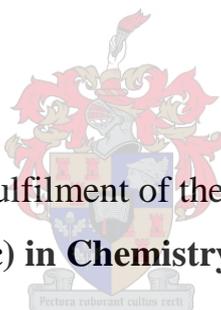


Development of GC-MS methods for the analysis of tyre pyrolysis oils

by

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Thesis presented in partial fulfilment of the requirements for the degree of
Master of Science (MSc) in Chemistry at Stellenbosch University



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March 2016

Declaration

By submitting this thesis electronically, I declare the entirety of the work contained therein is my own original work and that I am the owner of the copyright thereof (save to the extent explicitly otherwise stated) and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

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Summary

Gas chromatography coupled to mass spectrometry (GC-MS) and comprehensive two-dimensional gas chromatography (GC×GC) methods were developed for the analysis of tyre derived oils (TDOs). Using GC-MS with either solvent back extraction or liquid dilution for sample preparation, 33 volatile compounds were identified using standards, while an additional 71 compounds were tentatively identified in TDOs. The most abundant TDO constituents were found to be *dl*-limonene, *p*-cymene, benzothiazole, ethylbenzene, toluene, *p*-xylene, 3-ethyltoluene and α -terpinolene. For quantification of the volatile organic compounds which are known to have market value, both internal standard and standard addition methods were used. The quantitative data obtained from these two methods were comparable differing within $\pm 1-5\%$. To accommodate some of the compounds occurring in trace amounts in some TDO samples, a selected ion monitoring (SIM) method was also developed for better sensitivity. The developed GC-MS method was validated and demonstrated to be suitable for the quantitative analysis of target compounds in a range of TDOs.

Since 1-dimensional (1-D) GC failed to provide complete separation of the complex TDO samples, GC×GC was explored for their in-depth qualitative analysis. As proof of principle, a GC×GC-FID equipped with a novel single-stage thermal modulator was used to demonstrate the benefits of improved separation offered by GC×GC for TDO analysis. For detailed identification, a commercially available instrument fitted with a dual stage cryogenic modulator and hyphenated to time-of-flight mass spectrometer (TOFMS) was used. Analysis of the data obtained on this instrument allowed tentative identification of some 137 compounds using mass spectral and retention index data. The analytical methods reported in this thesis show promise both in terms of the routine quantification of market-value constituents of TDOs, and for the more detailed chemical analysis of these samples.

Opsomming

Gas chromatografie in kombinasie met massa spektrometrie (GC-MS) en omvattende twee dimensionele gaschromatografie (GC×GC) metodes is ontwikkel vir die analise van olie afkomstig van die pirolise van afval voertuigbande, bekend as ‘tyre derived oils (TDOs)’. Deur gebruik te maak van GC-MS met óf oplosmiddel terug-ekstraksie, óf vloeistof verdunning vir monstervoorbereiding is 33 vlugtige komponente met die gebruik van standaard in die olie geïdentifiseer en ‘n verdere 71 is tentatief geïdentifiseer. Die mees prominente verbindings in TDO wat gevind is was *dl*-limonene, *p*-cymene, benzothiazole, ethylbenzene, toluene, xylenes, ethyltoluenes and α -terpinolene. Vir die kwantifisering van vlugtige organiese komponente wat markwaarde het is beide die interne standaard metode en standaardbyvoeging gebruik. Die kwantitatiewe data wat verkry is met beide metodes het baie goed ooreengestem, met verskille van tussen 1 en 5%. Om komponente wat in uiters lae vlakke in die TDOs voorkom ook in te sluit, is ‘n selektiewe ion moniterings (SIM) GC-MS metode ingespan om verhoogde sensitiviteit te kry. Omdat een-dimensionele GC egter dikwels nie daarin slaag om volledige skeiding te bewerkstellig vir die komplekse TDO monsters nie, is GC×GC voorts ondersoek vir die in-diepte analisering van die olies.

Om die voordele van die beter skeiding wat GC×GC bied te illustreer, is GC×GC-FID, wat gebruik maak van ‘n nuut-ontwikkelde termiese enkelfase modulator, gebruik vir TDO analise. Vir die verdere identifikasie van die verbindings wat in TDOs voorkom is, is van GC×GC in kombinasie met ‘time-of-flight’ MS (GC×GC-TOFMS) gebruik gemaak. Op hierdie manier is 137 komponente tentatief geïdentifiseer met behulp van hulle massa spektra en retensie indeks data. Die analitiese metodes wat gerapporteer word hou heelwat belofte in vir biede die roetine analise van TDOs.

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Table of contents

Declaration	i
Summary	ii
Opsomming	iii
Acknowledgements	iv
List of abbreviations	viii
Manuscripts and conference presentations	x
Thesis layout	xi
CHAPTER 1	i
Introduction and literature review	i
1.1. Introduction	1
1.2. Chemical composition of tyre derived oils	2
1.2.1. Formation of limonene from tyres	3
1.2.2. Formation of aromatics from limonene decomposition	4
1.2.3. Formation of aromatics and polyaromatic hydrocarbons	5
1.2.4. Formation of hetero-atomic species	6
1.3. Analytical sample preparation techniques	7
1.3.1. Liquid-liquid extraction (LLE)	7
1.3.2. Solvent dilution	8
1.3.3. Solid phase extraction (SPE)	8
1.3.4. Solid phase micro extraction (SPME)	9
1.4. Chromatographic analysis	10
1.4.1. Introduction	10
1.4.2. Gas chromatography (GC)	10
1.4.2.1. Injection in GC	11
1.4.2.2. The capillary column	11
1.4.2.3. Detection in GC	13
1.4.2.3.1. Flame ionisation detector	13
1.4.2.3.2. Mass spectrometry	14
1.5. Comprehensive two-dimensional gas chromatography (GC×GC)	17
1.5.1. Introduction	17

1.5.2. Modulation.....	18
1.5.3. Detection in GC×GC	19
1.6. Analysis of TDOs	19
1.7. Goals of this study	23
1.7.1. Aims and objectives.....	24
1.8. References.....	25

CHAPTER 2

Development of a GC-MS method for the analysis of waste tyre pyrolysis oils*

Abstract.....	33
2.1. Introduction.....	34
2.2. Experimental.....	35
2.2.1. Materials and methods	35
2.2.2. Sample preparation procedures.....	36
2.2.2.1. Liquid-liquid back extraction.....	36
2.2.2.2. Solvent dilution.....	36
2.2.3. Instrumentation and chromatographic conditions.....	36
2.2.3.1. GC-MS method optimisation.....	36
2.2.3.2. Optimised GC-MS conditions.....	37
2.2.4. Data processing.....	37
2.2.4.1. Identification and quantification of TDO constituents	37
2.3. Results and discussion	38
2.3.1. Evaluation of sample preparation methods.....	38
2.3.1.1. Liquid-liquid back-extraction of polar constituents.....	38
2.3.1.2. Solvent dilution.....	41
2.3.2. Optimisation of GC-MS conditions	42
2.3.3. Identification of TDO constituents	44
2.3.4. Quantification of selected TDO constituents.....	51
2.3.4.1. Internal standard method.....	51
2.3.4.2. Standard addition method	52
2.3.5. Method validation	53
2.3.5.1. Selected ion monitoring (SIM) method	55

2.4. Conclusions.....	57
2.5. Acknowledgements.....	57
2.6. References.....	58

CHAPTER 3

Analysis of tyre-derived oils by comprehensive two-dimensional gas chromatography (GC×GC)*

Abstract.....	65
3.1. Introduction.....	66
3.2. Materials and methods	67
3.2.1. Chemicals and consumables	67
3.2.2. Sample preparation	68
3.2.2.1. Solid phase micro extraction (SPME) and liquid injection for GC×GC-FID analyses	68
3.2.2.2. Solid phase micro extraction (SPME) for GC×GC-TOFMS analyses	68
3.2.3. Instrumental conditions.....	68
3.2.3.1. GC×GC-FID instrumental conditions.....	68
3.2.3.2. GC×GC-TOFMS instrumental conditions.....	69
3.2.4. Data processing.....	69
3.3. Results and discussion	70
3.3.1. Evaluation of GC×GC-FID analysis of TDOs using a new single-stage modulator	70
3.3.2.1. Identification of compounds	75
3.4. Conclusions.....	84
3.5. Acknowledgements.....	84
3.6. References.....	85

CHAPTER 4

Conclusions and future recommendations

4.1. Conclusions.....	87
4.2. Recommendations for future research	88

List of abbreviations

AED	:	Atomic emission detector
CAR	:	Carboxen
CFCs	:	Chlorofluorocarbons
D _c	:	Diffusion coefficient
dc	:	direct current
DCM	:	Dichloromethane
d _f	:	Column film thickness
DVB	:	Divinylbenzene
ECD	:	Electron capture detector
EM	:	Electron multiplier
FID	:	Flame ionisation detector
GC	:	Gas chromatography
GC×GC	:	Comprehensive two- dimensional gas chromatography
GC-MS	:	Gas chromatography-mass spectrometry
HPLC	:	High performance liquid chromatography
HS-SPME	:	Head space solid phase micro extraction
i.d.	:	internal diameter
I.STD	:	Internal standard
LCMS	:	Longitudinal cryogenic modulator system
LLE	:	liquid-liquid extraction
LOD	:	Limit of detection
LOQ	:	Limit of quantification
mg	:	milligram
mL	:	millilitre
MSD	:	Mass spectrometric detector
NIST	:	National Institute of Standards and Technology (US Department of Commerce)
PA	:	Polyacrylate
PAHs	:	Polycyclic aromatic hydrocarbons
PDMS	:	Polydimethylsiloxane
PEG	:	Polyethylene glycol
ppm	:	parts per million

REDISA	:	Recycling and economic development initiative of South Africa
rf	:	radio frequency
RI	:	Retention index
RT	:	Retention time
SACI	:	South African Chemical Institute
SCD	:	Sulphur chemiluminescence detector
SDVB	:	Styrene-divinyl benzene
SPE	:	Solid phase extraction
SPME	:	Solid phase micro extraction
TCD	:	Thermal conductivity detector
TDO	:	Tyre derived oil
TIC	:	Total ion chromatogram
TOFMS	:	Time-of-flight mass spectrometry

Manuscripts and conference presentations

Manuscript 1: Development of a GC-MS method for the analysis of tyre pyrolysis oils

In preparation for publication

Presented orally at Stellenbosch University-REDISIA symposium

Presented orally at the 42nd SACI convention 2015 in Durban

Manuscript 2: Analysis of tyre derived oils (TDOs) by comprehensive two-dimensional gas chromatography (GC×GC)

In preparation for publication

Presented orally at Stellenbosch University at the REDISA symposium

Presented orally at the 42nd SACI convention 2015 in Durban

Thesis layout

Chapter 1: This chapter provides a brief literature review pertaining first of all to the waste tyre pyrolysis process and the chemistry of TDOs, as well as the challenges associated with the analysis of these samples, based on selected literature reports. Furthermore, a brief overview of gas chromatography based techniques for the analysis of volatile mixtures is presented, including sample preparation and GC and GC×GC separation principles and instrumentation, including injection and detection. The chapter also introduces the importance of the accurate analysis of tyre derived oils, and summarises the aims and objectives of this study

Chapter 2*: This chapter reports the development of GC-MS methods for the analysis of TDOs. Method development involved optimisation of GC and MS conditions, evaluation of several sample preparation processes and optimising quantification methods. Finally, method validation results are presented, as are qualitative and quantitative data obtained for several TDO samples.

Chapter 3*: This chapter reports the results for the evaluation of GC×GC for the comprehensive analysis of TDOs. Comparison of 1D-GC and GC×GC data illustrate the benefits of the latter approach for TDO analysis. The identification of 137 compounds in selected TDO samples by GC×GC-TOFMS is reported.

Chapter 4: This chapter contains the concluding summary of the work reported in the thesis and presents future recommendations for research in this field.

**The results for Chapters 2 and 3 are written in the format of publications, as these will be finalised for publication. For this reason, repetition between these Chapters is unavoidable.*

CHAPTER 1

Introduction and literature review

1.1. Introduction

Without tyres the automotive industry cannot exist, therefore the production and use, but also the disposal of tyres when not fit for use anymore, is unavoidable. The estimated number of waste tyres produced globally ranges from 1.5 to 3.3 billion [1]. Approximately the same number of tyres end up as waste tyres every year [2]. The majority of these waste tyres are disposed in landfills, resulting in a range of problems such as taking up large amounts of increasingly valuable landfill space and accidental fires resulting in highly toxic emissions such as sulphur dioxide (SO₂), nitrogen dioxide (NO₂), carbon monoxide (CO), hydrogen sulphide (H₂S) and hazardous polycyclic aromatic hydrocarbons (PAHs) [3–5]. Waste tyres are also sometimes controversially used as a direct source of energy via burning, for example in cement manufacturing [6]. Various strategies have been devised as alternatives to waste tyre management, all aiming at tyre recycling. Waste tyres can unfortunately not be recycled in ‘traditional’ ways such as metal, glass or plastic by melting them to obtain raw material for new products. This is as a result of the complex nature of tyres, which consist of rubber, steel, ash, carbon black, fillers, etc. [7]. Another complication is that the polymers in the tyres are cross-linked, and these bonds cannot be chemically broken easily [8]. Other options, receiving increasing attention include rubber reclaiming, crumb re-treading [2,9,10,11], grinding, incineration and pyrolysis [12].

Pyrolysis is defined as the process by which materials are thermally degraded by subjection to high temperature in the absence oxygen [13]. The pyrolysis process is effective in the recycling of waste materials, including waste tyres, and thereby contributes to reduce the environmental impact of waste tyres [14]. Various feed stocks have been investigated in pyrolysis processes, including biomass, tyres and plastic, amongst others. Since each feedstock results in oil with different chemical characteristics, they are named according to their original raw material [7]. For example, pyrolysis oils derived from tyres are referred to as tyre derived oils (TDOs). The pyrolysis process yields three main products: a gas, liquid and solid [15]. The ratio of these three products varies depending on the pyrolysis conditions used [16]. The most abundant and most investigated pyrolysis fraction in the case of tyres is the liquid (TDO) [8]. This is typically a dark brown to black coloured oily liquid of medium viscosity with a sulphurous, aromatic odour. It consists of a multitude of different organic compounds, some of which are of potential value in the chemicals industry [17,18]. In this context, the analysis of TDOs is of high importance to optimise pyrolysis processes to yield

high levels of these desirable compounds. However, the extraction and analysis of these oils, which comprise a very large number of compounds belonging to different chemical classes and spanning wide concentration ranges, is a severe analytical challenge.

1.2. Chemical composition of tyre derived oils

TDOs contain complex mixtures of C₆-C₂₄ organic compounds of various chemical classes such as paraffins, olefins, terpenes, aromatics (including PAHs), nitrogen and sulphur containing compounds as well as oxygenated compounds [19]. Several TDO constituents can be used for different purposes in a range of industries [17,20]. Some of the potentially significant market value compounds that have been reported in TDOs include *dl*-limonene, 4-vinylcyclohexene, toluene, ethylbenzene, xylenes, styrene and benzothiazole, amongst others, which have various industrial applications [12,21]. For example, xylenes are used in the production of industrial fibers, dyes and pigments [12], while benzothiazole is used in tyre manufacturing industries as an accelerator.

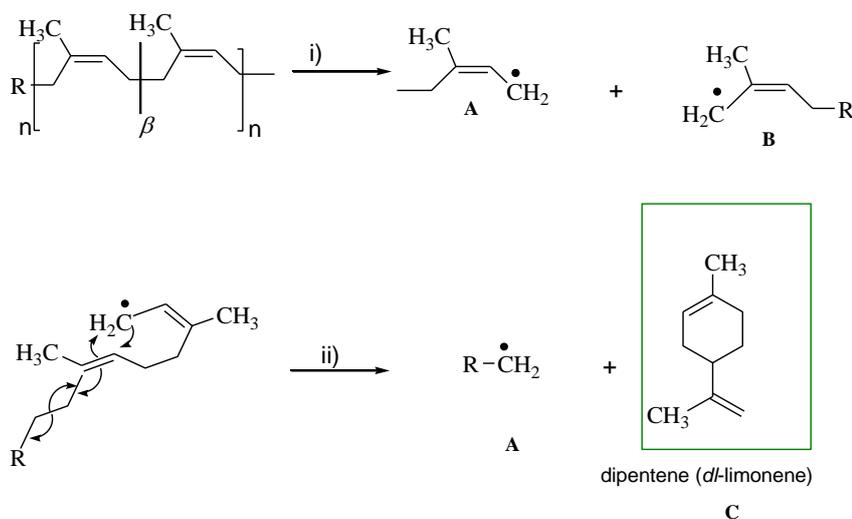
During pyrolysis, low molecular weight volatile aromatic compounds are formed as a result of decomposition of tyre polymeric materials at higher temperatures [5,22]. These low molecular weight products are recoverable as market value chemicals which can be used as sources of fuel [23]. The light aromatic fraction comprises compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX), which can be refined and used in petrochemical industries as feedstock chemicals [5]. The presence of PAHs and mono-aromatic compounds in TDOs is associated with secondary reactions that take place in the process of pyrolysis. These compounds mainly originate from the decomposition of primary products, with some of the higher molecular weight compounds formed via Diels Alder reactions [24].

Sulphur containing compounds are a known source of environmental pollution when they have undergone oxidation to produce SO₂, especially during tyre combustion [25] and this has been reported as an emission problem [26]. The presence of nitrogen and oxygen containing compounds in TDOs is attributed to the thermal degradation of accelerators such as *N,N*-di-isopropyl-2-benzothiazole-sulfenamide, 2-(4-morpholinylthio)-benzothiazole, *N,N*-caprolactamdisulphide and 2-mercaptobenzothiazole incorporated into tyres during the formulation process [27]. The terpene content is partly responsible for the potential recycle value associated with TDOs, with particularly *dl*-limonene occurring at high concentrations

[8,12]. *dl*-Limonene is one of the major market value compounds in TDO. This compound has a range of uses, including as an industrial solvent, application in resins and adhesives, as dispersing agent for pigments, as fragrance in cleaning products and as an environmental friendly solvent [1,11].

1.2.1. Formation of limonene from tyres

dl-Limonene is formed as a main product of the thermal degradation of tyre rubbers during the pyrolysis process. This compound has been identified as a major constituent in TDOs by several authors [2,8,13,18]. A schematic summary for the formation of *dl*-limonene is shown in **scheme 1a** below. The first step is the thermal degradation of polyisoprene rubber via a β -scission mechanism to form isoprene intermediate radicals (**A** and **B** in **scheme 1a**). The isoprene radical is then transformed via de-propagation to form isoprene in the gas phase. Isoprene then undergoes dimerization (intramolecular cyclization) to form dipentene (**C**, *dl*-limonene) [8].

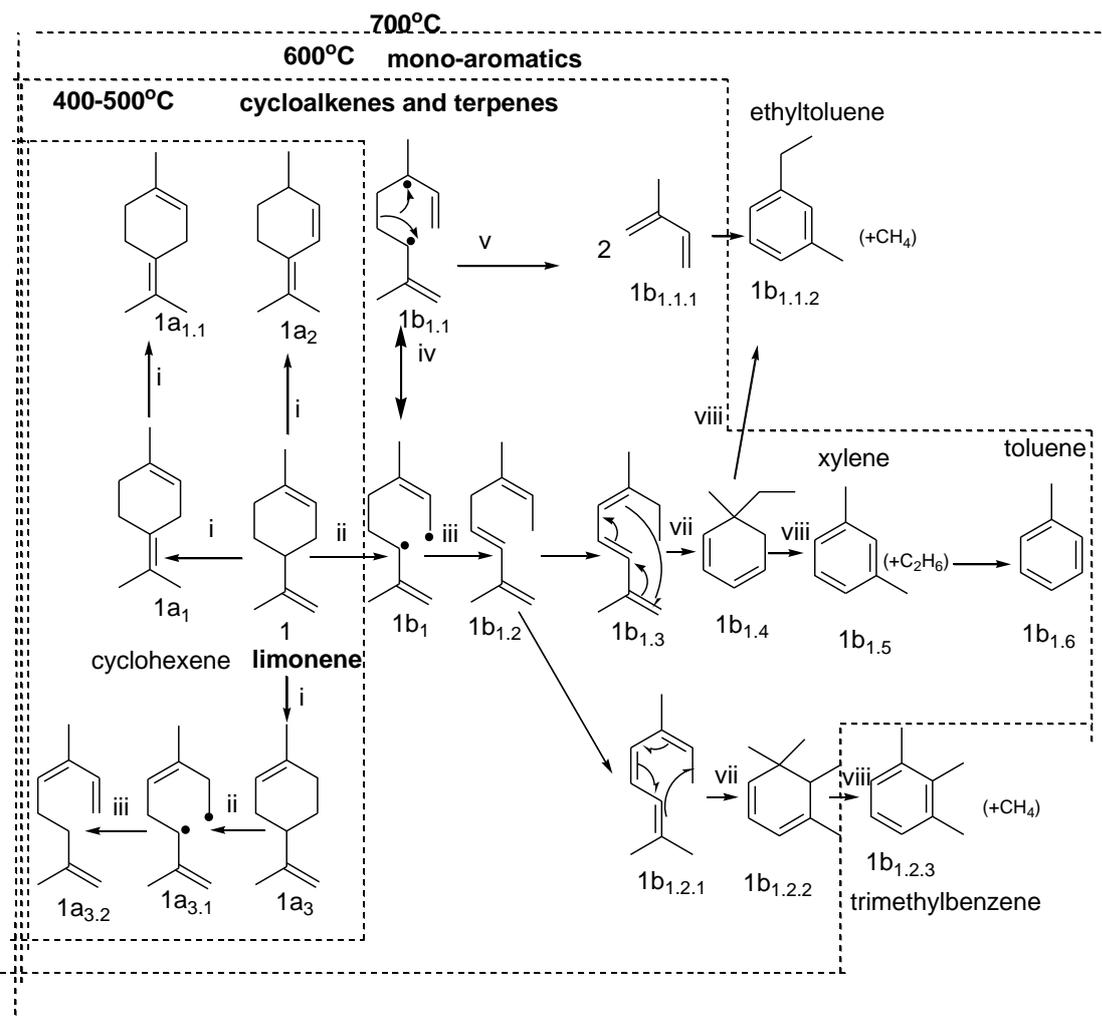


Scheme 1a. Pathway for the formation of dipentene (*dl*-limonene) during pyrolysis of tyre rubber i). Thermal degradation of polyisoprene rubber, ii). Intramolecular cyclization. Adapted from [13].

1.2.2. Formation of aromatics from limonene decomposition

Decomposition of limonene during pyrolysis occurs as the reactor temperature increases. Ding et al. [28] reported this process to occur between 400°C and 700°C. **Scheme 1b** below summarises the different processes involved as a function of temperature. Limonene first undergoes isomerisation at temperatures below 500°C to form cyclohexene isomers ($1a_1$, $1a_2$, $1a_3$ and $1a_{1.1}$) via pathway (i). This is a multi-step process leading to the production of several isomers. In the same temperature range, cyclohexene isomer $1a_3$ undergoes carbon-carbon bond cleavage via pathway (ii) at the allylic position to form *bi*-radical diene ($1a_{3.1}$). This is followed by intramolecular hydrogen transfer (iii) to form an alkatriene ($1a_{3.2}$ and $1b_{1.2}$). This cleavage-hydrogen-transfer pathway occurs at lower temperatures.

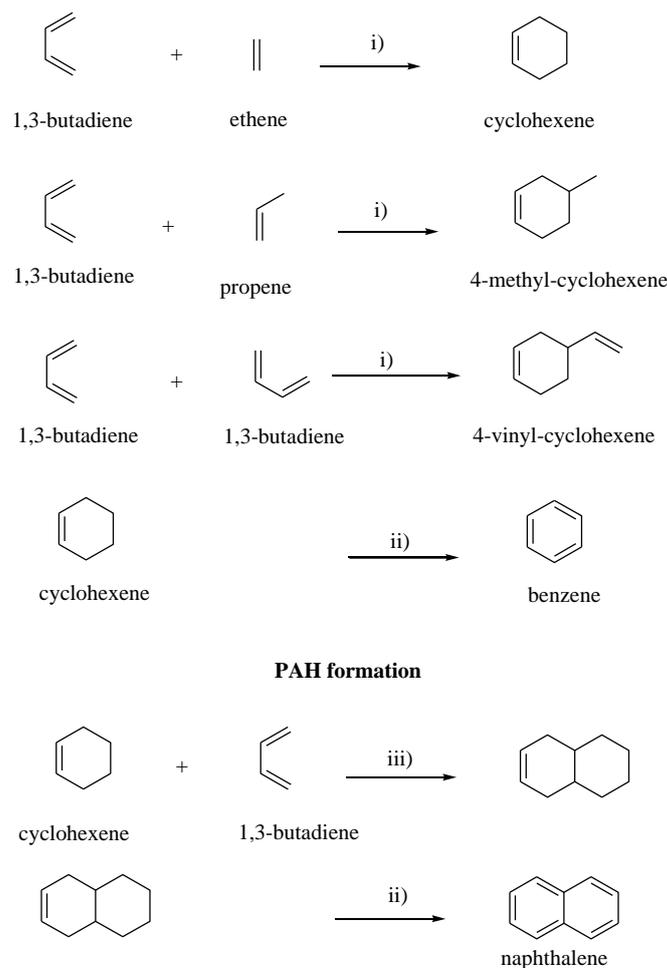
A similar pathway occurs at temperatures above 600°C to form aromatics (**scheme 1b**). Isoprene ($1b_{1.1.1}$) is formed via the internal cleavage of the C-C bond at the allylic position to form the *bi*-radical diene ($1b_1$), followed by allylic rearrangement (iv) of *bi*-radical diene ($1b_{1.1}$) through β -scission (v) to form isoprene ($1b_{1.1.1}$). In this temperature range (500-600°C), formation of xylene ($1b_{1.5}$) and toluene ($1b_{1.6}$) occurs via intra-molecular hydrogen transformation (vii) followed by the loss of ethane. Trimethylbenzene ($1b_{1.2.3}$) can be formed through a similar pathway although aromatisation only subsequently occurs at higher temperature. At 700°C, aromatic compounds are formed ($1b_{1.2.3}$) and ($1b_{1.1.2}$) via aromatization (viii), which will further transform as the temperature increases to form PAHs, as summarised in the next section.



Scheme 1b. Summary of the steps involved in the decomposition of limonene during pyrolysis. Adapted from [28,29]. (i). Isomerisation, (ii). Carbon-carbon bond cleavage, (iii) Intra-molecular hydrogen transfer, (iv). Internal cleavage, (v). Allylic rearrangement, (vi). Intra-molecular hydrogen transformation, (vii). β -scission, (viii). Aromatisation.

1.2.3. Formation of aromatics and polyaromatic hydrocarbons

In the pyrolysis of tyres, ethane, propene and 1,3-butadiene are formed, which then react as shown in **scheme 1c** below to form cyclic olefins. Dehydration of six-membered cyclic olefins occurs to produce single ring aromatic compounds. This mechanism is possible at pyrolysis temperatures higher than 600°C. The formation of PAHs at higher pyrolysis temperatures occurs via the Diels-Alder reaction as detailed in **scheme 1c** below according to Williams et al. [24].



Scheme 1c. Formation of cyclic olefins, aromatics and PAHs during waste tyre pyrolysis. Adapted from [24] i). Cyclisation, step ii). Aromatisation and iii). Diels-Alder reaction.

1.2.4. Formation of hetero-atomic species

Benzothiazolic acid and *N,N'*-caprolactam are amongst the commonly used accelerators added during tyre formulation. During the pyrolysis of tyres, the C-S and N-S bonds of these additives undergo cleavage to form benzothiazole and caprolactam, which are found in the oil [27]. Benzothiazole offers a wide range of industrial applications [30,31], and several authors have identified benzothiazole in significant concentrations in TDOs [9,11,17,29]. The polar nature of benzothiazole and related hetero-atomic species often requires the use of polar GC columns for improved chromatographic performance. Additional hetero-atomic compounds that have been identified in TDOs include phenol, aniline, cyclohexanone, cyclopentanone, benzonitrile, quinoline, thiophene and caprolactam to name the most important [1,14,32].

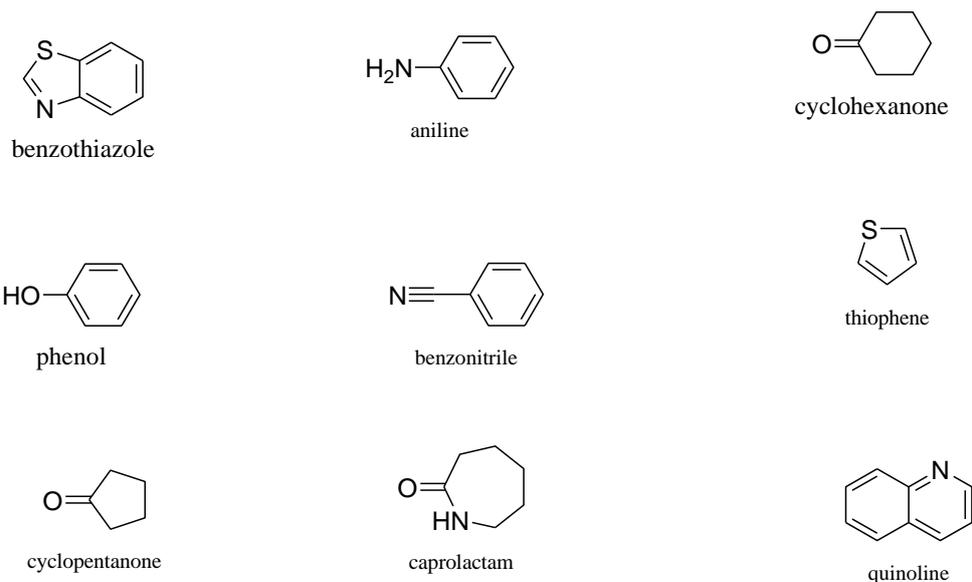


Fig. 1.1. Some examples of hetero-atomic species reported in TDOs.

1.3. Analytical sample preparation techniques

Different types of sample preparation techniques can be used, depending on the nature of the sample. Liquid-liquid extraction (LLE), Solid phase extraction (SPE) and solid phase micro extraction (SPME) are among the best-known and most utilised sample preparation techniques when dealing with complex ((semi-) volatile) samples. In the case of TDOs, simple sample dilution is also often used.

1.3.1. Liquid-liquid extraction (LLE)

Liquid-liquid extraction is a well-known sample preparation technique that involves the extraction of volatile organic compounds using two immiscible liquids governed by the affinity of compounds for the different phases as reflected by their distribution coefficients [33]. The advantages of this method include its simplicity, ease of use and the fact that dedicated instrumentation is not required. In LLE, the matrix is typically an aqueous medium, and an organic solvent is used to extract volatile organic compounds. The extraction of organic compounds from the aqueous medium depends on the polarity of target compounds; therefore the choice of solvent is governed by the properties of the target analytes. A range of solvents, varying in polarity, are typically evaluated for extraction optimisation. The main disadvantage of LLE is the relatively low extraction efficiency (depending on the phases used and the analytes of interest) and the consumption of hazardous solvents. The latter is a major

concern from an environmental point of view. In micro-LLE (μ LLE) small volumes of solvent are used to reduce solvent consumption, while also increasing extraction efficiency [34]. In the case of TDOs, the non-polar nature of the oil implies that addition of non-polar solvents essentially entails dilution of the oil. This is the most common approach to make TDOs compatible with GC separation [24]. However, the polarity of the solvent affect the recovery of different classes of compounds [35].

1.3.2. Solvent dilution

Solvent dilution is the simplest sample pre-treatment step prior to the GC analysis of complex hydrocarbon mixtures such as TDOs and petrochemical samples [36]. The method is easy to use for routine analysis, despite the fact that it requires relatively large amounts of solvent. Due to the solubility of TDOs in a range of different organic solvents, selection of a suitable solvent for dilution prior to analysis is a critical step. Properties such as polarity, solubility of the target analytes, and solvent volatility are important to consider. The principle of “like dissolve like” applies, and solvents are primarily selected according to their polarity as this property is the determining factor in analyte recovery. Mid-polar solvents are often preferred to give the most representative sample for analysis.

1.3.3. Solid phase extraction (SPE)

Solid phase extraction is one of the most popular sample preparation techniques used as an alternative to LLE [37]. SPE is an extremely versatile technique for the extraction of a wide range of compounds. SPE is performed in (purchased) cartridges packed with various packing materials ranging from polar to non-polar; typically similar phases as used in liquid chromatography are used. The stationary phase is conditioned prior to loading of the sample. Conditioning is performed using different solvents to remove any impurities and to wet the stationary phase. After conditioning the cartridge, the sample is loaded and the cartridge is rinsed with a weak eluent to remove sample impurities not of interest. Subsequently, the analytes of interest are eluted by a strong solvent with a polarity similar to target compounds. In order to improve the flow of the sample and solvents, vacuum can be used. The choice of the stationary phase depends on the nature of the analytes. The most commonly used apolar stationary phases used for the extraction of organic compounds are C18 and styrene-divinyl benzene (SDVB), which are known to offer high recoveries for these types of molecules. To the best of our knowledge, SPE has not been used in the analysis of TDOs.

1.3.4. Solid phase micro extraction (SPME)

SPME was invented in the early 1990's by Pawliszyn et al. [38]. This sample preparation technique involves the use of a fiber coated with stationary phase for the extraction of compounds from the gas or liquid phase. SPME is referred to as a sorptive technique since the analytes partition into the stationary phase [39]. Three different sampling modes can be used [40]: headspace (HS) extraction, direct immersion and membrane protected SPME. In HS-SPME, the extraction of volatile compounds is performed by exposing the fiber coating above the solvent-free liquid medium for extraction. This is the most commonly used form of SPME. Direct immersion is performed by immersing the fiber directly into the liquid sample, where the analytes are distributed between the fiber and sample matrix [41]. The membrane protected mode is mostly used in the extraction of highly polluted samples for the sake of protecting the fiber from being damaged [40]. After the extraction of volatile compounds, analytes are then desorbed from the fiber at high temperatures in a split/splitless GC injector for analysis [42]. **Figure 1.2** shows a typical experimental set-up for extraction of volatile organic compounds by HS-SPME.

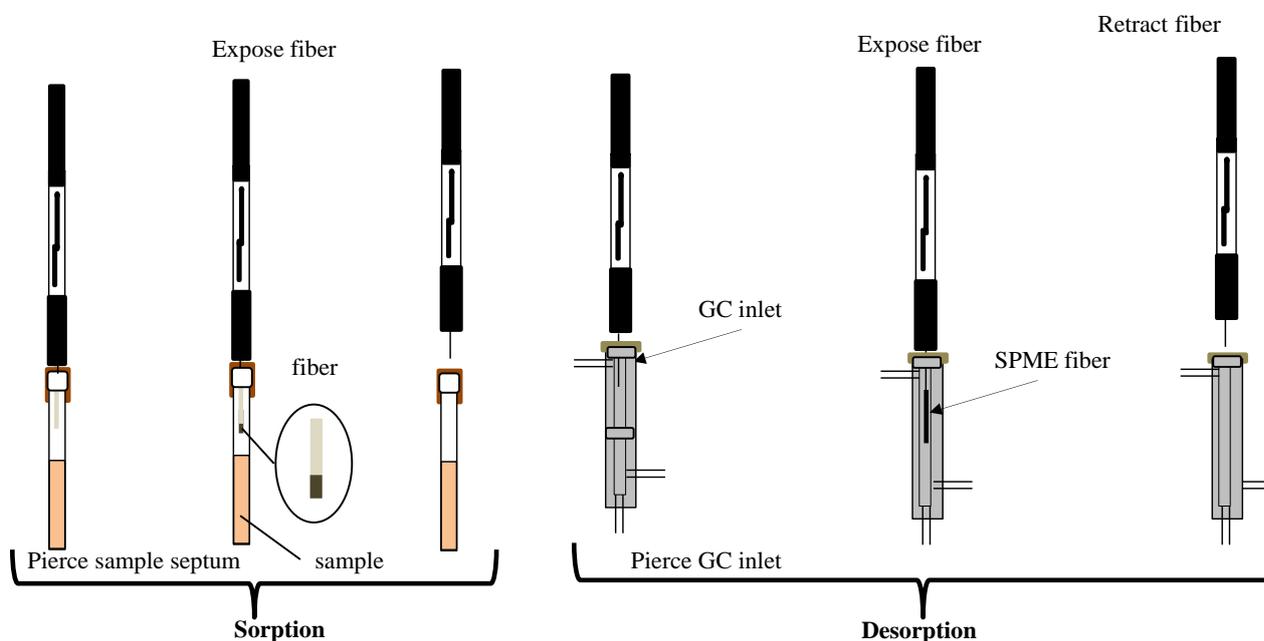


Fig. 1.2. Schematic representation of SPME sorption and desorption processes drawn by the author of this work.

Various polymeric fiber coatings such as polydimethylsiloxane (PDMS), carbowax (CAR), polyacrylate (PA) and polyethylene glycol (PEG), and also adsorbents such as divinylbenzene (DVB) as well as mixtures of these are commercially available. SPME is known to provide very good sensitivity, especially for the extraction of volatile compounds [40]. This technique extracts a wide range of volatile compounds, and is therefore potentially suitable for the analysis of TDOs. Since TDOs are typically viscous liquids, HS-SPME should preferably be used to avoid damaging the fiber's stationary phase. Using this method, interference by the non-volatiles in the sample would be reduced and less complex chromatograms can be obtained, simplifying identification and quantitation of compounds.

1.4. Chromatographic analysis

1.4.1. Introduction

The complexity of TDOs necessitates some form of separation for the chemical characterization of these samples; this is typically done using chromatographic techniques. Chromatography is a general term that describes the separation processes in which the components of a mixture are repetitively equilibrated between two phases, a fixed stationary phase and a mobile phase. Chromatography was first developed by the Russian scientist Mikhail Tswett in 1903 [43], who separated plant pigments on a column containing calcium carbonate stationary phase [44]. There are various forms of chromatography, which are distinguished based on the nature of the mobile phases [43,45]. One common aspect is that the components are transported through the stationary phase by the flow of the mobile phase. In this regard, separation is based on differences in migration rates among the components. Since chromatography is the most powerful separation method and allows separation, identification and quantification of the chemical components of complex mixtures, it is used extensively in all the chemical research and industry. In this study, GC with mass spectrometry and flame ionisation detection were used and these will be discussed briefly.

1.4.2. Gas chromatography (GC)

Gas chromatography is a powerful separation technique used in various fields of science such as forensic, environmental, food, agriculture and petrochemical industries [46,47]. In gas chromatography, the separation is mainly achieved as a result of partitioning of analytes between the gaseous mobile phase and a static phase (stationary phase) while transporting the

volatile and semi-volatile analytes through an open-tubular capillary column. A capillary GC column is coated with a thin film of liquid-like stationary phase which serves to retain the gaseous analytes transported by the mobile phase. The most commonly used mobile phases, referred to as carrier gases, include helium or hydrogen. Stationary phases are differentiated based on their polarity (see **section 1.4.2.2** for further details). Differential partitioning of analytes occurs as a function of properties such as polarity and boiling points [48]. Compounds which have greater affinity for the stationary phase spend more time in the column, whereas those with lower affinity spend less time in the stationary phase and thus elute earlier [45]. A GC instrument consists of a carrier gas supply, sample introduction unit (injector), capillary column, oven and a detector; the operation of the most important instrumental parts will be discussed briefly below.

1.4.2.1. Injection in GC

The injection port allows the volatile sample to be introduced in vapour form via the carrier gas stream into the capillary column. The most common injector used in contemporary GC is the vaporising split/splitless injector. This injector was invented to prevent overloading of the capillary column due to its low volume and capacity, which may affect resolution. The sample is introduced into a heated chamber, where vaporisation occurs. Two modes of injection, split and splitless, can be used depending on the concentration of the target analyte. Split mode is mostly used when the analyte is present at high concentrations, while splitless is used when the concentration of the analyte is low [49]. Splitless injection requires effective utilisation of focusing mechanisms such as the solvent effect, cold trapping and stationary phase focussing to avoid injection band broadening.

1.4.2.2. The capillary column

The capillary column is coated with a stationary phase that permits separation of compounds to take place. Stationary phases in a capillary GC are differentiated according to their polarity. Non-polar stationary phases such as PDMS, sometimes with 5 to 50% phenyl PDMS groups added are commonly used for the separation of compounds ranging from non-polar to medium polar. In these phases, separation is governed primarily by differences in vapour pressure, since non-specific dispersion interactions occur between the analytes and the stationary phase. Apolar phases have been used for the analysis of petrochemical samples and also for TDOs, since they primarily contain hydrocarbons. On semi-polar (14% cyanopropyl-phenyl 86% PDMS) or polar phases, mostly PEG, selective interactions such as hydrogen

bonding and dipole interactions occur, and compounds are separated according to their polarity. The column is housed in an oven for accurate temperature control. Since the separation of compounds in GC is primarily based on differences in the vapour pressures of compounds, temperature plays a crucial role. Temperature programming, where an initial low oven temperature is increased as a function of time, is used to provide optimal resolution for a range of weakly and strongly retained analytes within an acceptable analysis time.

Column dimensions such as length, internal diameter, film thickness and stationary phase are selected based on the analysis goals. Short (10-20 m) columns are used for fast separation of relatively simple mixtures. For complex samples, longer columns (50-60 m) provide improved separation efficiencies at the cost of longer analyses. Furthermore, reduction in the internal diameter (from e.g. from standard 0.25 mm i.d. to 0.1-0.18 mm) increases the efficiency per unit length and also provides higher optimal mobile phase flow rates, thereby allowing speeding up of the analysis. This is evident from the relationship between the column length, efficiency and optimal flow rate and the internal diameter:

$$N = \frac{L}{H} = \frac{L}{d_c} \quad (1.1)$$

$$u_{opt} = \frac{2D_M}{r_c} \quad (1.2)$$

Where N is the plate number, L is the length of the column, H is the height equivalent of a theoretical plate, u_{opt} is the optimal mobile phase linear velocity, D_M is the diffusion coefficient of the analyte in the mobile phase and d_c and r_c are the column internal diameter and radius, respectively [48]. An alternative measure of the efficiency of separation is the peak capacity (n_c). Peak capacity is defined as number of peaks that can theoretically be separated within the retention window [50]. According to Grushka [51], the peak capacity of a chromatographic separation depends on the plate number (N), the mobile phase linear velocity and the temperature. Peak capacity can be calculated according to Neue [50] using the equation below:

$$n_c = 1 + \frac{t_g}{w_{av}} \quad (1.3)$$

Where n_c is the peak capacity, t_g denotes the gradient run time and w_{av} average peak width at baseline. In GC, the oven ramping rate ($^{\circ}\text{C}/\text{min}$) affects the achievable peak capacity [52]. Slow ramping rates result in longer gradient times and generally higher peak capacities, although for very slow temperature programming rates peak widths increase and peak capacity decreases again. Evaluation of peak capacity in GC provides a measure of the separation performance as well as the optimum conditions for better separation.

1.4.2.3. Detection in GC

Detectors in chromatography should ideally obey certain characteristics such as adequate sensitivity, stability and reproducibility, linear response range to solute concentration over a wide dynamic range, as well as being reliable and easy to use. A wide range of detectors are compatible with GC, such as the nitrogen phosphorus detector (NPD), atomic emission detector (AED), thermal conductivity detector (TCD), sulphur chemiluminescence detector (SCD), electron capture detector (ECD), FID and MS, amongst others. Detectors are normally selected depending on the analyte of interest and the analysis goals (i.e. selective detection of the target analytes or screening of unknowns, trace level analysis, etc). Some detectors are universal, meaning that they respond to any or most sample constituents, for example FID, MS and AED. In contrast, selective detectors respond to certain group of compounds, for example the NPD (for nitrogen and phosphorus containing compounds) and the ECD (for halogenated compounds). Among all these detectors, MS and FID are the most commonly used detectors for analysis of a wide range of samples containing organic compounds. These detectors are also most commonly used in petrochemical analysis. MS is the most powerful and universal detector that provides detailed information about the identity of the chemical constituents, while FID only gives information about the quantitative chemical composition of the sample.

1.4.2.3.1. Flame ionisation detector

The FID is one of the most widely used detectors in gas chromatography. In this detector, the effluent from the column is directed into a small air and hydrogen flame; ions formed in the combustion of organic compounds in the flame are detected. Detection involves monitoring the current produced by collection of these ions by the collector electrode. The response of the FID is related to the number of carbon atoms entering the detector, thus it is a mass

sensitive detector. This detector is not sensitive towards non-combustible permanent gases such as CO₂, SO₂, NO₂, etc.[43]. A schematic diagram of an FID is shown in **Figure 1.3**.

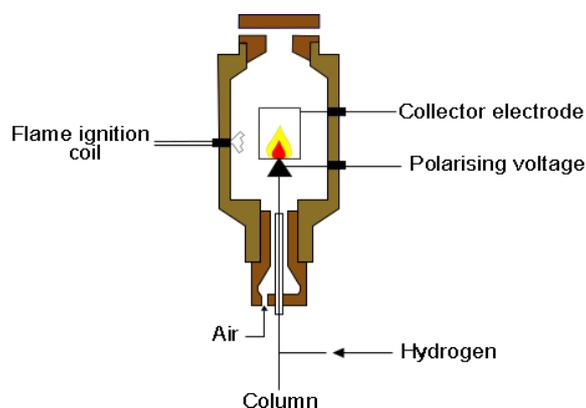


Fig. 1.3. Flame ionisation detector drawn by the author using Inkscape drawing software (<https://inkscape.org/en/download/windows/>).

The FID is extensively used in a variety of fields for qualitative and quantitative analyses [53–55]. Since FID is a mass sensitive universal detector for hydrocarbons, it can be used to estimate the mass % composition of hydrocarbon mixtures [56], and indeed has been used for this purpose in TDO analysis [5].

1.4.2.3.2. Mass spectrometry

Mass spectrometry measures the mass to charge ratio (m/z) of ions produced from the analytes. MS detection essentially involves 3 steps: ionisation, separation and detection. Each of these is briefly addressed below. The analyte enters the mass spectrometer via the ionisation source. Two types of ionisation sources are used in GC, namely electron impact (EI) and chemical ionization (CI), with the former being more common. In EI, the molecules are bombarded with a high energy (70 eV) beam of electrons that ionise the molecules entering the ion source in the gas phase by removing an electron. Because the formed molecular ions are unstable under such low pressure conditions, they fragment easily, and may be identified according to the characteristic fragmentation patterns formed [45].

In the second step, ions are separated according to their mass to charge ratio (m/z) in vacuum in the mass analyser. In this study, two of the most common mass analysers were used: quadrupole (q) and time-of-flight (TOF) systems. In quadrupole MS (qMS), separation

according to mass to charge ratio is performed by changing the rf and dc voltages applied across the four rods comprising the quadrupole (**Figure 1.4**). This changes the field in the quadrupole and allows only ions of a particular m/z ratio through to the detector for a given rf/dc ratio. By varying this ratio, ions of different m/z ratios can be detected. The quadrupole mass analyser consists of four parallel rods around the flight path of the ions. On two opposite rods a radio frequency (rf) is applied, whilst on the remaining two a direct current (dc) voltage is applied. This results in a magnetic field through which the ions travel which is changed continuously so that at any given setting of the rf and DC voltages only one ion will be resonant and arrive at the detector, while other ions are non-resonant and collide with the rods [45]. qMS instruments can be operated in one of two modes: full scan mode, which is used for identification of unknown compounds, and selected ion monitoring (SIM), which is used for analysis of target compounds and is more sensitive than scan mode.

In time of-flight mass analysers (**Figure 1.5**), ions formed in the source are accelerated into a flight tube by application of an extraction field on a back-plate or repeller. Ions attain the same kinetic energy in this process, and are forced through the acceleration region into the field-free drift region [58]. Because all ions have the same kinetic energy, but different masses, the time taken by the ions to travel through the flight tube depends on their mass to charge ratios [59]. Lighter ions reach the detector earlier, while the heavier ones reach the detector last. TOFMS detectors are capable of high resolution acquisition and/or very fast acquisition speeds, which makes them the MS detector of choice for GC×GC. The final step of MS involves detection of ions. This is typically done in qMS detectors using an electron multiplier, whereas in TOFMS detectors multi-channel plates are more common.

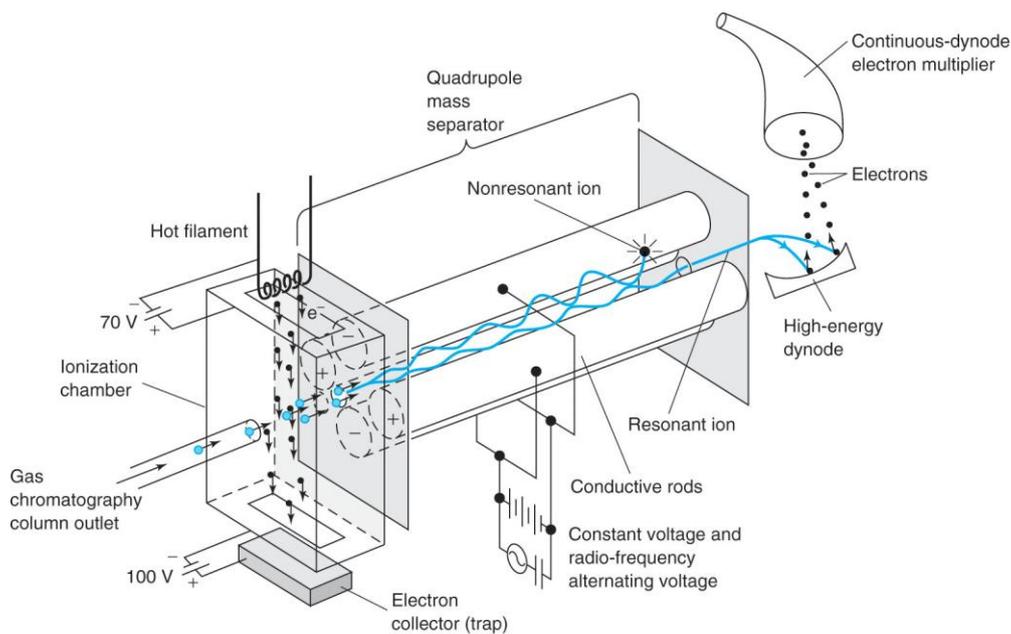


Fig. 1.4. A diagram showing a transmission quadrupole mass spectrometer equipped with an EI source. Reproduced from reference [45].

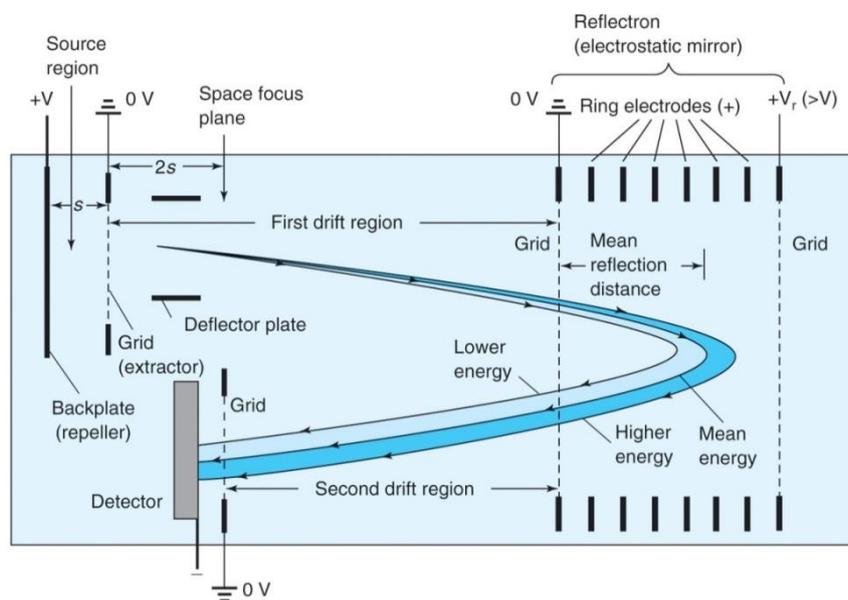


Fig. 1.5. Schematic illustration of a time-of-flight mass spectrometer. Reproduced from [45].

1.5. Comprehensive two-dimensional gas chromatography (GC×GC)

1.5.1. Introduction

GC×GC has become of increasing interest for the past few years in the analysis of complex samples. GC×GC is an advanced analytical technique that involves the separation of compounds via the utilisation of two columns with different stationary phases and hence different selectivities. The most common configuration uses an apolar column in the first dimension (¹D) and a polar column in the second dimension (²D) in order to improve the separation of compounds that cannot be separated on a single column [54,60]. Under ideal conditions, the peak capacity of GC×GC is equal to the product of peak capacities of the first and second dimension separations [61,62]:

$$n_{c,2D} = {}^1n_c \times {}^2n_c \quad (1.4)$$

Where $n_{c,2D}$ is the two-dimensional peak capacity, 1n_c the peak capacity of the first dimension column and 2n_c the peak capacity of the second dimension column. The improved resolution of GC×GC originates from the use of independent separation mechanisms in both dimensions to reduce component overlap. GC×GC separation is achieved by the use of interface between the two columns known as a modulator. Modulation involves the transfer of fractions of the ¹D column effluent to the ²D column. The modulator periodically traps the effluent and re-injects fractions as very sharp bands into the ²D column [63]. In the process of modulation, peaks eluting from the ¹D column are therefore sliced into different segments and each transferred to the ²D column for further separation. In GC×GC, the second dimension column is very short in order to allow the separation of target compounds within one modulation period [64]. To achieve this, a narrow internal diameter (i.d., normally 0.1 mm) column with a thin film is typically operated at a high mobile phase velocity. The ¹D column is long and specifically provides normal GC separation. GC×GC is arguably the most powerful separation method available for the analysis of volatile and semi-volatile compounds, and is increasingly being used in the analysis of complex of organic samples. For example, GC×GC has found extensive and increasing use in the analysis of complex samples in fields such as petrochemicals, environmental and food analysis [63,65–67]. Coupling of GC×GC with mass spectrometry increases the utility of the technique for qualitative and quantitative analysis.

1.5.2. Modulation

A typical GC×GC instrument configuration comprises two columns connected via the modulator, with standard GC injectors and detectors and an optional secondary oven (**Figure 1.6**). The function of the modulator is to trap, focus and re-inject the portions of effluent from the primary column onto the short second dimension column in a sequential and continuous way [68]. The time required to complete the process is called modulation period. An additional advantage of GC×GC operation is the improved sensitivity obtained as a result of the modulation process. This is because of the focusing of analytes during the trapping step followed by their very fast analysis in the second dimension. Modulators are categorised according to their operational characteristics as pneumatic (valve based) and thermal modulators [68,69]. Thermal modulators are further divided into two classes, i.e. heater based and cryogenic modulators [70,71]. Differences between these modulators have been discussed in detail [72]. Thermal modulators are most common, and will be discussed briefly here.

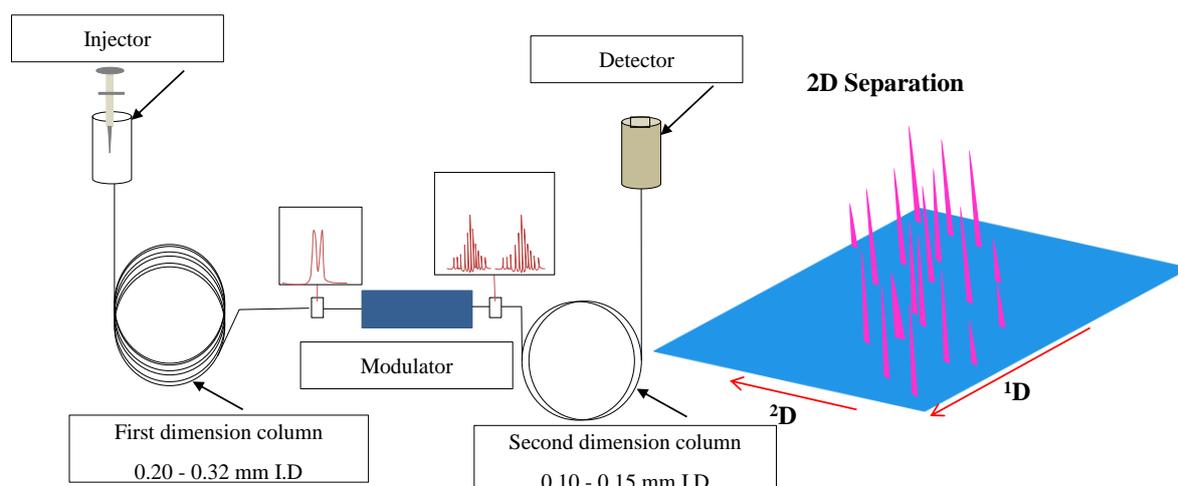


Fig. 1.6. Schematic illustration of a typical GC×GC instrument and representation of the two-dimensional separation. The figure was drawn by the author of this work.

In cryogenic modulators, trapping is performed at temperatures below the oven temperature, while for desorption the modulator temperature needs to be raised to or above the oven temperature [73]. The biggest advantages of cryogenic modulators are that even relatively highly volatile compounds can effectively be trapped without breakthrough occurring, and that excessive temperatures are not required for desorption [74]. Marriot and Kinghorn [75]

developed a longitudinal cryogenic modulator system (LCMS) which is capable of cryofocusing with carbon dioxide (CO₂) [76]. Several alternative configurations have since been developed, including non-moving modulators with two cryojets to allow analytes to be cryogenically trapped and the GC oven to provide warm air for releasing trapped analytes. Cryogenic modulators have found most widespread use in commercial GC×GC instrumentation. Recent interest in flow and heater-based modulators is aimed at developing more cost-effective alternatives to cryogenic modulators. For example, Górecki and co-workers [77] designed a consumable-free single stage thermal modulator utilising a trap for modulation where analytes are trapped at sub-oven temperatures and released by rapid electrical heating of the trap. Recently published work by Muscalu et al. [78] further detailed the applicability of this modulator for various samples.

1.5.3. Detection in GC×GC

Various detectors have been used in combination with GC×GC, including TCD, FID, MS and NPD. However, the most common detectors are FID and TOFMS due to their high acquisition rates [79]. The most important criterion for detection in GC×GC is a very fast acquisition rate to accurately define the very narrow (< 200 msec) peaks in the fast ²D separation. FID offers acquisition rates of up to 500 Hz, which is sufficient for GC×GC operation [80], and this detector is often used in quantitative GC×GC analyses. For detailed compound identification, however, MS is essential. TOF mass analysers are preferred due to their high acquisition rates, although the latest generation of quadrupole instruments have also successfully been used in combination with GC×GC. TOFMS systems typically used in combination with GC×GC separation offer scan speeds of up to 500 Hz, although the high resolution capabilities of the TOF are sacrificed for improved scanning speeds on these instruments, which therefore provide nominal mass accuracy [54].

1.6. Analysis of TDOs

The fuel properties of TDOs have been investigated by various authors [14,81,82]; these include physical properties such as caloric value, viscosity, water content, flash point and chlorine and fluorine content [24]. These properties illustrate the value of TDO as a potentially promising alternative fuel source. For the detailed chemical analysis of TDOs, however, their complexity implies that advanced instrumental analytical techniques are required. A typical TDO sample can contain hundreds to thousands of compounds of

different classes varying significantly in concentration levels. Since the majority of TDO constituents are low molecular weight semi-volatile organics, by far the most used analytical method is GC with either FID or MS detection [5,8,17]. Selective detectors such as sulphur chemiluminescence detector (SCD) and atomic emission detectors (AED) have also been used for TDO analysis [83,84].

The first challenge in TDO analysis is the choice of sample preparation technique to use prior to GC analysis [18]. TDOs are typically brown-black viscous oils, which would, if directly injected, severely contaminate the injection port and the column with high-boiling residues present in the oil. The formation of active sites in the injector, high noise levels, deterioration of chromatographic performance and irreproducible results are all possible consequences. One of the most common forms of sample preparation is therefore to dilute the TDO in an organic solvent prior to analysis [18,24]. In this approach, the most commonly used solvents typically include pentane, ethyl acetate, benzene, methanol and hexane. In a recent study, Rathsack et al. [32] used methyl acetate as a diluting solvent prior to GC×GC analysis. The use of different organic solvents in the fractionation of different classes of compounds in TDOs has been investigated in order to resolve the sample complexity [31]. Mirmiran et al. [84] used liquid-solid chromatography to fractionate TDOs. *n*-Pentane and ethyl acetate were used as eluents for hydrocarbons and methanol for nitrogen containing compounds. Williams et al. [15] reported a similar approach but used additional solvents to further fractionate the *n*-pentane fraction into two fractions, the first containing aliphatics and the second one low molecular weight aromatic compounds. However, in this study only selected compounds, as opposed to the overall composition, were of interest. Distillation has also been used as a pre-fractionation step prior to TDO analysis [82]. Alternative options for sample preparation which have to the best of our knowledge not been used to date for TDO analysis include solid phase micro extraction (SPME), solid phase extraction (SPE) and liquid-liquid extraction (LLE).

In terms of GC separation, the most commonly used stationary phases in the analysis of TDOs are apolar phases [8,18,85]. However, incomplete separation has been a challenge in previous studies due to the limited column efficiency provided by relatively short columns (typical dimensions are 30 m length × 0.25 mm internal diameter (i.d.) × 0.25 µm film thickness). A typical example of the GC-MS analysis of a TDO sample is presented in **Figure 1.7** [86]. In the study by Laresgoiti et al. [9], a longer column (50 m × 0.25 mm i.d. × 0.25

$\mu\text{m } d_f$) was used in order to attain better separation performance. Despite the improved efficiency of this column, however, under the conditions used incomplete separation was still observed (in the form of a ‘hump’ of unresolved material in the middle of the chromatogram). It is therefore clear that both high efficiency columns and optimised chromatographic conditions are needed for improved separation of TDOs.

FID detection is commonly used as a cheap and robust detection method for TDO analysis. The mass-dependent response of the FID is also often exploited to estimate the mass % composition of individual TDO constituents [29,32]. Because of the non-selective nature of the FID, however, optimal chromatographic resolution is critical in such applications.

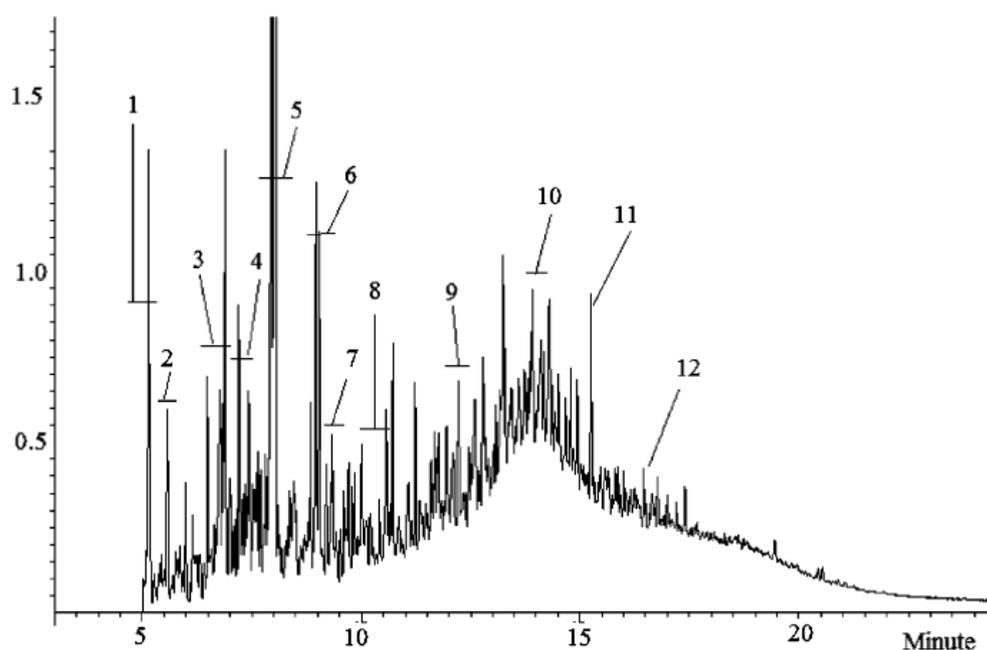


Fig. 1.7. Total ion chromatogram obtained for the GC-MS analysis of tyre pyrolysis oil on a $30 \text{ m} \times 0.25 \text{ mm i.d.} \times 0.25 \mu\text{m } d_f$ CP-Sil 8 CB low bleed/MS column. Reproduced from [86].

GC-MS is a more powerful alternative for the qualitative and quantitative analysis of TDOs. An additional benefit of MS detection is the better sensitivity compared to FID, thus allowing more detailed and accurate quantitative analyses. Quadrupole (qMS) instruments are most commonly used in TDO analysis. qMS instruments can be operated in one of two modes, scan and selected ion monitoring (SIM). The former is generally used for qualitative analyses, since compounds can be identified based on their mass spectra. In SIM mode on the other hand, the detector monitors only specific ions, and because it spends more time

acquiring data for each ion, this mode is much more sensitive and selective. For this reason, SIM allows the trace-level quantification of compounds. For example, since PAHs are found in trace levels in TDOs, the use of SIM is a promising approach for the accurate quantification of these compounds.

As alluded to above, complete separation of the large number of TDO constituents by GC is a challenging task. To further improve the separation of complex volatile mixtures, comprehensive two-dimensional gas chromatography (GC×GC) may be used. This advanced technique can potentially separate several hundreds of compounds present at low concentrations within a relatively short period of time [32,87]. GC×GC provides improved separation through the combination of two different columns (typically polar and apolar columns are combined) [61]. In this state-of-the-art equipment, compounds from the first dimension column (¹D) are periodically trapped by a modulator prior to their very fast injection into the second dimension column (²D) for fast separation while the subsequent fraction is trapped [88,89]. In addition to improved resolution, GC×GC also offers group-type separation and improved sensitivity due to the modulation process. GC×GC has in recent years found increasing application in TDO analysis [18,32]. The most commonly used column combination is an apolar column in the first dimension and a polar column in the second dimension (apolar × polar). For example, Rathsack et al. used an apolar × polar configuration for the analysis of TDO (**Figure 1.8** below) [18]. In a more recent study the same group have also used the reverse column configuration (polar × apolar) [32].

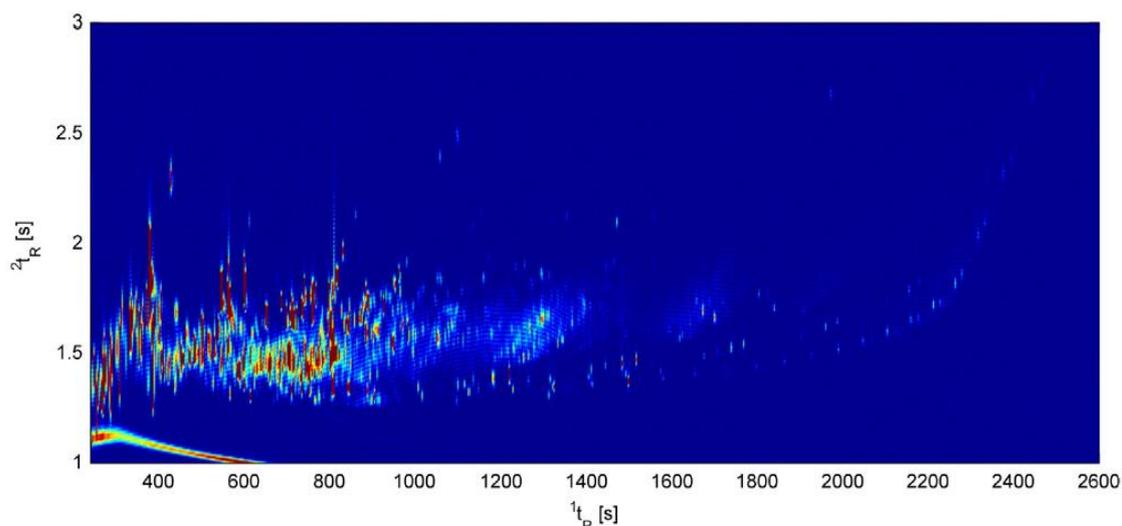


Fig. 1.8. Contour plot obtained for the GC×GC-qMS analysis of TDO. This analysis was performed using an apolar × polar column combination: ¹D 30 m × 0.25 mm i.d. × 0.25 μm d_f SLB-5MS × ²D 1.5 m × 0.15 mm i.d. × 0.15 μm d_f Rxi-SilMS. Reproduced from [18].

From the above brief overview, several general conclusions may be drawn: (1) no universal sample preparation method exists for the GC analysis of TDO volatiles and semi-volatiles; (2) chromatographic separation remains a critical challenge and conventional GC methods generally do not provide sufficient performance to separate all TDO constituents; (3) there is still limited quantitative data published for TDOs, and (4) GC×GC shows promise for the detailed analysis of TDOs.

1.7. Goals of this study

The physical properties of TDOs imply that suitable sample preparation strategies are required to effectively and reproducibly introduce a representative sample into the GC for analysis. The following means of achieving this will be evaluated: (i) direct analysis of the oils after dilution with an organic solvent, with the focus on selecting a suitable solvent for optimal recovery and (ii) liquid-liquid back-extraction of the water soluble compounds with an organic solvent to investigate polar constituents of the oil. For GC-MS analysis, a high efficiency GC column of length > 30 m and internal diameter < 250 μm will be selected to obtain maximum chromatographic performance and minimise co-elution. GC as well as MS conditions will be optimised for optimal separation and identification. Individual compounds will be identified using pure authentic standards where available, while for other compounds MS and RI data will be used for tentative identification. A second major goal is to develop an accurate quantitative GC-MS method for TDO analysis. To do this, both internal standard and standard addition methods will be evaluated. The final method will be validated and evaluated in terms of linearity, repeatability and recovery to ensure its suitability for routine analysis of diverse TDOs.

A more advanced, state-of-the-art technique for analysis of complex samples is comprehensive two-dimensional gas chromatography (GC×GC). This technique, where compounds are separated on the basis of two separation mechanisms, is characterised by much higher separation performance compared to 1-dimensional GC. This makes GC×GC an ideal tool for the analyses of highly complex samples such as TDOs [86]. Therefore, a third aim of this study was to explore the utility of GC×GC for the in-depth analysis of the chemical composition of TDOs. For this purpose, in the first instance the applicability of an in-house built GC×GC instrument equipped with a flame ionisation detector (FID) and a

consumable-free single stage thermal modulator [78] will be investigated to evaluate the potential benefits of GC×GC separation for TDOs. This will be followed by GC×GC with time-of-flight (TOFMS) analysis on a commercial instrument equipped with a dual-jet liquid-nitrogen cryogenic modulator to identify new TDO constituents based on comparison with deconvoluted mass spectra and RI values. This study will therefore greatly expand our knowledge in terms of the chemical composition of TDOs and offer several novel analytical methods for the in-depth analysis of these samples. The aims and objectives are stipulated below.

1.7.1. Aims and objectives

The overall research aim for this work is to develop GC-MS methods for routine quantitative analysis of tyre derived oils (TDOs). For this aim to be achieved, the following objectives are to be fulfilled:

- i. Optimisation of the GC separation of TDO components, including optimisation of GC parameters such as flow rate, column dimensions, injection volume, oven temperature program. At the same time, optimal MS parameters will be selected based on the GC conditions.
- ii. Evaluation of sample preparation techniques such as liquid-liquid extraction (LLE), SPE, solvent-dilution, SPME and liquid-liquid back extraction for the GC-MS analysis of TDOs.
- iii. Identification of TDO constituents by using MS spectra, retention index (RI) data and authentic standards.
- iv. Development of quantitative methods for quantification of TDO target compounds.
- v. Validation and evaluation of the method developed for routine analysis of a range of TDOs.
- vi. Evaluation of the applicability of GC×GC for TDO analysis using GC×GC-FID and GC×GC-TOFMS for identification of new TDO constituents.

1.8. References

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CHAPTER 2

Development of a GC-MS method for the analysis of waste tyre pyrolysis oils*

**This chapter is in preparation as a manuscript*

Abstract

The disposal of waste tyres is of big environmental concern. Currently most of these tyres still end up in landfill sites, not only taking up valuable space but also posing an environmental risk due to potential leaching of toxins and contamination of soil, water and air. The recycling of tyres using pyrolysis is an attractive means to deal with this problem. Tyre-derived pyrolysis oils contain potentially useful chemicals which are of obvious relevance to the recycling industry. However, these pyrolysis oils are extremely complex, thus complicating their chemical characterisation. In this study, several sample preparation procedures prior to gas chromatography-mass spectrometry (GC-MS) analysis were evaluated for the development of a GC-MS method for the quantitative analysis of tyre derived oils (TDOs). Selected compounds were identified using authentic standards, MS-spectral matches and calculated retention index comparison with literature. Two quantitative methods based on standard addition and the internal standard quantification, respectively, were developed; both are shown to be suitable for the analysis of TDOs. The two methods gave similar quantitative results and since the internal standard method is much less time consuming, this was selected as the method most suitable for the routine analysis of TDOs. Both methods were validated and proved to be repeatable and reproducible, with %RSDs averaging 2.9% in the linear concentration range of 3.91-125 mg/L (corresponding to 391-12500 mg/L in the oil). The limits of detection (LODs) and quantification (LOQs) ranged from 0.15-1.9 mg/L (corresponding to 15-190 mg/L in the oil) and 0.52-6.37 mg/L (corresponding to 52-637 mg/L in the oil), respectively. Good linearity ($r^2 \geq 0.998$) and good recoveries (81-114%) were achieved. Several TDO samples differing in their chemical composition were analysed in order to verify the general applicability of the method. Compounds which were found to be most abundant in the analysed TDO samples included *dl*-limonene, *p*-cymene, benzothiazole, toluene, ethylbenzene and xylenes, all compounds that have been reported to have significant market value.

Key words: Tyre derived oil (TDO), pyrolysis, gas chromatography mass spectrometry (GC-MS), volatile composition, sample preparation.

2.1. Introduction

Pyrolysis, the thermal decomposition of materials in the absence of oxygen, has been shown to be a very effective strategy to recycle waste tyres [1]. This relatively environmental friendly process (compared to alternative processes) results in the production of three principal products, namely a liquid, gas and solid char. The gases produced from pyrolysis can be used as fuels [2] and the solids as carbon black or activated carbon [3]. The liquid obtained during the process, pyrolysis oil, is considered the most valuable of the three, as it can be used as an alternative source of fuel that can be added to petroleum refinery feed stocks [4,5]. However, recently tyre derived oils (TDOs) and their production is receiving renewed attention as a result of increasing interest in the extraction of individual chemical compounds that are present in the complex oil and have considerable market value [6]. Therefore, in addition to the value of waste TDOs as a source of fuel, their chemical composition is becoming of increased interest. As a result of the complex composition of tyres, TDOs are also chemically very complex: they contain numerous different classes of chemicals such as aromatics [7], aliphatics [8], terpenes as well as sulphur, nitrogen and oxygen containing compounds [9].

Limonene, the main constituent of TDOs, is considered an environmentally acceptable solvent that can, amongst many other industrial uses, be utilised for cleaning of electrical circuit boards by replacing ozone depleting chlorofluorocarbons (CFCs) and as a dispersing agent in cleaning products, resins and adhesives [10,11]. In addition, besides limonene, several other TDO constituents have a range of different industrial applications, for example in the production of dyes, pesticides, surfactants and solvents [2,22,23]. For instance, xylenes are used in the production of industrial fibers, dyes and pigments [4], whereas benzothiazole is used in the tyre manufacturing industry as an accelerator. It is therefore clear that tyre-derived pyrolysis oil has potentially significant market value and that the extraction of particular chemicals for further use will add value to the product [14].

In light of the above, it is clear that the chemical analysis of TDOs is crucial in order to quantify the listed compounds and in addition to unveil potentially useful compounds. However, as a consequence of the abovementioned chemical complexity of TDOs, their analysis poses a major analytical challenge. Gas chromatography coupled with mass spectrometry (GC-MS) has been shown to be ideally suited for the separation and quantification of volatile and semi-volatile constituents of such complex samples. The use of MS allows tentative identification of various constituents [23]. Sample pre-treatment before GC-MS analysis of complex samples is also of

utmost importance to ensure that the compounds of interest are detectable and that the liquid to be injected is 'clean' enough not to cause excessive background noise and necessitate very frequent cleaning of the instrument.

In fact, previous GC-MS methods reported in literature for TDO analysis [16,17] highlight the complexity of these samples, and the need for both carefully optimised chromatographic separation and detection parameters to allow accurate quantification of TDO constituents. Indeed, relatively little quantitative data are available, and this is limited to the major TDO constituents such as limonene, toluene, benzothiazole, *p*-cymene, xylenes, ethylbenzene [1,18]. The goal of this study was therefore to develop a quantitative GC-MS method for TDO analysis, including investigation of sample preparation techniques such as liquid-liquid back-extraction and direct solvent dilution of the oil. The developed method was validated in terms of limit of detection (LOD), limit of quantification (LOQ), repeatability, recovery and linearity, and found to be robust and suitable for the analysis of various TDOs.

2.2. Experimental

2.2.1. Materials and methods

The TDO samples analysed were supplied by two different commercial waste tyre processing companies (Metsa and Malvinetix, Johannesburg, South Africa) and stored in the fridge at 4°C until analysis. An additional 18 experimental samples used were obtained from TDO researchers at the Department of Process Engineering, Stellenbosch University. TDO samples were filtered through hydrophilic PVDF 0.45 µm millex-HV filters (Millipore, Billerica, MA, USA) using a 5 mL sterile hypodermic syringe. Pure analytical standards, namely toluene (99.6% purity), 4-vinylcyclohexene (99.7%), ethylbenzene (99.9%), *p*-xylene (99.7%), *m*-xylene (99.6%), styrene (98.6%), *o*-xylene (99.8%), cumene (98.0%), 3-ethyltoluene (99%), α -methylstyrene (99.8%), 4-methylstyrene (98.6%), 4-ethyltoluene (95%), 2-ethyltoluene (99%), 1,3,5-trimethylbenzene (99.4%), 1,2,4-trimethylbenzene (98%), 1,2,3-trimethylbenzene (91.7%), *m*-cymene (99%), *p*-cymene (99.5%), *l*-limonene (99%) & *d*-limonene (99%), indane (97.5%), indene (96.7%), α -terpinolene (99%), benzothiazole (98.7%), naphthalene (99%), 1,4-dimethylnaphthalene (97.8%) and 2,6-dimethylnaphthalene (98.9%) were all purchased from Sigma-Aldrich (Steinheim, Germany). The internal standards, α -pinene (99.8%), deuterated toluene (99.7%) and deuterated naphthalene (99%), as well as hexane, methanol, cyclohexane, dichloromethane (DCM), ethyl acetate, acetone and 15 mL screw top vials were also purchased from Sigma-Aldrich. Anhydrous

sodium sulphate (Na_2SO_4 , 99.0%) was obtained from Sigma Aldrich. Linear alkanes ($\text{C}_7\text{-C}_{40}$) used for retention index (RI) calculations were purchased from Supelco (St. Louis, MO, USA).

2.2.2. Sample preparation procedures

2.2.2.1. Liquid-liquid back extraction

Back extraction of polar organic volatile compounds was performed by mixing 5 mL of de-ionised water purified by a Milli-Q water purification system (Millipore, Bedford, MA, USA) with 2 mL of TDO. The mixture was shaken vigorously and then centrifuged for 10 min at 3000 rpm to allow separation of the aqueous and 'organic' layers. The aqueous layer was removed and back-extracted with DCM using 4 mL of the aqueous layer and 2 mL of DCM. The DCM was removed and dried on anhydrous Na_2SO_4 . The extract was concentrated to ~ 50 μL under nitrogen (99.999%).

2.2.2.2. Solvent dilution

Solvents of different polarities such as hexane, DCM, ethyl acetate, methanol, cyclohexane, acetone, also purchased from Sigma-Adrich, were used for solvent selection using a dilution factor of 1:50. Based on the selected solvent (DCM), various dilution factors were further evaluated (TDO to solvent): 1:20, 1:50 and 1:100. A 1:100 (0.1 mL TDO added to 9.9 mL of DCM) was applied throughout the method development steps in this study.

2.2.3. Instrumentation and chromatographic conditions

2.2.3.1. GC-MS method optimisation

An HP 5890 series II GC instrument (Agilent, Midland, Canada) equipped with mass spectrometric detector (Agilent 5973, Palo Alto, CA) was used for all experiments. The two capillary columns used for optimisation were an apolar 60 m \times 0.25 mm i.d. \times 0.25 μm d_f Xti-5, (5%-Phenyl)-95% methylsiloxane (Agilent Technologies, Palo Alto, CA, USA) and an apolar 60 m \times 0.18 mm i.d. \times 0.10 μm d_f Rxi-5SilMS (Restek, Penn Eagle Park, CA, USA). Using the latter column, various oven temperature program rates (0.7, 1, 1.5, 2, 2.5, 3, 3.5 and $5^\circ\text{C}/\text{min}$), carrier gas flow rates (1, 1.2, 2 mL/min) and the split ratios (1:150, 1:100, 1:50, 1:20) were evaluated. All other instrumental conditions were kept constant as specified in the next section.

2.2.3.2. Optimised GC-MS conditions

For the final optimised GC-MS method, the following conditions were used: Helium (99.999% purity, Air Products, Cape Town, South Africa) was used as carrier gas with an initial inlet pressure of 348 kPa in constant flow mode (1.2 mL/min, linear velocity of 27.9 cm/s). 1 μ L sample was injected at a temperature of 280°C using a split/splitless injector operated in split mode with a split ratio of 1:20. A non-polar capillary column with dimensions: 60 m \times 0.18 mm i.d. \times 0.10 μ m d_f Rxi-5 Sil-MS (Restek) was used. The GC oven temperature was programmed as follows: 40°C (held for 5 min) ramped by 0.7°C/min up to 104°C and at 10°C/min to 280°C, held for 5 min. The transfer line to the MS was kept at 280°C and the MS was operated in full scan mode from 35 to 350 m/z at a scan rate of 4.5 scans/sec with standard electron ionisation energy of 70 eV. The electron multiplier (EM) voltage was 1 188 V. For the selective ion monitoring (SIM) experiments, 2 qualifiers and 1 quantifier ion were recorded (details in **Table 2.3**). For all experiments the MS source and quadrupole temperatures were 230°C and 150°C, respectively.

2.2.4. Data processing

2.2.4.1. Identification and quantification of TDO constituents

GC-MS data were recorded and processed using Agilent's MSD Chemstation software (D.01.02.16). For tentative identification by library matching the Nist 02 (National Institute of Standards and Technology, Gaithersburg, MD, USA) and Wiley 275 (Wiley, New York, USA) MS libraries were used. As criterion, a minimum spectral match factor of 70% was used, and further confirmation was obtained by comparison of retention indices with literature values. Experimental retention index values were determined relative to a series of linear alkanes (C₇-C₄₀) which were analysed under the same conditions as the TDOs. Data were manually integrated and exported to Microsoft Excel (Microsoft Office 2010) for retention index and other calculations.

Pure authentic standards (**Section 2.2.1**) were used for unambiguous identification and quantification of selected target compounds. Quantification of target compounds was performed using both the internal standard and standard addition methods and solvent dilution (**Section 2.4**) as sample pretreatment. The internal standards were introduced by adding 40 μ L of each of the internal standard solutions (5 000 mg/L in DCM) with the solvent (DCM) to dilute each TDO sample 1:100. Calibration curves were constructed with the following concentration levels: 3.91,

7.81, 15.6, 31.3, 62.5 and 125 mg/L with 20 mg/L of the internal standards at each calibration point. For standard addition, a 1:100 dilution factor of TDO to DCM was again used and 10 μ L of each standard stock solution (12.5, 6.25, 3.13, 1.56, 0.781 and 0.391 g/L) was added to achieve spiked concentrations of the standards at 3.91, 7.81, 15.6, 31.3, 62.5 and 125 mg/L. All solutions were preserved at 4°C in the fridge until needed. Calibration curves for both internal standard (IS) and standard addition methods were prepared in Microsoft Excel using characteristic extracted ions (shown in **Table 2.2**) for all the compounds using the same ions as also used in selected ion monitoring conditions (SIM) experiments. The method was only validated using the IS method. The same IS method was also used for SIM method development. The calibration curves were constructed using the following calibration levels: 0.12, 0.24, 0.49, 0.98 and 1.9 mg/L using 1:100 as a dilution factor. Two qualifiers and one quantifier ion were recorded (details are recorded in **Table 2.3**).

2.3. Results and discussion

2.3.1. Evaluation of sample preparation methods

In initial work, different sample preparation procedures were evaluated in an attempt to obtain a GC amenable sample that is representative of the TDO. This was necessitated by the fact that TDOs, which are typically dark oily liquids, also contain non-volatile impurities due to the nature of the starting product (rubber) and the pyrolysis process.

2.3.1.1. Liquid-liquid back-extraction of polar constituents

Liquid-liquid back extraction was utilised in an attempt to extract polar compounds from TDO samples such as compounds containing sulphur, nitrogen and oxygenated functional groups. Water was used to 'extract' these polar compounds from the oil, followed by back-extraction of organic compounds from the water with an organic solvent. Various dilution ratios of the oil to water were evaluated: 1:5, 2:5 and 3:5 (v/v). A ratio of 2:5 was found to be optimal, as this gave clear fractionation of the oil and water after centrifugation, and the proportionally large volume of oil increased sensitivity. This water fraction was then back-extracted using DCM for the recovery of polar organic compounds. The major compounds extracted included benzothiazole, aniline, cyclohexanone, phenol, *p*-cresol, quinoline and cyclopentanone. Some of these are considered to have considerable market value and therefore their determination is of interest.

The good extraction efficiency observed for benzothiazole hints at the possibility of using water for the removal of sulphur containing compounds from TDOs during processing either for their recovery or to remove unwanted compounds, for example when used for fuel production [19,20]. In **Figure 2.1** a typical GC-MS chromatogram (split into four parts for clarity) obtained using liquid-liquid back extraction is shown. It is important to note the overlap of some compounds detected using this approach and solvent dilution (discussed below, **2.3.1.2**), respectively. Some compounds were detected using both methods (labelled ‘ab’ in **Figure 2.1**), whereas others such as phenol were detected only in the back-extracted sample (‘b’ in **Figure 2.1**).

Note that the poor chromatographic performance observed for polar compounds is a result of using an apolar column – for analysis of these compounds a polar column would certainly provide better peak shapes. This was not attempted in the current work, since the goal was only a qualitative evaluation of the polar constituents of TDOs.

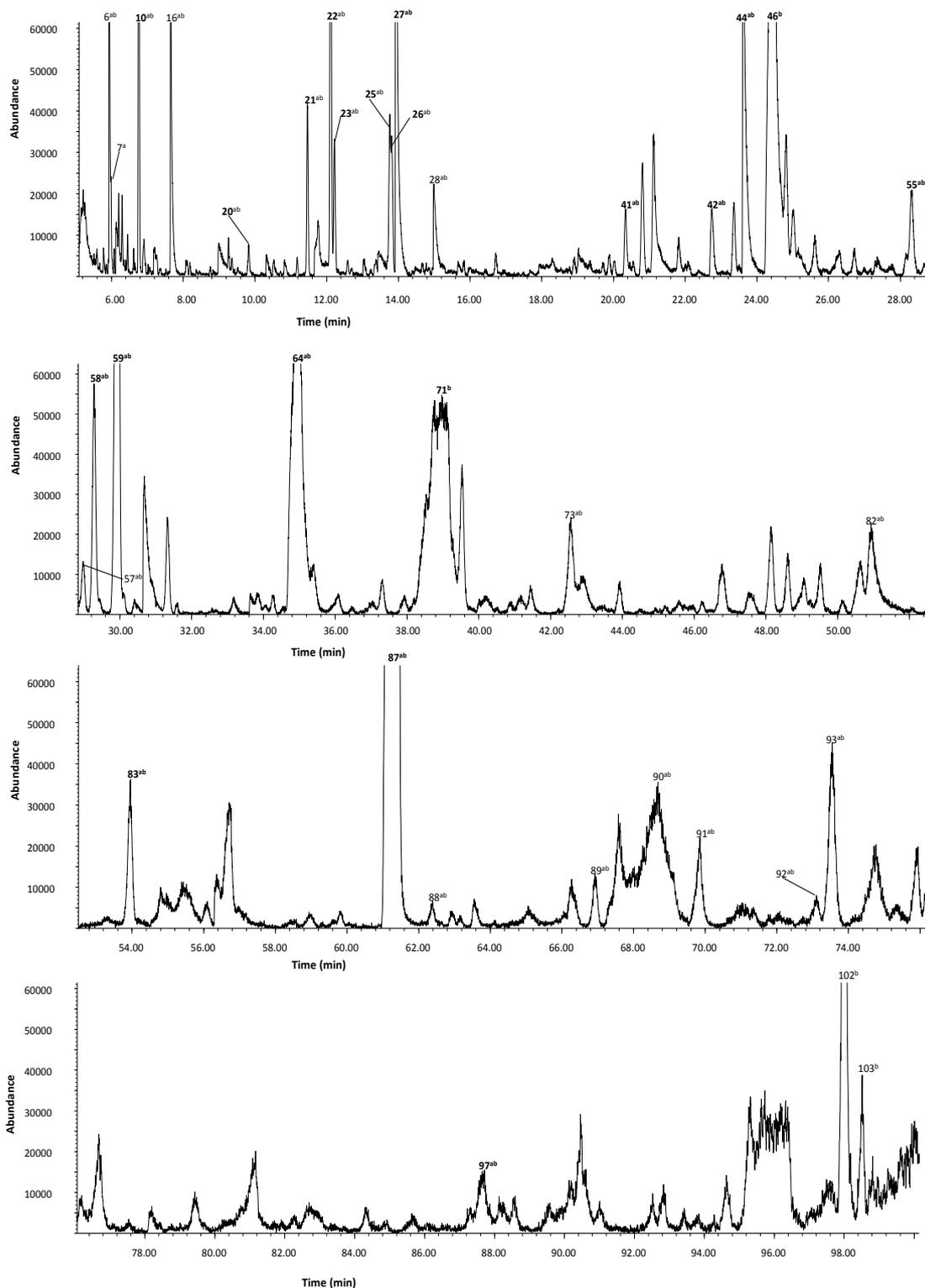


Fig. 2.1. Total ion chromatogram of TDO1 showing compounds identified using liquid-liquid back extraction. Peak numbering corresponds to **Table 2.1.** ^{ab} denotes compounds identified from both solvent dilution and in liquid-liquid back extraction, ^b denotes compounds identified only in the liquid-liquid back extraction sample.

2.3.1.2. Solvent dilution

Direct injection of a relatively dirty sample, even with a high split ratio, is normally not a desired method of sample introduction in GC. Injection of a sample of such nature could lead to several instrumental complications, most notably the injection port and the column becoming contaminated with high-boiling or non-volatile residues present in the oil. This may furthermore lead to the formation of active sites that can potentially lead to a high level of noise, the deterioration of chromatographic performance and irreproducible results. Since all the sample preparation strategies discussed above discriminate to some degree against certain classes of compounds, solvent dilution was investigated as a way to obtain a more representative sample. A range of organic solvents, ranging from relatively polar to non-polar, were evaluated for this purpose using a constant dilution ratio of 1:50. The solvents included were acetone, ethyl acetate, methanol, DCM, cyclohexane and hexane.

The objective here was to identify the solvent that gives the best recovery, acceptable chromatographic performance and high sensitivity for the widest range of compounds. For this evaluation, several compounds belonging to different chemical classes were used, including mono-aromatics, terpenes, cyclic alkenes, PAHs and heterocyclic compounds. The compounds selected cover a wide range of retention properties and volatilities. The results are graphically depicted in **Figure 2.2**, where the internal standard corrected peak areas are plotted for each of the target compounds following dilution with the respective solvents. From the results it is clear that the mid-polar solvent DCM was most suitable, since it gave the best recoveries for most of the compounds. The TDO samples were highly soluble in DCM, and this solvent is also well suited for GC injection and provided the best chromatographic performance. Thereafter, in order to minimise undesired system contamination, an optimal dilution factor together with an adequate injector split ratio had to be determined. The goal was on the one hand to obtain adequate sensitivity for the compounds of interest, and on the other to avoid unwanted contamination. With the injector split ratio kept constant at 1:50, different dilution ratios (1:20, 1:50 and 1:100) were evaluated. As it was found that a 1:100 dilution still provided adequate sensitivity, this ratio was selected in order to avoid contamination issues. Thereafter the injector split was optimised (described in **Section 2.3.2**) and 1:20 was found to be optimal.

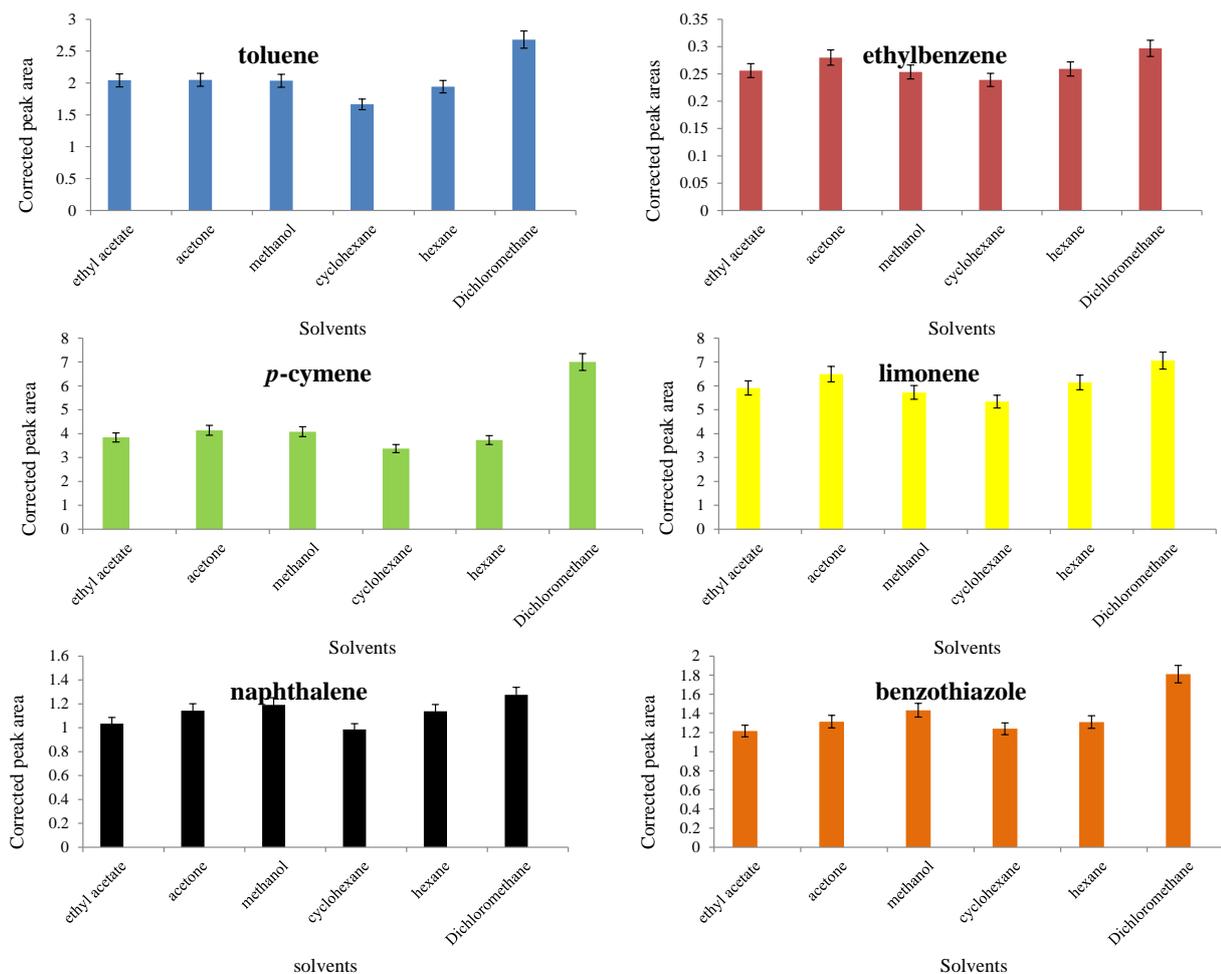


Fig. 2.2. Internal standard corrected peak areas for selected TDO constituents following dilution (1:50) in a range of solvents. Error bars indicate the standard deviation of duplicate injections.

2.3.2. Optimisation of GC-MS conditions

For the separation of TDO constituents, non-polar capillary columns were selected. As a first step, column efficiency was evaluated, since this is an important consideration in light of the complexity of the sample. For this, two columns were used: a long, conventional 60 m × 0.25 mm i.d. × 0.25 μm d_f Xti-5 column and a narrow-bore alternative, a 60 m × 0.18 mm × 0.10 μm Rxi-5SilMS column. It was clear that the more efficient 0.18 mm column, which also offered faster analyses due to the higher optimal mobile phase linear velocity (29.7 cm/sec), provided better performance for this application. The performance of this column was evaluated in terms of its peak capacity, defined as the maximum number of peaks that can be theoretically separated on a column under given chromatographic conditions [21]. The peak capacity was determined as a function of oven ramping rate, calculated using equation 2.1 below:

$$n_c = 1 + \frac{t_g}{w_{av}} \quad 2.1$$

Where n_c is the peak capacity, t_g denotes the gradient time (the time of the oven temperature programme) and w_{av} the average peak width at baseline. The average peak width was obtained by manual integration of the following major compounds; toluene, 4-vinylcyclohexene, ethylbenzene, *p*-xylene, *m*-xylene, styrene, cumene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethylbenzene, 2-ethyltoluene, 1,2,4-trimethylbenzene, α -methylstyrene, 4-methylstyrene, 1,2,3-trimethylbenzene, *m*-cymene, *p*-cymene, *dl*-limonene, indene, terpinolene, naphthalene, benzothiazole, 1,4-dimethylnaphthalene, 2,6-dimethylnaphthalene and biphenyl. Oven ramping rates of 5.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0 and 0.7°C/min were evaluated using starting and end temperatures of 40°C and 280°C, respectively. The results are presented in **Figure 2.3**.

A maximum peak capacity of 1060 was obtained at an oven ramping rate of 0.7°C/min. From a practical point of view, however, this resulted in an unrealistically long analysis time (352 min). Therefore, this slow ramping rate was used up to 104°C as it was found that most compounds of interest elute before this temperature. A ramp rate of 10°C/min to 280°C was subsequently used to elute high-boiling compounds. Using this temperature programme, the analysis time was reduced to 119 min. Although still long, this is acceptable for routine analysis and warranted by the complexity of the oil. In terms of injection, splitless injection proved to be unsuitable due to column overloading observed for many high-level constituents. Split injection using various split ratios (1:150, 1:100, 1:50 and 1:20) was therefore evaluated. The lower split ratio of 1:20 provided better sensitivity and was used for all further analyses.

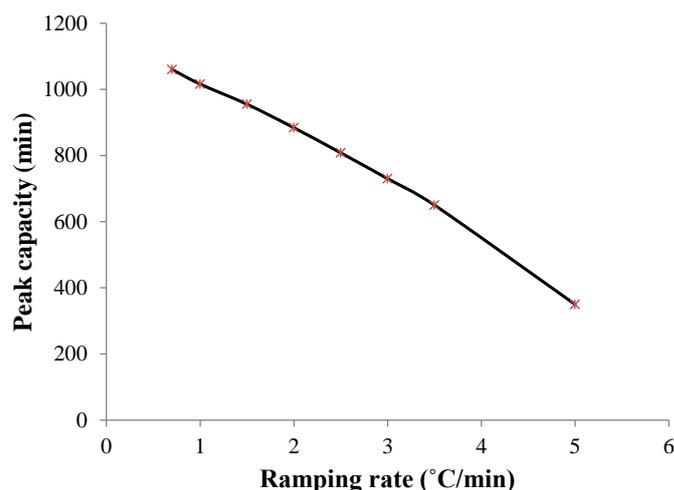


Fig. 2.3. Plot of peak capacity as a function of oven ramping measured for TDO constituents on a 60 m × 0.18 mm i.d. × 0.10 μm d_f Rxi-5 SilMS column. Carrier gas flow rate: 1.20 mL/min (constant flow). The GC oven temperature was programmed as follows: 40°C (held for 2 min) ramped by 5.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0 and 0.7°C/min respectively until 280°C.

2.3.3. Identification of TDO constituents

Identification of compounds in a complex mixture such as TDO, which can contain in the order of hundreds of organic molecules [22], is challenging. Absolute, unambiguous identification is only possible by comparing retention times and mass spectra with authentic reference standards. For compounds for which standards were available this was used as basis for identification. However, for a large number of compounds standards were not available and for those, tentative identification was performed using mass spectra and retention indices. For MS identification the mass spectral data obtained for the separated compounds were compared with commercial MS databases (NIST and Wiley libraries). Retention indices were calculated relative to n-alkanes (C₇–C₄₀) and compared with reported literature values [23–28] and other cited references as in **Table 2.1**. Retention indices were calculated using van den Dool and Kratz retention index method on a non-polar column [29–31]:

$$RI = 100 \left[n + \left(\frac{t_{rx} - t_{rn}}{t_{rN} - t_{rx}} \right) \right] \quad 2.2$$

In this equation, RI denotes the retention index, n is the number of carbon atoms in the smaller n-alkane, N is the number of carbon atoms in the larger n-alkane and t_r is the retention time. The combination of these two complementary identification strategies has been used extensively in

literature [32] and is generally accepted to provide accurate information, albeit still ‘tentative’. Literature retention index values for the relevant column stationary phase were obtained from the references indicated in **Table 2.1**. A tolerance (Δ RI) of 20 as maximum difference between the calculated and published RI values was accepted for tentative confirmation of identity.

The compounds identified as outlined above in two TDO samples are presented in **Table 2.1**. **Figures 2.4** and **2.5** show typical total ion chromatograms (TIC’s) for the two samples. The chromatograms have each been split into 4 parts for the sake of clarity. From **Table 2.1** and **Figures 2.4** and **2.5**, it is evident that the TDO samples contain a large number of compounds that vary significantly between the two samples. This underlines the necessity for a high-efficiency and robust analytical method. The chromatographic performance of the optimised GC method on the 60 m, 0.18 mm i.d. column is also evident. The strategies outlined above allowed for the identification or tentative identification of 81 compounds in TDO1, and 84 compounds in TDO2, respectively. This represents a significant improvement in the number of compounds tentatively identified in TDO in literature reports, which are typically in the order of 10-20 compounds [14,17]. This can largely be ascribed to the improved separation obtained under optimised conditions on the column used here. *dl*-Limonene was one of the major compounds identified in both samples. The isomers of limonene were not resolved on the apolar column used here. For the separation of these isomers, a chiral column [33] or comprehensive two-dimensional gas chromatography (GC \times GC) [34] may be used. Even with the high-efficiency column and slow rate ramp used, problematic pairs such as *dl*-limonene and indane, *p*- and *m*-xylene and *o*-xylene and styrene were not completely resolved. Nevertheless, these compounds could be accurately quantified, in the case of co-eluting compounds by extracting unique *m/z* mass fragment ions (see further).

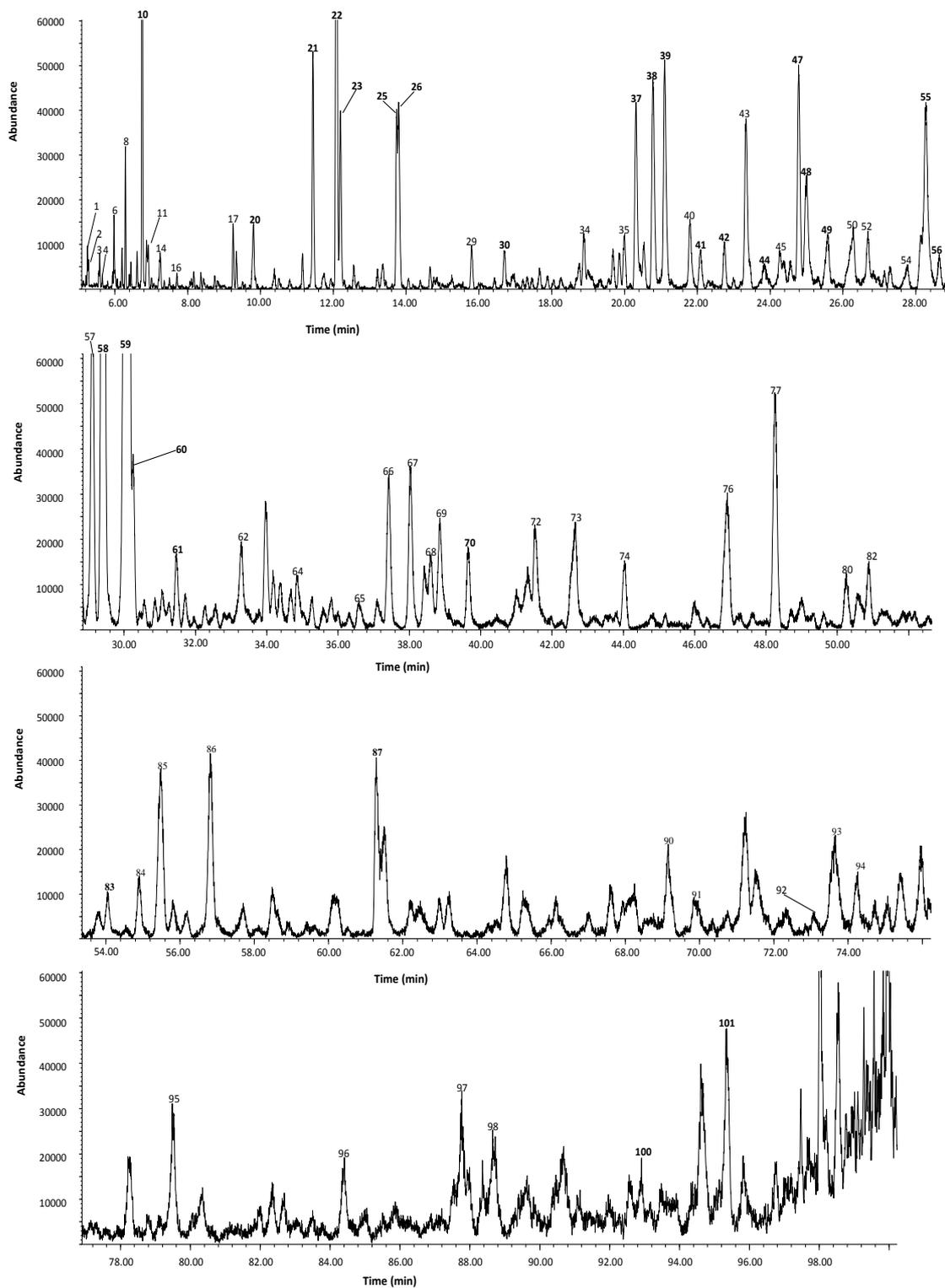


Fig. 2.4. Total ion chromatogram of TDO sample 1 obtained under optimised conditions. Peak numbers correspond to **Table 2.1**. Sample preparation: solvent dilution in DCM (1:100). For chromatographic details, refer to **Section 2.2.2.4**.

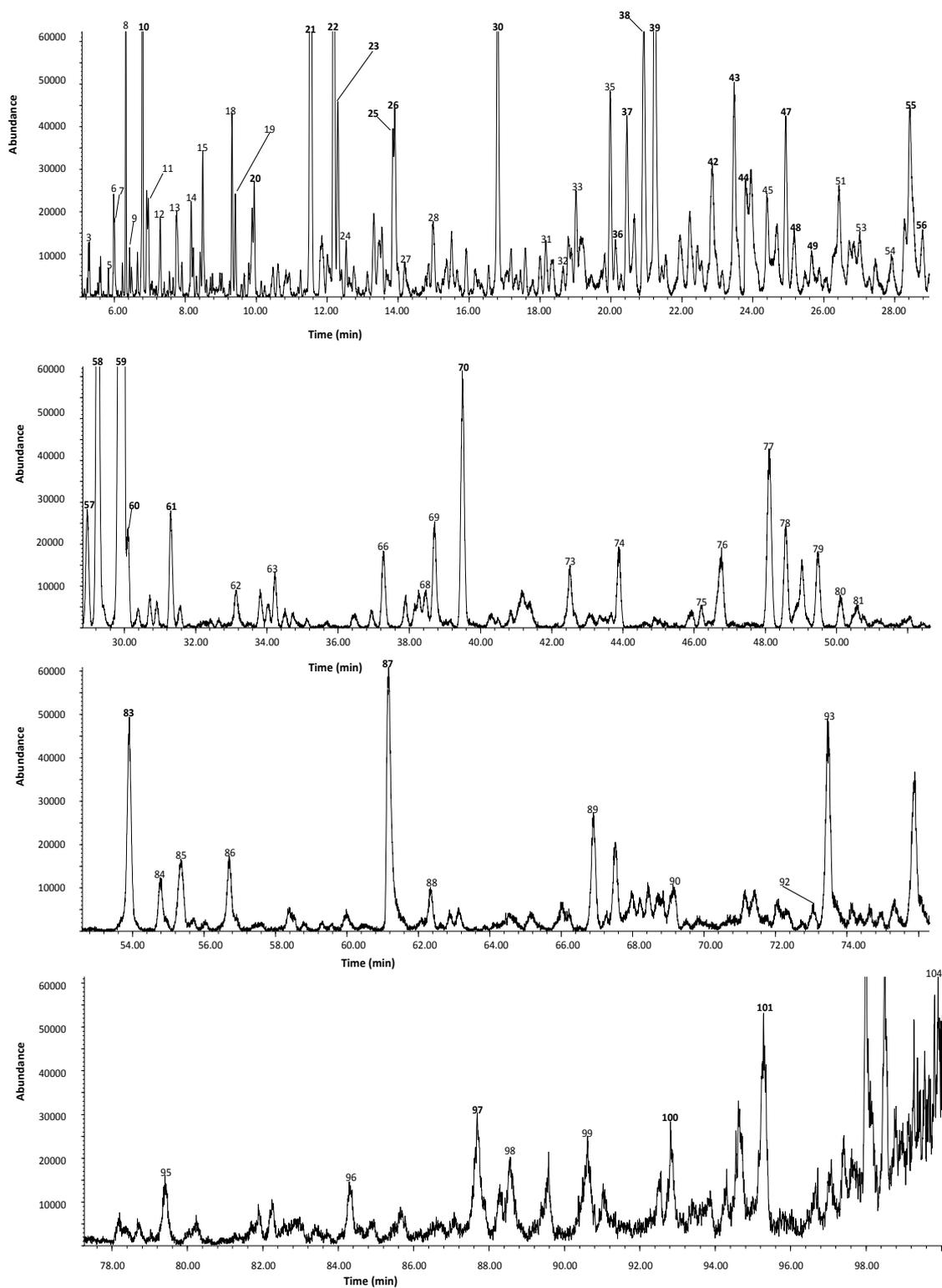


Fig. 2.5. Total ion chromatogram of TDO sample 2 obtained under optimised conditions. Peak numbers correspond to **Table 2.1**. Sample preparation: solvent dilution in DCM (1:100). For chromatographic details, refer to **Section 2.2.2.4**.

Table 2.1

Compounds identified in the two TDO samples using solvent dilution and liquid-liquid back extraction methods. Quantification was only done for the solvent dilution method using the internal standard method (for details, refer to **Section 2.3.4**). Concentrations given in mg/L represent values in the undiluted oil.

Peak #	t_R (min)	Class	Compound	RI _{Calc.}	RI _{Lit.}	Δ RI	TDO1 (g/L)	TDO2 (g/L)	References
1	5.23	<i>al</i>	2-Heptene(<i>E</i>) ^a	707	707	0	nq	nq	[35]
2	5.25	<i>al</i>	2,4,4-Trimethyl-1-pentene ^a	708	705	3	nq	nq	[36]
3	5.58	<i>al</i>	Methylcyclohexane ^a	718	725	7	nq	nq	[24]
4	5.61	<i>al</i>	2,4,4-Trimethyl-2-pentene ^a	719	722	3	nq	nq	[36]
5	5.83	<i>al</i>	Ethylcyclopentane ^a	726	733	7	nd	nq	[24]
6	5.93	<i>ox</i>	4-Methyl-2-pentanone ^{ab}	730	730	0	nq	nq	[37]
7	5.98	<i>ox</i>	3-Methyl-2-pentanone ^a	731	734	3	nq	nq	[38]
8	6.29	<i>al</i>	4-Methylcyclohexene ^a	741	740	1	nq	nq	[36]
9	6.43	<i>al</i>	1-Ethylcyclopentene ^a	746	754	8	nd	nq	[25]
10	6.76	<i>ma</i>	Toluene ^{ab}	756	756	0	2.18	3.03	[32]
11	6.88	<i>al</i>	3-Methyl-1-cyclohexene ^a	760	756	4	nq	nd	[39]
12	6.91	<i>al</i>	1-Methyl-cyclohexene ^a	761	763	2	nd	nq	[39]
13	6.96	<i>al</i>	2,2,5-Trimethylhexane ^a	771	789	18	nd	nq	[40]
14	7.25	<i>al</i>	3-Methyl-3-ethylpentane ^a	772	774	2	nq	nd	[38]
15	7.55	<i>al</i>	2-Methyl-1-heptene ^a	782	783	1	nd	nq	[35]
16	7.64	<i>ox</i>	Cyclopentanone ^{ab}	793	794	1	nq	nd	[24]
17	9.25	<i>al</i>	1,3-Dimethylcyclohexene ^a	817	825	8	nq	nd	[36]
18	9.57	<i>al</i>	1,4-Dimethyl-1-cyclohexene ^a	822	825	3	nd	nq	[36]
19	9.79	<i>al</i>	Propyl-cyclopentane ^a	825	836	11	nd	nq	[24]
20	9.81	<i>al</i>	4-Vinylcyclohexene ^{ab}	826	838	12	0.404	<LOQ	[24]
21	11.44	<i>ma</i>	Ethylbenzene ^{ab}	849	849	0	0.754	4.26	[41]
22	12.09	<i>ma</i>	<i>p</i>-Xylene ^{ab}	860	861	1	3.92	2.95	[29]
23	12.2	<i>ma</i>	<i>m</i>-Xylene ^{ab}	862	864	2	0.813	0.775	[29]
24	12.53	<i>al</i>	3-Methyl-octane ^a	865	867	2	nd	nq	[35]
25	13.74	<i>ma</i>	Styrene ^{ab}	885	886	1	0.895	0.736	[42]
26	13.8	<i>ma</i>	<i>o</i>-Xylene ^{ab}	886	889	3	0.967	1.16	[29]
27	13.93	<i>ox</i>	Cyclohexanone ^{ab}	896	897	1	nq	nq	[24]
28	15.00	<i>ox</i>	2-Methyl-2-cyclopenten-1-one ^{ab}	901	912	11	nq	nd	[26]
29	15.79	<i>al</i>	2,5-Dimethyl-3-vinyl-1,4-hexadiene ^a	908	908	0	nq	nd	[43]
30	16.7	<i>ma</i>	Cumene ^a	916	919	3	<LOQ	<LOQ	[29]
31	18.65	<i>al</i>	Tricylene ^a	932	925	7	nd	nq	[44]
32	18.89	<i>ter</i>	β -Pinene ^a	934	934	0	nd	nq	[45]
33	19.03	<i>ter</i>	Camphene ^a	935	943	8	nd	nq	[46]
34	19.84	<i>ma</i>	Isocumene ^a	942	943	1	nq	nd	[47]
35	19.98	<i>ma</i>	Propylbenzene ^a	943	958	15	nd	nq	[47]
36	20.3	<i>ter</i>	Camphene ^a	947	947	0	nd	nq	[46]

Peak #	t_R (min)	Class	Compound	RI _{Calc.}	RI _{Lit.}	Δ RI	TDO1 (g/L)	TDO2 (g/L)	References
37	20.78	ma	3-Ethyltoluene ^a	952	958	6	1.32	1.27	[29]
38	21.13	ma	4-Ethyltoluene ^a	954	960	6	1.75	2.83	[29]
39	21.69	ma	1,3,5-Trimethylbenzene ^a	960	967	7	0.597	0.479	[29]
40	21.98	ma	1,3,4-trimethylbenzene ^a	961	969	8	nq	nd	[47]
41	22.75	ni	Aniline ^{ab}	967	958	9	nq	nd	[48]
42	22.85	ma	2-Ethyltoluene ^{ab}	968	972	4	0.436	0.892	[49]
43	23.34	ter	α -Pyronene ^a	972	980	8	nq	nd	[50]
44	23.62	ni	Benzonitrile ^{ab}	975	981	6	nq	nq	[51]
45	23.96	ma	3-Menthene ^a	977	987	10	nq	nq	[52]
46	24.41	ox	Phenol ^b	981	981	0	nq	nd	[53]
47	24.78	ma	1,2,4-Trimethylbenzene ^a	984	985	1	1.63	1.81	[54]
48	25.01	ma	α -Methylstyrene ^a	986	987	1	0.444	<LOQ	[24]
49	25.58	ma	4-Methylstyrene ^a	991	980	11	0.404	<LOQ	[55]
50	26.2	ter	3-Carene ^a	997	1000	3	nq	nd	[56]
51	26.43	al	2,6-Dimethyl-2-trans-6-octadiene ^a	998	988	10	nd	nq	[57]
52	26.68	al	3,3-Dimethyl-6-methylenecyclohexene ^a	1000	1001	1	nq	nd	[57]
53	27.01	ma	sec-Butylbenzene ^a	1003	1006	3	nd	nq	[29]
54	28.28	ter	<i>o</i> -Ocimene ^a	1011	1018	7	nq	nq	[44]
55	28.43	ma	1,2,3-Trimethylbenzene ^{ab}	1011	1016	5	4.82	2.09	[47]
56	28.65	ma	<i>m</i>-Cymene ^a	1013	1010	3	0.402	0.461	[58]
57	28.95	ma	<i>p</i> -Menthene ^{ab}	1016	1016	0	nq	nq	[36]
58	29.26	ma	<i>p</i>-Cymene ^a	1018	1020	2	0.459	1.29	[32]
59	29.97	ter	<i>dl</i>-limonene ^{ab}	1022	1025	3	11.7	11.8	[54]
60	30.05	ma	Indane ^a	1023	1015	8	0.732	0.252	[55]
61	31.31	ma	Indene ^{ab}	1031	1023	8	1.19	0.662	[55]
62	33.29	ma	<i>m</i> -Propyltoluene ^a	1042	1053	11	nq	nq	[59]
63	34.23	ma	3-Ethyl- <i>o</i> -xylene ^a	1048	1055	7	nq	nd	[60]
64	34.83	ox	<i>o</i>-Cresol ^{a,b}	1052	1052	0	nq	nq	[51]
65	35.28	ma	1-Methyl-2-propylbenzene ^a	1061	1075	14	nd	nq	[60]
66	37.27	ma	4-Ethyl- <i>o</i> -xylene ^a	1067	1078	11	nq	nq	[61]
67	37.4	ma	<i>o</i> -Cymene ^a	1068	1050	18	nd	nq	[62]
68	37.88	ma	1-Methylindan ^a	1072	1079	7	nq	nq	[29]
69	38.42	ma	5-Ethyl- <i>m</i> -xylene ^a	1075	1074	1	nq	nq	[62]
70	38.7	ter	α -Terpinolene ^a	1077	1063	14	1.36	1.40	[30]
71	38.92	ox	<i>p</i>-Cresol ^{a,b}	1078	1075	3	nq	nd	[51]
72	39.63	ma	<i>p</i> -Cymene ^a	1082	1087	5	nd	nq	[63]
73	42.56	ox	2,5-Xylenol ^{ab}	1101	1108	7	nq	nq	[64]
74	42.59	ma	1-Methyl-4-(1-methylpropyl)-benzene ^a	1101	1100	1	nq	nq	[29]
75	43.88	ma	1,2,4,5-Tetramethylbenzene ^a	1109	1109	0	nd	nq	[29]
76	46.77	ma	5-Methylindan ^a	1125	1135	10	nq	nq	[29]
77	48.03	ma	4-Methylindene ^a	1131	1141	10	nq	nq	[29]
78	48.57	ma	1-Methylindene ^a	1135	1124	11	nd	nq	[29]

Peak #	t_R (min)	Class	Compound	RI _{Calc.}	RI _{Lit.}	Δ RI	TDO1 (g/L)	TDO2 (g/L)	References
79	48.58	<i>ma</i>	3-Methylindene ^a	1138	1155	17	nd	nq	[65]
80	48.98	<i>ma</i>	1,2,4,5-Tetramethylbenzene ^a	1139	1140	1	nd	nq	[24]
81	50.88	<i>ma</i>	Pentylbenzene ^a	1148	1159	11	nq	nq	[24]
82	50.94	<i>ox</i>	2,3-Dimethylphenol ^{ab}	1148	1151	3	nq	nd	[26]
83	52.22	<i>ma</i>	Naphthalene ^{ab}	1165	1177	12	1.69	<LOQ	[51]
84	54.78	<i>ma</i>	1,3,5-Trimethylbenzene-2-ethenyl ^a	1177	1192	15	nq	nq	[27]
85	55.34	<i>ma</i>	1,2-Dimethyl-2,3-dihydro-1H-indene ^a	1179	1199	20	nq	nq	[27]
86	56.72	<i>ma</i>	2,2-Dimethyl-2,3-dihydro-1H-indene ^a	1186	1201	15	nq	nd	[27]
87	61.16	<i>su</i>	Benzothiazole ^{ab}	1206	1195	11	4.89	3.81	[66]
88	62.33	<i>ma</i>	4,6-Dimethylindan ^{ab}	1228	1235	7	nq	nq	[27]
89	66.89	<i>ma</i>	1,1-Dimethyl-1H-indene ^{ab}	1237	1238	1	nq	nq	[27]
90	68.66	<i>ox</i>	Caprolactam ^{ab}	1247	1244	3	nq	nd	[60]
91	69.86	<i>ni</i>	Phthalonitrile ^{ab}	1273	1204	17	nq	nq	
92	73.46	<i>pah</i>	2-Methylnaphthalene ^{ab}	1274	1281	7	nq	nq	[24]
93	73.55	<i>su</i>	2-Methylbenzothiazole ^{ab}	1277	1288	11	nq	nq	[62]
94	75.88	<i>pah</i>	1-Methylnaphthalene ^a	1287	1301	14	nq	nq	[62]
95	79.41	<i>ma</i>	1,1,3-Trimethylindan ^a	1307	1306	1	nq	nq	[27]
96	87.69	<i>ma</i>	1,2,3-Trimethylindene ^a	1354	1349	5	nq	nq	[27]
97	88.55	<i>pah</i>	Biphenyl ^{ab}	1359	1368	9	0.705	0.399	[29]
98	89.58	<i>su</i>	2,7-Dimethylbenzo(b)thiophene ^a	1361	1343	18	nq	nd	[67]
99	90.61	<i>pah</i>	1,3-Dimethylnaphthalene ^a	1381	1397	16	nq	nd	[62]
100	92.83	<i>pah</i>	2,6-Dimethylnaphthalene ^{ab}	1383	1390	7	0.524	<LOQ	[29]
101	95.27	<i>pah</i>	1,4-Dimethylnaphthalene ^{ab}	1423	1424	1	0.568	<LOQ	[29]
102	98.01	<i>su</i>	2,4-Dimethylquinoline ^b	1442	1454	12	nq	nd	[67]
103	98.49	<i>su</i>	1,2,3-Trimethyl-1,2-dihydro-2-quinoline ^b	1459	1470	11	nq	nd	[67]
104	100.43	<i>pah</i>	Acenaphthene ^a	1472	1472	0	nd	nq	[62]

Compounds for which standards were available are indicated in **bold**, ^acompounds identified in TDOs using solvent dilution method, ^bcompounds identified in TDOs using liquid-liquid back extraction, ^{ab}compounds identified using both solvent dilution and liquid-liquid back extraction, ^{nq}compounds detected in TDOs but were not quantified, ndcompounds not detected in TDOs. Compound classes: *al*-aliphatic compounds, *ox*-oxygen containing compounds, *ma*-mono-aromatic compounds, *ter*-terpenes, *ni*-nitrogen containing compounds, *su*-sulphur containing compounds, *pah*-polycyclic aromatic hydrocarbons, *LOQ*: limit of quantification, *LOD*: limit of detection.

Both TDO samples contain volatiles comprising several chemical classes ranging from aliphatics (*al*), oxygen containing compounds (*ox*) mono-aromatics (*ma*), terpenes (*ter*), nitrogen containing compounds (*ni*), sulphur containing compounds (*su*) and PAHs (*pah*) (as assigned in **Table 2.1**). Of the identified compounds, most were mono-aromatics (49), followed by aliphatic compounds (21).

2.3.4. Quantification of selected TDO constituents

For quantification of TDO constituents, two independent quantification methods were used to ensure accurate results: internal standard (IS) and standard addition methods. The standard addition method was used as the reference method to account for potential matrix effects and the results were compared to those obtained using the IS method to ensure accuracy of the latter method for use in routine analysis.

2.3.4.1. Internal standard method

The internal standard method entails the construction of calibration curves by plotting the relative peak area (peak area divided by IS peak area) for each compound to be calibrated against a known concentration of the analyte [68]. This graph is then used with relative peak area for the compound of interest in the sample to determine its concentration. In this way inaccuracy that might result from the sample preparation and injection processes are accounted for. Effective use of the IS method requires that the internal standard not be present in the sample, and that the compound(s) used as internal standards should be chemically as close as possible to the compound to be calibrated.

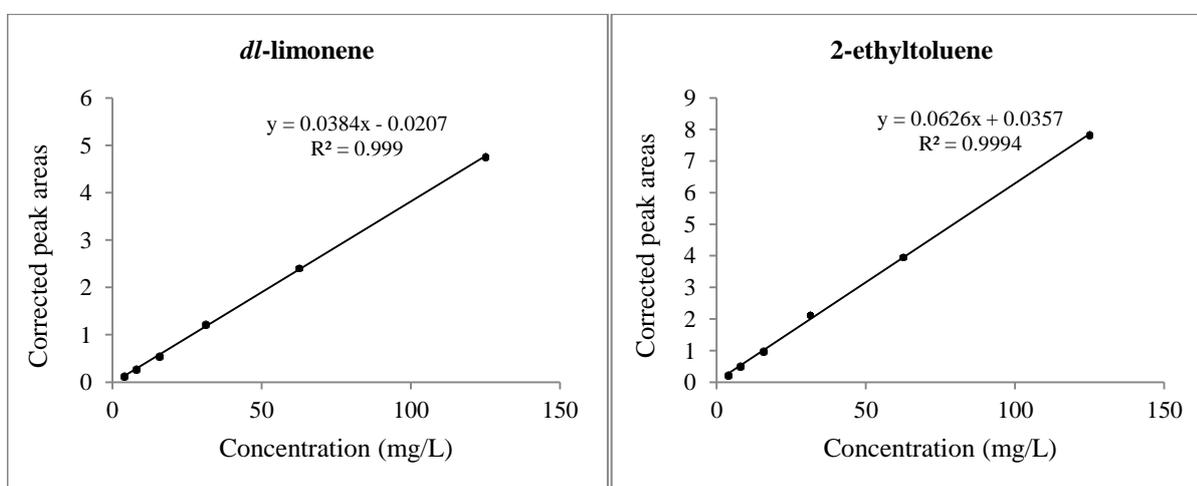


Fig. 2.6. Typical calibration curves obtained for toluene and 2-ethyltoluene using the internal standard method.

Due to the large chemical and physical diversity of TDO constituents, three different internal standards were used for quantification of selected target classes: deuterated toluene (toluene- d_8) was used for mono-aromatics, deuterated naphthalene (naphthalene- d_8) for PAHs and α -pinene

for terpene-like compounds. Internal standards were added during the solvent dilution step for the construction of calibration curves and for quantification in the samples. As an example, **Figure 2.6** shows typical IS calibration graphs obtained for limonene, with α -pinene as IS, and 2-ethyltoluene with deuterated toluene as IS. Note that quantification of compounds that partially co-eluted, such as for example *dl*-limonene (**59**) and indane (**60**) was achieved by using unique ions extracted for each compound. For example, for *dl*-limonene, ion 93 was used, and for indane, ion 117 was used. Since these ions were unique to each of these compounds, accurate quantification could be achieved even though they were not completely resolved chromatographically.

2.3.4.2. Standard addition method

The standard addition method is considered to be more accurate than the internal standard method as possible matrix effects are accounted for, and as the assumption is not made that the behaviour of a large number of analytes are the same as an IS [68]. Here the sample is spiked with known amounts of standard compounds at different concentration levels to obtain calibration graphs as shown in **Figure 2.7**. The concentration of a specific analyte is derived from this graph as the point where the graph intercepts the x-axis.

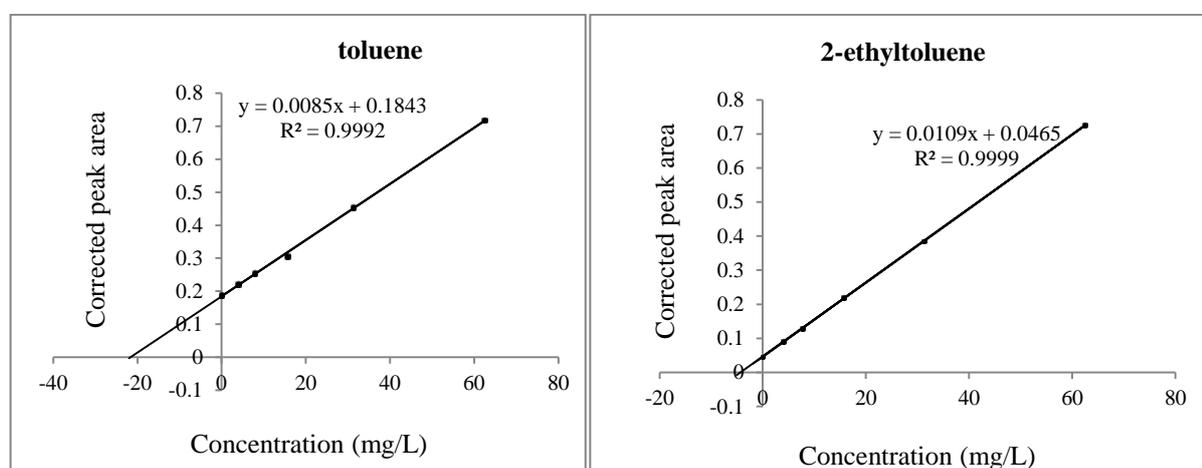


Fig. 2.7. Typical calibration curves obtained for toluene and 2-ethyltoluene using the standard addition method.

The comparative quantitative results obtained for the two methods are summarised in **Table 2.2**. Compounds such as toluene, *p*-xylene, *m*-cymene, *dl*-limonene and benzothiazole were present at high concentrations, whereas compounds such as cumene and *m*-cymene were not quantified as their levels were below their minimum quantification levels. Both quantitative methods were

found to be in good agreement, and based on this the IS method was deemed fit for routine analysis since the standard addition method, although potentially more accurate, is more labour intensive. Further method validation was therefore done using the internal standard method only.

2.3.5. Method validation

The optimised IS GC-MS method developed for analysis of TDOs was validated in terms of linearity, reproducibility, repeatability, sensitivity, recovery and robustness [69]. The results are summarised in **Table 2.2**. Repeatability was based on triplicate injections of a sample prepared daily on three different days. This was determined as inter-day repeatability as well as intra-day repeatability as tabulated in **Table 2.2**. For the majority of compounds, the %RSD values were between 1-5%. Linearity was evaluated from the calibration curves of the triple injections. Recoveries were determined using the spiked and unspiked TDO sample with the same amount of internal standards as also added in the calibration curve (averages of three determinations are reported). The LOD's and LOQ's were determined by measuring the peak-to-peak noise of the baseline around the target analyte (lowest calibration point, 3.91 mg/L, n = 3). The signal was manually measured as the peak height of the analyte. The signal to noise ratio was then used to calculate the concentrations that would give signal to noise ratios of 3 and 10:1, respectively. The applicability of the validated internal method has been demonstrated for the analysis of more than 20 TDO samples (results not shown).

Table 2.2

Quantitative data obtained for TDO sample 1 using the internal standard (IS) and standard (STD) addition methods. Concentrations are reported in mg/L in the oil. Validation data for the IS method are also summarised.

Internal standard method validation											
No:	Compounds	Ions (<i>m/z</i>)	STD addition (g/L in the oil)	ISTD. method (g/L in oil)	r^2	Inter-day repeatability		Intra-day repeatability		LOD (mg/L)	LOQ (mg/L)
						% RSD (<i>n</i> = 3)	% RSD (<i>n</i> = 9)	% Recovery ^a			
10	Toluene	91	2.17	2.18	0.9992	3.1	3.3	96	0.17	0.57	
20	4-Vinylcyclohexene	79	0.409	0.404	0.9994	3.0	2.2	109	0.27	0.91	
21	Ethylbenzene	91	0.771	0.754	0.9988	2.1	1.8	81	0.16	0.52	
22	<i>p</i> -Xylene	106	3.99	3.92	0.9989	2.1	1.8	95	0.17	0.57	
23	<i>m</i> -Xylene	106	0.850	0.813	0.999	2.8	3.7	96	0.2	0.67	
25	Styrene	104	0.905	0.893	0.9994	4.3	3.8	112	0.25	0.85	
26	<i>o</i> -Xylene	106	0.928	0.967	0.9991	3.4	3.7	90	0.21	0.71	
30	Cumene	105	0.377	0.379	0.9982	2.3	2.1	96	0.19	0.63	
37	3-Ethyltoluene	105	1.35	1.32	0.9986	3.2	3.5	107	0.26	0.88	
38	4-Ethyltoluene	105	1.72	1.75	0.9981	4.9	4.6	106	0.33	1.09	
39	1,3,5-Trimethylbenzene	105	0.622	0.597	0.9978	1.7	2.1	94	0.21	0.69	
42	2-Ethyltoluene	105	0.427	0.436	0.9994	2.2	1.6	107	0.35	1.18	
47	1,2,4-Trimethylbenzene	105	1.65	1.63	0.9984	2.3	2.1	107	0.42	1.39	
48	α -Methylstyrene	118	0.457	0.444	0.9981	1.3	0.8	101	0.41	1.38	
49	4-Methylstyrene	117	0.416	0.404	0.9987	4.4	3.6	98	0.51	1.70	
55	1,2,3-Trimethylbenzene	105	4.99	4.82	0.9986	4.7	3.9	90	0.41	1.36	
56	<i>m</i> -Cymene	119	0.403	0.402	0.9988	2.8	2.9	114	0.24	0.79	
58	<i>p</i> -Cymene	119	4.78	4.59	0.9988	2.9	3.2	103	0.34	1.14	
59	<i>dl</i> -Limonene	93	11.9	11.7	0.992	2.8	2.2	81	0.27	0.90	
60	Indane	117	0.707	0.733	0.9999	2.4	2.3	83	0.27	0.90	
61	Indene	115	1.25	1.19	0.9999	3.6	2.3	81	0.32	1.04	
70	α -Terpinolene	136	1.32	1.36	0.9996	1.7	4.6	93	0.54	1.79	
83	Naphthalene	128	1.61	1.70	0.9998	3.4	2.7	84	0.43	1.43	
87	Benzothiazole	135	4.79	4.89	0.9996	2.9	3.1	83	1.91	1.37	
97	Biphenyl	154	0.691	0.705	0.9998	3.5	2.8	85	0.35	1.17	
100	2,6-Dimethylnaphthalene	156	0.527	0.524	0.9999	0.9	15	92	0.55	1.84	
101	1,4-Dimethylnaphthalene	156	0.567	0.568	0.9999	2.5	2.7	86	0.34	1.14	

^a Recoveries were determined by spiking samples with known amounts of standards, and quantifying the spiked samples. The recovery was then calculated according to [68]: Average values of 3 measurements are reported. RSD: relative standard deviation, LOD: limit of detection, LOQ: limit of quantification, I.STD: internal standard.

2.3.5.1. Selected ion monitoring (SIM) method

During method validation, a range of additional TDO samples were analysed using the validated GC-MS method. For one of these samples, denoted TDO3, quantification was not successful using full scan mode. This oil differed extensively from the other samples, with several compounds found to be present in very low concentrations. This is due to the fact that the oil was obtained from a different pyrolysis process which was done under very low temperature conditions. For analysis of such samples, an alternative method using SIM detection was developed. Chromatographic conditions and sample preparation were otherwise the same as for the validated GC-MS IS method. Three ions that were uniquely characteristic for the compounds of interest were selected; two served as qualifiers and one as quantifier (**Table 2.3**). A calibration range of 0.12 to 2.91 mg/L (before solvent dilution) was used. Good linearity of $r^2 \geq 0.9998$ was achieved and this method was found to be sensitive enough to quantify the compounds present at low concentrations in TDO sample 3 (**Table 2.3**). The SIM method also proved to be suitable for the quantification of compounds below the quantification range of the scan method in additional samples (results not shown).

Table 2.3

Quantifier and qualifier ions used to quantify compounds in TDO 3 using the internal standard method in combination with SIM detection and quantitative values obtained using this method (reported as mg/L in the oil).

Peak no:	Compounds	Quantifier (m/z)	Qualifiers (m/z)	Start time (min)	TDO3 (mg/L)
	Toluene_d8	98	70, 100	5.01	I. STD1
10	Toluene	91	65, 92	6.73	70.23
20	4-Vinylcyclohexene	79	54, 108	9.6	77.25
21	Ethylbenzene	106	77, 91	11.43	80.01
22	<i>p</i> -Xylene	106	77, 91	12.12	291
23	<i>m</i> -Xylene	106	77, 91	12.12	36.13
25	Styrene	104	51, 78	13.66	182.3
26	<i>o</i> -Xylene	106	77, 91	13.91	66.15
30	Cumene	105	77, 105	16.55	43.17
	α-Pinene	136	93, 121	17.39	I. STD2
37	3-Ethyltoluene	105	77, 120	20.37	97.35
38	4-Ethyltoluene	105	77, 121	21.37	192
39	1,3,5-Trimethylbenzene	105	77, 122	22.37	31.69
42	2-Ethyltoluene	105	77, 120	20.37	51.34
48	α -Methylstyrene	118	78, 103	23.27	73.23
49	4-Methylstyrene	117	91, 115	25.5	63.14
55	1,2,3-Trimethylbenzene	105	77, 120	28.01	nq
56	<i>m</i> -Cymene	119	91, 134	28.59	35.34
58	<i>p</i> -Cymene	119	91, 134	28.59	97.14
60	Indane	117	68, 91	31.2	<LOD
61	Indene	115	89, 116	31.2	98.16
	Naphthalene_d8	136	108, 132	53.47	I. STD3
83	Naphthalene	128	102, 127	53.76	33.32
87	Benzothiazole	135	69, 108	61.28	<LOD
97	Biphenyl	154	76, 153	88.43	102
100	2,6-Dimethylnaphthalene	156	115, 141	92.01	30.23
101	1,4-Dimethylnaphthalene	156	115, 141	92.01	30.23

<LOD: compound below limit of detection, <LOQ: compound below limit of quantification, **bold**: internal standards.

2.4. Conclusions

In this contribution, efficient and robust GC-MS methods were developed and validated for the accurate quantitative analysis of TDO constituents in support of research aimed at improving tyre recycling through pyrolysis. A simple solvent dilution step found to give the most representative sample, whereas a liquid-liquid back-extraction procedure suitable for the analysis of polar TDO constituents was also developed. Using an optimised GC-MS method on a high-efficiency column, a total of 104 volatile organic compounds were identified and 33 of them unambiguously identified using authentic standards. Two quantitative methods based on internal standard and standard addition methods were evaluated, and gave comparable results. The internal standard method was selected for routine analysis and was successfully validated. 27 selected compounds ascribed with considerable market value were successfully quantified using the developed method. For TDO samples containing some compounds at trace levels, an additional GC-MS SIM method was also developed and successfully applied. The methods developed in this work will play an important role in pyrolysis research aimed at producing TDOs with high yields of target compounds from waste tyre crumbs for recycling purposes.

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CHAPTER 3

Analysis of tyre-derived oils by comprehensive two-dimensional gas chromatography (GC×GC)*

**This chapter is in preparation as a manuscript.*

Abstract

Tyre derived oil (TDO) is obtained by the pyrolysis of the rubber from waste tyres. These oils are very complex and their detailed chemical composition is far from fully understood. Therefore advanced analytical techniques are needed to further our knowledge with regards to the chemical make-up of TDOs. Comprehensive two-dimensional gas chromatography (GC×GC) is a powerful analytical technique increasingly being used for the analysis of such complex samples. GC×GC is characterised by very high peak capacities and unsurpassed resolution. This high performance is achieved by subjecting samples to two different separation mechanisms in one analysis. In this study the use of GC×GC with flame ionisation detection (FID), after using solid phase micro extraction (SPME) for sample preparation, is evaluated for TDO analysis. This was done using 27 representative reference standards commonly found in TDOs. For modulation, a novel consumable free single stage thermal modulator was utilised. It is illustrated that markedly improved separation compared to 1-dimensional (1D) GC is obtained.

The use of FID in the identification of compounds is limited since it requires the use of reference standards. Therefore GC×GC hyphenated to time-of-flight mass spectrometry (GC×GC-TOFMS) was also explored for the analysis of TDOs. This instrument makes use of a cryogenic modulator, which is most commonly used in GC×GC, but costly to operate. Sample preparation was performed using SPME and based on GC×GC-TOFMS analysis of two oils it was possible to collectively tentatively identify 137 compounds. In this study, a total of 36 new compounds were tentatively identified in TDO's. Identification was performed using both mass spectral database matching and retention index comparisons with literature values. Moreover, separation of several compounds co-eluting in 1D such as *m*-xylene and styrene as well as indane and *dl*-limonene was achieved. It is thus concluded that GC×GC-TOFMS is very well suited for the separation and identification of the constituents of complex TDO samples.

Keywords: Comprehensive two-dimensional gas chromatography (GC×GC), time-of-flight mass spectrometry (TOFMS), tyre derived oil (TDO), volatiles, selectivity, peak capacity, single stage thermal modulator, cryogenic modulator.

3.1. Introduction

Tyre derived oil (TDO) is the crude oil obtained from the pyrolysis of tyres (essentially rubber crumb). These complex liquids consist of hundreds of chemical compounds, many of which are of value and used in several industries; therefore their recovery from the oil is of interest. An analytical technique capable of providing very high resolving power is required to unravel the highly complex composition of these oils. Gas chromatography mass spectrometry (GC-MS) is one of the most well-known and widely used analytical techniques for analysis of volatiles and semi-volatiles since it allows for separation, identification and quantitation [1,2] of many individual compounds. However, even this technique often fails to provide sufficient resolving power to separate highly complex mixtures due to limited peak capacity. Comprehensive two-dimensional gas chromatography (GC×GC) is one of the most powerful separation techniques available nowadays for the analysis of very complex samples. The exceptional performance of GC×GC is achieved by subjecting a sample to two different and independent separation mechanisms in one analysis. An increased peak capacity is obtained via the combination of two chromatographic columns that ideally provide orthogonal separation [3]; in theory the peak capacity of GC×GC is equal to the product of peak capacities of the two respective separations.

In GC×GC, the two columns are connected via an interface known as a modulator, whose function is to continuously trap and refocus the effluent from the conventional first dimension (¹D) column and re-inject it as a narrow band onto the second dimension (²D) column, which is typically very short for rapid further separation [4,5]. The time taken to complete a single cycle of these events is known as the modulation period [6]. The most popular and widely used modulators are cryogenically cooled dual stage thermal modulators, as they provide good performance and reproducibility for a wide range of analytes and are easy to use and maintain. However, their high consumption of cryogenic agents such as liquid nitrogen renders them very costly to operate. Recently Górecki and co-workers [4,7] described and evaluated the use of a novel single stage thermal modulator as an attractive alternative that requires no cryogenics and offers consumable-free operation. This modulator consists of a trap and a narrow-bore fused silica restriction capillary installed between the ¹D column and a trap that retains the analytes at sub-oven temperatures. The trap is resistively heated to inject the compounds onto the second dimension, while the expansion of the heated gas, due to the presence of the restriction, briefly stops the flow from the first dimension. This modulator has been shown to provide extremely reproducible performance, thereby simplifying further data processing strategies such as multivariate data analysis [4,5,8]. The short length of the second

dimension column in GC×GC provides extremely fast separation [9], resulting in very narrow peaks with high signal-to-noise ratios. This however requires the use of a detector capable of very fast data acquisition rates. In practice, the two most common detectors used to meet this criterion are the flame ionisation detector (FID) and time-of-flight mass spectrometer (TOFMS).

The aim of this work was to evaluate applicability of GC×GC to TDO analysis. For this purpose, two instruments were used: a GC×GC-FID instrument equipped with the custom built single stage thermal modulator, and a commercial GC×GC-TOFMS instrument equipped with a dual stage cryogenic modulator. For both configurations, solid phase micro-extraction (SPME) was used for sample preparation as the technique allows for the extraction of a wide range of diverse analytes, in addition to being relatively easy to perform and sensitive. For GC×GC-FID a mixture of standards were injected and compounds in the oil were identified using retention time comparison. Some compounds not separated in 1D-GC were successfully separated using this technique. GC×GC-TOFMS was subsequently used for the detailed qualitative analysis of TDOs. Tentative identification was performed based on mass spectral database matching and using retention indices (RIs). A total of 137 compounds were tentatively identified in this manner. Both instrumental configurations were found to provide highly sensitive and reproducible performance, making them well suited for the analysis of TDOs.

3.2. Materials and methods

3.2.1. Chemicals and consumables

The two TDO samples analysed were collected from private companies and stored at 4°C until analysis. The oils were filtered using Hydrophilic Polyvinylidene Fluoride (PVDF) 0.45 µm pore size millex-HV syringe filters (Millipore, Billerica, MA, USA) prior to sample preparation. Authentic reference standards as well as dichloromethane (DCM) and 15 mL screw top vials were purchased from Sigma-Aldrich (Steinheim, Germany). The standards were 3-ethyltoluene (99%), α -methylstyrene (99.8%), 4-methylstyrene (98.6%), 4-ethyltoluene (95%), 2-ethyltoluene (99%), 1,3,5-trimethylbenzene (99.4%), 1,2,4-trimethylbenzene (98%), 1,2,3-trimethylbenzene (91.7%), *m*-cymene (99%), toluene (99.6%), 4-vinylcyclohexene (99.7%), ethylbenzene (99.9%), *p*-xylene (99.7%), *m*-xylene (99.6%), styrene (98.6%), *o*-xylene (99.8%), cumene (98.0%), *p*-cymene (99.5%), *l*-limonene (99%) & *d*-limonene (99%), indane (97.5%), indene (96.7%), α -terpinolene (99%), benzothiazole

(98.7%), naphthalene (99%), 1,4-dimethylnaphthalene (97.8%), and 2,6-dimethylnaphthalene (98.9%). A standard stock solution in DCM was prepared at a concentration of 5000 ppm for all compounds. The internal standards (ISs), α -pinene (99.8%), deuterated toluene (99.7%) and deuterated naphthalene (99%) were also from Sigma-Aldrich and a stock solution of 5000 ppm of each was prepared in DCM. Linear alkanes (C₇-C₄₀) used for retention index determination were obtained from Supelco (St. Louis, MO, USA). A 65 μ m poly(dimethyl)siloxane/divinylbenzene ((PDMS/DVB) SPME fiber (Supelco)) was used.

3.2.2. Sample preparation

3.2.2.1. Solid phase micro extraction (SPME) and liquid injection for GC \times GC-FID analyses

Prior to use, the SPME fiber was conditioned in a GC injection port at 240°C for 30 min under a split flow of 50 mL/min helium. The SPME fiber was then exposed in the headspace of the sample, 5 mL in a 15 mL vial, for 30 min at room temperature (23 \pm 1°C) with a stirring speed 300 rpm for extraction of volatile constituents from the headspace of the TDO sample. After extraction, the fiber was immediately desorbed in the GC injector at 240°C for 2 min in split mode with a split ratio of 1:10. For liquid injections, the standard mixture of 27 compounds was spiked with 40 μ L of each of the three ISs, resulting in a concentration of 20 ppm in the solvent (DCM), and 1 μ L was injected in split mode (split ratio 1:10). A detector temperature (FID) of 250°C was used and a makeup gas flow of nitrogen (45 mL/min) was used.

3.2.2.2. Solid phase micro extraction (SPME) for GC \times GC-TOFMS analyses

The sampling process was completely automated using a Gerstel (Mülheim an der Ruhr, Germany) auto-sampler. The fiber was first conditioned at 240°C for 30 min in the sampler's fiber conditioning station, followed by extraction of volatiles in the headspace of the oil (1 mL) at a temperature of 50°C at an agitation speed of 250 rpm. After extraction, the sampler inserted the fiber directly into the GC injector at 240°C for desorption during 10 min at a split ratio of 1:10.

3.2.3. Instrumental conditions

3.2.3.1. GC \times GC-FID instrumental conditions

Analyses were performed using an Agilent 6890 GC-FID (Agilent Technologies, Palo Alto, CA, USA) retrofitted with a custom built single stage thermal modulator. Modulation was

controlled by a capacitive discharge power supply for heating of the modulator trap. An apolar \times polar column set was used. The ^1D column was a 60 m \times 0.18 mm i.d. \times 0.10 μm d_f Rxi-5Sil MS supplied by Restek (Restek corp., Penn Eagle Park, CA, USA), while the ^2D column was a 0.6 m \times 0.15 mm i.d. \times 0.15 μm d_f Stabilwax (Restek). The PTV injector used was programmed from initial temperature of 40°C and ramped by 10°C/sec to 240°C directly before injection with a split ratio of 1:10. Hydrogen was used as carrier gas at a constant inlet pressure of 2.5 bar (linear velocity of 26.5 $\text{cm}\cdot\text{s}^{-1}$ under initial conditions). The oven GC temperature program was as follows: 40°C, held for 5.33 min, ramped at 0.7°C/min to 104°C, held for 0 min, ramped at 9.4°C/min to 240°C and held for 5.33 min. This oven temperature program was calculated using the Agilent method translation software with as input the initial conditions as described in Chapter 2. A modulation period of 5 sec was used with a discharge voltage of 30 V. The FID temperature was set to 240°C with H_2 flow of 30 mL/min and air, 350 mL/min and an acquisition rate of 100 Hz.

3.2.3.2. GC \times GC-TOFMS instrumental conditions

Analyses were performed on a LECO Pegasus 4D GC \times GC-TOFMS system (LECO Corp., St. Joseph, MA, USA). This instrument contains a dual stage cryogenic modulator housed in the primary GC oven. The columns used were for ^1D a 30 m \times 0.25 mm i.d. \times 0.25 μm d_f Rxi-5 Sil MS (Restek) and for ^2D , a 0.6 m \times 0.25 mm i.d. \times 0.25 μm d_f Stabilwax (Restek) housed the secondary GC oven. The primary oven temperature program started at 40°C, held for 2 min and ramped by 5°C/min to 240°C, held for 5 min. The offset temperature between the ^1D and ^2D ovens was +10°C. A modulation period of 5 sec was used. The split ratio was 1:10 and helium was used as carrier gas. The injector temperature was 240°C. For detection, TOFMS was used with electron ionisation at 70 eV with a scan range of 45-400 amu at 100 Hz.

3.2.4. Data processing

Data acquired from the GC \times GC-FID system were exported as csv format files and imported into MATLAB 2010a (Math Works Inc., Natick, MA, USA) for further processing using an in-house developed script to generate as output both contour plots and chromatograms. GC \times GC-TOFMS data analysis was performed using LECO ChromaTOF software (LECO). For identification, the spectral deconvolution algorithm of the software was used to obtain pure mass spectra and comparison of these with MS spectra in the NIST 2005 library (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used to create

a peak list of candidate compounds. Using the retention data for linear alkanes, RIs of the candidate compounds were calculated and manually compared to RIs reported in literature for further confirmation of identity.

3.3. Results and discussion

The qualitative and quantitative analysis of TDO constituents is important when designing pyrolysis processes for tyre recycling and also for the determination of market value chemicals. One dimensional GC-MS has extensively been used for this purpose. However, partial co-elution is unavoidable for such complex samples containing compounds with similar boiling points and/or polarity. This challenge cannot easily be resolved by 1-dimensional GC (1D-GC), since separation in a single column is governed by a fixed number of interactions. Notwithstanding the power of 1D-GC-MS in the analysis of pyrolysis oils, the resolving power of GC×GC, especially coupled with TOFMS, has become an attractive alternative to 1D-GC. In this work, the utility of GC×GC for TDO analysis is explored using two distinct instruments. In the first instance, a novel single-stage modulator capable of consumable-free operation will be evaluated with FID detection. Secondly, a commercial GC×GC instrument equipped with a dual-stage cryogenic modulator and hyphenated to a high-speed TOFMS detector was used for the detailed qualitative analysis of TDOs. For sample preparation, HS-SPME was used for extraction of volatile compounds. Since this study was focussed on the comprehensive analysis of TDO constituents, a mixed stationary phased SPME fiber (65 μm PDMS/DVB) was used.

3.3.1. Evaluation of GC×GC-FID analysis of TDOs using a new single-stage modulator

Initial work focussed on the evaluation of a recently developed single-stage modulator for TDO separation. Compared to the much more common commercial cryogenic modulators, this modulator offers the advantage of consumable-free, and therefore much cheaper, operation. This single stage thermal modulator functions by trapping analytes eluting from the first dimension at sub-oven temperatures. This is achieved by sandwiching a coated stainless steel trapping capillary between two ceramic pads connected to heat sinks (cooling fins) situated outside the oven, ensuring that the temperature between the pads is always lower than the oven temperature. A schematic drawing showing the main components of this modulator is presented in **Figure 3.1**.

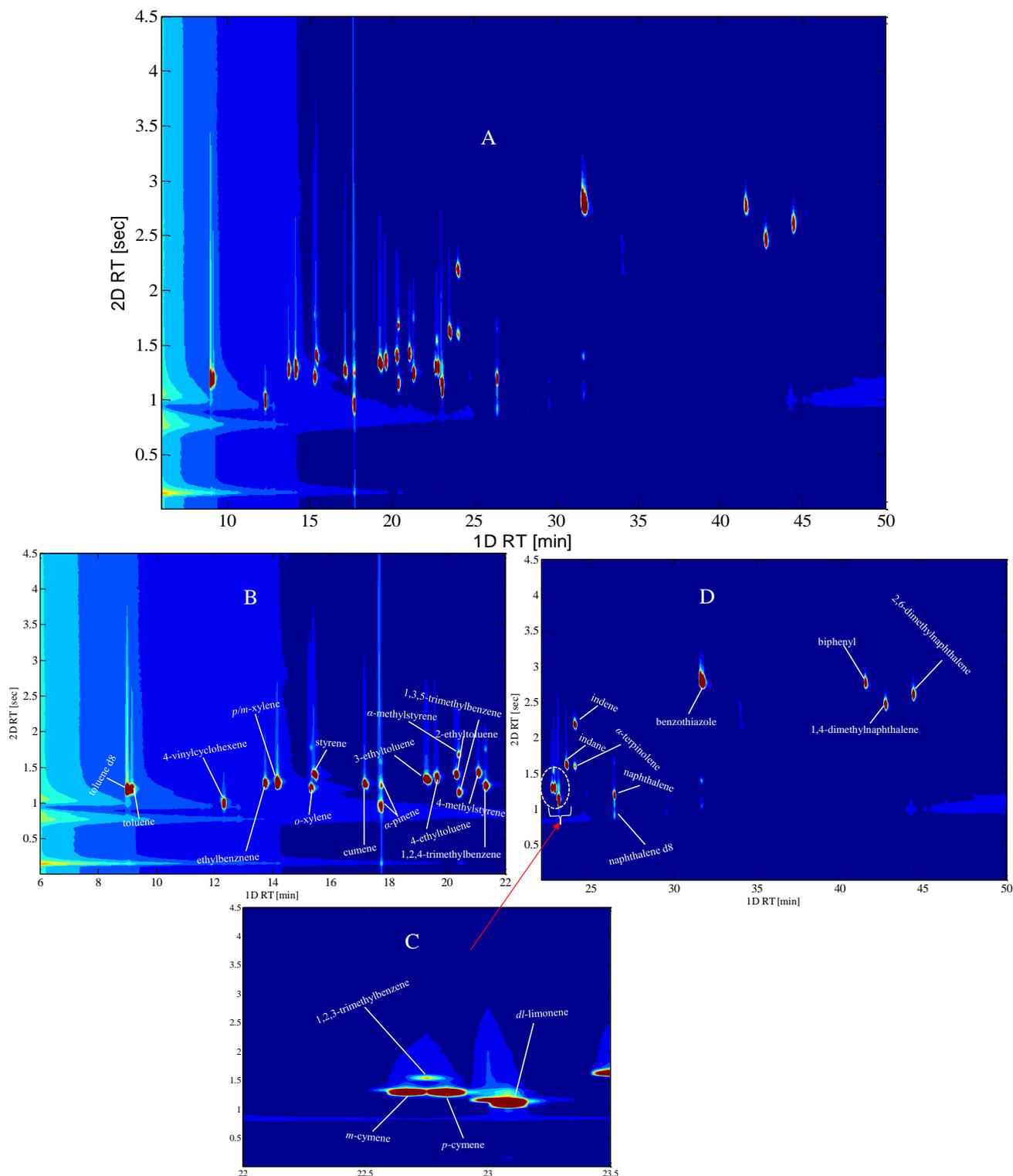


Fig. 3.2. GC×GC-FID contour plots showing TDO standards analysed by GC×GC-FID using the single-stage thermal modulator. (A) Shows the complete contour plot and (B-D) illustrate the separation of selected compounds.

Figure 3.3 illustrates that incomplete separation of styrene and *o*-xylene as well as *dl*-limonene and indane was obtained by 1D-GC. The top chromatograms illustrate the relevant parts of the 1D-GC-FID chromatograms, and the bottom contour plots the corresponding

parts of the GC×GC-FID contour plots. The incomplete separation of these compound in 1D-GC is a consequence of the fact that separation of compounds in an apolar column is only based on non-specific dispersion interactions. However, these compounds were separated in ²D based on differences in their polarities. For example, styrene was more retained in the ²D polar column. The same phenomenon was noticed in the case of *dl*-limonene and indane, which co-elute in 1D-GC because of their similar boiling points [11]. However, these compounds exhibit different polarities, allowing their separation in the ²D column. The separation of *d* and *l*-limonene was not achieved by either 1D or GC×GC separation, since these isomers have very similar physical properties. **Figure 3.3** therefore illustrates the benefits of improved selectivity offered by GC×GC separation, where compounds co-eluting in the first dimension are separated in two dimensions.

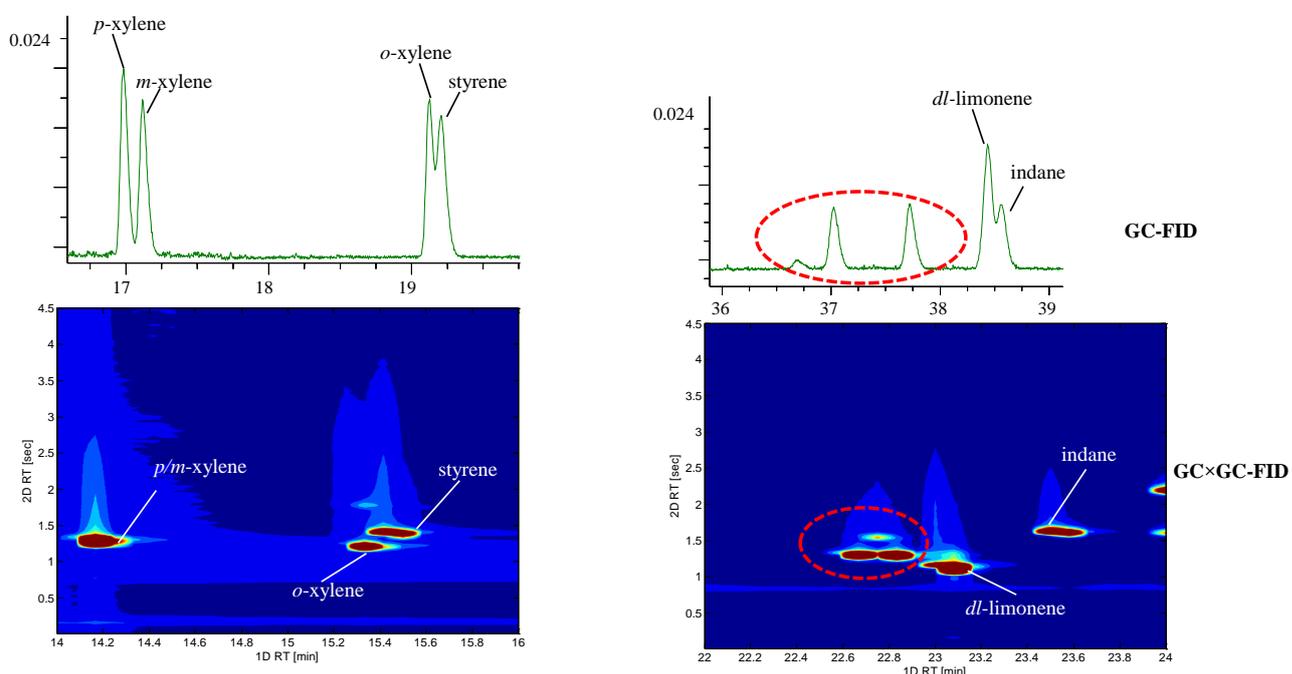


Fig. 3.3. Top: Selected parts of GC-FID chromatograms obtained for the analysis of TDO standard compounds. Bottom: corresponding contour plots obtained for the analysis of the same standards by GC×GC-FID.

Subsequently, TDO samples were analysed under the same conditions following HS-SPME extraction of the volatiles. An example of a contour plot obtained for one of the samples is presented in **Figure 3.4**. This figure once again confirms the complexity of the TDO sample, as well as the improved separation offered by GC×GC. Many compounds co-eluting in either dimension are resolved in the two-dimensional separation space provided by the combination of apolar and polar columns in GC×GC.

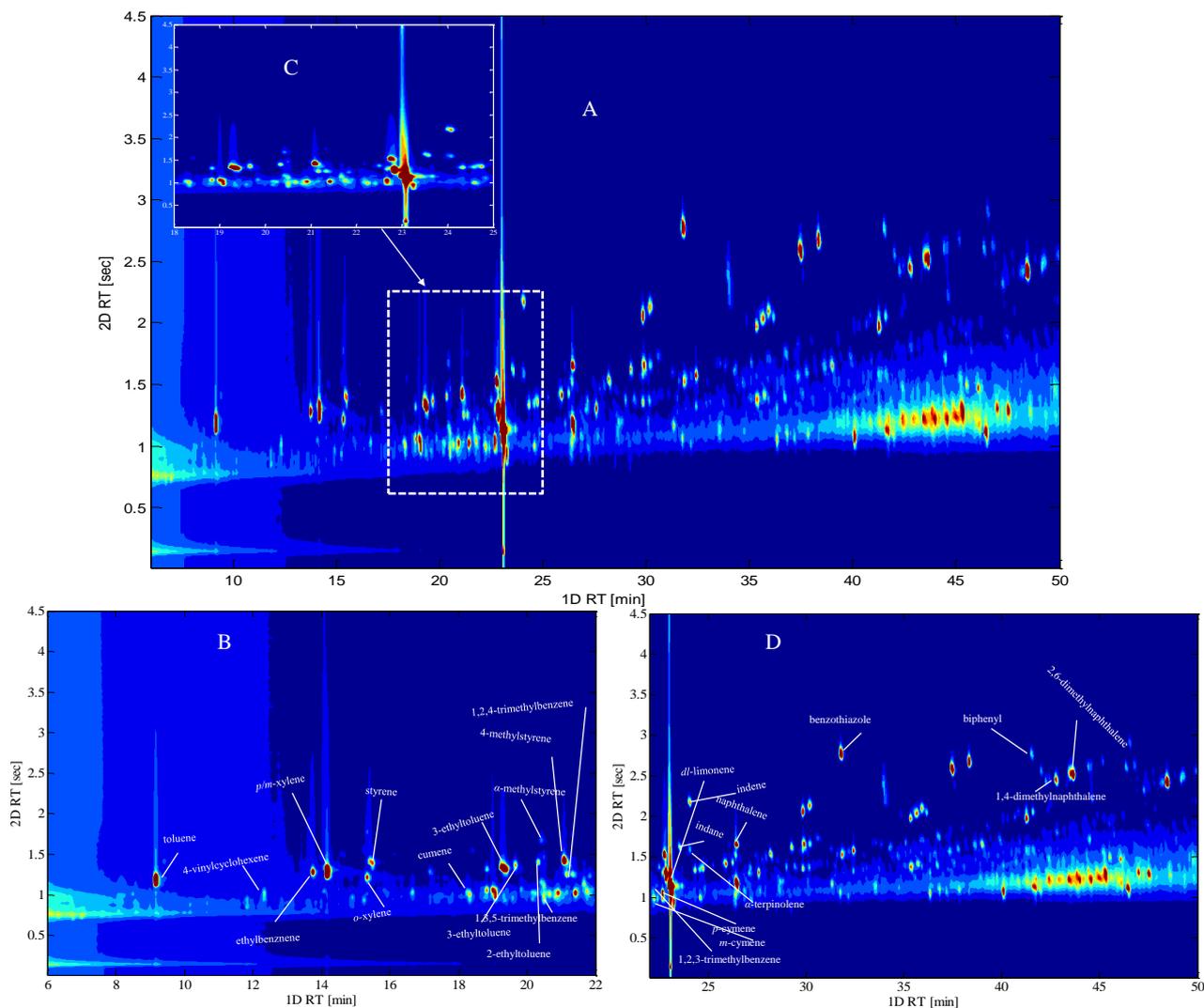


Fig. 3.4. Contour plots showing the results obtained for the HS-SPME-GC×GC-FID (apolar × polar column combination) analysis of a TDO sample. (A). Shows the complete contour plot and (B-D) present enlargements of sections of the contour plot highlighting the improved resolving power of the technique.

The column set used for GC×GC-TOFMS analyses was once again an apolar × polar combination. In contrast to the GC×GC-FID experiments, however, a conventional column (30 m × 0.25 mm i.d. × 0.25 μm d_f) was used in the first dimension, and a 0.25 mm i.d. wax column (0.6 m, 0.25 μm d_f) in the second dimension. The carrier gas for these experiments was helium, and a faster oven ramp rate, 5°C/min from 40 to 240°C, was used. The secondary oven was operated at an offset of +10°C compared to the oven and the modulation period was 5 sec. Under these experimental conditions, some first-dimension resolution was lost compared to 1D-GC-MS and GC×GC-FID data obtained on a 60 m × 0.18 mm i.d. column operated with a slow oven ramp. For example, the isomers *p*- and *m*-xylene (**28** and **29**) were not completely separated (**Figure 3.5**). However, similar separation of *o*-xylene (**34**) and

styrene (**35**), and *dl*-limonene (**71**) and indane (**72**) was obtained by GC×GC-TOFMS as observed for the GC×GC-FID system utilising a longer ¹D column (compare **Figures 3.3** and **3.5**). Furthermore, HS-SPME-GC×GC-TOFMS allowed identification of low-level compounds due to the combination of the inherent sensitivity of HS-SPME and solute band re-focusing by the modulator. The good performance of the cryogenic modulator used here is confirmed by the good peak shapes observed for most compounds with peak widths in the second dimension of ~300 msec.

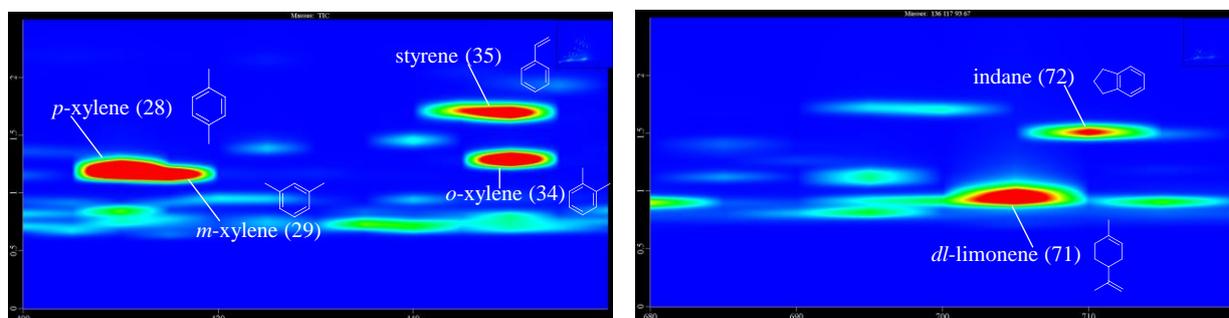


Fig. 3.5. Selected regions of the contour plots obtained for the GC×GC-TOFMS (apolar × polar column combination) analysis of a TDO sample. The plots illustrate the partial separation of *p*-xylene (**28**) with *m*-xylene (**29**), *o*-xylene (**34**) with styrene (**35**) and *dl*-limonene (**71**) with indane (**72**). Peak numbers correspond with **Table 3.1**.

3.3.2.1. Identification of compounds

For the tentative identification of the compounds in the TDOs, two complementary strategies were used. As a starting point the recorded mass spectra were compared with mass spectral databases. A minimum similarity of 70% was used. The high data acquisition rate of the TOFMS allowed deconvolution of mass spectra for partially co-eluting compounds, thereby providing clean mass spectra for most compounds. In addition to this, experimental retention indices were determined (relative to a homologous series of straight chain alkanes) and compared with literature values using the van de Dool and Kratz method [13,14], where a deviation maximum of 20 between calculated and literature values was used as a criterion for further confirmation of identity. The data of the acquired chromatogram were processed using a retention index method in the ChromaTOF software. In this manner, the combination of GC×GC separation with TOFMS detection enabled the tentative identification of 76 and 113 compounds in the two TDO samples analysed. These are listed in chronological order in **Table 3.1** and the corresponding contour plots are presented in **Figures 3.6** and **3.7**.

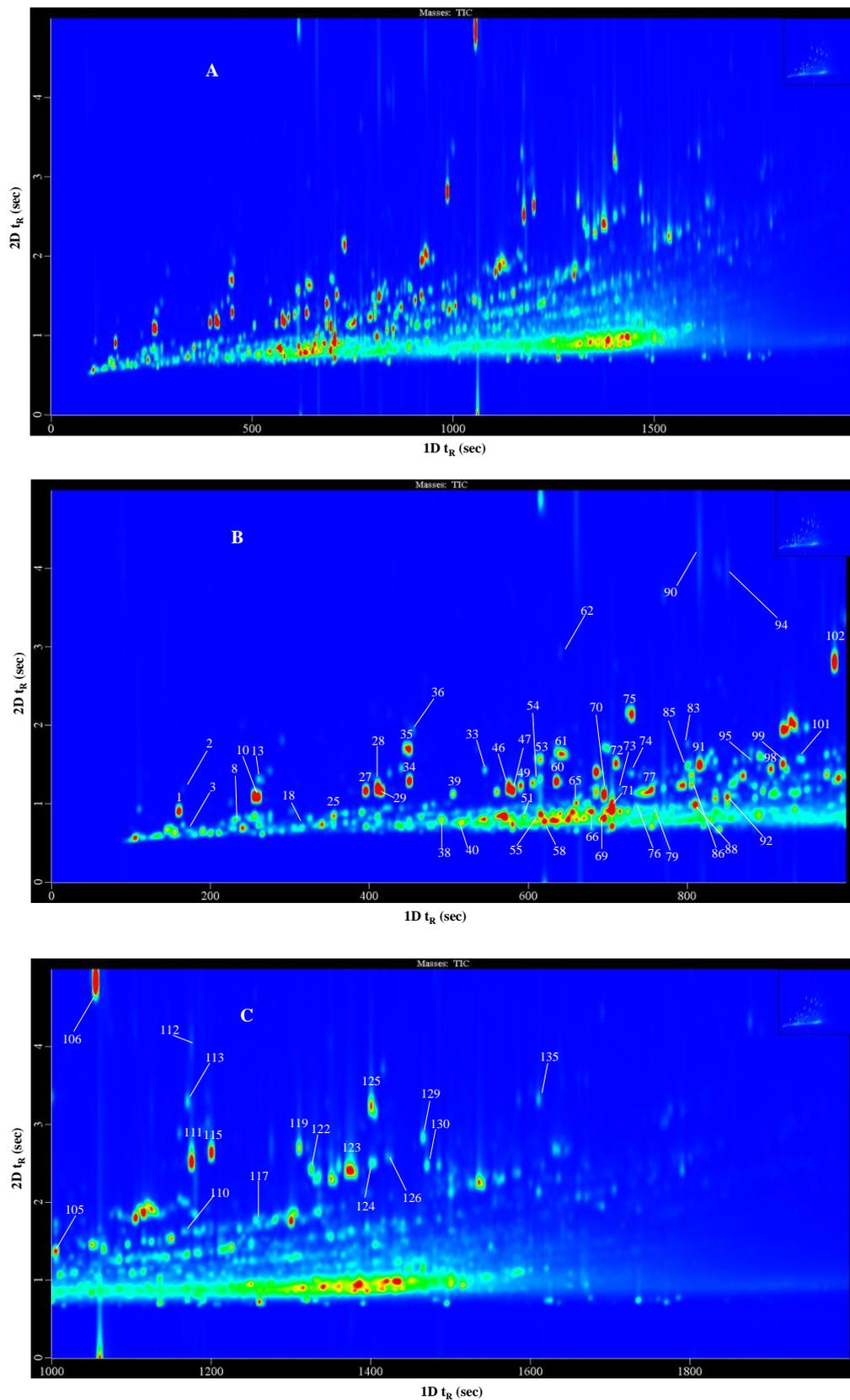


Fig. 3.6. (A) Contour plot obtained for the GCxGC-TOFMS (apolar × polar column combination) analysis of sample TDO1. (B) (0-1000 sec) and (C) (1000-2000 sec) show selected parts of the contour plot with the tentatively identified compounds numbered. Peak labels correspond to **Table 3.1**.

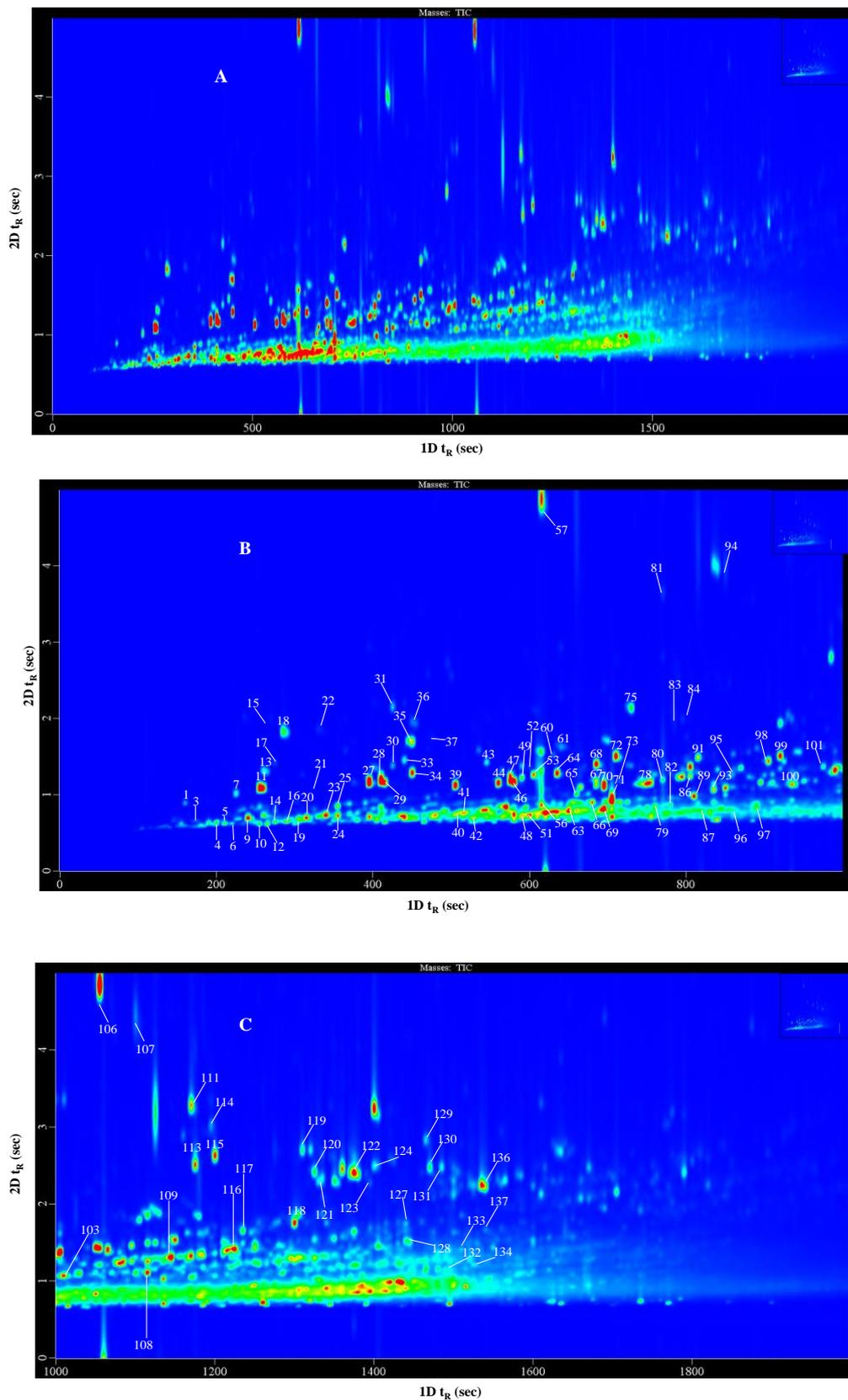


Fig. 3.7. (A) Contour plot obtained for the GCxGC-TOFMS (apolar \times polar column combination) analysis of sample TDO2. (B) (0-1000 sec) and (C) (1000-2000 sec) show selected parts of the contour plot with the tentatively identified compounds numbered. Peak labels correspond to **Table 3.1**.

Table 3.1

List of compounds tentatively identified in two TDO samples (TDO1 and TDO2) by GC×GC-TOFMS.

No:	Compound	$t_{r,D}^1$ (sec)	$t_{r,D}^2$ (sec)	RI_{calc}	RI_{lit}	TDO 1	TDO 2
1	Benzene	160	0.91	707	694	√	√
2	Thiophene	165	1.19	710	700	√	×
3	Cyclohexene	175	0.66	714	701	√	√
4	2,4,4-trimethyl-1-pentene	200	0.62	732	712	×	√
5	Methylcyclohexane	210	0.63	738	736	×	√
6	Vinylcyclopentane	210	0.66	738	737	×	√
7	Methyl isobutyl ketone	225	1.02	748	749	×	√
8	Bicyclo[2.2.1]hept-2-ene	230	0.8	751	755	√	×
9	1-Ethylcyclopentene	245	0.7	760	754	×	√
10	2,5-Dimethyl-2-hexene	250	0.64	763	751	×	√
11	Toluene	255	1.1	766	769	√	√
12	2-Methyl-heptane	255	0.61	766	763	×	√
13	3-Methyl-thiophene	260	1.32	770	767	√	√
14	2,2,4,4-Tetramethyl-pentane	265	0.62	772	775	×	√
15	Pentanenitrile	270	2.01	776	777	×	√
16	cis-1,3-Dimethylcyclohexane	275	0.64	779	786	×	√
17	3-Methyl-thiophene	275	1.42	779	779	×	√
18	Cyclopentanone	285	1.83	786	788	√	√
19	3-Methyl-1-ethyl-trans-cyclopentane	290	0.65	788	793	×	√
20	trans-1,3-Dimethyl-cyclohexane	310	0.67	800	808	×	√
21	tetrahydro-Thiophene	310	1.27	801	806	×	√
22	2-Methyl-pyridine	330	1.87	814	818	×	√
23	2,6-Dimethyl-heptane	345	0.62	822	828	×	√
24	Propylcyclopentane	350	0.67	825	836	×	√
25	4-Vinylcyclohexene	355	0.85	829	838	√	√
26	2-Methylcyclopentanone	365	1.58	835	836	√	√
27	Ethylbenzene	395	1.17	854	857	√	√
28	p-Xylene	410	1.28	863	864	√	√
29	m-Xylene	415	1.16	866	866	√	√
30	2,4-Dimethylthiophene	425	1.38	873	878	×	√
31	Hexanenitrile	425	2.15	873	874	×	√
32	trans-4-Nonene	440	0.68	882	884	×	√
33	2,3-Dimethylthiophene	440	1.46	882	893	×	√
34	o-Xylene	450	1.29	888	888	√	√
35	Styrene	450	1.7	889	889	√	√
36	Cyclohexanone	450	1.96	889	891	√	√
37	2-Ethylpyridine	475	1.75	904	901	×	√
38	2,5-Dimethyl-3-vinyl-1,4-hexadiene	490	0.8	912	914	√	×
39	Cumene	505	1.13	919	919	√	√
40	Camphene	515	0.77	924	928	√	√
41	n-Propylcyclohexane	520	0.71	926	926	×	√
42	3,6-Dimethyloctane	525	0.65	929	929	×	√
43	(Z)-1-Phenylpropene	545	1.43	940	958	√	√

No:	Compound	t_{rD}^1 (sec)	t_{rD}^2 (sec)	RI _{calc}	RI _{lit}	TDO 1	TDO 2
44	2-Propylthiophene	565	1.32	950	961	×	√
45	(-)- <i>trans</i> -Pinane	570	0.76	955	959	√	×
46	3-Ethyltoluene	575	1.19	956	955	√	√
47	2-Ethyl-5-methylthiophene	575	1.26	956	959	√	√
48	4-Methylnonane	580	0.66	958	958	×	√
49	4-Ethyltoluene	590	1.23	963	963	√	√
50	2-Methyl-1-octen-3-yne	595	0.95	970	974	√	×
51	3-Methylnonane,	595	0.66	966	962	×	√
52	Thiophene, 2-(1-methylethyl)	600	1.36	973	976	×	√
53	1,3,5-Trimethylbenzene	605	1.27	976	975	√	√
54	α -Myrcene	615	0.88	981	981	√	×
55	2,3,4-Trimethylthiophene	615	1.32	981	983	√	×
56	Aniline	615	1.09	981	977	×	√
57	Benzonitrile	615	4.88	983	984	√	√
58	2-Methyl-1-nonene	620	0.7	983	991	√	×
59	1-Butenylenecyclohexane	635	0.81	992	999	×	×
60	1,2,4-Trimethylbenzene	635	1.29	992	993	√	√
61	α -Methylstyrene	640	1.63	995	994	√	√
62	Benzofuran	640	2.93	996	993	√	×
63	2-Carene	655	0.91	1003	1003	×	√
64	3-Carene	660	0.86	1006	1005	×	√
65	<i>sec</i> -Butylbenzene	660	1.09	1006	1009	√	√
66	α -Terpinene	680	0.9	1017	1017	√	√
67	1,2,3-Trimethylbenzene	685	1.41	1020	1020	√	√
68	<i>m</i> -Cymene	685	1.12	1020	1021	√	√
69	<i>p</i> -1-Menthene	695	0.82	1025	1025	√	√
70	<i>p</i> -Cymene	695	1.13	1025	1025	√	√
71	<i>dl</i> -Limonene	705	0.93	1030	1030	√	√
72	Indane	710	1.51	1033	1034	√	√
73	<i>o</i> -Cymene	715	1.18	1036	1036	√	√
74	2,4-Dimethylstyrene	730	1.39	1044	1050	√	×
75	Indene	730	2.14	1044	1041	√	√
76	α -Ocimene	735	0.98	1047	1049	√	×
77	1-Methyl-2-propylbenzene	750	1.14	1055	1057	√	×
78	Butylbenzene	750	1.16	1055	1054	×	√
79	γ -Terpinene	760	0.96	1060	1060	√	√
80	2-Propyltoluene	770	1.2	1066	1063	×	√
81	Acetophenone	770	3.65	1067	1066	×	√
82	<i>p</i> -Mentha-3,8-diene	780	0.97	1071	1071	×	√
83	<i>o</i> -Toluidine	785	2.00	1074	1072	√	√
84	Octanenitrile	795	1.99	1080	1079	×	√
85	Dehydro- <i>p</i> -cymene	800	1.49	1082	1086	√	×
86	2-Ethyl- <i>m</i> -xylene	805	1.25	1085	1086	√	√
87	1-Methylindan	805	1.37	1085	1087	×	√
88	1-Methyl-4-(1-methylethylidene)-cyclohexene	810	0.99	1087	1088	√	×

No:	Compound	t_{rD}^1 (sec)	t_{rD}^2 (sec)	RI_{calc}	RI_{lit}	TDO 1	TDO 2
89	α -Terpinolene	810	0.98	1087	1087	×	√
90	<i>p</i> -Cresol	815	4.23	1092	1093	√	×
91	<i>p</i> -Cymene	815	1.49	1090	1090	√	√
92	2-Ethyl-1,3-dimethyl-benzene	840	1.34	1103	1100	√	×
93	1-Methyl-4-(1-methylpropyl)-benzene	850	1.09	1109	1112	×	√
94	2,6-Dimethyl-phenol	850	3.97	1111	1111	√	√
95	Prehnitol	870	1.36	1120	1122	√	√
96	3,7-dimethyl-decane	885	0.66	1128	1127	×	√
97	Hexylcyclopentane	905	0.72	1139	1136	×	√
98	2,3-Dihydro-4-methyl-1H-indene	905	1.45	1140	1138	√	√
99	2,3-Dihydro-5-methyl-1H-indene	920	1.51	1148	1140	√	√
100	Pentylbenzene	935	1.14	1156	1159	×	√
101	1,2,3,4-Tetrahydronaphthalene	945	1.57	1162	1162	√	√
102	Naphthalene	985	2.81	1185	1184	√	√
103	Benzene, (1,1-dimethylpropyl)	995	1.25	1190	1182	×	√
104	2,6-Dimethylundecane	1035	0.67	1213	1214	×	√
105	1,2,3,4-Tetrahydro-2-methylnaphthalene	1040	1.44	1216	1218	√	×
106	Benzothiazole	1055	4.84	1227	1227	√	√
107	Caprolactam	1100	4.42	1254	1253	×	√
108	Hexylbenzene	1115	1.11	1261	1261	×	√
109	Pentamethylbenzene	1145	1.48	1280	1282	×	√
110	1,2,3,4-Tetrahydro-5-methyl-naphthalene	1165	1.63	1291	1288	√	×
111	2-Methyl-benzothiazole	1170	3.28	1296	1288	√	×
112	2-Methyl-5-(1-methylethyl)-phenol	1175	4.05	1299	1294	√	×
113	1-Methyl-naphthalene	1175	2.51	1299	1297	√	√
114	2-Methylquinoline	1195	3.34	1311	1312	×	√
115	2-Methylnaphthalene	1200	2.63	1314	1314	√	√
116	1-Ethyl-1,2,3,4-tetrahydronaphthalene	1220	1.31	1325	1324	×	√
117	4-Phenylcyclohexene	1235	1.65	1334	1345	√	√
118	5-Ethyl-1,2,3,4-tetrahydro-naphthalene	1280	1.47	1362	1362	×	√
119	Biphenyl	1310	2.7	1380	1380	√	√
120	1-Ethyl-naphthalene	1330	2.29	1392	1393	×	√
121	2-Methyl-1,1'-biphenyl	1335	2.09	1395	1397	×	√
122	2,6-Dimethylnaphthalene	1350	2.3	1405	1407	√	√
123	1,4-Dimethylnaphthalene	1375	2.41	1422	1424	√	√
124	2,3-Dimethylnaphthalene	1400	2.49	1438	1438	√	√
125	2,4-Dimethylquinoline	1400	3.25	1439	1454	√	×
126	1,2-Dimethylnaphthalene	1425	2.56	1455	1452	√	×
127	2-(1-Methylethyl)naphthalene	1425	2.07	1455	1454	×	√
128	Curcumene	1465	1.15	1481	1480	×	√
129	Acenaphthene	1465	2.83	1482	1481	√	√
130	3-Methylbiphenyl	1470	2.48	1485	1488	√	√
131	4-Methylbiphenyl	1485	2.48	1495	1497	×	√

No:	Compound	$t_{r,D}^1$ (sec)	$t_{r,D}^2$ (sec)	RI_{calc}	RI_{Lit}	TDO 1	TDO 2
132	Cuparene	1505	1.24	1508	1505	×	√
133	1,1,4,5,6-Pentamethyl-2,3-dihydro-1H-indene	1515	1.48	1514	1522	×	√
134	Cadina-1(10),6,8-triene	1530	1.2	1524	1523	×	√
135	1H-Phenalene	1585	3.31	1562	1558	√	×
136	Fluorene	1610	3.31	1579	1579	×	√
137	3,3'-Dimethylbiphenyl	1635	2.31	1595	1594	×	√

$t_{r,D}^1$: retention time on the first dimension column, $t_{r,D}^2$: retention on the second dimension column, RI_{calc} : calculated retention index, RI_{Lit} : published retention index.

It is clearly illustrated (**Figures 3.6 and 3.7**) in these contour plots that the TDOs consist of large numbers of apolar compounds of which the majority are not separated according to their boiling points. However, some polar compounds are also present in high abundance. Several different classes of compounds were identified in the TDO samples analysed, including aliphatics, terpenes, mono-aromatics, PAHs and heterocyclic compounds. Some co-elution was still observed, for example for the aliphatic hydrocarbons which were not resolved in the apolar column. Further optimisation of the 1D separation should improve separation of these compounds, or alternatively a polar × apolar column combination can be used to improve the separation of these compounds [15]. By extracting unique fragmentation ions for particular classes of compounds, the group-type separation of these different chemical classes was confirmed (**Figure 3.8**). A schematic representation of the overall elution pattern observed is shown in **Figure 3.9**. Each of the classes of compounds identified is briefly addressed below.

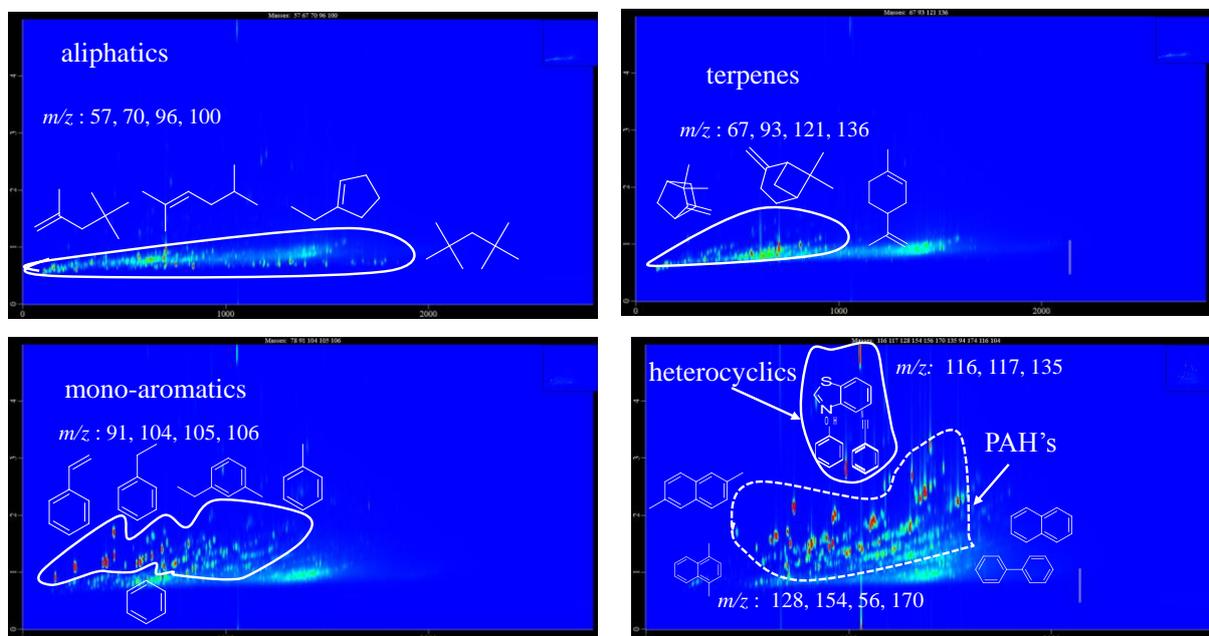


Fig. 3.8. Extracted ion contour plots obtained for the GC×GC-TOFMS analysis of a TDO sample showing the group type separation obtained for different classes of chemical constituents.

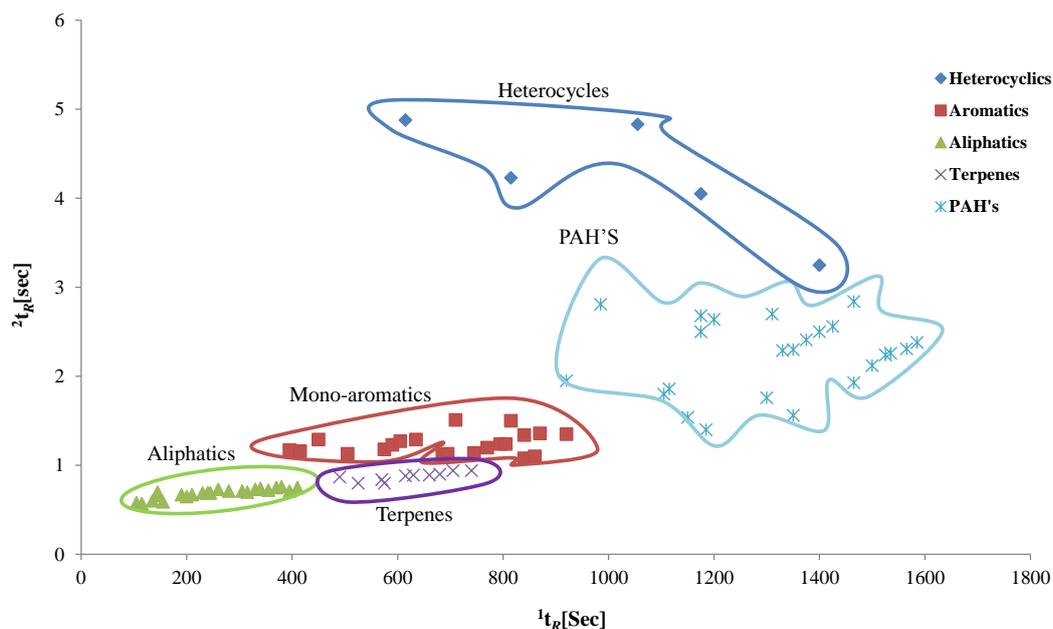


Fig. 3.9. Schematic representation of the elution pattern obtained for different chemical classes detected in TDO analysis by GC×GC-TOFMS.

Aliphatic hydrocarbons

Ions m/z 57, 70, 96 and 100 were extracted to visualise the distribution of aliphatic hydrocarbons in the TDO samples (**Figure 3.8**). A total of 21 compounds belonging to this class were identified. Aliphatic compounds are mostly observed at the bottom left of the

counter plots; this is can be attributed to the low boiling points and low polarities of these compounds and the use of an apolar \times polar column combination in this work.

Terpenes

Terpenes are relatively high boiling apolar compounds [16], and accordingly displayed higher retention than the aliphatic hydrocarbons on the non-polar ^1D column but were also found in the lower part of the contour plot. Characteristic ions at m/z 67, 93, 121 and 136 were used to detect terpenes [17]. The major compounds belonging to this class tentatively identified in TDOs include *dl*-limonene, α -terpinolene, camphene, γ -terpinene and α -terpinene, with *dl*-limonene (**71**) detected at high levels in both samples [18,19]. Of these, α -terpinolene (**89**) is used in the food industry as fragrance and flavour additive [20]. In total, 12 terpenes were tentatively identified in the analysed samples.

Mono-aromatic compounds

Characteristic ions extracted for the selective detection of mono-aromatics were m/z 91, 104, 105 and 106. These compounds are present in TDOs at relatively high concentrations, as confirmed by quantification of selected compounds by GC-MS (Chapter 2). Mono-aromatics showed moderate retention on the second dimension polar column, and were separated from terpenes by this characteristic. 37 mono-aromatics were detected, including as major compounds: toluene, ethylbenzene, *p/m*-xylene, styrene, *o*-xylene, 1,2,4-trimethylbenzene and 3-ethyltoluene.

Poly-aromatic hydrocarbons

TDOs are known to contain trace levels of PAHs, depending on the pyrolysis conditions used [18]. GC \times GC analysis using an apolar \times polar column combination offers improved separation of PAHs, since their relatively high retention in both dimensions partially separates these compounds from other TDO constituents (**Figure 3.9**). Characteristic fragmentation ions used to visualise PAHs include m/z 128, 154, 156 and 170. A total of 29 PAHs were tentatively identified by GC \times GC-TOFMS, significantly more than could be identified by 1D GC-MS (Chapter 2).

Sulphur, oxygen and nitrogen containing compounds

Ions 135, 108 and 116 were used for selective detection of sulphur, nitrogen and oxygen-containing compounds. These are highly polar compounds and therefore appear on the upper right part of the contour plot [22]; in some cases wraparound was observed for these classes of compounds. In total, 12 sulphur, 8 oxygen and 12 nitrogen containing compounds were identified in the analysed TDO samples. Benzothiazole (**106**) was identified as one of the major components of both TDO samples, in agreement with quantitative results obtained by GC-MS (Chapter 2).

3.4. Conclusions

This Chapter reports the evaluation of GC×GC for the detailed analysis of the chemical composition of TDOs. Two different instrumental configurations were utilised. In the first instance, a novel consumable-free single stage thermal modulator was used in combination with HS-SPME and FID detection to demonstrate the improved separation offered by GC×GC. The improved selectivity offered by the combination of apolar and polar columns was shown to provide significant benefits in terms of the separation of compounds co-eluting in 1D-GC. Secondly, a commercial GC×GC-TOFMS instrument equipped with a cryogenic modulator was used for the detailed qualitative analysis of two TDO samples. Using this state-of-the-art instrument, a total of 137 compounds were tentatively identified in the two samples analysed based on mass spectral and retention index data. This was achieved even though experimental parameters used were not fully optimised for TDOs, thus indicating the possibility of identifying many more components following method optimisation. The group-type separation observed for aliphatics, mon-aromatics, terpenes, PAHs and sulphur-, oxygen- and nitrogen-containing compounds proved especially useful in combination with deconvoluted mass spectra for the tentative identification of a range of TDO constituents.

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3.6. References

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CHAPTER 4

Conclusions and future recommendations

4.1. Conclusions

The research reported in this thesis was aimed at developing reliable GC methods for the quantitative and qualitative analysis of selected market-value compounds in tyre-derived pyrolysis oils (TDOs) in support of further tyre recycling research. This objective was met by successfully developing both qualitative and quantitative gas chromatography-mass spectrometric (GC-MS) methods for TDO analysis. Compounds were tentatively identified in TDOs based on retention index and mass spectral data, while 33 market-value compounds were confirmed using authentic standards and subsequently quantified. Chromatographic separation was optimised on a high-efficiency apolar column, and several sample preparation and quantitation procedures were evaluated for this purpose. The accuracy of quantitative data obtained using the internal standard (IS) method was confirmed using standard addition. The final GC-MS method utilising solvent dilution in dichloromethane and internal standard quantitation was validated for routine analysis, and was found to be stable, robust and accurate when utilised by different users. Compared to methods reported in literature for TDO analysis, the developed method offers improved chromatographic separation and quantitative accuracy, and allowed tentative identification of more compounds in a single analysis.

The applicability of the method to a wide range of samples differing in their chemical composition was confirmed by analysis of 20 TDO samples and various distillates produced from waste tyres. A more sensitive method using MS in selected ion monitoring (SIM) mode was also successfully developed in order to quantify compounds which were below the detection limit of the method utilising full scan mode. The application of this method for the low-level quantification of compounds in selected TDOs was demonstrated. Initial findings following the transfer of the validated GC-MS method to GC-FID indicate that the latter is a realistic cheaper alternative for quantitation of major compounds and for determining the mass percentage of compounds without the need for time-consuming calibrations. Each of the developed methods have been used extensively by fellow REDISA students for the analysis of a range of TDO samples in support of research aimed at the establishment of novel pyrolysis conditions favouring particular products. This confirms their suitability for the intended routine analysis of TDOs.

In the second part of this project, the potential of comprehensive two-dimensional gas chromatographic (GC×GC) analysis of TDOs was evaluated as a means of allowing detailed investigation of the chemical composition of these samples. This powerful analytical tool is increasingly being used in the many industries in order to resolve complex samples such as Fischer-Tropsch oils, wine and food samples, amongst others. Initial research was performed on a custom built GC×GC instrument equipped with flame ionisation detector (FID) and a novel consumable-free single stage thermal modulator. Using this technique, the separation of compounds co-eluting in 1D-GC such as *o*-xylene and styrene, *dl*-limonene and indane was improved, as confirmed by the analysis of authentic standards. This is due to the presence of the second dimension column. Subsequently, a commercially available GC×GC-time-of-flight MS (TOFMS) instrument equipped with a cryogenic modulator was used to identify constituents of selected TDOs. Initial data analysis allowed identification of 137 compounds based on deconvoluted mass spectra and retention index data in the first dimension. GC×GC was found to offer improved sensitivity and selectivity, which resulted in improved separation, as illustrated in this work for compounds that could not be resolved using the optimised 1D GC-MS method. The technique therefore holds promise for the much more detailed analysis of these complex samples, as reflected by the increased use of GC×GC for TDO analysis reported in literature.

4.2. Recommendations for future research

Notwithstanding the power and applicability of conventional GC-MS methods illustrated in this work, it would be interesting to perform more detailed fractionation of TDOs, using for example high performance liquid chromatography (HPLC), in order to reduce the complexity of these samples and allow the much more detailed analysis of particular compound classes. Further optimisation of sample preparation methods would also be beneficial in the development of improved GC-MS methods for TDO analysis. This is especially relevant for the analysis of market-value polar compounds, which are not effectively analysed using conventional methods. In addition to the use of GC×GC as a powerful tool to resolve the complexity of TDOs, it will be of benefit to evaluate different GC×GC detectors for selective detection of particular compounds such as hetero-atomic species. Also, the applicability of GC×GC-FID for quantification of market value chemicals should be explored as a more accurate method compared to 1D GC-FID. Finally, since TDOs contain quite a large number of enantiomers, which cannot be distinguished by GC-MS using an apolar column, it would

be interesting to use a chiral column (in 1D or GC×GC) to separate enantiomers like *d* and *l*-limonene.