Cold-EI total ion chromatograms of the standard before (top) and after (bottom) fractionation by SPE using silica gel. (Peak labels as defined in Table 6.1).

It can be observed that the diol and alcohols were successfully retained. Because of the non-polar column used, the organic acids are not visible in Fig. 6.7, 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 pre-fractionation procedure tested 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 a modifier in the mobile phase. In the SFC separation, the oxygenates were backflushed 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  $\mu$ L) containing 2000  $\mu$ g/g of each of the components listed in Table 6.1 was separated by SFC according to the procedure described in the previous section.

Fig. 6.8 shows stacked GC-MS with Cold-EI mass chromatograms of the standard before and after fractionation by SFC.

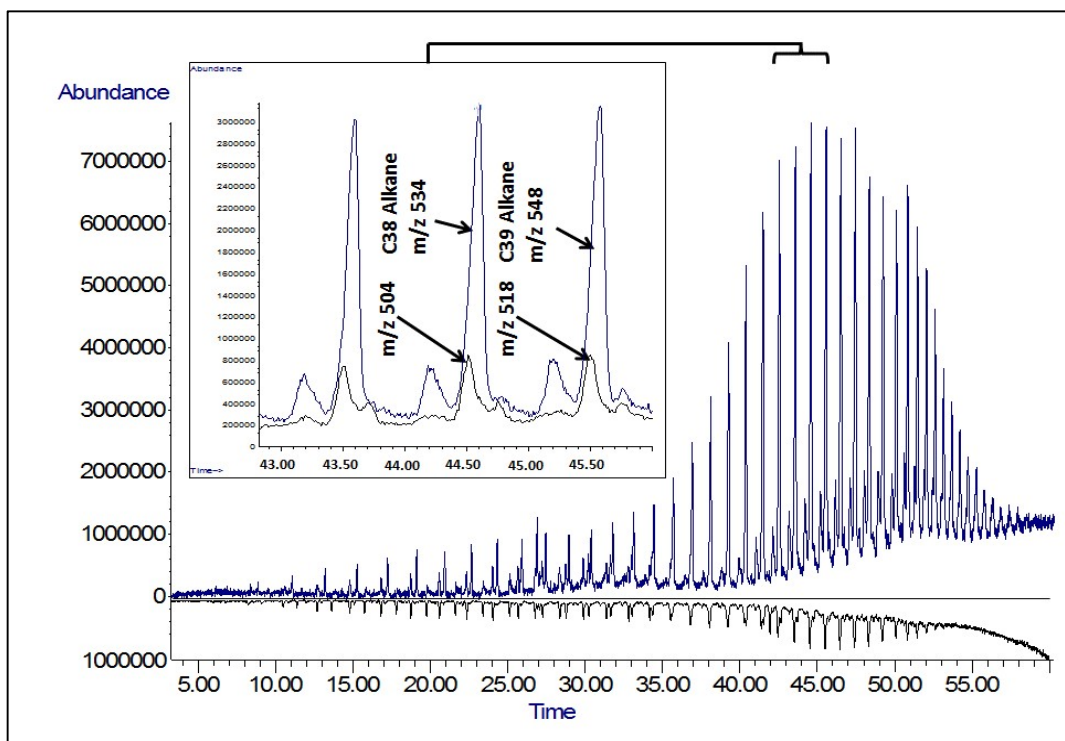


**Figure 6.8** GC-MS with Cold-EI total ion chromatograms of the standard before (top) and after (bottom) fractionation by SFC using a silica column. (Peak labels as defined in Table 6.1).

Analysis by GC-MS with Cold-EI showed that the paraffins and olefins (compounds a, b and c) 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 (Fig. 6.8 bottom) due to the high concentration of these oxygenates trapped in the liner that lead to column overload.

### 3.4. Separation of an oxidised heavy paraffinic sample

Both procedures were applied to an oxidised heavy paraffinic sample with the aim of accurately identifying the oxygenates present in the sample. Fig. 6.9 shows the GC-MS with Cold-EI mass chromatograms of the oxidised heavy paraffinic sample before (top) and after (bottom) fractionation by SPE.



**Figure 6.9** 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.

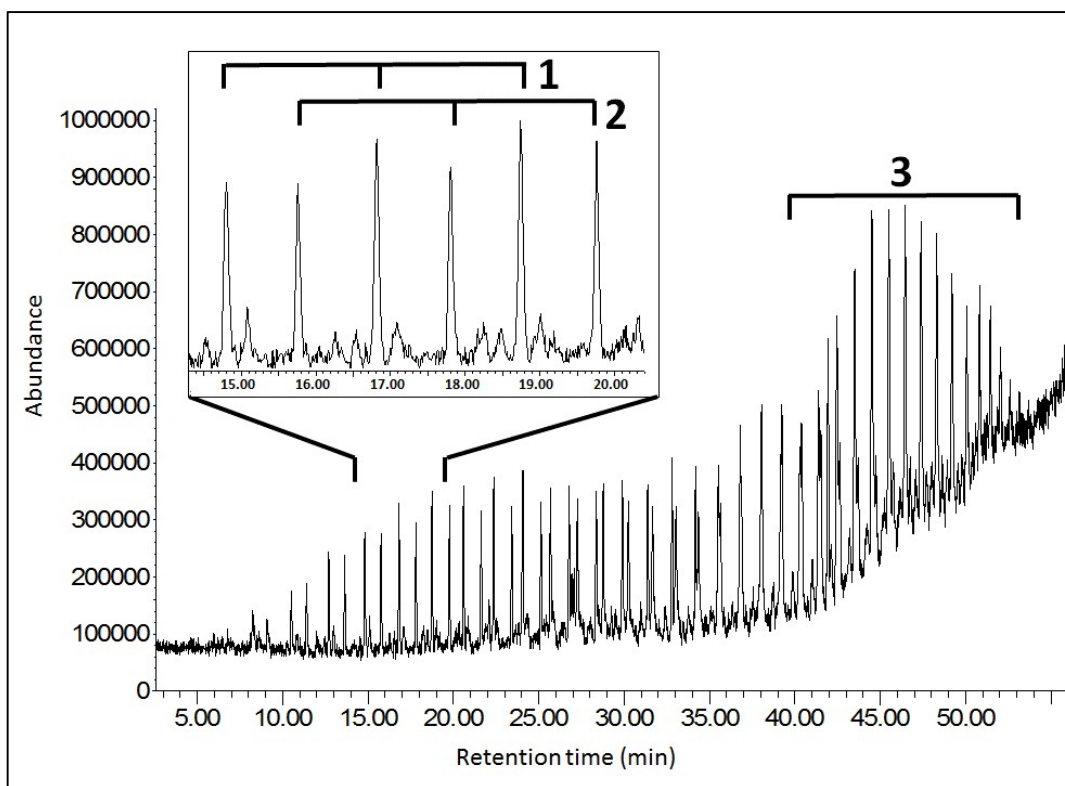
Fig. 6.9 clearly shows that the n-alkanes that dominated the oxidised heavy paraffinic fraction were completely removed by the SPE fractionation procedure. After the selective retention of the oxygenates by SPE and elution of the overlapping n-alkanes, only the retained oxygenates were observed in the total ion chromatogram (see Fig. 6.9 insert). The oxygenates with molecular masses  $m/z$  504 and 518 remained with the C38 and C39 alkanes completely removed.

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. 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



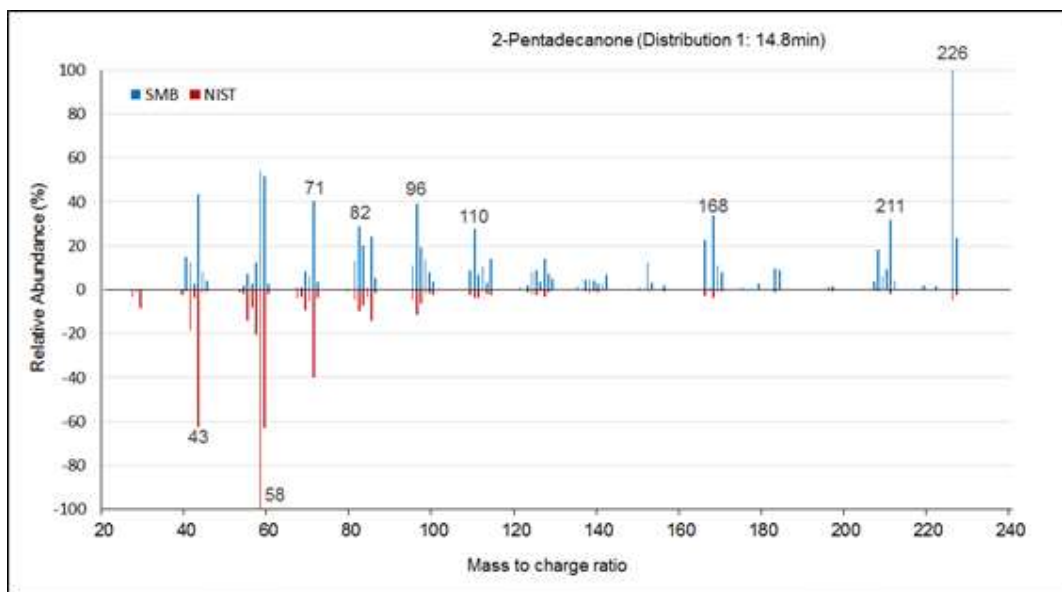
this fraction could only be observed when selected masses were extracted. Additionally, the concentrations of the oxygenates were a lot lower compared to the SPE separation procedure due to the SFC instrument requiring more dilute samples and smaller injection volumes. More work is needed to optimise and develop the SFC separation procedure. For this reason only the results from the oxidised heavy paraffinic sample after fractionation by SPE are discussed.

The GC-MS with Cold-EI mass chromatogram of the oxidised heavy paraffinic sample after fractionation by SPE is shown in Fig. 6.10. The two oxygenate distributions at the start and the third distribution at the end of the chromatogram is also indicated.



**Figure 6.10** GC-MS with Cold-EI total ion chromatogram of the oxidised heavy paraffinic sample after fractionation by SPE.

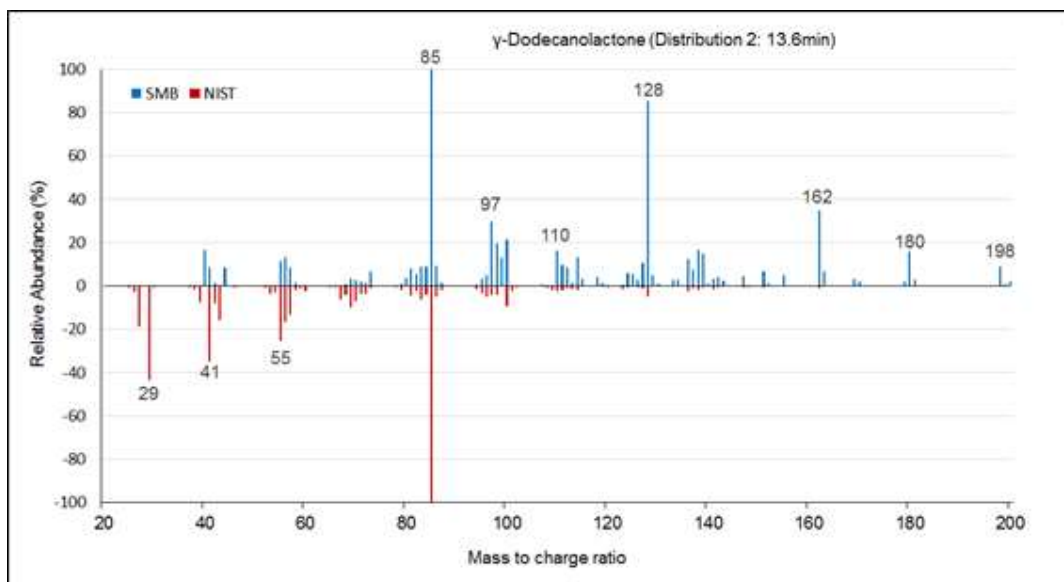
The oxygenates in the first distribution in Fig. 6.10 were identified as 2-ketones with the peaks eluting at 14.8, 16.8 and 18.8 min identified as 2-pentadecanone ( $C_{15}H_{30}O$ ), 2-hexadecanone ( $C_{16}H_{32}O$ ) and 2-heptadecanone ( $C_{17}H_{34}O$ ), respectively. The Cold-EI mass spectrum for the peak at 14.8 min in the oxygenate distribution labelled 1 is shown in Fig. 6.11 (top) as well as the NIST library mass spectrum (bottom).



**Figure 6.11** Mass spectra of the oxygenate eluting at 14.8 min (labelled 1 in Fig. 6.10).

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 in Appendix A as supplementary material. The Cold-EI behaviour of these 2-ketones is consistent with that of 2-octadecanone (Fig. 6.4A, top), where the substantially increased molecular ion is observed as the base peak and the abundance of the heavy mass fragments ( $[M - CH_3]^+$  and  $[M - H_2O]^+$ ) 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.

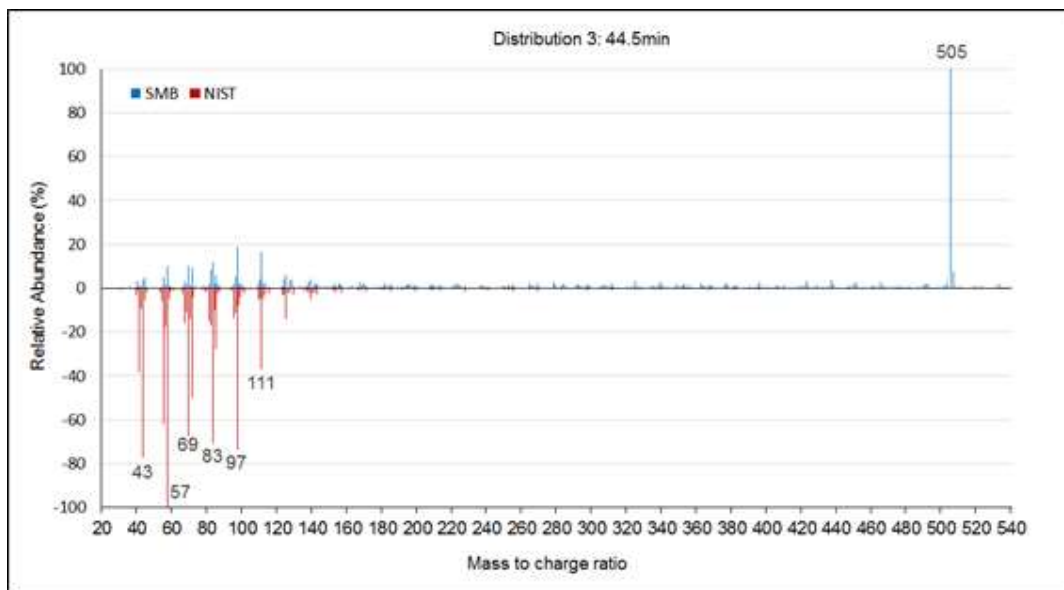
The peaks eluting at 13.6 and 25.1 min as part of the second distribution in Fig. 6.10 were identified by NIST library matching as  $\gamma$ -dodecanolactone ( $C_{12}H_{22}O_2$ ) and  $\gamma$ -stearolactone ( $C_{18}H_{34}O_2$ ), respectively. The Cold-EI mass spectrum for the oxygenate eluting at 13.6 min and that forms part of the second distribution is shown in Fig. 6.12 (top) together with the NIST library mass spectrum (bottom). The conventional EI and Cold-EI mass spectra for  $\gamma$ -stearolactone ( $C_{18}H_{34}O_2$ ) is included in Appendix A as supplementary material.



**Figure 6.12** Mass spectra of the oxygenate eluting at 13.6 min that form part of the second distribution (labelled 2 in Fig. 6.10).

Very weak (<5%) or no molecular ions were observed for the  $\gamma$ -lactones in the NIST library mass spectra (Fig. 6.12, bottom). The base peak observed for both these  $\gamma$ -lactones was at  $m/z$  85, corresponding to the  $\gamma$ -butyrolactone fragment ( $C_4H_5O_2$ ). In the Cold-EI mass spectrum of  $\gamma$ -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  $\pm 10\%$ . For the  $\gamma$ -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  $\gamma$ -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  $\gamma$ -lactones. The formation of  $\gamma$ -lactones as the major ester product during the autoxidation of hydrocarbons is consistent with the observations from other studies [41 - 42] (as discussed in Chapter 5) where an intramolecular pathway from alkyl hydroperoxides for the formation of these  $\gamma$ -lactones was presented. Extracting the molecular ions of the  $\gamma$ -lactone homologous series showed that all the  $\gamma$ -lactones from C10 to C41 were present in the oxidised heavy paraffinic sample.

The third oxygenate distribution eluted towards the end of the GC-MS (Cold-EI) chromatogram and is labelled 3 in Fig. 6.10. 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 Fig. 6.13.



**Figure 6.13** Mass spectra of the oxygenate eluting at 44.5 min that form part of the third distribution (labelled 3 in Fig. 6.10).

(Note that 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 in Appendix A 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 Fig. 6.10. 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.

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 the third 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 ( $m/z = 504.6$ ; note 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 in Appendix A) suggests that this peak is an alkene or cycloalkane ( $C_{36}H_{72}$ ) or an oxygenate ( $C_{35}H_{68}O$ ). The  $C_{36}$  alkenes or cycloalkanes do not elute at 44.5 min, 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. Based on the assumption that that these compounds are carbonyls containing a cyclic or a double bond functionality, a homologous series from  $C_{14}$  to  $C_{51}$  was observed to be present in the oxidised heavy paraffinic sample when the expected molecular ions of these compounds were extracted.

Characteristic molecular and fragment ions for the other oxygenates present in the standard (Table 6.1) were also extracted to check for the presence of these components in the oxidised heavy paraffin. Low concentrations of linear acids from  $C_8$  to  $C_{21}$  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 are also consistent with the typical oxygenates that

are formed during the autoxidation of saturated hydrocarbons reported in other studies [41 - 42, 44 - 45] and in Chapter 5. 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) and 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, e.g. 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] (see Chapter 5) 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 alkanes and alkenes oxidised paraffinic sample 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 need for prior separation.

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# Chapter 7

## Conclusions and Final Remarks

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## 1. Conclusions

The primary goal of this study was to develop chromatographic techniques and to investigate the hyphenation of these techniques to comprehensively characterise compounds and compound classes of interest in petrochemical streams. These developments were aimed at addressing specific analytical challenges in the petrochemical industry. Although GC×GC is an essential analytical tool in petrochemical analysis, several challenges remain that need to be addressed by the use and hyphenation of other techniques.

The use of on-line hyphenation of SFC to a GC×GC system as a pre-separation technique successfully addressed the challenge of separating alkenes and alkanes, both cyclic and non-cyclic. The use of SFC was also found to be less complicated than the hyphenation with HPLC as the removal of the supercritical CO<sub>2</sub> was easily achieved without any loss of volatile sample components, and the risk of co-eluting solvents and dilution effects were eliminated. The hyphenation of SFC to GC×GC was easily achieved by decompression of the supercritical fluid through a restrictor into the GC injection port. Although initial attempts to trap the solutes was unsuccessful due to the trapping temperature being outside the recommended operating conditions of the primary column used in the reversed column configuration, it was addressed by trapping the solutes on an appropriate thick phase column inside the PTV injector. The developed SFC pre-separation method not only focussed on the separation of the alkenes and alkanes, but the samples was also pre-separated into other chemical groups (saturates, unsaturates, oxygenates and aromatics). These chemical groups could then be characterised independently by means of individual GC×GC methods (not included in this study).

The developed SFC-GC×GC could not be utilised for the separation of isomeric cyclic and double bond containing compounds with the same (two or more) double bond equivalents, since the silver-modified column forms complexes with double bond compounds, irrespective of the number of double bonds. It was demonstrated that on-line hydrogenation after GC×GC separation successfully addresses the challenge of distinguishing between these isomeric compounds. The number of rings and alkene double bonds in specific compounds can be determined from the mass spectra of the compounds before and after hydrogenation. A

unique challenge in the development of this method was to achieve hydrogenation after GC×GC separation without instrument modifications. It was found that complete hydrogenation could be achieved by installing a capillary reactor in the TOF-MS transfer line. This required a high dispersion of platinum within the capillary reactor and the parameters of the preparation procedure were optimised to achieve this. The influence of the capillary reactor diameter and temperature on the degree of hydrogenation was also extensively investigated and the developed method made it possible, for the first time, to determine the backbone of cyclic/olefinic structures in complex petrochemical streams and thereby fully addressed the challenge of differentiation between classes like dienes and cyclic olefins in these streams.

Another challenge that this study focussed on was the characterisation and monitoring of oxygenates in oxidised heavy paraffinic fractions. The traditionally used titrimetric procedures used for the control of the oxidation process of these heavy samples are tedious and lack selectivity toward specific oxygenate classes. The aim of this study was to develop a HT-GC×GC method to address these shortcomings. HT-GC×GC column sets for the optimum separation of oxygenates in oxidised heavy paraffinic fractions were evaluated for the first time. It was found that the developed HT-GC×GC method has clear advantages over the titrimetric methods in monitoring oxidation reactions, with the selective quantification of oxygenate classes and the possibility of determining the concentrations of each oxygenate class by carbon number being the most significant. The proposed HT-GC×GC analysis therefore allows for the further optimisation of oxidation conditions to produce higher value heavy paraffinic fractions.

Another challenge in identifying oxygenates present in oxidised heavy paraffinic fractions is the fact that the use of EI libraries is limited for heavy oxygenates. The absence of the molecular ions ( $M^+$ ) from the mass spectra of most of these heavy oxygenates further contributes to the identification challenge. This study aimed at the pre-separation of these heavy oxygenates and subsequently utilising Cold-EI, that provides EI spectra with an enhanced molecular ion, to aid in their identification. Since very little is known about oxygenate behaviour on GC-SMB-MS, the investigation of the Cold-EI behaviour of various oxygenate classes was required before studying the feasibility of pre-separation procedures

on these oxidised heavy paraffinic fractions. It was found that the Cold-EI mass spectra are characterised by a substantial increase in the relative abundance of the molecular ion peaks as well as characteristic heavy mass fragments for all the oxygenates investigated. In most cases the molecular ion was observed as the base peak ion in the mass spectrum. It was also found that the oxygenates could be successfully pre-separated by both SPE and SFC before Supersonic GC-MS analysis, of which SPE was favoured. The advantages of this procedure were clearly illustrated, whereby the heavy oxygenates in an oxidised heavy paraffinic sample could be better characterised. This study successfully addressed various analytical challenges in the field of petrochemical analysis.

## 2. Original contributions

Original contributions were made in the field of the comprehensive analysis of petrochemical streams and products. The SFC separation of petrochemical samples into different chemical groups enabled the subsequent GC×GC characterisation of each chemical group. The developed SFC method has also been used as a screening method to determine the chemical composition of different fuels [1]. The technique utilising capillary hydrogenation after GC×GC separation that was developed to address the challenge of separating isomeric cyclic and double bond containing compounds, has also been used for determining the backbone of unknown contaminants in various petrochemical products. This method has the added advantage that instrument modifications are not required.

The developed HT-GC×GC method for the characterisation and monitoring of oxygenates in oxidised heavy paraffinic fractions allows for the optimisation of the conditions used for the oxidation of these heavy paraffinic fractions. This method has also been used for the characterisation of other oxygenate containing heavy petroleum fractions. The knowledge gained from the investigation of the behaviour of various oxygenate classes with Cold-EI also allowed the accurate identification of these oxygenates in other oxygenate containing petroleum fractions from the Cold-EI spectra. The SPE pre-separation procedure could also be applied to other oxygenate containing petrochemical samples.

### 3. The future of the petrochemical industry

Looking at the global future of the petrochemical industry, it is clear that the world of petrochemicals and refining needs to change since it has to rapidly reduce its carbon emissions, while continuing to meet the energy needs of a growing global population. In petrochemicals, the demand has grown steadily over the past ten years and more growth is forecast, mostly since the key drivers behind this growth will continue to increase but also since some petrochemical products (improved manufacturing materials, insulation materials, improved packaging) will also play an important role in the global efforts to cut carbon emissions [2]. The production of chemicals from cleaner energy sources than petroleum or coal will play a significant role in the future to enhance growth and curb emissions in this sector. Bioethanol, natural gas, hydrogen and methanol are some of the most attractive alternative sources for cleaner fuels and chemicals. Recently, technology has been demonstrated whereby a fuel cell and electrolyser is utilised to produce green hydrogen from wind and solar energy, which can then be converted into chemicals and fuels [3].

This long term growth in petrochemicals as well as the expansion into cleaner sources will require development of the analytical capabilities required to monitor, optimise and streamline production processes. This will require characterisation of feedstock and final products over vast molecular weight and concentration ranges. GC×GC and HT-GC×GC will therefore continue to play an important role with other comprehensive hyphenated techniques also coming to the fore, for example techniques like SFC×GC whereby the selectivity achieved on SFC in the first dimension is utilised [4]. Hyphenation between pre-separation, the abovementioned comprehensive analysis techniques and selective detection techniques (high resolution time-of-flight detector (HRT), O-FID, SMB-MS) will be areas that will continue to grow in attempts to characterise streams more selectively and at lower concentrations. The development of multi-target compound analysis methods is also foreseen to demonstrate that streams and products comply with environmental legislation.

Heavier feedstock and heavy speciality chemicals produced will also require new methods for their characterisation. These developments may include LC×LC with gel permeation



chromatography (GPC) in the first dimension to accommodate the large carbon number range combined with a selective second dimension separation to improve characterisation capabilities. Developments in the detection capabilities of LC×LC in the petrochemical sector also need to be pursued. This improved characterisation will allow for the optimisation of production processes as well as the production of improved final products.

The carbon footprint of the refining industry also needs to be drastically reduced. The development and increased production of electric cars is already making an impact on the refining industry. However, electric cars only make up ±0.2% of the world's current car fleet and an increase to ±7.5% by 2040 is predicted, leaving the majority requirement to other fuel sources. If the fuel requirements for heavy vehicles, ships and airplanes are added to the equation, it is clear that the world's medium term future still includes refinery industries and that the petroleum industry will continue to be a big role player [5]. It is therefore of the utmost importance that these refinery industries need to become more integrated and efficient to reduce their operational carbon intensity, and opportunities like digitalisation to streamline production processes need to be fully utilised. The utilisation of lower value heavy petroleum fractions for the production of fuel as well as chemicals will be critical to improve production efficiency, thereby reducing their carbon footprint.

Also in the refining industry, analytical capabilities will continue to play a very important role in the efforts to integrate and streamline processes. Fingerprinting of process streams by comprehensive analysis will enable the identification of integration and optimisation opportunities, while chemometric analysis of on-line or at-line analysis data will allow the close control of production processes at very fast response rates. The ongoing identification of new environmental concerns and the ability to monitor these in both petrochemical and refining products will continue to grow in importance, in turn requiring that the available analytical methods keep up with the legislative requirements.

## 4. Recommendations

During this study, various improvements and alternatives to the developed methods could be identified for future investigation. In our investigation on the analysis of oxidised heavy paraffinic fractions by HT-GC×GC, it was reported that peak tailing was still observed in the second dimension for the compounds present in high concentrations, and the use of a reverse fill/flush (RFF) differential flow modulator needs to be investigated to reduce the observed tailing [6]. Although the reduced tailing will improve quantification accuracy, the use of an internal standard quantification method will also need to be studied to make this method more robust and applicable to routine analysis. The use of HT-GC×GC with an oxygen selective detector (O-FID) will also be investigated for the more selective detection of oxygen containing compounds [7]. Using an O-FID detector can also improve the quantification accuracy and may be easy to adapt in a routine laboratory. In our investigation on the pre-separation of oxygen containing compounds in oxidised heavy paraffinic fractions and the identification by supersonic GC-MS it was suggested that pulsed flow modulation GC×GC Supersonic GC-MS [8] needs to be investigated to improve the GC separation and eliminate the use of a pre-separation procedure. These projects are currently under investigation or are planned for investigation at Sasol in the future.

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# Appendix A

## Additional Information

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**Table A:** Standards used for optimisation of SFC fractionation (Chapter 3).

Hexane	Butylbenzene
Dodecane	Naphthalene
Pentadecane	Phenanthrene
Cyclohexane	Ethanol
1-Octene	Isopropanol
Cycloheptene	Hexanal
2,4-Octadiene	Nonanone
1,3-Cyclooctadiene	Cyclopentanone
Toluene	

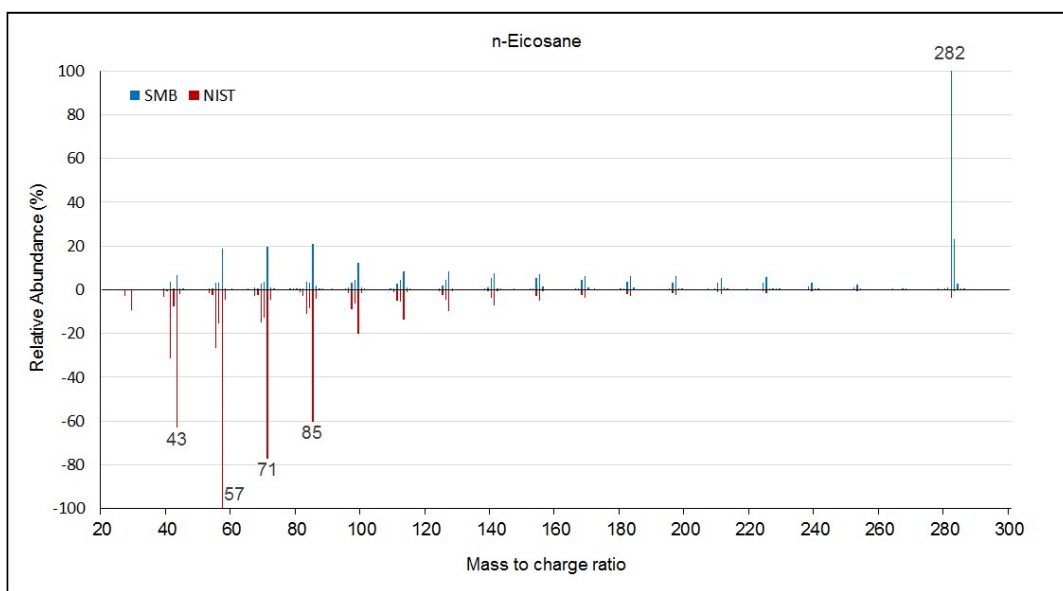
**Table B:** Standards used to determine the relative response factors for the quantification of oxidised heavy paraffinic fraction samples by HT-GC×GC (Chapter 5).

n-Eicosane	Hexadecyl Dodecanoate
n-Docosane	2-Octadecanone
1-Eicosene	n-Docosanal
Didecyl-Ether	1,12-Octadecandiol
Undecanoic Acid	1-Tetradecanol
Tetradecanoic Acid	1-Hexadecanol
Arachidic Acid	1-Heptadecanol
n-Docosanal	1-Docosanol
1,12-Octadecandiol	2-Octyl-1-dodecanol

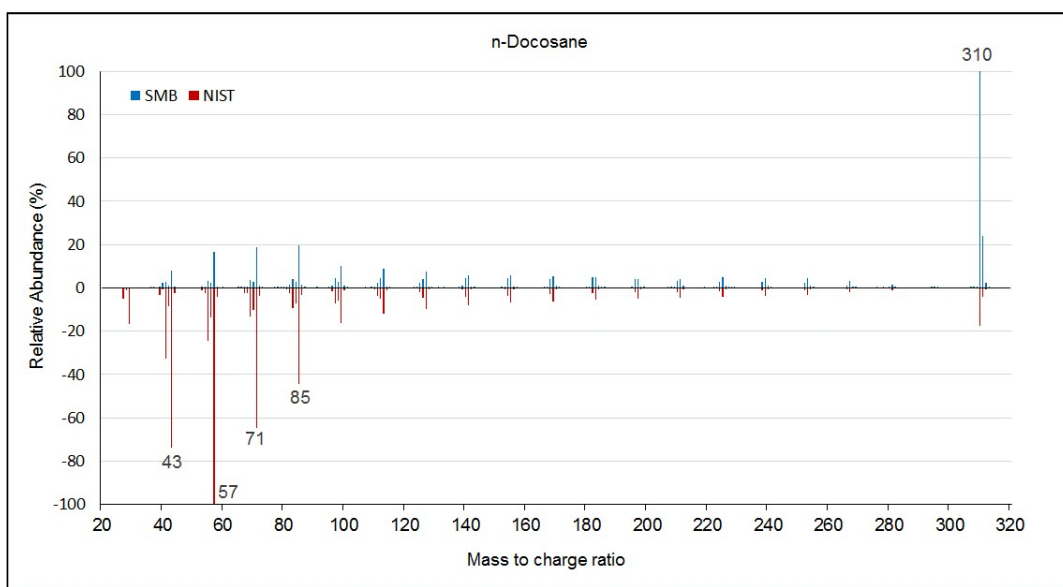
**Table C:** Relative response factors used for the quantification of oxidised heavy paraffinic fraction samples by HT-GC×GC (Chapter 5).

Compounds	Relative response factor
Paraffins (linear, branched)	1.0
2-Ketones	0.8
>2-Ketones	0.8
γ-Lactones	0.6
Acids	0.5
Other oxygenates	0.8

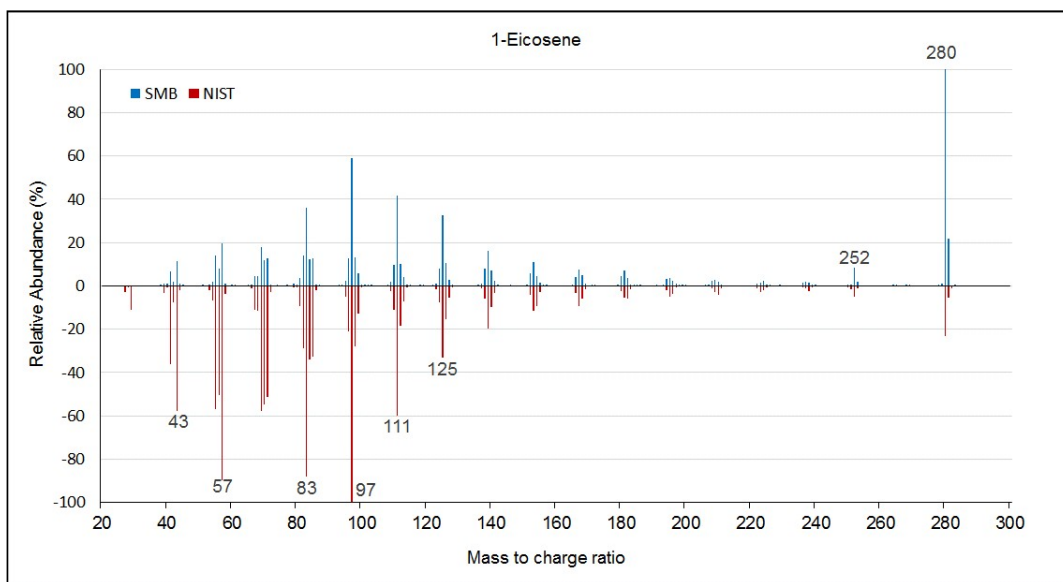
# Additional Mass Spectra



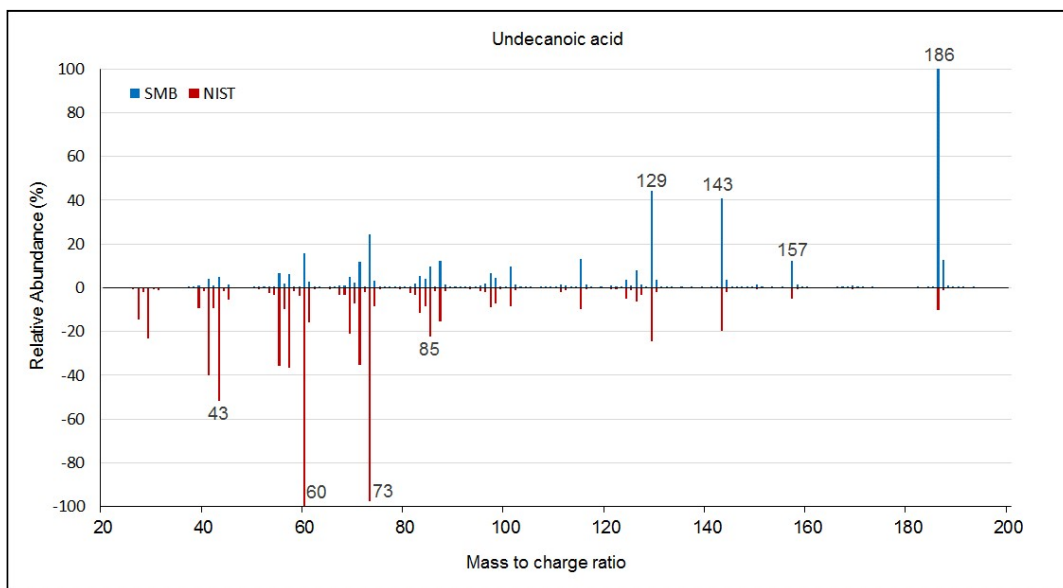
**Figure A:** Mass spectra of *n*-Eicosane with conventional EI (bottom) and Cold-EI (top).



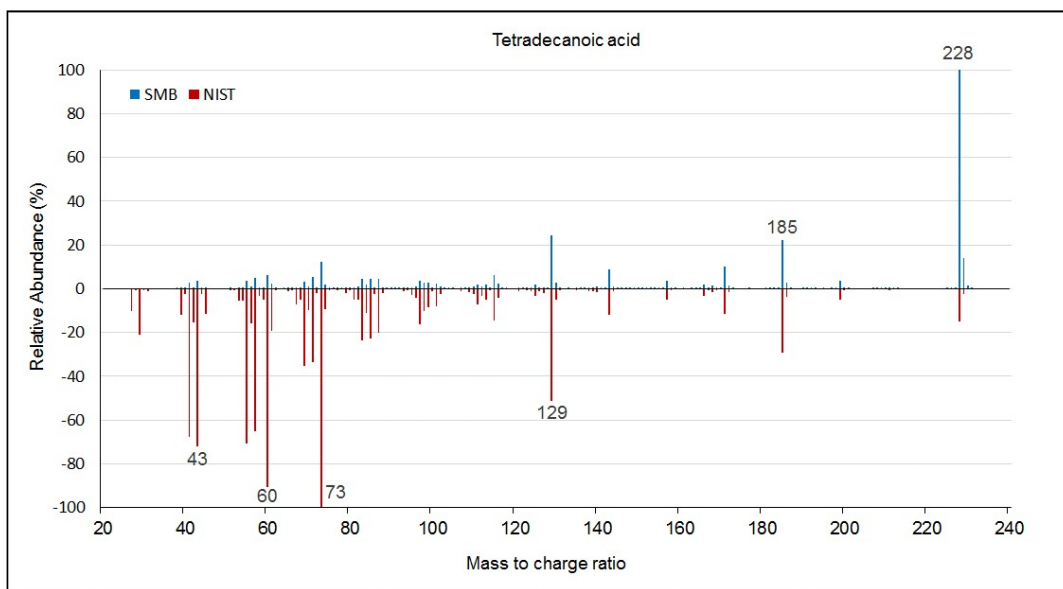
**Figure B:** Mass spectra of *n*-Docosane with conventional EI (bottom) and Cold-EI (top).



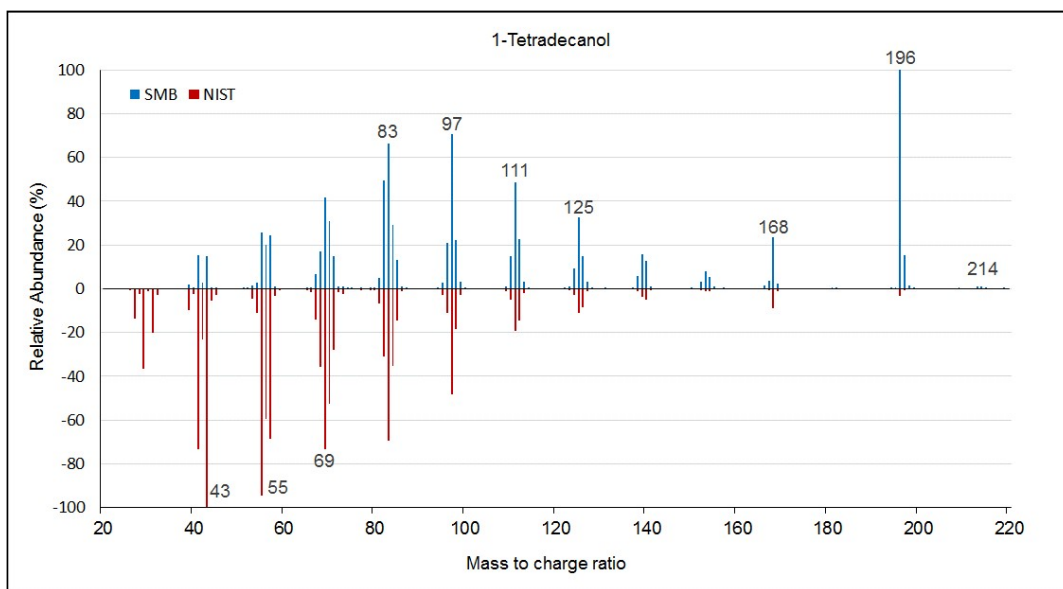
**Figure C:** Mass spectra of *n*-Eicosene with conventional EI (bottom) and Cold-EI (top).



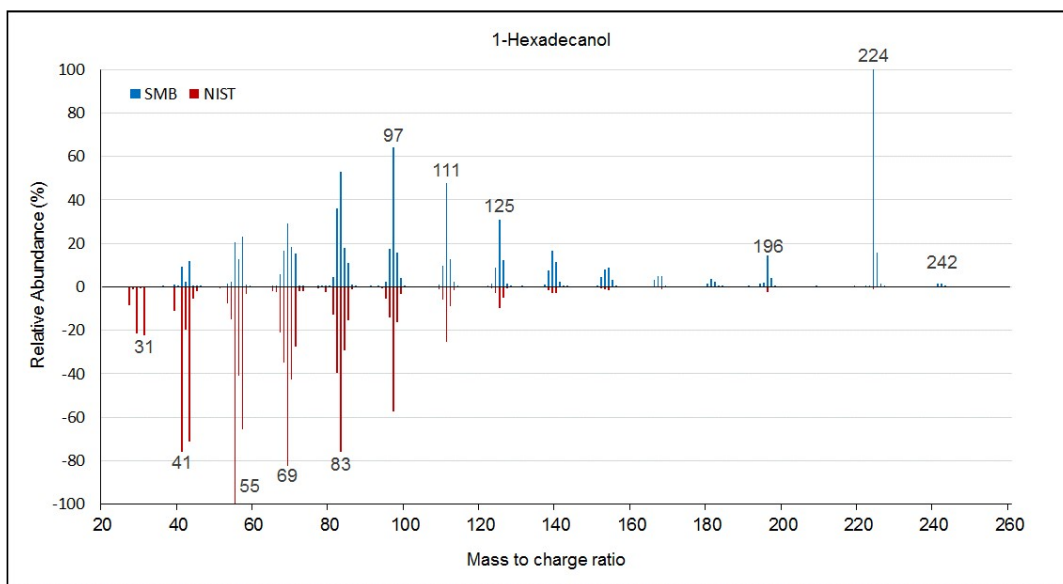
**Figure D:** Mass spectra of Undecanoic acid with conventional EI (bottom) and Cold-EI (top).



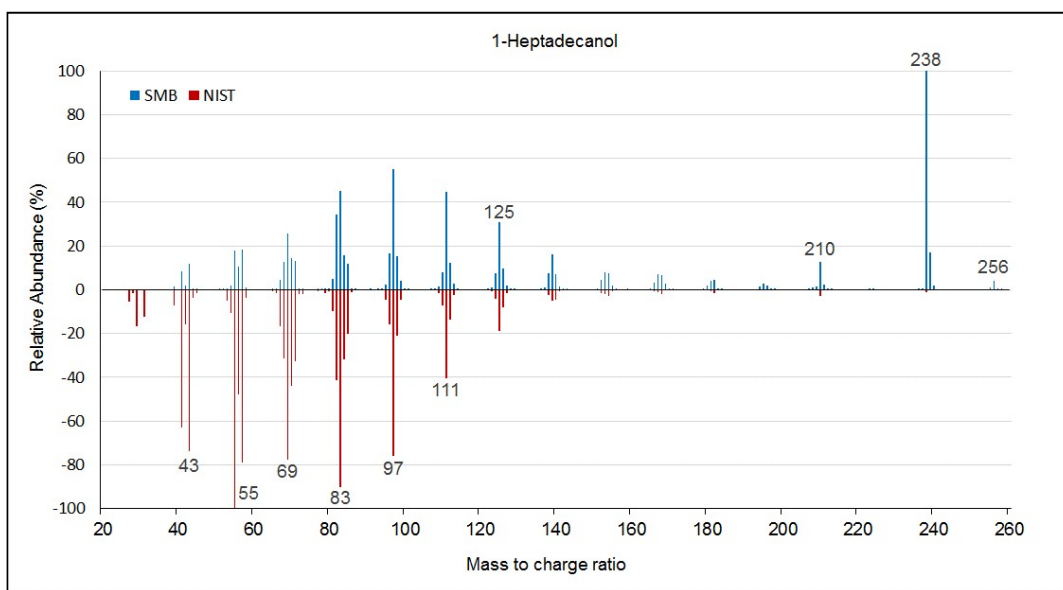
**Figure E:** Mass spectra of Tetradecanoic acid with conventional EI (bottom) and Cold-EI (top).



**Figure F:** Mass spectra of 1-Tetradecanol with conventional EI (bottom) and Cold-EI (top).

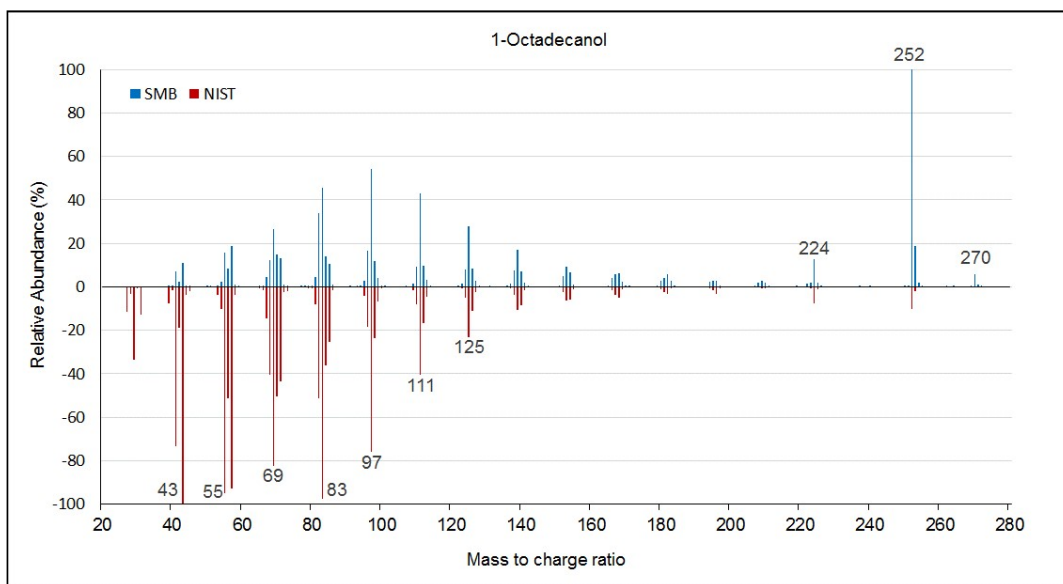


**Figure G:** Mass spectra of 1-Hexadecanol with conventional EI (bottom) and Cold-EI (top).

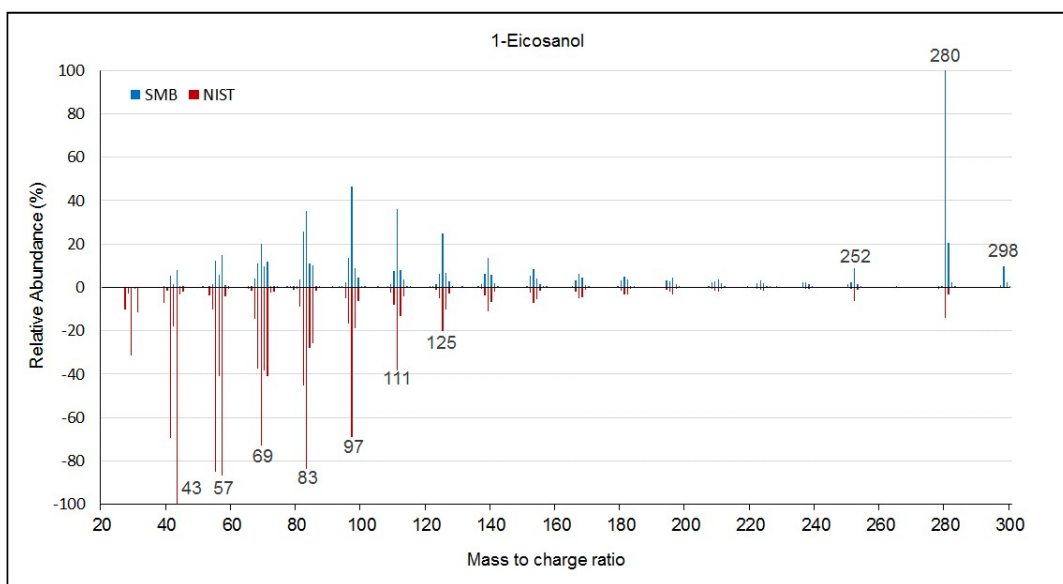


**Figure H:** Mass spectra of 1-Heptadecanol with conventional EI (bottom) and Cold-EI (top).

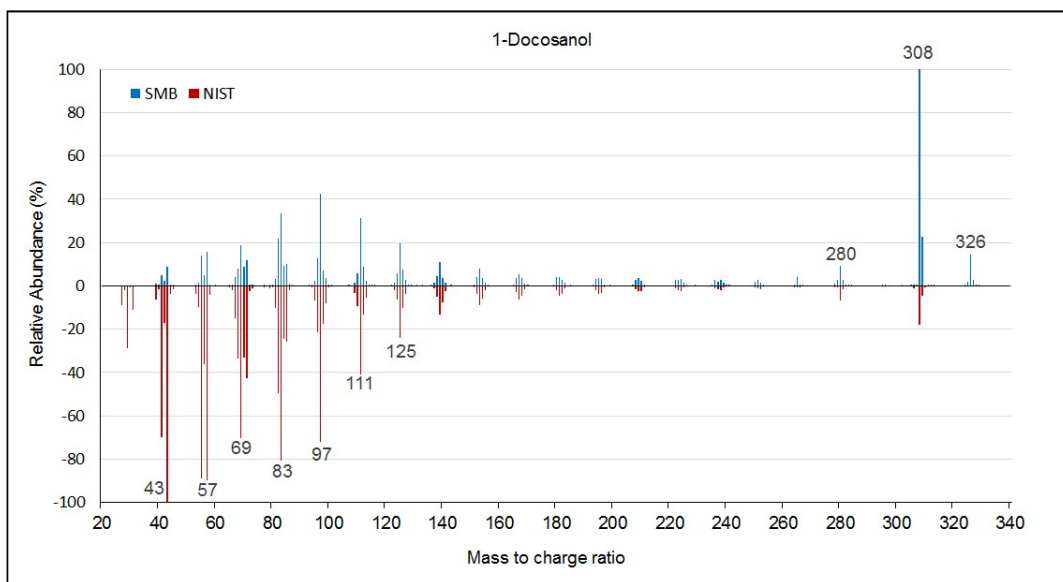




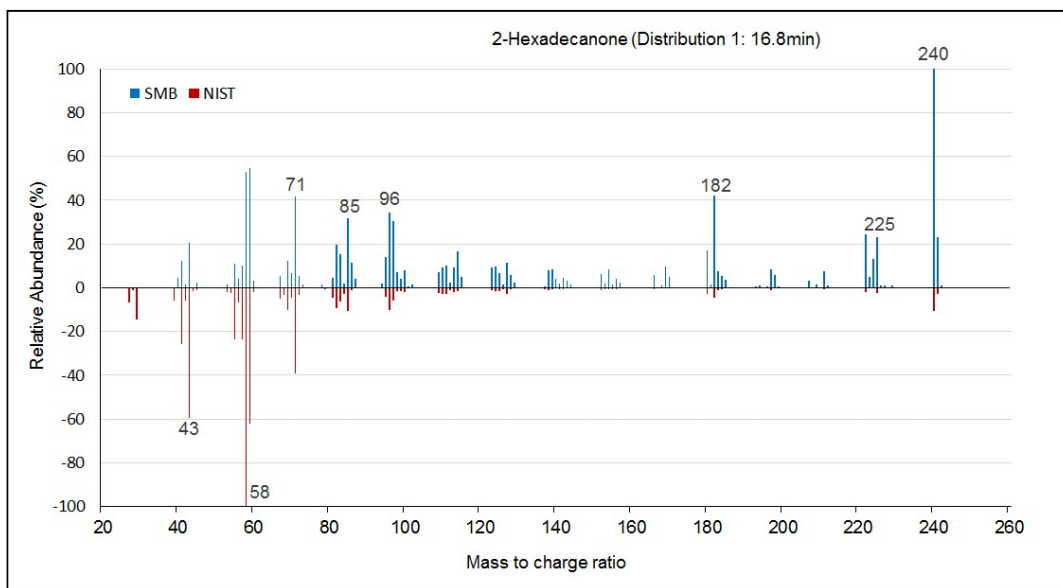
**Figure I:** Mass spectra of 1-Octadecanol with conventional EI (bottom) and Cold-EI (top).



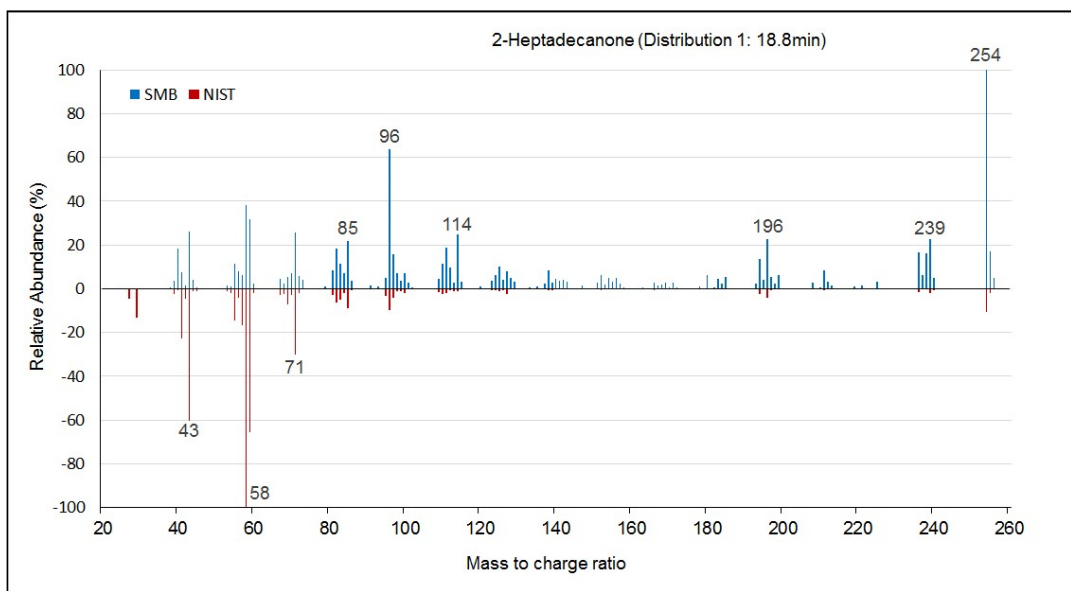
**Figure J:** Mass spectra of 1-Eicosanol with conventional EI (bottom) and Cold-EI (top).



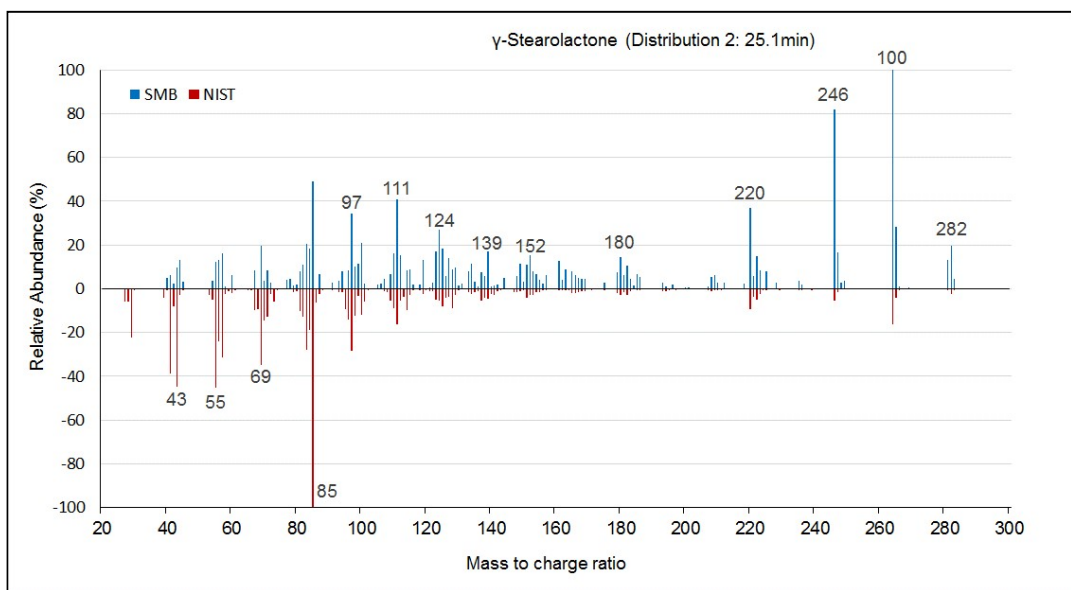
**Figure K:** Mass spectra of 1-Docosanol with conventional EI (bottom) and Cold-EI (top).



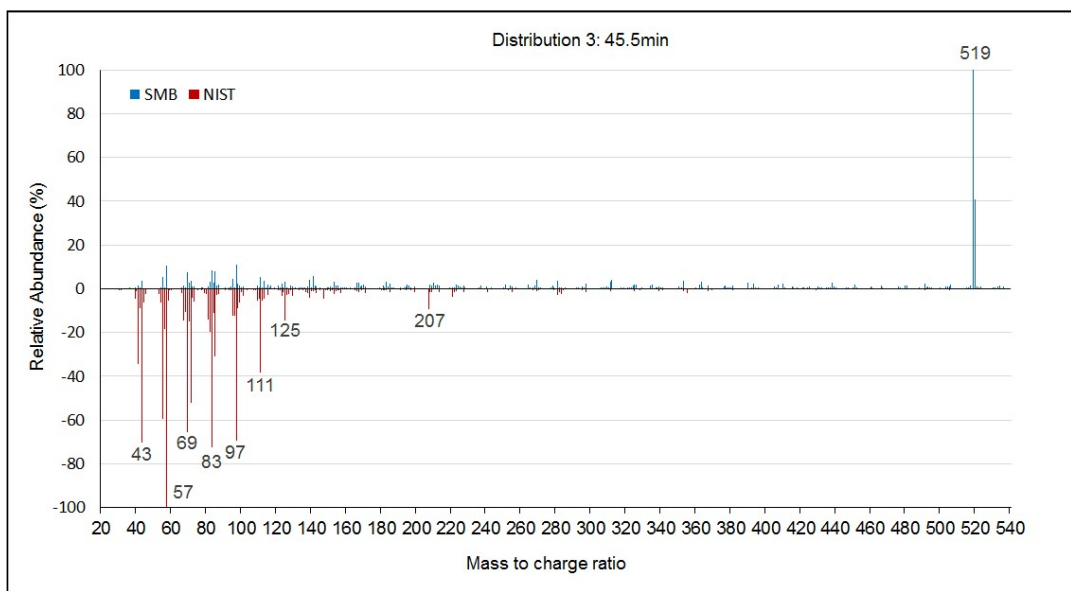
**Figure L:** Mass spectra of 2-Hexadecanone at 16.8 min (Distribution 1) with conventional EI (bottom) and Cold-EI (top).



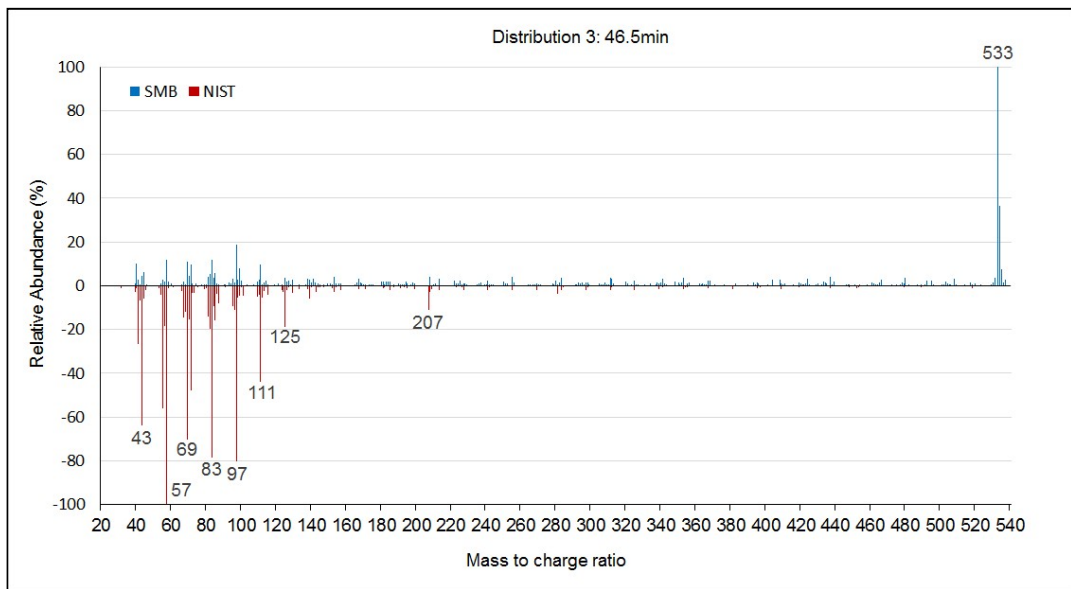
**Figure M:** Mass spectra of 2-Heptadecanone at 18.8 min (Distribution 1) with conventional EI (bottom) and Cold-EI (top).



**Figure N:** Mass spectra of  $\gamma$ -Stearolactone at 25.1 min (Distribution 2) with conventional EI (bottom) and Cold-EI (top).



**Figure O:** Mass spectra of the oxygenate eluting at 45.5 min (Distribution 3) with conventional EI (bottom) and Cold-EI (top).



**Figure P:** Mass spectra of the oxygenate eluting at 46.5 min (Distribution 3) with conventional EI (bottom) and Cold-EI (top).