University of Strathclyde
Department of Pure and Applied Chemistry

# The Discrimination of Ignitable Liquids and Ignitable Liquid Residues using Chemometric Analysis

By
Wan Nur Syuhaila Mat Desa

A thesis presented in fulfilment of the requirements for the degree of Doctor of Philosophy

2012

This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

Signed:
Date:

# Abstract

Hydrocarbon fuels such as petrol and petroleum distillate products are commonly used to set deliberate fires. In fire debris analysis, characterisation and identification of these accelerants are based on subjective pattern matching to a reference collection or database. Such procedures involving manual comparison, is often hampered by the complex nature of the samples when exposed to heat, especially in the presence of interfering products and can be extremely challenging.

The application of chemometrics and Artificial Neural Networks (ANNs) pattern recognition techniques are examined in this work to determine their abilities to objectively match chromatographic profiles derived from evaporated ignitable liquid samples to their un-evaporated source. The abilities of the mathematical methods to further resolve ignitable liquid patterns when in the presence of interfering pyrolysis and combustion products is also investigated. Data pre-treatment via normalisation and power transformation prior mathematical analysis is examined and discussed.

Petrol and petroleum distillate products of light, medium and heavy fractions, obtained from a variety of manufacturers, were examined. Their objective classification and discrimination using the mathematical techniques under study is exposed and discussed. The link between evaporated and unevaporated samples was poorly established by conventional chemometric techniques using Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA). In contrast, Self Organising Feature Maps (SOFM), an ANN technique, provided excellent classification and full discrimination of light and medium petroleum distillate samples by specific brand. Classifications of petrol and diesel samples by brand were less successful. However, some meaningful associations were possible within the petrol groupings using SOFM, and all evaporated samples were correctly associated into the clusters containing their un-evaporated counterparts. In addition, SOFM provided successful and unequivocal discrimination of ignitable liquid residues recovered from fire debris according to the class of ignitable liquid in all samples tested. The findings from this work prompt further exploration on the potential use of SOFM as a mathematical strategy for the objective comparison of ignitable liquids and their residues from fire debris samples.

# Acknowledgement

Firstly I wish to express my sincere gratitude to my supervisor (adviser), Prof. Dr. Niamh Nic Daéid who was abundantly helpful, dedicated and has offered invaluable assistance, guidance and support throughout this project. Deepest gratitude is also due to the members of the supervisory committee, Dr. Kathleen Savage and Dr. Chief for invaluable skills and expertise assistance given during this entire experience. Many thanks to Lynn Curran, Jim Christie (fantastic), Georgina Scott and all staff in the Centre for Forensic Science for kind assistance through the duration of my studies.

A special thank you also go to the FFBs PhD colleagues for friendship and words of encouragements, motivations and help in making this challenging journey a pleasant one; Chief, Kevin, Anika, Sara, Yuva, Aude, Lucy, Ice, Graham, Aree, Majid, Greg, Felicity, Kachi, Alaia, Alistair, Nicola, Four, Nick, Hillary, Vanitha and Ainsley. Thanks are also due to all my good friends of Malaysian student community in Glasgow; you all have been great.

Scholarship funding from the Ministry of Higher Education (Malaysia) and Universiti Sains Malaysia is duly acknowledge.

Finally, I wish to convey my heartiest thank you and love to my beloved families; husband and best friend, Dzulkiflee and my most wonderful princesses, Aisyah and Aein, and my parents for their endless love, understanding, patience and lots of prayers.

# Publications, Posters and Presentations

**Wan N. S. Mat Desa,** Dzulkiflee Ismail and Niamh Nic Daeid, Classification and Source Determination of Medium Petroleum Distillates by Chemometric and Artificial Neural Networks: A Self Organizing Feature Approach, *Analytical Chemistry*, 2011, 83(20), pp 7745-7754

**Wan N. S. Mat Desa,** Niamh Nic Daeid, Dzulkiflee Ismail and Kathleen Savage, Application of Unsupervised Chemometric Analysis and Self-organising Feature Map (SOFM) for the Classification of Lighter Fuels, *Analytical Chemistry*, 2010**,** *82* (15), pp 6395–640

**Wan N.S. Mat Desa,** Dzulkiflee Ismail, Kathleen Savage, and Niamh Nic Daeid, The Application of Self-organising Feature Maps (SOFM) for Lighter Fuel Classification, Proceedings American Academy of Forensic Science 63rd Meeting, February 2011, Chicago, IL, USA - Oral presentation

**Wan N.S. Mat Desa,** Dzulkiflee Ismail, Kathleen Savage, and Niamh Nic Daeid, Multivariate Pattern Recognition Analysis of Petroleum Based Accelerants, Proceedings American Academy of Forensic Science 63rd Meeting, February 2011, Chicago, IL, USA - Poster presentation.

**Wan N.S. Mat Desa,** Dzulkiflee Ismail, Kathleen Savage, and Niamh Nic Daeid, Clustering of Medium Petroleum Distillates Products: A Self Organising Feature Map (SOFM) Approach Proceedings American Academy of Forensic Science 63rd Meeting, February 2011, Chicago, IL, USA - Poster presentation

**Wan Nur Syuhaila Mat Desa,** Niamh Nic Daeid, Kathleen Savage, Petroleum accelerants discrimination by pattern recognition techniques, Strathclyde University Research Day 2010, Glasgow, Scotland – Poster presentation.

**Wan Mat Desa,** Niamh Nic Daeid, The Application of Multivariate Pattern Recognition for Petroleum Based Accelerant Identification and Classification, Proceedings of The 5th European Academy of Forensic Science Conference 2009, Glasgow, Scotland – Poster presentation.

# Abbreviations

| | |
|---|---|
| **ACS** | Activated Carbon Strips |
| **ASTM** | American Society for Testing and Materials |
| **ANN** | Artificial Neural Network |
| **CSV** | Comma Separated Value |
| **DFLEX** | Diffusive Flammable Liquid Extraction |
| **EIC** | Extracted Ion Chromatograms |
| **EIP** | Extracted Ion Profiling |
| **ENFSI** | European Network Forensic Sciences Institute |
| **GC-FID** | Gas Chromatography – Flame Ionisation Detector |
| **GC-MS** | Gas Chromatography – Mass spectrometry |
| **HCA** | Hierarchical Cluster Analysis |
| **HPD** | Heavy Petroleum Distillates |
| **IP** | Interfering Products |
| **LPD** | Light Petroleum Distillates |
| **MPD** | Medium Petroleum Distillates |
| **m/z** | Mass-to-charge ratio |
| **NIST** | National Institute of Standards and Technology (USA) |
| **PAH** | Poly Aromatic hydrocarbon |
| **PCA** | Principal Component Analysis |
| **PPMC** | Pearson Product Moment Correlation |
| **R** | Regression Coefficient |
| **RSD** | Relative Standard Deviation |
| **SOFM** | Self Organising Feature Map |
| **SIMCA** | Sift Independent Model Cluster Analysis |
| **SPME** | Solid Phase Micro-extraction |
| **TCC** | Target Compound Chromatogram |

# Table of Contents

**Abstract** iii

**Acknowledgement** iv

**Publications, Posters and Presentations** v

**Abbreviations** vi

**Table of Contents** vii

**List of Figures** xvi

**List of Tables** xxviii

**Thesis Overview** xxxii

**CHAPTER 1: INTRODUCTION**

1.1 Background 1

1.2 Fire Investigation Process 2

1.3 Examination of Fire Debris Samples 4

1.4 Collection and Storage of Fire Debris Samples 5

1.4.1 Fire Debris Packaging Materials 5

1.5 Developments in Fire Debris Analysis 6

1.5.1 Ignitable Liquid Classification Scheme 8

1.6 Extraction Techniques of Ignitable Liquid Residues 10

1.6.1 Steam Distillation 10

1.6.2 Solvent Extraction 11

1.6.3 Direct Headspace/ Simple Headspace 12

1.6.4 Dynamic /Swept Headspace / Purge and trap (Adsorbent Sampling) 12

1.6.5 Dynamic Headspace Diffusion (Tenax TA) 12

1.6.6 Passive Headspace Diffusion (Activated Carbon) 13

1.6.7 Passive Headspace Extraction by Solid Phase Microextraction 14

(SPME)
1.7 Instrumental Analysis of Ignitable Liquid Residue 15

1.7.1 Chromatography 16

1.7.2 Gas chromatography 17

1.7.2.1 GC Inlet/Injection Port 18

1.7.2.2 Carrier Gas 18

1.7.2.3Analytical Column 18

1.7.3 Flame Ionisation Detectors (GC–FID) 19

1.7.3.1 Limitations of GC-FID 20

1.7.4 Gas Chromatography-Mass Spectrometry (GC-MS) 20

1.7.4.1 Ionisation Source 21

1.7.4.2 Quadrupole Mass Analyser 22

1.7.4.3 MS Detector 23

1.7.4.4 Limitations of GC-MS 24

1.8 Interpretation of Ignitable Liquid and Ignitable Liquid Residues 25

1.8.1 Target Compound Chromatogram (TCC) 28

1.8.2 Mass Chromatography Techniques 32

1.8.3 Problems and Challenges in Ignitable Liquid Residue Interpretation 35

1.9 Introduction to Multivariate Pattern Recognition 35

1.9.1 Application of Multivariate Pattern Recognition for Ignitable Liquid and Ignitable Liquid Residue Analysis. 36

1.10 Research Aims 46

1.11 References 47

## CHAPTER 2: GAS CHROMATOGRAPHY MASS SPECTROMETRY (GC-MS) METHOD VALIDATION

2.1 Introduction 59

2.2 Materials and Methodology 60

  2.2.1 GC-MS Experimental Set-Up 60

  2.2.2 Solvent Study 61

  2.2.3 Preparation of Ignitable Liquid Test Mixtures 62

  2.2.4 Instrumental Precision 62

  2.2.5 Peak Shape Evaluation (Resolution and Asymmetry) 63

  2.2.6 Limit of Detection 63

    2.2.6.1 Preparation of Calibration Curve Standard Solution 63

  2.2.7 Inter and Intra Ignitable Liquid Sample Variations 64

2.6 Results and Discussions 65

  2.6.1 Solvent Study 65

  2.6.2 Assessment of Instrumental Performance 66

  2.6.3 Peak Evaluation (Resolution and Asymmetry) 66

  2.6.4 Limit of Detection 68

  2.6.5 Within and Between Sample Variations 72

2.7 Conclusions 73

2.8 References 74

## CHAPTER 3: PREPARATION AND ANALYSIS OF IGNITABLE LIQUIDS, EVAPORATED IGNITABLE LIQUIDS, BURNT SUBSTRATES AND IGNITABLE LIQUID SPIKED BURNT SUBSTRATES

3.1 Introduction 76

  3.1.1 Ignitable Liquids (IL) 76

3.1.2 Petroleum Based Ignitable Liquid: Production and Process 78

3.1.2.1 Petrol 82

3.1.2.2 Light and Medium Petroleum Distillates (LPD and MPD) 84

3.1.2.3 Heavy Petroleum Distillates (HPD) 84

3.2 Materials and Methods 85

3.2.1 Ignitable Liquid Collection 85

3.2.2 Preparation of Evaporated Petrol Samples 89

3.2.3 Preparation of Evaporated Ignitable Liquids (LPD, MPD and HPD) 90

3.2.4 GC-MS Analysis of Unevaporated and Evaporated Ignitable Liquid Samples 90

3.2.5 Reproducibility of the Ignitable Liquid Evaporation Technique 91

3.3 Optimisation 91

3.3.1 Optimisation of Passive Headspace Methods for the Recovery of Volatile Materials from Substrates 91

3.3.2 Optimisation of Carbon Strip Size for Passive Headspace Extraction 92

3.3.3 Reproducibility of ACS Sample Recovery 93

3.3.4 Optimisation of the Volume Of Ignitable Liquid Spiked onto the Substrate 93

3.4 Preparation of Substrate Materials 94

3.4.1 Collection of Substrate Materials 94

3.4.2 Preparation of Burnt Substrate Samples 96

3.4.3 Preparation of Burnt Substrates Spiked with Ignitable Liquid. 97

3.4.4 Passive Headspace Extraction of Burnt Substrates and Ignitable Liquid Spiked Burnt Substrates. 98

3.5 Results and Discussions 98

3.5.1 Ignitable Liquid Reference Collection 98

3.5.2 Chromatographic Patterns of Fresh and Evaporated Petrol Samples 98

3.5.3 Chromatographic Pattern of Fresh and Evaporated LPD Samples 101

3.5.4 Chromatographic Pattern of Unevaporated and Evaporated MPD Samples 103

3.5.5 Chromatographic Pattern of Unevaporated and Evaporated HPD Samples 105

3.5.6 Reproducibility of the Ignitable Liquid Evaporation Technique 108

3.5.7 Optimisation of Carbon Strip Size for Passive Headspace Extraction 111

3.5.8 Reproducibility of ACS Sample Recovery 113

3.5.9 Optimisation of the Volume of Ignitable Liquid Spiked onto the Substrate 116

3.5.10 Preparation of Burnt Substrate Samples and Burnt Substrate Samples Spiked with Ignitable Liquids 120

3.5.11 Reproducibility of Interfering Products Sampling 121

3.6 Conclusions 124

3.7 References 125

**CHAPTER 4: MATHEMATICAL ANALYSIS OF CHROMATOGRAPHIC DATA DERIVED FROM UNEVAPORATED AND EVAPORATED IGNITABLE LIQUIDS**

4.1 Introduction 128

4.2 Multivariate Analysis for Pattern Recognition 129

4.2.1 Data Pre-processing and Pre-treatment 132

4.2.1.1 Power Transformation 133

4.2.1.2 Row Scaling 135

4.3 Cluster Analysis 135

4.4 Principal Component Analysis (PCA). 135

4.4.1 Issues with PCA 137

4.5 Hierarchical Cluster Analysis 138

4.5.1 Proximity/Distance measurement 139

4.5.2 Issues with Hierarchical Analysis 141

4.6 Self Organising Feature Map (SOFM) 142

4.6.1 SOFM Algorithm 142

4.6.2 SOFM Visualisation 143

4.6.3 SOFM Classification on Sample Dataset 144

4.6.4 Limitations of SOFM 146

4.7 Experimental Methodology 146

4.7.1 Chromatographic Pattern Examination and Identification 146

4.7.2 Data Pre-treatment 147

4.7.3 Data Analysis 149

4.8 Results and Discussion 150

4.8.1 SOFM Model Validation 150

4.8.2 Light Petroleum Distillate 155

4.8.2.1 Chromatographic Examination and Identification of Light Petroleum Distillates 155

4.8.2.2 PCA Classification for LPD (Lighter Fluid) Samples 157

4.8.2.3 HCA Classification for LPD (Lighter Fluid) Samples 159

4.8.2.4 SOFM Classification for LPD (Lighter Fluid) Samples 160

4.8.3 Medium Petroleum Distillate 162

4.8.3.1 Chromatographic Examination and Identification of Medium Petroleum Distillates 162

4.8.3.2 PCA Classification for MPD Samples 166

4.8.3.3 HCA Classification for MPD Samples 167

4.8.3.4 SOFM Classification for MPD Samples 168

4.8.4 Heavy Petroleum Distillate 170

4.8.4.1Chromatographic Examination and Identification of Diesel Samples 170

4.8.4.2 PCA Classification for HPD (diesel) Samples 173

4.8.4.3 HCA Classification for HPD (diesel) Samples 174
4.8.4.4 SOFM Classification for HPD (diesel) Samples 175
4.8.5 Petrol 176
4.8.5.1Chromatographic Examination and Identification of Petrol 176
4.8.5.2 Petrol Data Matrices 180
4.8.5.3 PCA Classification for Petrol Samples 181
4.8.5.4 HCA Classification for Petrol Samples 184
4.8.5.5 SOFM Classification for Petrol Samples 188
4.8.6 Multivariate Analysis of Combined Ignitable Liquid Samples 191
4.8.6.1 PCA Classification 193
4.8.6.2 HCA Classification 194
4.8.6.3 SOFM Classification 195
4.9 Conclusions 197
4.10 References 198

**CHAPTER 5: ASSESSMENT OF THE ABILITIES OF SOFM TO ASSOCIATE IGNITABLE LIQUIDS TO BRAND IN THE PRESENCE OF INTERFERING PRODUCTS**

5.1 Introduction 206
5.1.1 Pyrolysis 208
5.1.1.1 Random Chain Scission 209
5.1.1.2 Side Group Scission 210
5.1.1.3 Depolymerisation 211
5.1.1.4 Other Pyrolysis Mechanisms 212
5.1.2 Combustion Products 213
5.1.3 Background Substrates 215
5.2 Experimental Methods 218
5.2.1 Preparation of Interference Products 218
5.2.2 Prediction by SOFM Model 219
5.3 Results and Discussions 219
5.3.1 Pyrolysis and Combustion Products from Common Substrates 219

5.3.1.1 Flooring Materials 219
5.3.1.2 Polymeric House Hold Materials 226
5.3.1.3 Wood 230
5.3.1.4 Newspaper 233
5.3.2 General Conclusions in Relation to Substrate Interfering Products 234
5.3.3 Burning of Selected Substrate Materials in the Presence of Ignitable Liquids 235
5.3.4 Classification of Ignitable Liquid Residues using SOFM Model 238
5.3.5 Chromatographic Observation and SOFM Predictions for Light Petroleum Distillates Residues 239
5.3.6 Chromatographic Observation and SOFM Predictions for Medium Petroleum Distillate Residues 243
5.3.7 Chromatographic Observation and SOFM Predictions for Heavy Petroleum Distillates Residues 247
5.3.8 Chromatographic Observation and SOFM Predictions for Petrol Residues 250
5.4 Conclusions 253
5.5 References 255

**CHAPTER 6: GENERAL CONCLUSION AND FURTHER WORK**

6.1 Summary of Conclusions 260
6.2 Recommendations for Further Work 264
6.3 References 265

**APPENDICES**

**Appendix A:** Statistical Calculation to Determine Instrumental Limit of Detection (LOD) 266

**Appendix B:** Overlay of Total Ion Chromatograms (TICs) of Unevaporated and Evaporated Light Petroleum Distillates Samples 270

**Appendix C:** Overlay of Total Ion Chromatograms (TICs) of Unevaporated and Evaporated Medium Petroleum Distillate Samples 272

**Appendix D:** Overlay of Total Ion Chromatograms (TICs) of Unevaporated and Evaporated High Petroleum Distillate Samples 276

**Appendix E:** Overlay of Total Ion Chromatograms (TICs) of Unevaporated and Evaporated Petrol Samples 280

**Appendix F:** Total Ion Chromatograms (TICs) of Interfering Products from Burnt Substrates 287

**Appendix G:** Extracted Ion Profiles of Unevaporated Ignitable Liquids 290

**Appendix H:** Extracted Ion Profile of Burnt Substrates 325

**Appendix I:** The SOFM Validation Map for Medium Petroleum Distillate Classifications 336

**Appendix J:** The SOFM Validation Map for Heavy Petroleum Distillate Classifications 339

**Appendix K:** The SOFM Validation Map for Petrol Classifications 342

**Appendix L:** Journal publications 345

# List of Figures

Chapter 1

Figure 1.1 Current fire investigation practises in the United Kingdom as suggested by Young and Cooper. 2

Figure 1.2 Fire investigation process. 3

Figure 1.3 Percent composition from 1770 samples submitted for fire debris analysis. 4

Figure 1.4 Schematic diagram showing laboratory procedures for examination of fire debris samples. 8

Figure 1.5 Illustration of differential affinity in chromatography system. 17

Figure 1.6 General lay out of a typical gas chromatograph instrumental set-up. 17

Figure 1.7 Structure of non polar of methylsilicone and phenylmethylsilicone (synonymous with phenylmethylpolysiloxane). 19

Figure 1.8 Basic diagram showing major elements of a mass spectrometer. 20

Figure 1.9 Quadrupole mass analyser. 22

Figure 1.10 Illustration of electron multiplication in mass spectrometer detector. 23

Figure 1.11 An example of toluene mass spectrum. 24

Figure 1.12 Interpretation and classification of ignitable liquid and ignitable liquid residue based on previous ignitable liquid classification scheme. 26

Figure 1.13 Classification flow chart of IL and ILR based on recent IL classification scheme ASTM E1618. 27

Figure 1.14 A, B, C and D illustrate summed EIPs of hydrocarbon groups from a petrol sample. E, F and G are the individual EICs of alkyl benzene profiles. 34

Figure 1.15 Chromatogram section of C0–C2-naphthalenes obtained by selected ion monitoring of the three isomer groups. 38

Figure 1.16 PCA score plot of 35 petrol samples collected petrol stations in Sydney, Australia. 38

Figure 1.17 PCA score plot of 35 petrol samples at five different levels of evaporation (0, 25, 50, 75 and 90% by weight). 39

Figure 1.18 PCA score plot of petrol samples collected New Zealand compared to samples collected in Australia. 40

Figure 1.19 PCA score plot of New Zealand petrol samples collected during summer and winter time. 40

Figure 1.20 PCA scores plot of five neat diesels (each colour represent one brand) and the burnt test sample (purple squares). 44

**Chapter 2**

Figure 2.1 Partial TICs showing chromatographic profile of blank solvents. 65

Figure 2.2 TIC of 1 mg/mL standard test mixture in pentane. 66

Figure 2.3 Shows a linear relationship between the peak area and commercial test mixtures (concentration 0.001% to 0.05% vol/vol). 69

Figure 2.4 Presents the regression lines of 12 compounds from the commercial standard mixture at concentrations between 0.001% to 0.05% vol/vol. 70

Figure 2.5 Chromatogram of Zippo lighter fluid at 2% dilution in pentane. 72

**Chapter 3**

Figure 3.1 Crude oil refinery process flow diagram. 81

Figure 3.2 Illustration of typical refinery plant process and produce from crude oil. 82

Figure 3.3 Molecular structure of octane rating compounds. 83

Figure 3.4 Molecular structures of cetane rating compounds. 85

Figure 3.5 Location map showing fuelling station where petrol and diesel samples were obtained. Sample F (leaded petrol) was obtained from regulated garage in England. 87

Figure 3.6 Location map showing local stores in Glasgow where LPD and MPD samples were obtained. 89

Figure 3.7 Fractional distillation set-up for evaporation of ignitable liquids. 90

Figure 3.8 Illustration of the experimental set up for the passive headspace adsorption phase. 93

Figure 3.9 Illustration of burnt substrate sample preparation. 96

Figure 3.10 TICs of unevaporated petrol from regular unleaded petrol, premium unleaded petrol and leaded petrol. 99

Figure 3.11 An example of unevaporated to highly evaporated chromatographic pattern of petrol sample (BP unleaded premium grade). TICs of other samples are included in appendix section. 100

Figure 3.12 TICs of unevaporated LPD (lighter fluid) samples from 5 different brands. 101

Figure 3.13 An example of unevaporated to highly evaporated chromatographic pattern of LPD sample (lighter fluid of Zippo). 102

Figure 3.14 TICs of unevaporated MPD samples from 3 types of MPD (white spirit, paint brush cleaner and lamp oil) from various brands. 103

Figure 3.15 An example of unevaporated to highly evaporated chromatographic pattern of MPD sample (B&Q white spirit). 104

Figure 3.16 Representative TICs of some of unevaporated HPD samples (i.e. diesel) from different brands. 106

Figure 3.17 An example of unevaporated to highly evaporated chromatographic pattern of diesel sample (Tesco diesel). 107

Figure 3.18 TIC of 50% evaporated petrol sample. 109

Figure 3.19 TIC of 50% evaporated Zippo lighter fluid sample. 110

Figure 3.20 An example of chromatogram section obtained from ACS passive headspace concentration of petrol sample. 111

Figure 3.21 Graph showing volatile compounds recovery (10μL petrol sample) by headspace passive extraction in closed container. 113

Figure 3.22 TIC profile obtained from 50% evaporated petrol and 50% evaporated diesel at 1:1 ratio extracted using passive headspace with ACS C (5 mm x 20 mm) and ACS D (5 mm x 25). 114

Figure 3.23 A comparisons of TICs profiles obtained from ACS extracts of unevaporated petrol, burnt carpet substrate and simulated fire debris samples (carpet and petrol) at 80°C for 16hrs. 117

.

Figure 3.24 Zoomed section to enhance detail in chromatographic profile from simulated fire debris sample (carpet burnt with petrol). Peaks Pyp 1-4 were chosen for ratio analysis. 118

Figure 3.25 Peak area ratio calculated from the simulated fire debris sample with various petrol drop sizes. 119

Figure 3.26 Recorded temperatures during the burning of high density polyethylene (HDPE) showing the temperature range between replicates sample preparations. 121

Figure 3.27 TIC patterns of volatiles extracted using passive headspace concentration technique from HDPE polymer sample burnt with a maximum temperature in the range of 249.28°C - 267.52°C. 122

Figure 3.28 Volatiles extracted using passive headspace concentration technique from a high density polyethylene (HDPE) polymer sample. 123

**Chapter 4**

Figure 4.1 Representation of typical multivariate data matrix arrangements. 131

Figure 4.2 Multivariate analysis scheme. 132

Figure 4.3 The effect of power transformation illustrates a) the reduction in scale or magnitude and b) comparison in data distribution of raw data and power transformed for data from table 4.1. 134

Figure 4.4 An example of PCA score plot to illustrate sample clustering in two dimensional spaces. Overall, samples are clustered in two big groups. 136

Figure 4.5 Loading plot for PC 1 and PC2 that convey correlation among the variables. 137

Figure 4.6 Biplot for PC 1 and PC2 representing information about variables and their relationship with sample clustering as indicated by their distances. 137

Figure 4.7 Illustration of cluster analysis scheme by agglomerative and divisive methods. 138

Figure 4.8 Illustration of single linkage (nearest neighbour or minimum distance). 139

Figure 4.9 Illustration of complete linkage (furthest neighbour or maximum distance). 140

Figure 4.10 Illustration of average linkage (average distance). 140

Figure 4.11 Dendrogram from HCA of ignitable liquid samples clustered based on previous ASTM ignitable liquid classification scheme. 141

Figure 4.12 Two layer structure of SOFM neural network. Each input variable is connected to all neurons on the platform. 142

Figure 4.13 Output map shows similarities within the animal dataset. 144

Figure 4.14 Simplified schematic presentations that illustrate the framework of component maps in SOFM. Each component map correlates to a single attribute which clearly show, for example the distinction between animals in term of physical attributes (e.g size). 145

Figure 4.15 Output map of the training (left) and test set (right) showing correct association of the unevaporated (neat),to highly (95%) evaporated LPD samples to their group by brand. Samples code are D=Dunhill, P=Perma, R=Ronsonol, S=Swan and Z=Zippo and numbers designated level of evaporation. Test samples were coded in green italic font. 151

Figure 4.16 Chromatograms of unevaporated lighter fluid samples (2% in pentane with 0.5mg/ml tetrachloroethylene ISTD). Numbered peaks correspond to identification in table 4.5. 155

Figure 4.17 Chromatographic pattern of neat (unevaporated) to highly evaporated LPD using Zippo brand as an example. Full chromatographic profile (in boxed area) illustrates the peaks selected for multivariate analysis. Chromatographic patterns of other LPD samples are included in appendix B. 157

Figure 4.18 Principal component score plots of pure and evaporated samples. A, B, C and D represent plots of raw data, normalised, normalised square root and normalised fourth root transformation datasets respectively. 158

Figure 4.19 Hierarchical clustering of pure and evaporated samples. A, B, C and D represent dendrograms of raw data, normalised, normalised square root and normalised fourth root transformation datasets respectively. (D=Dunhill, P=Perma, R=Ronsonol, S=Swan and Z=Zippo). 159

Figure 4.20 SOFM maps of pure and evaporated samples. A,B,C and D represent the maps of raw, normalised, normalised square root and normalised fourth root transformation dataset respectively. (D=Dunhill, P=Perma, R=Ronsonol, S=Swan and Z=Zippo). 161

Figure 4.21 TICs pattern from unevaporated MPD samples from eight different brands. Target compounds for MPD class are identified and numbered according to identification table 4.6. Keycode for the samples are BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO= After Dark lamp oil. 163

Figure 4.22 Chromatographic pattern of neat (unevaporated) to highly evaporated MPD using white spirit as an example. Partial chromatographic profile (in boxed area) illustrates the peaks selected for multivariate analysis. Chromatographic patterns of other MPD samples are included in appendix C. 165

Figure 4.23 PCA score plot of MPD samples from sixteenth root dataset. PC1 and PC2 explain 55.49% of total variance in the dataset. Keycode for the samples are BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO= After Dark lamp oil. 167

Figure 4.24 Dendrogram of HCA for MPD classification from sixteenth root power transformed dataset. Misclassified samples are highlighted. Keycode for the samples are BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO= After Dark lamp oil. 168

Figure 4.25 U-matrix output map of MPD samples. Dotted lines are drawn to emphasise the boundaries between the samples. Keycode for the samples are BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO= After Dark lamp oil. Black lines emphasises sample groupings. 169

Figure 4.26 Representative TICs of unevaporated diesel from different brands. For brevity, prominent peaks are numbered as identified in table 4.7 accordingly as similar pattern are observed in other samples. 170

Figure 4.27 Chromatographic pattern of neat (unevaporated) diesel to highly evaporated diesel. Partial chromatographic profile (in boxed area) showed the peaks included for multivariate analysis. 172

Figure 4.28 Score plot (accounted for 72.1% and 8.63% variation in PC1 and PC2) showing the groupings of 8 diesel samples obtained from different stations. Sample codes are; DA=Diesel Asda, DB=Diesel Esso, DC=Diesel Jet, DD=Diesel Sainsbury, DE=Diesel Shell, DF=Diesel Morrison, DG=Diesel BP and DH=Diesel Tesco. The code numbering designates level of sample evaporation. 173

Figure 4.29 Dendrograms showing the linking of unevaporated, moderately and severely evaporated diesel samples. Sample codes are; DA=Diesel Asda, DB=Diesel Esso, DC=Diesel Jet, DD=Diesel Sainsbury, DE=Diesel Shell, DF=Diesel Morrison, DG=Diesel BP and DH=Diesel Tesco. The code numbering designates level of sample evaporation. 174

Figure 4.30 SOFM Output map revealing no apparent groupings from neat (unevaporated) and evaporated diesel samples of different brands. Sample codes are; DA=Diesel Asda, DB= Diesel Esso, DC= Diesel Jet, DD= Diesel Sainsbury, DE= Diesel Shell, DF= Diesel Morrison, DG= Diesel BP and DH= Diesel Tesco. The code numbering designates level of sample evaporation 175

Figure 4.31 TICs of unevaporated petrol from regular unleaded petrol, premium unleaded petrol and leaded petrol. For brevity, the prominent peaks are numbered as identified in table 4.8 accordingly as similar pattern are observed across all petrol samples. 177

Figure 4.32 Zoomed TICs showing an example of pattern shift as petrol gradually evaporates.. Data matrices strategies are highlighted to illustrate full, partial and extracted ion chromatogram region for PCA, HCA and SOFM analysis. 179

Figure 4.33 EIP of indane from petrol sample. 181

Figure 4.34 Scores plot of full chromatographic profiles (data matrix 1) of unevaporated and evaporated samples from 14 petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. 182

Figure 4.35 Scores plot of C2-C4 alkylbenzenes region (data matrix 2) of 183 neat (unevaporated) and evaporated constituents from 14 petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation.

Figure 4.36 Score plot of indanes profile of 14 neat (unevaporated) and evaporated petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation. 184

Figure 4.37 Dendrogram of full TIC chromatogram (data matrix 1) consisting of 14 petrol samples Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BP regular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation. 185

Figure 4.38 Dendrogram of C2-C4 alkylbenzenes region of neat (unevaporated) and evaporated constituents from 14 petrol samples Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation. 186

Figure 4.39 Dendrogram of indane profiles of neat and weathered constituents from 13 unleaded and 1 leaded petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation. 187

Figure 4.40 U-matrix of SOFM of the samples using full chromatographic profiles of neat (unevaporated) and evaporated constituents from 14 petrol samples Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, 188

J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation.

Figure 4.41 SOFM U-matrix map of C2 to C4 alkylbenzenes profile of neat (unevaporated) and evaporated constituents of 14 petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation. Black lines emphasises sample groupings. 189

Figure 4.42 SOFM U-matrix map of indane profiles of neat (unevaporated) and evaporated constituents from 14 petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation. 190

Figure 4.43 Representative TICs of unevaporated ignitable liquid samples- of the LPD, MPD, HPD and petrol samples. 191

Figure 4.44 Representative TICs of moderately evaporated (50%) ignitable liquid samples- of the LPD, MPD, HPD and petrol samples. 192

Figure 4.45 Representative TICs of highly evaporated (95%) ignitable liquid samples- of the LPD, MPD, HPD and petrol samples. 192

Figure 4.46 Score plot of PC1 and PC2 for the combined data matrix of petrol and petroleum distillate products. 194

Figure 4.47 Dendrograms for the combined data matrix of petrol and petroleum distillate products. 195

Figure 4.48 The SOFM output map for the combined data matrix of petrol and petroleum distillate products. 196

**Chapter 5**

Figure 5.1 Conversion from solid to vapour phase by different pathways. 207

Figure 5.2 Thermal decomposition pathways of cellulosic materials. 209

Figure 5.3 Illustration of random scission mechanism of polyethylene. 210

Figure 5.4 Side group scission of polyvinylchloride. 211

Figure 5.5 Depolymerisation mechanism of polymethylmethacrylate substrate. 212

Figure 5.6 Simplified reaction of chain stripping mechanism. 212

Figure 5.7 Cross linking mechanism of polyacrylonitrile. 213

Figure 5.8 Char layers of wood structure. 214

Figure 5.9 Summarisation of sources of interference products in fire debris. 217

Figure 5.10 Chromatogram of sample S1. 100% Polypropylene carpet with rubber backing. 221

Figure 5.11 Chromatogram of sample S2 100% polypropylene carpet with jute backing. 222

Figure 5.12 Chromatogram of sample S3 Vinyl sheet. 224

Figure 5.13 Chromatogram of sample S4 vinyl tiles. 225

Figure 5.14 Chromatogram of sample S5 polystyrene CD casing. 226

Figure 5.15 Chromatogram of sample S6 polyurethane foam. 228

Figure 5.16 Chromatogram of sample S7 carrier bags. 229

Figure 5.17 Chromatogram of sample S8 pine wood. 231

Figure 5.18 Chromatogram of sample S9 Medium density fibreboard (MDF). 232

Figure 5.19 Chromatogram of sample S10 plywood. 233

Figure 5.20 Chromatogram of sample S11 burnt newspaper. 234

Figure 5.21 SOFM output maps showing the classification of ignitable liquid residues based on the class characteristic. Sampling code for LPD samples were reassigned to avoid confusion with petrol sample labelling. Key code for LPD are LP=Perma, LS=Swan, LR=Ronsonol, LZ=Zippo and LD=Dunhill. 238

Figure 5.22 TICs of LPD residues in comparison to neat IL and IP profiles of Zippo lighter fluid on polypropylene carpet with rubber backing( code =S1Z). 240

Figure 5.23 TICs of LPD residues in comparison to neat ignitable liquid and interference product profiles of Swan lighter fluid on vinyl sheeting( code = S3S). 240

Figure 5.24 TICs of LPD residues in comparison to neat IL and IP profiles of Perma lighter fluid on carrier bag( code = S7 P). 241

Figure 5.25 The output map of residues (in green) and reference liquid (in black) LPD. (For residue sample, code S numerical represent the substrate followed by the ignitable liquid code which are R=Ronsonol, Z=Zippo, S=Swan, P=Perma and D=Dunhill). 242

Figure 5.26 TICs of MPD residues in comparison to neat ignitable liquid and interfering product profiles of Bertoline lamp oil on polyurethane foam (code=S6BLO). 244

Figure 5.27 TICs of MPD residues in comparison to neat ignitable liquid and interfering product profiles of Polycell brush cleaner on polyurethane foam (code= S7PBC). 244

Figure 5.28 TICs of MPD residues) in comparison to neat ignitable liquid and interfering product profiles of Bertoline white spirit on polypropylene carpet (code= S1BWS). 245

Figure 5.29 TICs of MPD residues) in comparison to neat ignitable liquid and interfering product profiles of Homebase brush cleaner on vinyl sheet (code= S3HBC). 245

Figure 5.30 The output map of residues (in green) and reference liquid (in black) MPD. (For residue sample, code Snumerical represent the substrate followed by the ignitable liquid code, BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO= After Dark lamp oil). 246

Figure 5.31 Representative TICs of Diesel residues from fire debris samples extracted using ACS-passive headspace method. The samples are ASDA diesel burnt on polypropylene carpet (S1DA), Jet diesel burnt on vinyl carpet (S3DC), Sainsbury diesel burnt on polyurethane foam (S7DD, Tesco diesel burnt on polypropylene carpet – jute backing (S2DH) and Shell diesel burnt on CD casing. 248

Figure 5.32 The output map of diesel residues (in green) and diesel reference liquid (in black). For residue sample, code S numeric represents the substrate followed by the diesel brand code. 249

Figure 5.33 TIC of petrol residue (Tesco super petrol on polypropylene carpet, S1 C), in comparison to neat petrol and interference product reference sample. 250

Figure 5.34 TIC of petrol residue (Leaded 4 Star petrol on polypropylene carpet with jute backing, S2F), in comparison to neat petrol and interference product reference sample. 251

Figure 5.35 TIC of petrol residue (Asda regular grade petrol on vinyl sheet, S3N), in comparison to neat petrol and interference product reference sample. 251

Figure 5.36 TIC of petrol residue (Jet regular grade petrol on carrier bag, S7L), in comparison to neat petrol and interference product reference sample. 252

Figure 5.37 The output map of petrol residues (in green) and neat reference liquid (in black). For residue sample, code S numeric represents the substrate followed by the petrol brand code. 253

# List of Tables

## Chapter 1

Table 1.1 Previous ASTM International flammable and combustible liquid classification systems. 9

Table 1.2 Current ASTM International flammable and combustible liquid classification systems. 10

Table 1.3 Petrol Target Compounds. 28

Table 1.4 Medium Petroleum Distillate (MPD) Target Compounds. 29

Table 1.5 Heavy Petroleum Distillate (HPD) Target Compounds. 30

Table 1.6 Typical ions that corresponds to hydrocarbon group common in ignitable. 33

## Chapter 2

Table 2.1 Physical and chemical properties of suitable solvents for ignitable liquid dilution and extraction of ILR from fire debris sample. 61

Table 2.2 Hydrocarbon compounds used in test mixtures. 62

Table 2.3 Hydrocarbon compounds comprised in the commercial standard mixtures. 64

Table 2.4 Percent Relative Standard Deviation (% RSD) of 14 compounds in IL standard mixture. 67

Table 2.5 Instrumental or method LOD obtained from linear equation of IL standard mixture (0.001% vol/vol – 0.05% vol/vol). 71

Table 2.6 Percent RSD of 19 peaks detected from Zippo lighter fluid sample. 73

## Chapter 3

Table 3.1 Characteristics of hydrocarbon compounds commonly associated with petroleum based ignitable liquid composition. 77

Table 3.2 Petroleum refining operation process terminologies. 80

Table 3.3 List of petrol samples collected. 86

Table 3.4 List of diesel samples collected. 86

Table 3.5 List of LPD samples. 88
Table 3.6 List of MPD samples. 88
Table 3.7 ACS sizes tested for the passive headspace adsorption technique. 92
Table 3.8 Polymers resin used to generate interfering pyrolysis products. (n=14). 94
Table 3.9 Wood used to generate interfering pyrolysis products (n=10). 95
Table 3.10 House hold items used to generate interfering pyrolysis products. Floorings(n=9), fabrics(n=8) and others(n=4). 95
Table 3.11 Materials chosen for substrate study. 97
Table 3.12 Reproducibility of compounds in 50% evaporated petrol (ISTD= internal standard and TPA=total peak area). 109
Table 3.13 Compounds reproducibility from 50% evaporated Zippo lighter fluid (ISTD= internal standard and TPA=total peak area). 110
Table 3.14 Variations (%RSD) of hydrocarbon compounds extracted from ACS of different sizes. 112
Table 3.15 Percent RSD of vapour compounds from 50% petrol and 50% diesel (1:1). 115
Table 3.16 Calculated RSD values of prominent peaks from triplicate analysis of HDPE pyrolysis product. 124

**Chapter 4**

Table 4.1 The effect of power transformation on randomly generated sample (hypothetical data). The lowest and highest values in the dataset are highlighted. 134
Table 4.2 List of ignitable liquid datasets subjected to multivariate analyses. 148
Table 4.3 K-fold cross validation strategy devised to determine the predictive abilities of the SOFM network for ignitable liquid samples. 149
Table 4.4 Evaluation table for training set and test set of SOFM model. 154
Table 4.5 Peaks from LPD samples identified using the NIST mass spectral library. Highlighted (in bold) are the target compounds as listed in ASTM 1618 and other literature. 156

Table 4.6 Compound identification for MPD samples. Peaks were identified using the NIST mass spectral library. Highlighted (in bold) are the target compounds as listed in ASTM 1618 and other literature. 164

Table 4.7 Compound identification for HPD (i.e diesel) samples identified using the NIST mass spectral library. Highlighted (in bold) are the target compounds as listed in ASTM 1618 and other literature. 171

Table 4.8 Peaks from petrol samples are identified using the NIST mass spectral library. The target compounds as listed in ASTM 1618 and other literature are highlighted in bold. 178

**Chapter 5**

Table 5.1 Identified compounds encountered from the controlled burning experiment of 35 samples. 217

Table 5.2 Eleven materials chosen for ignitable liquid - substrate study. 218

Table 5.3 Peak identification of volatile compounds extracted from burnt polypropylene carpet (rubber backing). 221

Table 5.4 Peak identification of volatile compounds extracted from burnt polypropylene carpet (jute backing). 222

Table 5.5 Peak identification of volatile compounds extracted from burnt vinyl sheet. 224

Table 5.6 Peak identification of volatile compounds extracted from burnt vinyl tiles. 225

Table 5.7 Peak identification of volatile compounds extracted from polystyrene CD casing. 227

Table 5.8 Peak identification of volatile compounds extracted from burnt polyurethane foam from furniture. 228

Table 5.9 Peak identification of volatile compounds extracted from carrier bags. 229

Table 5.10 Peak identification of volatile compounds extracted from burnt pine wood. 231

Table 5.11 Peak identification of volatile compounds extracted from burnt medium density fibre board. 232

Table 5.12 Peak identification of volatile compounds extracted from burnt plywood. 233

Table 5.13 Maximum temperature recorded during the burnings for simulated fire debris samples. Highlighted are the samples which produced chromatographic patterns which contained interfering products (in total 128) which were tested for prediction using the SOFM model. 236

# Thesis Overview

Chapter 1 of this presents an introduction to the topic focusing on the laboratory techniques used for fire debris sample analysis and the interpretation of the chromatographic results using pattern recognition techniques.

Chapter 2 provides an in depth description of the methods employed to validate the instrumentation used in the chromatographic analysis of the samples under study.

Chapter 3 provides a background to the production of petroleum distillates. The chapter explains the experimental methodology used to generate the evaporated ignitable liquid samples used in the study including measures taken to examine reproducibility of the sample production techniques. Identification of the main components within the ignitable liquids are presented and the changes in the chromatographic profiles as the sample evaporates are comprehensively exposed and explored.

Chapter 4 describes the principles of multivariate pattern recognition techniques, specifically, Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA) and Self Organising Feature Maps (SOFM), an Artificial Neural Network. Each of these mathematical methods were used and their abilities to link unevaporated and evaporated light, medium, heavy petroleum distillate products and petrol to their original brands was evaluated. A number of data pre-processing strategies are evaluated and a validation method using this type of data for the SOFM model is discussed.

Chapter 5 examines the chromatographic patterns generated by interfering products in the presence of various ignitable liquids. The ability of SOFM to provide an objective method of linking these samples to unevaporated and evaporated ignitable liquids both by class (LPD, MPD, HPD and petrol) and by brand are comprehensively explored and discussed.

Finally, Chapter 6 provides the overall conclusions of the study together with suggestions for potential and future work to explore the data analysis approaches used within this research.

# CHAPTER 1: INTRODUCTION

## 1.1 Background

Fires, whether accidentally or deliberately ignited, can result in extensive damage, economic cost and in some cases loss of life. Key facts in arson trends in England and Wales were revealed in the Arson Control Forum Annual Report (2006) that reported a weekly average of 1,600 deliberate fires, causing 50 injuries and 2 fatalities [1]. Recently, according to the Fire Statistics Great Britain report, produced by the UK Department of Communities and Local Government (DCLG), a total of 287,000 fires (outdoor and dwelling fires) were attended by local authority and fire rescue services in 2010-2011[2]. In Scotland, similar data reveals that between 2010 and 2011, a total of 38,927 deliberate fires involving 47 fatalities [3].

Statistics also reveal the substantial financial cost of arson. Recent data available in the DCLG Fire Research Report 2010/2011estimated a total fire damage cost (in England and Wales) of over £7 billion pounds[4]. However, notwithstanding the high economic and social costs, the conviction rate for arson remains low and is generally considered to be less than 10%[5].

Fire scene investigations are conducted in order to determine the origin, cause and development of the fire. In cases of accidental fires, investigations are conducted to understand fire occurrence and to deduce if negligence, carelessness, hazardous environment, spontaneous combustion of materials, product failure or other causes has led to the incident. In the cases of deliberately set fires the circumstances of the event and mechanism of ignition need to be discerned. Fire investigations therefore involve personnel from various organisations working together, to determine origin, cause and spread of the fire as outlined in figure 1.1.

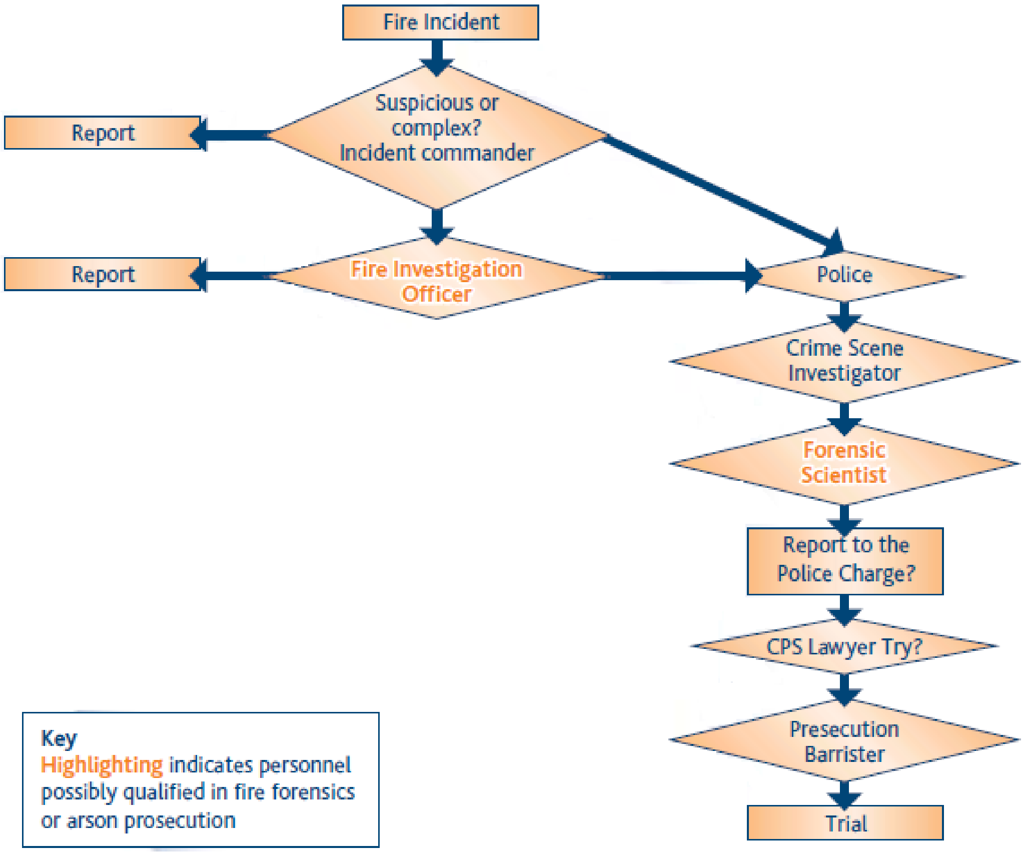


**Figure 1.1 Current fire investigation practises in the United Kingdom as suggested by Young and Cooper. Reproduced from [5].**

## 1.2 Fire Investigation Process

Fire investigation can be divided into two stages; the first stage is the investigation of the fire scene where the origin, cause and development of the fire is determined. The second stage involves the examination of materials recovered from the scene either physically (for example the examination of an electrical appliance) or through a systematic chemical analysis in order to determine whether or not an ignitable liquid residue (ILR) may be present. These investigative stages are presented in figure 1.2.

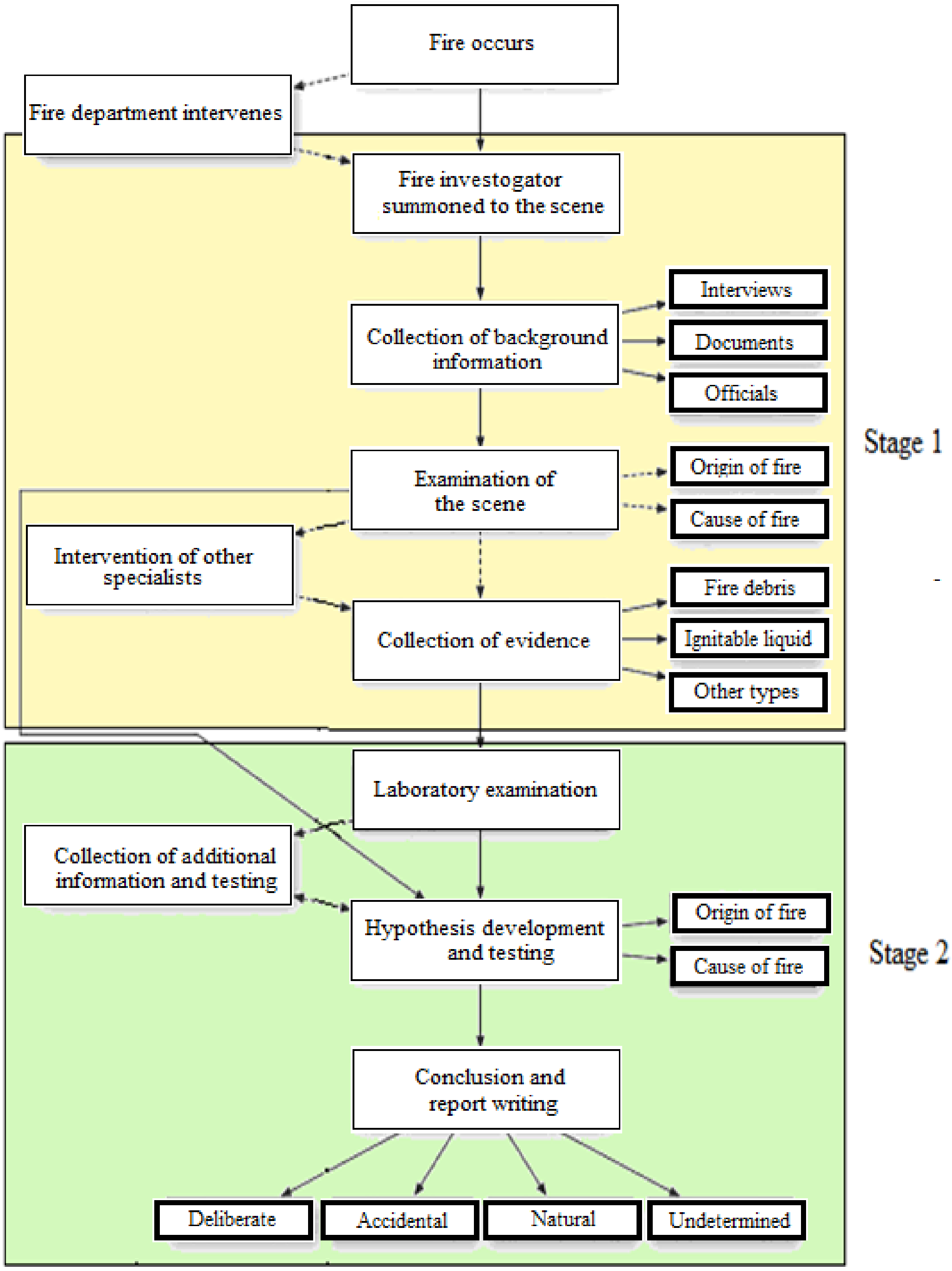


**Figure 1.2 Fire investigation process. Adapted from Stauffer, Dolan and Newman[6].**

## 1.3 Examination of Fire Debris Samples

At the scene, indicators to predict the presence of liquid accelerants can include eyewitness reports, the detection of chemical odours and/or interpretation of burn patterns during the scene investigation, or the use of trained hydrocarbon canines and/or field instruments used for the detection of hydrocarbon residues[7-10]. Fire debris samples removed from the scene and commonly submitted to the forensic laboratory for analysis usually contain burnt or charred materials. The type of burned material present in the sample matrix can greatly influence the identification of ignitable liquid traces as they can contribute directly to the final chromatographic results produced by laboratory analysis. Other factors that influence the analytical results include the type of ignitable liquid present, time of burning, air availability, arrangement of burned material and dispersion of the ignitable liquid on the matrix [11].

In practise, the type of sample collected at the scene depends primarily on the materials present. In 1990, Bertsch and Zhang indicated the type of samples commonly submitted for fire debris analysis and this is summarised in figure 1.3 [12].

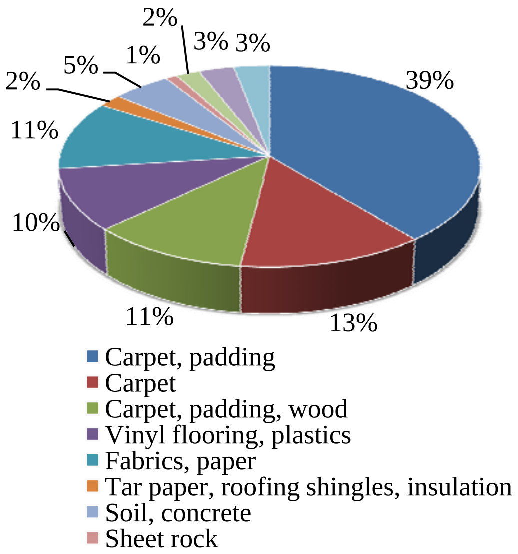


**Figure 1.3 Percent composition from 1770 samples submitted for fire debris analysis. Reproduced from Berstch and Zhang[12].**

The majority of the submitted samples have included carpet, carpet padding and wood, followed by fabrics and paper, vinyl flooring, plastics and other items. For example, Almirall and Furton, suggested that 54.6% of fire debris samples submitted to the Florida Fire Marshal’s laboratory contained burned materials or building material such as the remains of burnt structural materials including timbers, masonry and other building parts such as floorings, window sills and doors [17].

## 1.4 Collection and Storage of Fire Debris Samples

The quality and appropriateness of the packaging materials used and the use of an appropriate sample extraction technique are major issues in fire debris analysis. Packaging material is chosen in order to contain and transport fire debris samples from the scene to the laboratory, such that loss of volatile ignitable liquid residues and any potential contamination is minimised. Appropriate packing material should be gas tight, inert, impermeable to hydrocarbon vapours, durable and devoid of any residues that may interfere with the test results [13]. The physical attributes of the sample may also need to be considered. The types of packaging material commonly used are untreated paint cans with lid, glass jars with screw lid and various types of plastic bags.

### 1.4.1 Fire Debris Packaging Materials

Metal tins are robust, impermeable to vapour residues and available in various sizes. This type of packaging material is most commonly used for fire debris sampling in the USA [6]. Its suitability of the tins have been investigated and have proven to retain volatile materials with minimal degree of hydrocarbon vapour leakage [14-15]. The author also suggested that sample loss could be higher if the container was stored for longer at elevated temperature. A more recent study by William and Sigman found that tin cans perform better than glass jars in terms of minimising sample loss and permeability[16]. The metal can is susceptible to corrosion over time and as a consequence the cans may be lined with a plastic or epoxy coating to prevent corrosion, however the lining can bleed or diffuse into the can when the sample is treated for subsequent analysis[9].

Glass jars are used widely in many European countries [17]. Glass is transparent, rust free and has a long life span but is susceptible to breakage, cannot easily contain large samples and the screw lid is not particularly airtight [18]. Glass jars have been shown to have the fastest leakage rates compared with other packaging materials and contamination (<0.1µL/L concentration) from the rubber seal screw caps have also been reported [16, 19].

Polymer bags such as polyethylene bags, polyester bags, nylon bags and copolymer (nylon/polyester/polyolefin or nylon/polyethylene) bags are the most frequently used for fire debris as they are flexible, transparent, inexpensive, water resistant, light weight and convenient to transport and store [20]. Leakage and background contamination issues from plastic bags are known and extensive research to evaluate the robustness of this type of packaging for sampling of fire debris exhibits have been performed [15-17, 19, 21-25]. Another concern for plastic packaging is the difficulty in sealing the bags. Heat sealing, although not very practical in the field, is the most effective sealing method [16]. Other sealing techniques include folding taping, sealing with a cable tie and knotting the bag [6, 26].

### 1.5 Developments in Fire Debris Analysis

Fire debris analysis was first reported in the early 20th century using steam distillation and solvent extraction of an ignitable liquid residue and a simple identification using odour recognition. By the 1950s, most ignitable liquids were still being isolated from debris using either distillation or solvent extraction techniques and most detection was undertaken by boiling point, refractive index and specific gravity determination on the isolated samples. Around this time, spectroscopic analysis using emission spectroscopy and infrared spectrophotometer were also being reported for the analysis of volatile compounds from ignitable liquid residues [27-28].

Fire debris analysis was revolutionised in the 1960s with the introduction of gas chromatographic techniques together with new developments in ignitable liquid residue extraction methods. Simpler and essentially non-destructive extraction methods involving passive headspace analysis was introduced by Ettling and Adam in 1968[29]. Improvements in terms of instrumental sensitivity and robustness of extraction methods have developed considerably since then. Further discussions on extraction techniques are included in section 1.6.

In tandem with technological advancements, efforts to “regulate” practises within fire debris analysis were also developing with the establishment of an ignitable liquid classification scheme, standard methods and guidelines for laboratory analysis, [6, 26]. The American Society for Testing and Materials (ASTM) E 30 committee on Forensic Sciences has published a comprehensive ignitable liquid classification scheme and has compiled guides[1], practises[2] and test method[3] procedures for the preparation, extraction and analysis of fire debris extracts[30-31].

Similar procedures have been developed by the European Network of Forensic Science Institutes (ENFSI) Fire and Explosion Investigation working group [32-33]. A refined structure for fire debris analysis has been presented by Stauffer *et al* and is simplified in figure 1.4 [6].

---

[1] According to the Form and Style for ASTM Standards; guide means “a compendium of information or series of options that does not recommend a specific course of action”

[2] Practise means “a definitive set of instructions for performing one or more specific operations that does not produce a test results”

[3] Test method means “a definitive procedure that produces a test result”

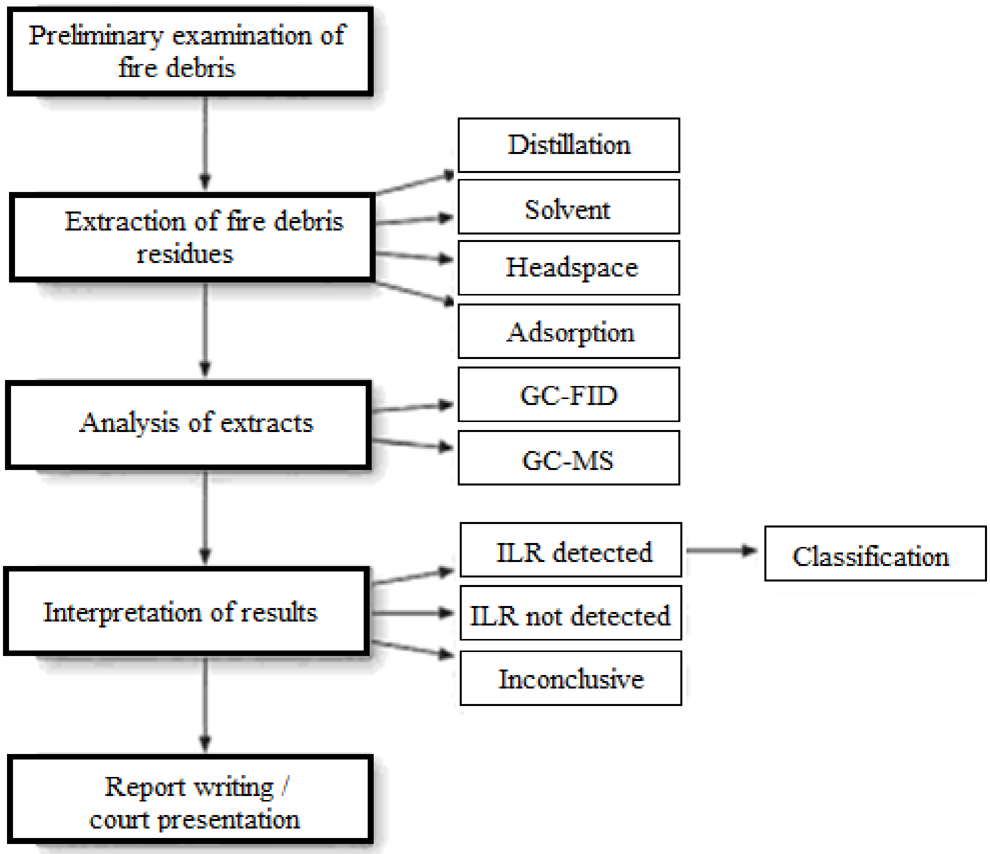


**Figure 1.4 Schematic diagram showing laboratory procedures for examination of fire debris samples. Reproduced from Stauffer, Dolan and Newman [6].**

### 1.5.1 Ignitable Liquid Classification Scheme

The identification of an ignitable liquid is based on class characterisation. Systematic groupings of ignitable liquids have been established by the ASTM which in principle groups the ignitable liquids on the basis of hydrocarbon composition, boiling point and raw material source[34]. This classification scheme featured in ASTM E 1387 and ASTM E1618 had undergone several revisions since it was first introduced in the 1980s. Initially, classification of ignitable liquids was limited to six groupings with a miscellaneous class further divided into five sub-classes and is presented in table 1.1.

**Table 1.1 Previous ASTM International flammable and combustible liquid classification systems [34-35].**

| Class number | Class name | Example |
|---|---|---|
| 1 | Light petroleum distillates (LPD) | Pocket lighter fuel |
| 2 | Gasoline | Gasoline, gasohol |
| 3 | Medium petroleum distillates (MPD) | Mineral spirits, charcoal lighter fluid |
| 4 | Kerosene | Jet A-fuel, No.1 fuel oil |
| 5 | Heavy petroleum distillates (HPD) | Diesel fuel, No. 2 fuel oil |
| 0 | Miscellaneous | |
| 0.1 | Oxygenated solvents | Alcohols, ketones |
| 0.2 | Isoparaffins | Copier toners, specialty solvents |
| 0.3 | Normal alkanes | Solvents, candle oils |
| 0.4 | Aromatic solvents | Xylenes, insecticide solvents |
| 0.5 | Naphthenic/paraffinic solvents | Lamp oils, insecticide solvents |

This classification system was revised in 2000 to take into account the growing range of ignitable liquid products available on the market [36]. The revised system is presented in table 1.2 and allows each class, with the exception of petrol, to be sub-categorised into light, medium and heavy carbon compounds. However, in certain products, when the carbon number cannot be specified by one subclass, combinations of “light to medium” or “medium to heavy” is permitted in order to correctly describe the sample[34].

**Table 1.2 Current ASTM International flammable and combustible liquid classification systems [34-35].**

| Class name | Light (C4-C9) | Medium (C8-C13) | Heavy (C8-C20) |
|---|---|---|---|
| Gasoline | Fresh gasoline typically falls in the range of C4–C12, including gasohol | | |
| Petroleum Distillates | Camp fuels | Charcoal starters | No. 1& No.2 fuel oils |
| Isoparaffinic products | Aviation gas | Copier toners | Specialty solvents |
| Aromatic products | Xylene/toluene | Fuel additives | Cleaning solvents |
| Naphthenic/paraffinic products | Solvents | Lamp oils | Copier toners |
| Normal alkane products | Pentane | Candle oils | |
| De-aromatised distillates | Fuel additives | Metal cleaners | |
| Oxygenated solvents | Alcohols/ketones | Industrial solvents | |
| Other / miscellaneous | | Turpentine | |

## 1.6 Extraction Techniques of Ignitable Liquid Residues

The main aim of the extraction process is to isolate the ignitable liquid residue from the fire debris substrate and pre-concentrate the extracted residues prior to analysis. Various techniques are used and are discussed in the following sections.

### 1.6.1 Steam Distillation

The use of steam distillation in the extraction of ignitable liquid residues from fire debris dates back to the 1940s though it is now rarely used [6, 37]. This method is time consuming, destructive and provides poor sample recovery. Guidelines for steam distillation are provided in ASTM E1385 however, recent literature and confirmation from ASTM International have reported that this method has now been withdrawn[6, 38].

### 1.6.2 Solvent Extraction

This procedure is reported as a relatively good technique to recover hydrocarbon compounds of C18 and higher [39]. However, contamination from matrices such as fine particulate material or fire suppressant (if used) can carry over into the sample, resulting in deterioration of any ignitable liquid residue which may be present and as such, has restricted the use of the method. The method involves washing of the debris sample with a fixed volume of solvent followed by a filtering stage (if needed). The sample is then concentrated prior to analysis.

Solvent extraction can also be applied to non porous samples such as glass and plastic materials and guidelines are presented in the ASTM E1386 [40]. Common solvents used include;

i. carbon disulfide : very toxic, highly flammable but clean in terms of matrix carryover, has high desorption efficiency and is very effective. Despite concerns over health and safety, it is able to desorb aromatics and aliphatic hydrocarbons very well [6, 12, 39, 41]

ii. diethyl ether: effective for aromatics and aliphatic hydrocarbon desorption, however it is also highly flammable and subject to rapid evaporation [6, 12, 39, 42]

iii. pentane : common solvent and less hazardous relative to others [6, 39, 41]

iv. methylene chloride : effective for all hydrocarbons but in relation to other solvents, is reported to have tendency to dissolve plastic material, hence can possibly carry a significant amount of contamination from sample matrix [6, 39].

### 1.6.3 Direct Headspace/ Simple Headspace

In principle, volatile ignitable liquids present in a debris sample may reach equilibrium when placed inside a closed container [39]. The vapours fill the headspace of the container and can be extracted using gas tight syringes, where a small volume of the vapour is withdrawn from the container and injected directly into the gas chromatograph. To assist the sample to reach a vapour equilibrium, the container is heated for a certain period of time at moderate temperatures as suggested by DeHaan [20]. This technique was, however, reported to be insufficient for the removal of higher molecular weight compounds such as diesel hydrocarbon fractions, but can be very useful as a screening tool. ASTM E 1388 provides a recognised international guideline for direct headspace extraction [43].

### 1.6.4 Dynamic /Swept Headspace / Purge and Trap (Adsorbent Sampling)

Adsorbent sampling techniques, such as passive and dynamic headspace analysis, are arguably the most commonly used methods of sample extraction and concentration ASTM E1413 outlines the method used for dynamic headspace analysis [44]. This technique requires the fire debris sample container to be placed on a heated platform and a source of carrier gas passed into the sample container. The heated headspace (containing any ignitable liquid vapours) from the sample container is then drawn through an activated charcoal adsorbent to retain the volatile components. The trapped sample is desorbed by either a solvent wash or thermally [37, 45]. The overall sampling procedure is rapid and sensitive.

### 1.6.5 Dynamic Headspace Diffusion (Tenax TA)

Polymeric material adsorbent, commercially known as Tenax® is a synthetically produced porous polymer resin (2,6-diphenylene oxide) that is packed into tubes [46]. It is specifically designed for the trapping of volatiles and semi-volatiles from air or from samples which have been purged from liquid or solid sample matrices [46-47]. Due to its low affinity for water, Tenax is useful for trapping hydrophobic volatiles from samples with a high moisture content. Tenax is suitable for the extraction of compounds with boiling point ranges from 50-300°C, and it is thus less efficient for the adsorption of lower boiling point compounds such as alcohols and other oxygenated compounds [48].

There are various literature methods involving the use of Tenax as a medium for fire debris extraction which are similar to the direct headspace approach [6, 18, 45]. The fire debris container is preheated (60-80°C) and the headspace is drawn through the Tenax tube using a syringe. The Tenax tube is then thermally desorbed using an automated thermal desorber (ATD) at the injection port of the gas chromatograph. All adsorbed compounds are thermally removed and analysed, resulting in better sensitivity in terms of compound recovery. The process time is relatively short and the process facilitates repetitive analysis of the sample [49].

### 1.6.6 Passive Headspace Diffusion (Activated Carbon)

This method is similar to direct headspace method except that any volatile organic components are trapped or absorbed passively onto a suspended adsorbent. Twibel and Home first reported the use of a wire coated with activated charcoal as the solid adsorbent [50]. Since then, the method has been modified to improve extraction sensitivity and charcoal adsorbents now include charcoal coated plexiglass, charcoal bags and activated carbon strips (ACS) commercially known as Diffusive Flammable Liquid Extraction (DFLEX®) which have been shown as appropriate and effective adsorbents for most ignitable liquid classes [51-55].

Activated carbon is usually derived from substances with high carbon content such as coal, wood and coconut shells [56]. It has a random imperfect structure which is highly porous over a broad range of pore sizes. This structure provides a very large surface area which allows the carbon to adsorb a wide range of compounds (boiling point range 0 – 250°C) and has high affinity for non polar hydrocarbon compounds [48]. In passive adsorption, the carbon strip adsorbs $C_7$ – $C_{10}$ hydrocarbons when exposed to a sample for short periods of time while longer exposure times results in the adsorption of higher $C_{14}$ - $C_{20}$ hydrocarbon compounds [6, 37].

Adsorption is conducted in an appropriate container where the activated carbon is suspended over the fire debris sample and is left to equilibrate at room temperature or more commonly heated at 60°C to 80°C for 12 to 16 hours. After incubation of the sample, the volatiles are desorbed from the adsorbent using a solvent such as carbon disulfide, pentane, diethyl ether or methylene chloride which is then injected directly into the gas chromatograph. A recommended guideline for this procedure is provided in ASTM E1412[57].

Because headspace using activated charcoal is a non-destructive technique, it facilitates further analysis of the sample if necessary. Sample archiving is also possible using ACS strips. This technique requires simple apparatus and the actual sample preparation is short apart from the adsorption time in the oven.

Optimisation issues such as temperature and duration of incubation, adsorbent properties, volatile component concentration and desorption solvent may directly influence the representation of the actual content from the sample and have been studied in depth [42, 53, 58-61]. These issues are also addressed in ASTM E1412 [57].

### 1.6.7 Passive Headspace Extraction by Solid Phase Microextraction (SPME)

In the early 1990s the development of solid-phase micro extraction (SPME) by Pawliszyn [62] provided a new variant of the passive adsorption technique. This technique combined the sample extraction and concentration into one step and was easily automated for the analysis of volatile compounds from liquids, solids and gases. The fibre coating within the SPME system is exposed to the headspace of the sample in question and any volatile organic compounds adsorbed onto its surface. The SPME fibre is then inserted directly into the gas chromatograph injection port for thermal desorption [63]. A recommended procedure for this method is presented in ASTM E2154 [64].

A silica fibre coated with polymer, commonly the polydimethylsiloxane (PDMS) is used for extraction of hydrocarbons from fire debris samples [39]. Because it is synthetically made, the properties of the SPME fibre, such as the sorbent type and the size or thickness of the needles, can be manipulated [65]. PDMS fibre is known to be suitable for polar and non polar analytes but less efficient for compounds with lower boiling ranges [48]. More polar SPME fibres such as Carboxen/PDMS fibres have been suggested to benefit the extraction of more polar target compounds [48]. Depending on the fibre type and temperature, SPME fibres may have some preferential affinity towards aliphatic or aromatic compounds from the headspace such as PDMS and Carboxen/PDMS show preferential extraction of aliphatic or aromatic compounds [66]. The optimisation of various types of SPME fibres have been shown by Furton *et al*. and more recently by Yoshida *et al*. [67-68].

Earlier work by Almirall, Bruna and Furton demonstrated the use of SPME for the rapid extraction and higher sensitivity detection of pocket lighter fluid, petrol and diesel from aqueous solutions [63]. The sensitivity of this method over ACS with hexane elution demonstrated that traces of liquid accelerants at 50ppm were detectable and chromatographically comparable to its unevaporated form.

Thermal and chemical desorption of SPME fibres was studied by Harris and Wheeler [69]. The authors claimed that the SPME–chemical desorption technique produced results which were comparable to the ACS method using micro amount of solvents (carbon disulfide). Although they believed that SPME with conventional desorption was as effective as the ACS technique, the variation from the SPME extraction method was high, with 15-20% relative standard deviation (RSD). Other literature reported the presence of background peaks after a number of repeat use of the fibres even after cleaning [35, 66].

## 1.7 Instrumental Analysis of Ignitable Liquid Residue

At present gas chromatography (GC) is the most widely accepted technique used to screen, characterise and identify ignitable liquid residues in fire debris samples and was first reported for this application in 1960 [37]. At present, gas chromatography coupled with a flame ionisation detector (GC-FID) or a mass spectrometer (GC-MS) are both widely used and a standard method pertaining to these procedures are outlined in ASTM 1387 and ASTM E1618 standard test method respectively [70-71]. The application of GC-MS in fire debris analysis is increasingly popular because it provides confirmation of the identity of specific compounds.

### 1.7.1Chromatography

Chromatography, which means ‘colour writing’ was developed by Twsett in 1903 [72]. Modern scientific explanation by The International Union of Pure and Applied Chemistry (IUPAC) defines chromatography as “a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary (stationary phase) while the other (the mobile phase) moves in a definite direction” [73].

Two critical elements in a chromatographic system are the stationary and mobile phases. The stationary phase can be a solid, a liquid coated on a solid or a gel which are prepared in the form of either packed tubes (i.e. a column) or thin layers coated onto inert supports such as glass, plastic or aluminium [74]. Liquid or gas is utilised as a mobile phase to move the samples contained within mixtures of components (or analytes) through the stationary phase.

In principle, chromatographic separation is based upon an analyte’s differential affinity (interaction) and equilibrium between the mobile and stationary phases [74]. As the analytes migrate through the chromatographic system, they separate from one another based on their affinity to the stationary phase. Analytes with less affinity towards the stationary phase travel more rapidly while those with greater affinity towards the stationary phase move fairly slowly through the chromatographic column (figure 1.5). Affinity towards the stationary phase may be based either on adsorption, size or polarity depending on the sample and the chromatographic system being employed. During the process, equilibration of the analytes between stationary and mobile phase occur and separation become more pronounced as the samples progress through the system.

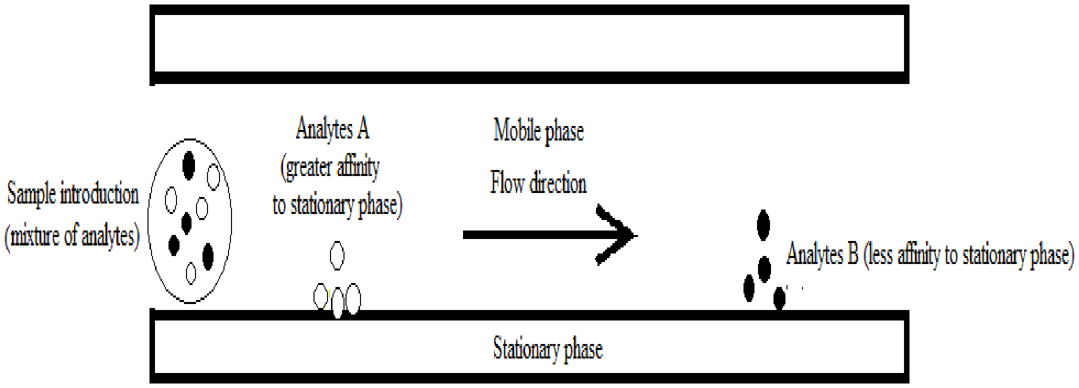


**Figure 1.5 Illustration of differential affinity in chromatography system.**

Among the many chromatographic systems available, gas chromatography is mainly use for ignitable liquid analysis.

### 1.7.2 Gas Chromatography

When a sample is introduced into a gas chromatographic system, it travels through a number of analytical compartments, each of which plays an important role. A diagram of a general gas chromatographic system as presented in figure 1.6, and consists of an injector port, carrier gas, analytical column, detector and recorder.

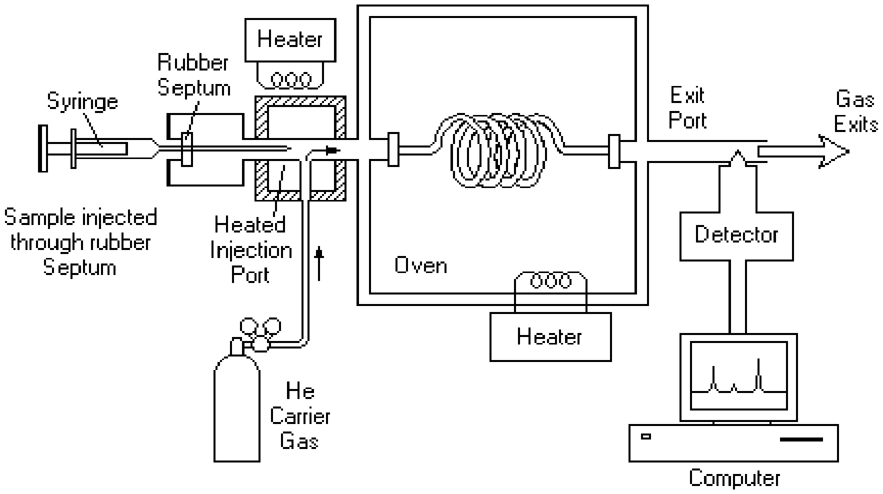


**Figure 1.6 General lay out of a typical gas chromatograph instrumental set-up [75].**

### *1.7.2.1 GC Inlet/Injection Port*

The injection port is a heated compartment sealed by a septum. Upon sample introduction, the sample will vaporise and be swept into the column by the carrier gas. At the injection port, split or splitless mode allows either a portion or the whole of the injected sample respectively, to be analysed in the column. Split mode is required to prevent overloading of the column whereas splitless mode is normally used in the analysis of trace samples[74].

### *1.7.2.2 Carrier Gas*

High purity inert gases such as nitrogen, helium or hydrogen are used to transport analytes throughout the system as they do not chemically react or interact with the compound being analysed. When GC is coupled to a mass spectrometer (MS), helium gas is the carrier gas of choice, as it is not only chemically inert, but also does not contribute or interfere with the mass spectral patterns of the compounds under analysis [74, 76].

### *1.7.2.3Analytical Column*

The column is the heart of a GC. Inside an oven, it is fixed between the injection port and the detector. For effective separation to occur, two main variables need careful consideration, the choice of column and the correct temperature settings. The oven temperature is monitored or adjusted according to the experimental procedure required. Automated temperature programming allows the oven to gradually increase it’s temperatures within a specified time to allow the separation of the analytes at different rates.

There are two types of GC column, packed columns and capillary columns. Packed columns are less sensitive and no longer used for fire debris analysis. Capillary columns have the advantage of being able to provide high efficiency separations of complex mixtures [6, 26].

A bonded, non-polar capillary column, methylsilicone or phenylmethylsilicone (phenylmethylpolysiloxane) column or equivalent is required for ignitable liquid analysis and are recommended in ASTM E1618 [70]. The structures of both stationary phases are presented in figure 1.7.

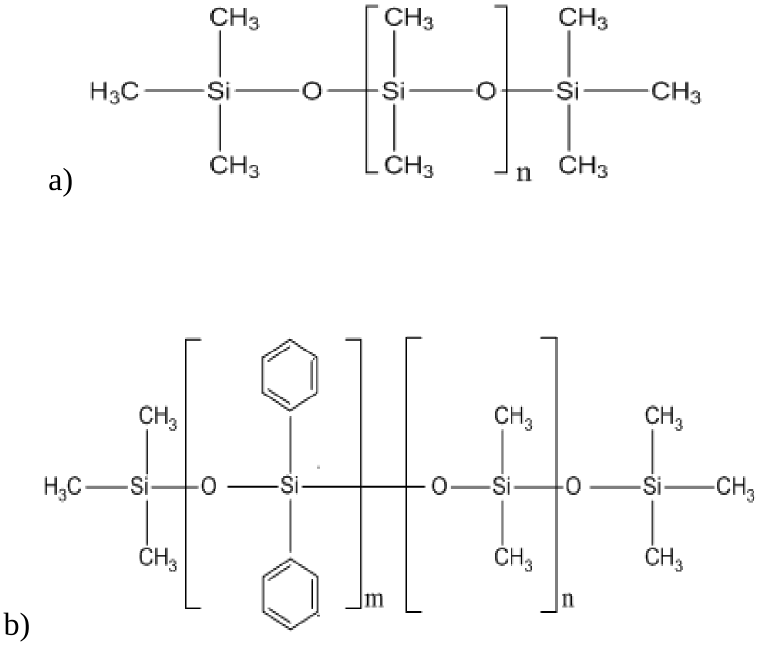


**Figure 1.7 Structure of non polar a) methylsilicone and b) phenylmethylsilicone (synonymous with phenylmethylpolysiloxane).**

### 1.7.3 Flame Ionisation Detectors (GC–FID)

The flame ionisation detector is a universal detector generally responding to any compound containing organic carbon with a relatively low detection limit [39]. The hydrocarbon compound eluting from the column is transformed into an ionic form by combustion with the flame at the point of exit into the detector. These ions are converted into a current which is amplified, and presented as a chromatogram.

GC-FID has been widely used within forensic laboratories in fire debris analysis and ASTM E1387 outlines a standard method for its use in this application [71]. Typically, the instrument is used for routine analysis where the chromatogram is compared against a collection of chromatograms of known reference standards.

Extensive literature regarding the characterisation and identification of ignitable liquid residue from fire debris samples using GC-FID is available [6, 18, 20, 26, 39, 77-79].

#### *1.7.3.1 Limitations of GC-FID*

GC-FID is particularly useful when the presence of ignitable liquid residue is in abundance, but becomes less useful for samples containing lower concentrations or in highly evaporated or highly contaminated samples [80]. The development of a high resolution capillary column, oven-temperature programming and method optimisation has definitely improved component separation, but for complex samples, the problem of co-elution is still prominent. Despite these limitations, it is a well established method and is still widely accepted in the analysis of fire debris samples.

### 1.7.4 Gas Chromatography-Mass Spectrometry (GC-MS)

A GC-MS system consists of two instruments bridged together to create a powerful analytical instrument that can separate, characterise and identify volatile components within complex mixtures. The mass spectrometer is comprised of three major elements, which are the ioniser for ionising and fragmenting the sample, the mass analyser for separating the ionised particles and a detector, as presented in figure 1.8.

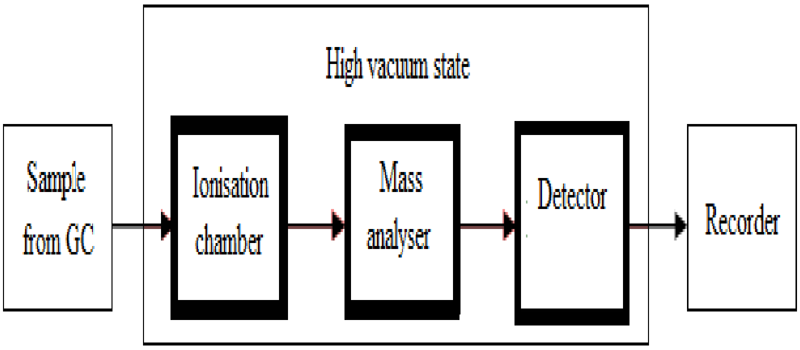


**Figure 1.8 Basic diagram showing major elements of a mass spectrometer.**

### *1.7.4.1 Ionisation Source*

The mass spectrometer operates within a high temperature (200°C-300°C) and low pressure ($10^{-5}$ to $10^{-6}$ torr) vacuum system. This maintains the sample in a vapour state on emergence from the GC, so that it can be readily introduced into the ionisation chamber. In addition, keeping the system under vacuum prevents collision between air particles and sample molecules, provides a ‘clean’ enclosed atmosphere for the ionisation process and reduces the production of background mass spectra [81].

MS analysis begins with the ionisation of the sample molecule. Numerous ionisation techniques are available, though electron impact ionisation (EI) is the most widely used for organic samples [81-82]. In EI mode, a high energy electron beam (70eV), is generated using a heated tungsten filament. This is accelerated towards an anode and in doing so, collides with molecules of the sample to be analysed [81]. The collision removes an electron from the sample molecule, producing a charged molecule or radical cation known as the molecular ion (or parent ion) and denoted as $M^{+\bullet}$.

$$M\,(g) + e^- \rightarrow M^{+\bullet} + 2e^-$$

Continuous bombardment causes the molecular ion to break down further producing more fragment ions or daughter ions.

$$M^{+\bullet} \rightarrow m_1^+ + m_2^\bullet \quad \text{or}$$

$$M^{+\bullet} \rightarrow m_1^+ + m_2$$

All of these ions are then separated according to their mass to charge ratio (m/z ratio) by the mass analyser and detected in proportion to their abundance. Neutral particles such as $m_2\bullet$ or $m_2$ are not detected.

### *1.7.4.2 Quadrupole Mass Analyser*

The mass analyser separates ions according to their mass to charge (m/z) ratio using magnetic or electrical fields. A common mass analyser is the quadrupole ion analyser. The quadrupole analyser consists of four parallel rods positioned along the direction of travel of the generated ions as presented in figure 1.9.

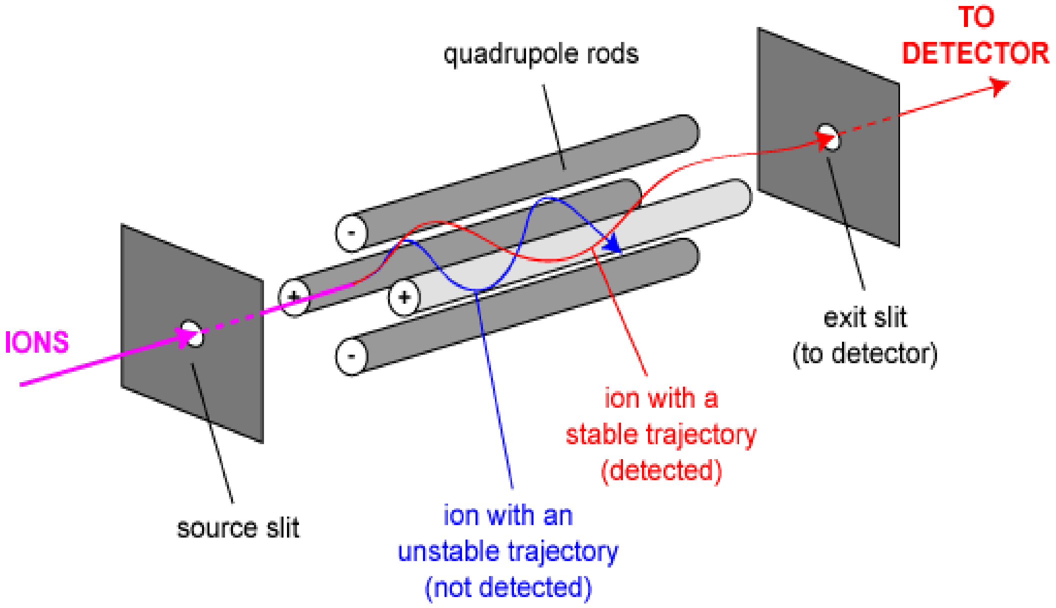


**Figure 1.9 Quadrupole mass analyser. Reproduced from[83].**

Adjacent rods are of opposite charge and have fixed direct current (DC) and alternating radio frequency (RF) fields. As a result, an electromagnetic field is created within the region of the four rods, causing the ions generated from the fragmented sample to travel in a spiral path down through the quadrupole. The electromagnetic field around the poles is manipulated so that ions with a certain m/z range reach the detector without colliding with the rods. Ions outwith the range will be deflected out or collide with the rods, and are not detected. Only molecular ions and fragment ions will pass to the detector, which then records the abundance of each m/z ratio species [82, 84-85].

### 1.7.4.3 MS Detector

After separation of the fragmented ions according to their m/z ratio, the ion is attracted into a tube detector, usually a dynode electron multiplier. When the ion strikes the dynode conductive surface, a secondary electron is produced. A typical electron multiplier tube consists of 12 to 24 dynodes. As electrons accelerate along the detector tube, they continually strike the dynode surface, causing further electron multiplication. The process is illustrated in figure 1.10.

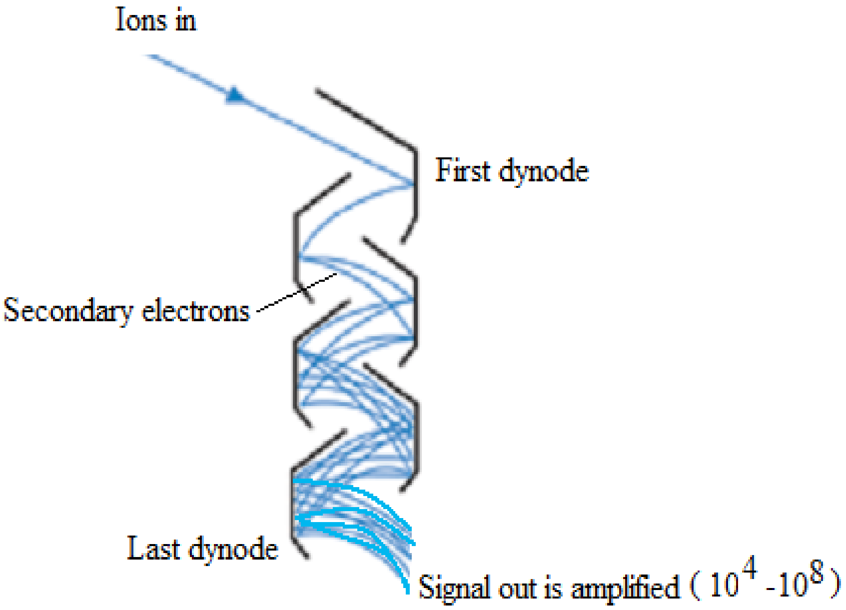


**Figure 1.10 Illustration of electron multiplication in mass spectrometer detector (adapted from[86]).**

As a result, the low original signal is amplified, producing a stronger signal with a gain of in the order of $10^4$-$10^8$ [86]. A typical mass spectrum is illustrated in figure 1.11, shown as a bar graph of relative abundance versus mass to charge ratio.

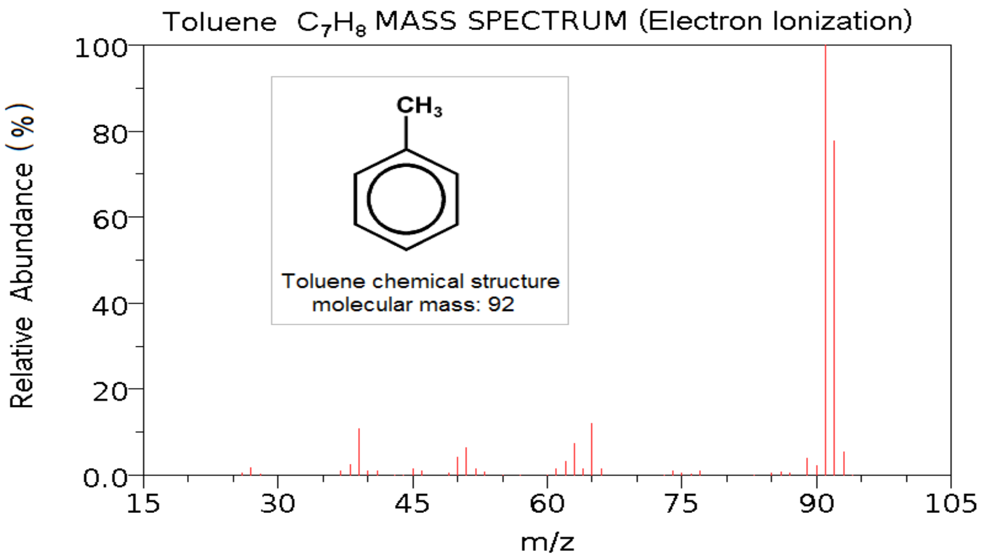


**Figure 1.11 An example of toluene mass spectrum [87].**

Mass spectral data is collected either in scan acquisition mode (SCAN), or selected ion monitoring mode (SIM). Scan acquisition mode provides a wide range of ion detection, commonly set between 10 – 400 amu (atomic mass units) in fire debris analysis. Scan mode produces a total ion chromatogram (TIC). SIM mode on the other hand, scans ions that are pre-selected to detect the compounds of interest. SIM mode increases the detector sensitivity and can also be performed on data acquired using the scan acquisition mode.

### *1.7.4.4 Limitations of GC-MS*

Identification of every peak in a total ion chromatogram of an ignitable liquid mixture can be very time consuming and challenging due to the often complex samples presented. The MS detector is unable to distinguish and discriminate between compounds with similar chemical structures or co-eluting compounds having the same ion mass. Problems can be encountered in the examination of isomeric molecules such as ortho, meta, para-xylene or when examining interferences which have originated from materials that are derived from petroleum based products.

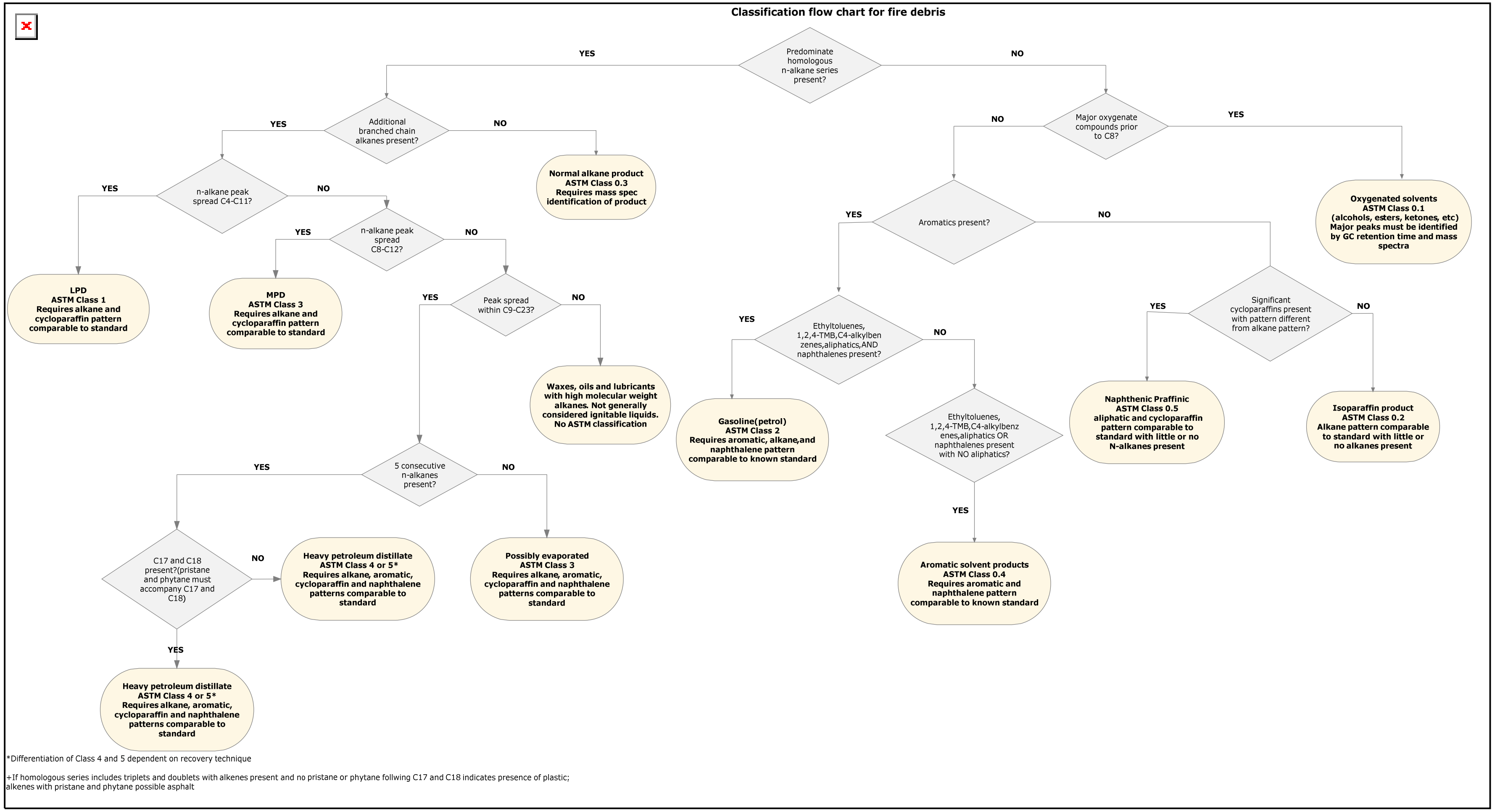
## 1.8 Interpretation of Ignitable Liquid and Ignitable Liquid Residues

The GC-MS total ion chromatogram (TIC) is analogous to a conventional GC chromatogram. Identification of ignitable liquid and ignitable liquid residues are made based on visual pattern matching methods. The TIC pattern and relative peak (area or height) ratio obtained from the sample are visually compared to an ignitable liquid reference collection or database to identify the class of ignitable liquid present. Early citation of interpretation and applications of GC-MS data for ignitable liquid and ignitable liquid residue from fire debris samples is discussed by Mach [88] who achieved good separation when a shorter GC column was utilised.

The feasibility of GC-MS in ignitable liquid analysis was described by Smith who demonstrated the utilisation of mass chromatography, selective ion monitoring and extracted ion profiles to distinguished ignitable liquid samples, ignitable liquid residues and substrate residues [89-90]. The benefits and advantages of using GC-MS in fire debris analysis was further elaborated in various publications in which the authors suggested a more systematic approach to sample analysis [91-93]. Interpretation of various range of ignitable liquids including samples from real case work by mass spectral profiles are also discussed [94-95].

In general, for confirmation of the presence of a given compound, matching of the ion profiles can be done by isolating a single peak from the TIC and using the mass spectral data to identify the compound to which the peak relates. In addition, the use of a target compound chromatogram (TCC) with mass chromatography techniques are routinely employed to identify the ignitable liquid class which may be present in a given sample [39, 89-90, 92, 94-99].

Some authors have suggested that, once the sample has been analysed, a schematic flow diagram, presented in figures 1.12 and figure 1.13, can assist in the decision making required to assign the sample to a specific ignitable liquid classification [9,117].



*Differentiation of Class 4 and 5 dependent on recovery technique

+If homologous series includes triplets and doublets with alkenes present and no pristane or phytane follwing C17 and C18 indicates presence of plastic; alkenes with pristane and phytane possible asphalt

**Figure 1.12 Interpretation and classification of ignitable liquid and ignitable liquid residue based on previous ignitable liquid classification scheme. Reproduced from Newman[99].**

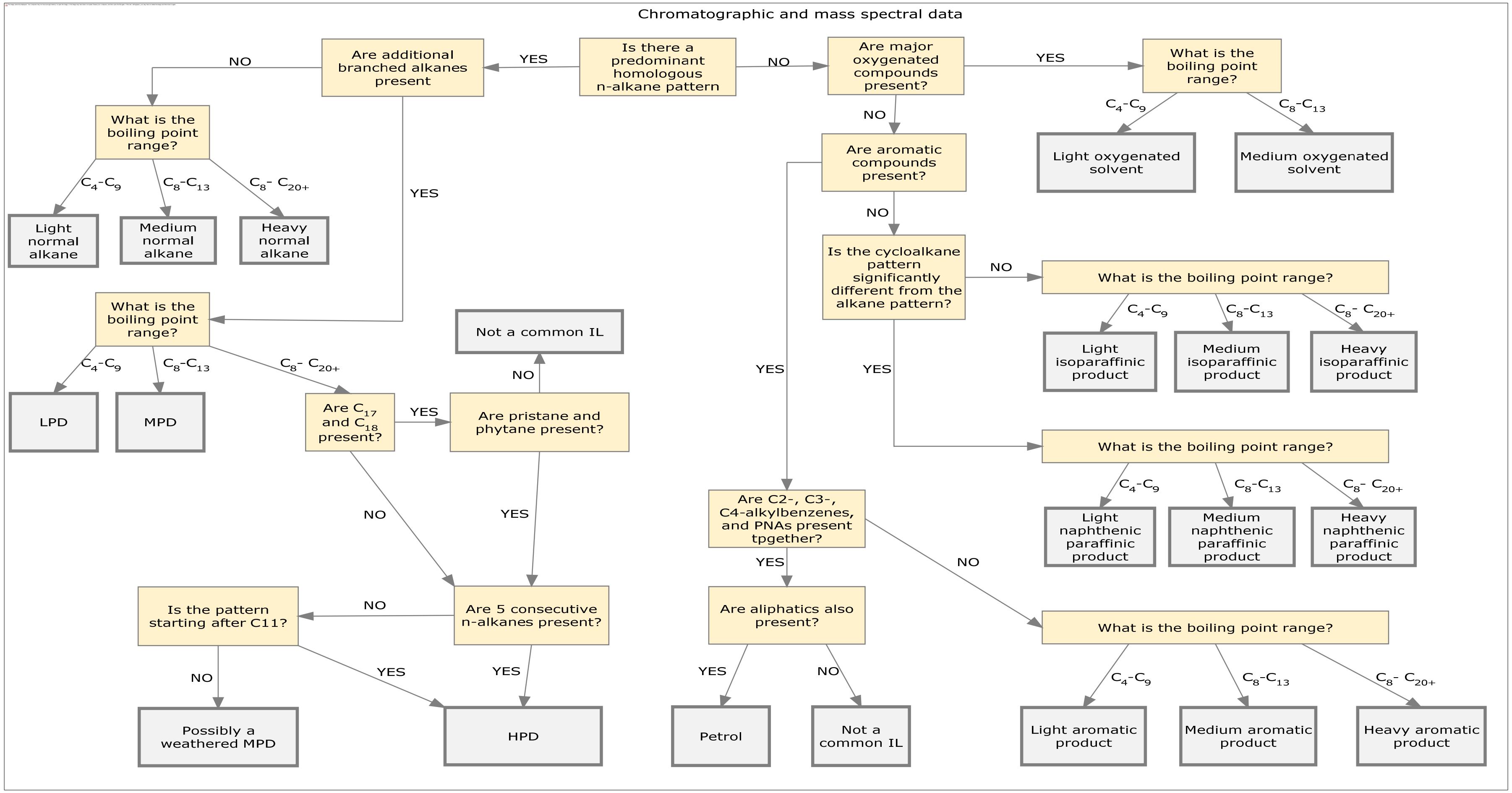


**Figure 1.13 Classification flow chart of IL and ILR based on recent IL classification scheme ASTM E1618. Reproduced from Stauffer [6].**

### 1.8.1Target Compound Chromatogram (TCC)

The production of a target compound chromatogram (TCC) involves the selection of certain class compound data that can be used to characterise and identify the sample [20, 26, 37, 48]. It is carried out by pre-setting information within the computer software to characterise the sample, such as retention time, relative abundance and the m/z value of key specific compounds. Typical target compounds for ignitable liquid analysis are listed in tables 1.3 - 1.5 [70].

**Table 1.3 Petrol Target Compounds [11].**

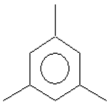
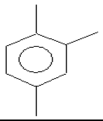
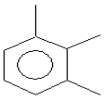
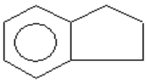
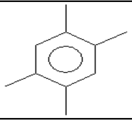
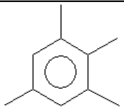
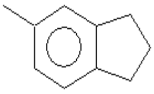
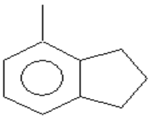
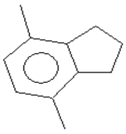
| Compound | CAS Number | Molecular structure |
|---|---|---|
| 1,3,5-Trimethylbenzene<br>($C_9H_{12}$) | 108–67–8 |  |
| 1,2,4-Trimethylbenzene<br>($C_9H_{12}$) | 95–36–3 |  |
| 1,2,3-Trimethylbenzene<br>($C_9H_{12}$) | 526–73– 8 |  |
| Indane<br>($C_9H_{10}$) | 496– 11– 7 |  |
| 1,2,4,5-Tetramethylbenzene<br>($C_{10}H_{14}$) | 95– 93– 2 |  |
| 1,2,3,5-Tetramethylbenzene<br>($C_{10}H_{14}$) | 527– 53–7 |  |
| 5-Methylindane<br>($C_{10}H_{12}$) | 874– 35– 1 |  |
| 4-Methylindane<br>($C_{10}H_{12}$) | 824– 22– 6 |  |
| Dodecane<br>($C_{12}H_{26}$) | 112–40– 3 |  |
| 4,7-Dimethylindane<br>($C_{11}H_{14}$) | 6682– 71– 9 |  |

***Table 1.3 Continued***

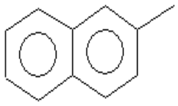
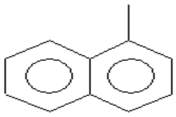
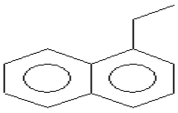
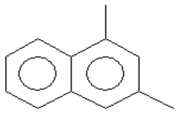
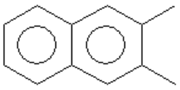
| | | |
|---|---|---|
| 2-Methylnaphthalene<br>$(C_{11}H_{10})$ | 91– 57– 6 |  |
| 1–Methylnaphthalene<br>$(C_{11}H_{10})$ | 90–12– 0 |  |
| Ethylnaphthalenes (mixed)<br>$(C_{12}H_{12})$ | 1127–76– 0 |  |
| 1,3-Dimethylnaphthalene<br>$(C_{12}H_{12})$ | 575– 41– 7 |  |
| 2,3-Dimethylnaphthalene<br>$(C_{12}H_{12})$ | 581–40–8 |  |

**Table 1.4 Medium Petroleum Distillate (MPD) Target Compounds [11].**

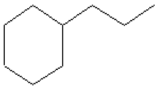
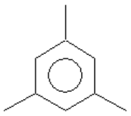
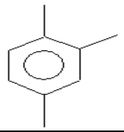
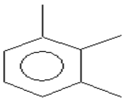
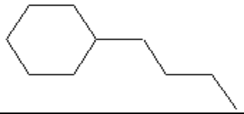
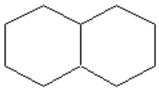
| **Compound (chemical formula)** | **CAS Number** | **Molecular structure** |
|---|---|---|
| Nonane<br>$(C_9H_{20})$ | 111–84– 2 |  |
| Propylcyclohexane<br>$(C_9H_{18})$ | 1678–92–8 |  |
| 1,3,5-Trimethylbenzene<br>$(C_9H_{12})$ | 108– 67–8 |  |
| 1,2,4-Trimethylbenzene<br>$(C_9H_{12})$ | 95–36–3 |  |
| Decane<br>$(C_{10}H_{22})$ | 124–18– 5 |  |
| 1,2,3-Trimethylbenzene<br>$(C_9H_{12})$ | 526– 7–8 |  |
| n-Butylcyclohexane<br>$(C_{10}H_{20})$ | 1678– 93– 9 |  |
| Trans-decalin<br>$(C_{10}H_{18})$ | 493– 02– 7 |  |
| Undecane<br>$(C_{11}H_{24})$ | 1120– 21– 4 |  |

***Table 1.4 Continued***

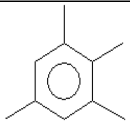
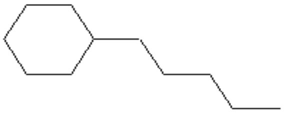
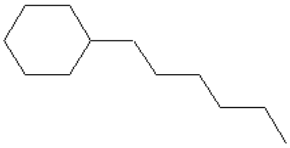
| | | |
|---|---|---|
| 1,2,3,5-Tetramethylbenzene<br>($C_{10}H_{14}$) | 527– 53–7 |  |
| n-Pentylcyclohexane<br>($C_{11}H_{22}$) | 4292– 92– 6 |  |
| Dodecane<br>($C_{12}H_{26}$) | 112– 40– 3 |  |
| n-Hexylcyclohexane<br>($C_{12}H_{24}$) | 4292– 75– 5 |  |

**Table 1.5. Heavy Petroleum Distillate (HPD) Target Compounds [11].**

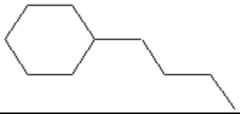
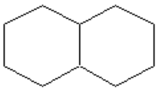
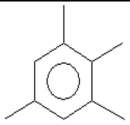
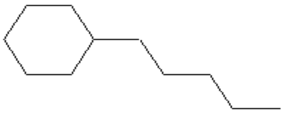
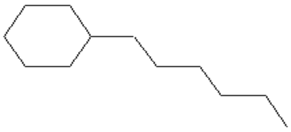
| **Compound**<br>**(chemical formula)** | **CAS Number** | **Molecular structure** |
|---|---|---|
| Decane<br>($C_{10}H_{22}$) | 124–18– 5 |  |
| n-Butylcyclohexane<br>($C_{10}H_{20}$) | 1678– 93– 9 |  |
| Trans-decalin<br>($C_{10}H_{18}$) | 493– 02– 7 |  |
| Undecane<br>($C_{11}H_{24}$) | 1120– 21– 4 |  |
| 1,2,3,5-Tetramethylbenzene<br>($C_{10}H_{14}$) | 527– 53–7 |  |
| n-Pentylcyclohexane<br>($C_{11}H_{22}$) | 4292– 92– 6 |  |
| Dodecane<br>($C_{12}H_{26}$) | 112– 40– 3 |  |
| n-Hexylcyclohexane<br>($C_{12}H_{24}$) | 4292– 75– 5 |  |

***Table 1.5 Continued***

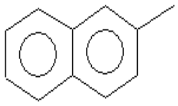
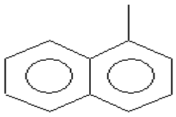
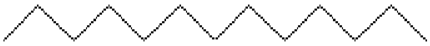
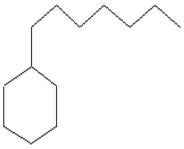
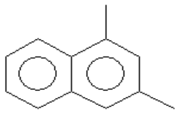
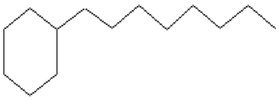
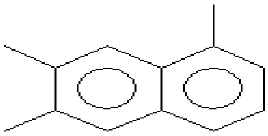
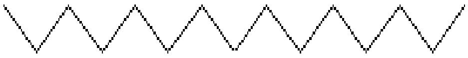
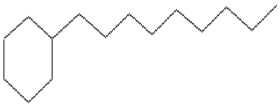
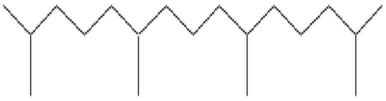
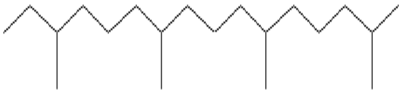
| | | |
|---|---|---|
| 2-Methylnaphthalene<br>$(C_{11}H_{10})$ | 91– 57– 6 |  |
| 1–Methylnaphthalene<br>$(C_{11}H_{10})$ | 90–12– 0 |  |
| Tridecane<br>$(C_{13}H_{28})$ | 629–50–5 |  |
| n-Heptylcyclohexane<br>$(C_{13}H_{26})$ | 005617–41–4 |  |
| 1,3-Dimethylnaphthalene<br>$(C_{12}H_{12})$ | 575– 41– 7 |  |
| Tetradecane<br>$(C_{14}H_{30})$ | 629–59–4 |  |
| n-Octylcyclohexane<br>$(C_{14}H_{28})$ | 1795–15–9 |  |
| 2,3,5-Trimethylnaphthalene<br>$(C_{13}H_{14})$ | 2245–38–7 |  |
| Pentadecane<br>$(C_{15}H_{32})$ | 629–62–9 |  |
| n-Nonylcyclohexane<br>$(C_{15}H_{30})$ | 2883–02–5 |  |
| Hexadecane<br>$(C_{16}H_{34})$ | 544–76–3 |  |
| Heptadecane<br>$(C_{17}H_{36})$ | 629–78–7 |  |
| Pristane<br>$(C_{19}H_{40})$ | 1921–70–6 |  |
| Octadecane<br>$(C_{18}H_{38})$ | 593–45–3 |  |

***Table 1.5 Continued***

| | | |
|---|---|---|
| Phytane<br>($C_{20}H_{42}$) | 638–36–8 |  |
| Nonadecane<br>($C_{19}H_{40}$) | 629–92–5 |  |
| Eicosane<br>($C_{20}H_{42}$) | 112–95–8 |  |
| Heneicosane<br>($C_{21}H_{44}$) | 629–94–7 |  |

Comparison between petroleum based ignitable liquids and standards from GC-MS data using target compound chromatograms has been presented in the literature by Nowicki, Keto and many other authors [94-95, 97]. Keto and Wineman [97, 100] demonstrated TCC comparison of the sample and reference standard eliminated the pyrolysate (contaminant from interference product) from wood spiked with evaporated petrol. This approach simplifies complex chromatograms and facilitates the detection of a compound of interest, especially when dealing with a complex sample matrix. Current standards only list target compound chromatograms for petrol, medium petroleum and heavy petroleum distillates. In addition, because only a limited numbers of compounds are targeted, other interpretative approaches may be required if an unfamiliar total ion chromatographic pattern is encountered.

### 1.8.2 Mass Chromatography Techniques

Most GC-MS data processing software packages are capable of compiling the retention time and structural information of characteristic hydrocarbons such as alkenes, cycloparaffins, aromatics, naphthalenes, terpenes and dihydro-indanes from common ignitable liquids [48]. Mass chromatography facilitates the selection of sets of m/z ratios, indicative of one or more hydrocarbon groups, producing simpler chromatograms of hydrocarbon profiles in the sample.

The m/z information is used to produce filtered chromatographic profiles, either by identifying the presence of an individual ion using an Extracted Ion Chromatogram (EIC) or the presence of more than one ion, producing an Extracted Ion Profile (EIP). These techniques are more widely employed in ignitable liquid residue analysis and can be used to produce simplified chromatograms, reducing the impact of interfering matrices or background peaks. The use of EIP and EIC can facilitate the identification of an ignitable liquid especially in the case of inconclusive identification [101]. Examples of extracted ion chromatograms and profiles are given in figure 1.14.

Extracted ion chromatography can be applied to distinguish between compounds of the same ignitable liquid class. Table 1.6 lists mass spectral data corresponding to the specific hydrocarbon compound classes.

**Table 1.6: Typical ions that corresponds to hydrocarbon group common in ignitable liquid [8, 23].**

| **Compound class** | **m/z values** |
|---|---|
| Alkanes | 29,43,57,71,85,99 |
| Cycloalkanes | 41,55,69,83 |
| Alkenes | 41,55,69,83,97 |
| Alkylbenzenes | 91,92,105,106,119,120 |
| Naphthalanes | 128,142,156,170 |
| Indanes | 117,118,131,132 |
| Terpenes | 93,136 |
| Alcohols | 31,45,59 |
| Ketones | 44,58,72,86 |

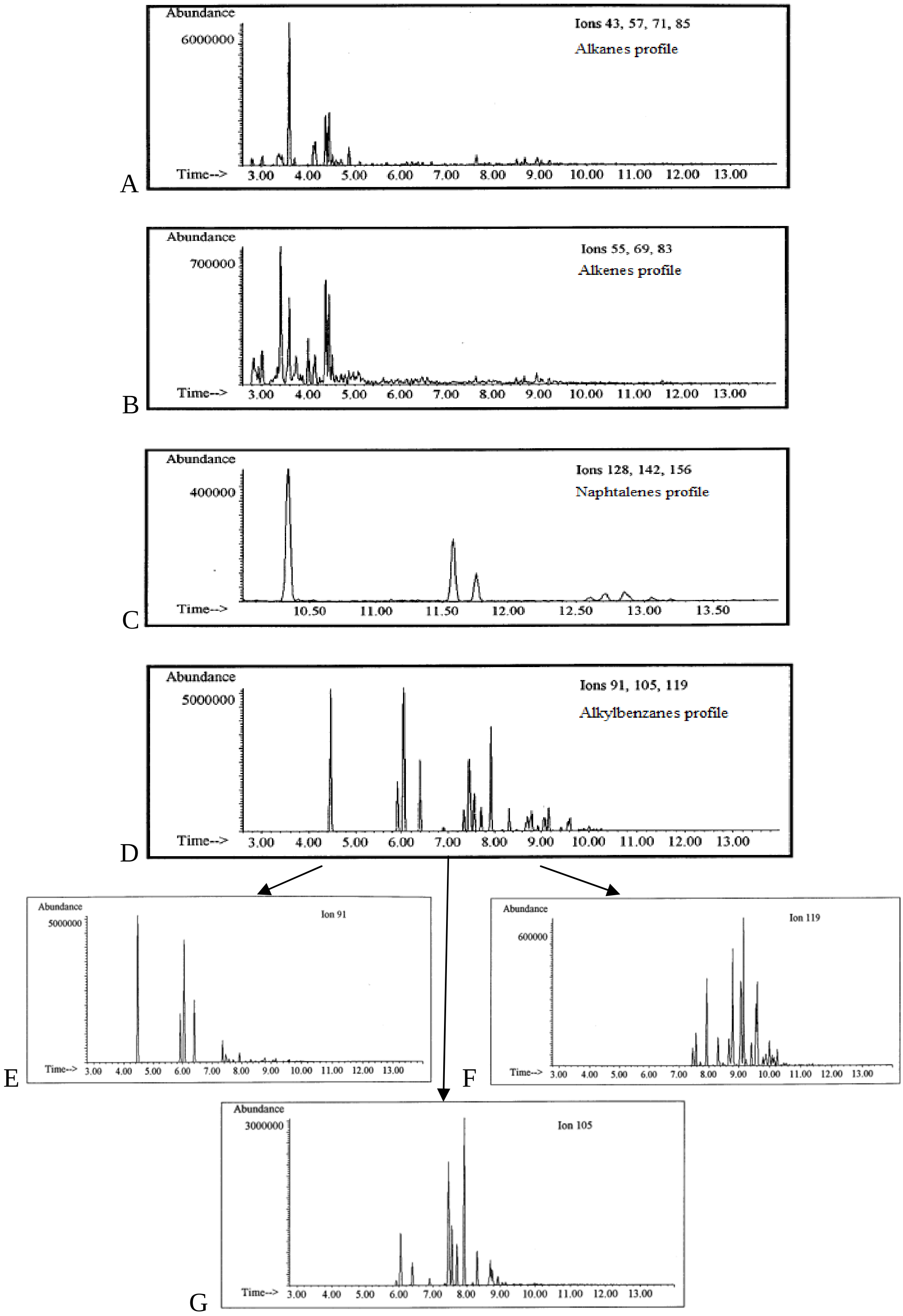


**Figure 1.14 A, B, C and D illustrate summed EIPs of hydrocarbon groups from a petrol sample. E, F and G are the individual EICs of alkyl benzene profiles. Adapted from[37].**

### 1.8.3 Problems and Challenges in Ignitable Liquid Residue Interpretation

The interpretation and identification of data produced from ignitable liquid residue analysis can be difficult and challenging [102]. Visual comparison of chromatograms derived from samples with those generated from reference ignitable liquids is a generally subjective procedure and successful detection and identification of ignitable liquid in fire debris samples can be difficult due to various factors.

When exposed to heat, ignitable liquids undergo compositional changes, resulting in chromatographic changes. These changes in composition result in variations in the number of peaks present in the chromatogram, peak heights and chromatogram pattern shift.

Other common complications in the interpretation of fire debris analysis is the presence of “interfering hydrocarbon by-products” derived from background material, combustion products, pyrolysis products or other factors such as microbial degradation. Numerous studies on the sources of interference for volatile compounds are reported [93, 103-107]. While in many circumstances this can be overcome using target compound chromatography or mass chromatographic techniques, this is not always the case. In some circumstances the application of a more objective form of comparison of the chromatographic data using mathematical techniques using multivariate analysis has been useful.

## 1.9 Introduction to Multivariate Pattern Recognition

Multivariate pattern recognition is a powerful statistical tool that can interpret large datasets and distinctively characterise these data into a more understandable graphical form. Chemometric analysis is used to describe the approach when dealing with data derived specifically from chemical analysis [108-111].

Datasets produced from analytical instruments, in their original numerical form, are often difficult to interpret as raw numerical information. The majority of outputs generated from analysis are translated into a graphical mode, such as chromatograms and spectra, to facilitate result interpretation. When one is dealing with a wide range of samples compared across a large number of variables, multivariate pattern recognition techniques may be advantageous. Several methods of pattern recognition have been developed for the classification and/or discrimination of samples from multivariate datasets. Essentially, these differ in the way they achieve the objective [111-112]. These techniques include Linear Discriminate Analysis (LDA), Principal Component Analysis (PCA), Cluster Analysis (CA), Hierarchical Analysis (HA), k-Nearest neighbour (kNN), Soft Independent Model Cluster Analysis (SIMCA) and Artificial Neural Networks (ANN). The main differences between the techniques are the algorithm used in the mathematical analysis and the visual presentation of the multivariate data analysis results.

### 1.9.1 Application of Multivariate Pattern Recognition for Ignitable Liquid and Ignitable Liquid Residue Analysis.

Over a decade ago, Bertsch suggested the application of expert mathematical systems to the interpretation of the analytical results derived from fire debris samples [102]. The author hoped for an automated procedure where the “evaluation procedures starting with sample injection and ending with a printout of the name of a matching accelerant standard” may become common place. The application of multivariate pattern recognition for ignitable liquid classification in an effort to automate, minimise and possibly eliminate subjectivity has increasingly been given attention [35]. The ASTM E1618-06 also suggests that “computerised pattern matching techniques are acceptable, provided the analyst visually verifies results”[70].

One of the earliest works presented by Ichikawa and co-workers in 1993 used discriminant analysis, K-nearest neighbour and PCA to differentiate between samples of premium and regular unleaded petrol based on octane numbers [113]. The values of the MS fragment ions of aromatics, naphthalenes and branched paraffinic compounds were used in the chemometric analysis which successfully discriminated the two types of unevaporated petrol samples. Tan *et al*. further demonstrated the use of PCA and SIMCA to classify a wide range of ignitable liquids using GC-MS data [110]. Here the datasets were processed using “binning techniques” before uploading chemometric analysis. The application of PCA to the unevaporated ignitable liquids dataset grouped the samples into their corresponding class. A SIMCA model was used to successfully predict the sample class. Diluted ignitable liquids spiked onto unburned woods and carpets as well as onto a burned matrix were also tested. The work concluded that many ignitable liquids could be successfully classified provided that sample analyses were carried out at 20°C and within 3 hours post collection. These restrictions however may be incompatible with many operational circumstances.

Sandercock and Du Pasquier investigated the use of multivariate analysis to establish a common origin in 35 petrol from various petrol stations in Australia, using compound specific methods with PCA [114]. In contrast to common practise, the authors abandoned the use of alkylbenzenes for petrol classification and focused instead on polar and poly aromatic hydrocarbon (PAH) components (which are suggested to differentiate crude oils from each other, a difference which is believed to persist through the refining process [115].

Polar compounds were harder to detect and did not present significant variation compared to the PAH compounds which included naphthalenes, fluorenes, anthracene and phenantrenes and also their isomeric compounds. The PAH compounds identified using SIM scan, were uploaded and processed using PCA. Examples of a partially selected chromatogram and the PCA results from the 35 petrol samples are reproduced in figure 1.15 and figure 1.16 respectively.

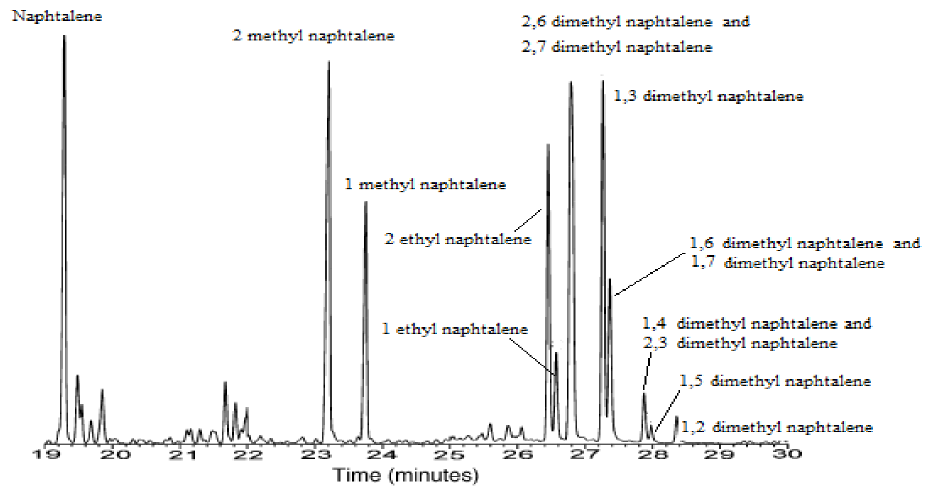


**Figure 1.15. Chromatogram section of C0–C2-naphthalenes obtained by selected ion monitoring of the three isomer groups. Reproduced from Sandercock and Du Pasquier [114].**

In most cases, petrol samples from the same station were clustered together except for six samples of premium and regular grade petrol (highlighted in figure 1.16) that were tightly grouped together even though they came from different fuel stations.

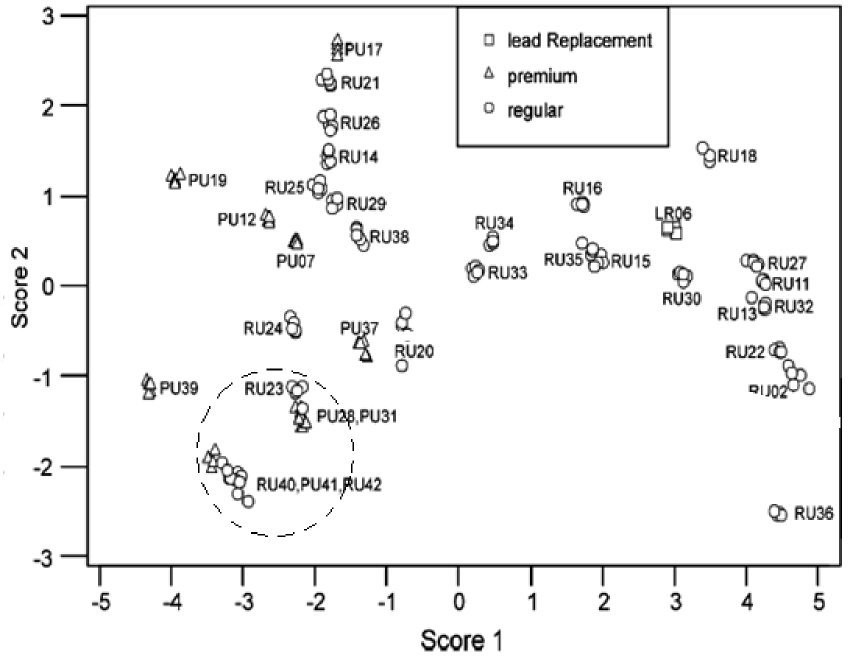


**Figure 1.16 PCA score plot of 35 petrol samples collected petrol stations in Sydney, Australia. Sample designation by fuel grade; LR-lead replacement, PU-premium and RU-regular. Reproduced from Sandercock and Du Pasquier [114].**

The same authors conducted further research on the effect of petrol evaporation using a similar approach [116]. Using the same set of petrol samples, evaporated samples to 25, 50, 75 and 90 percent (by weight) were generated. Data from the resultant chromatograms were analysed by PCA and LDA in an attempt to group the evaporated petrol back to the relevant unevaporated sample. The PCA-LDA plot is shown in figure 1.17. Eighteen sample groups were identified and the authors suggested that the closeness of the groups potentially indicated that the petrol was supplied from one refinery, though this was not corroborated through information relating to petrol distribution networks. The work has also suggested that multivariate analysis could be used to establish linkages between evaporated samples and their original unevaporated petrol.

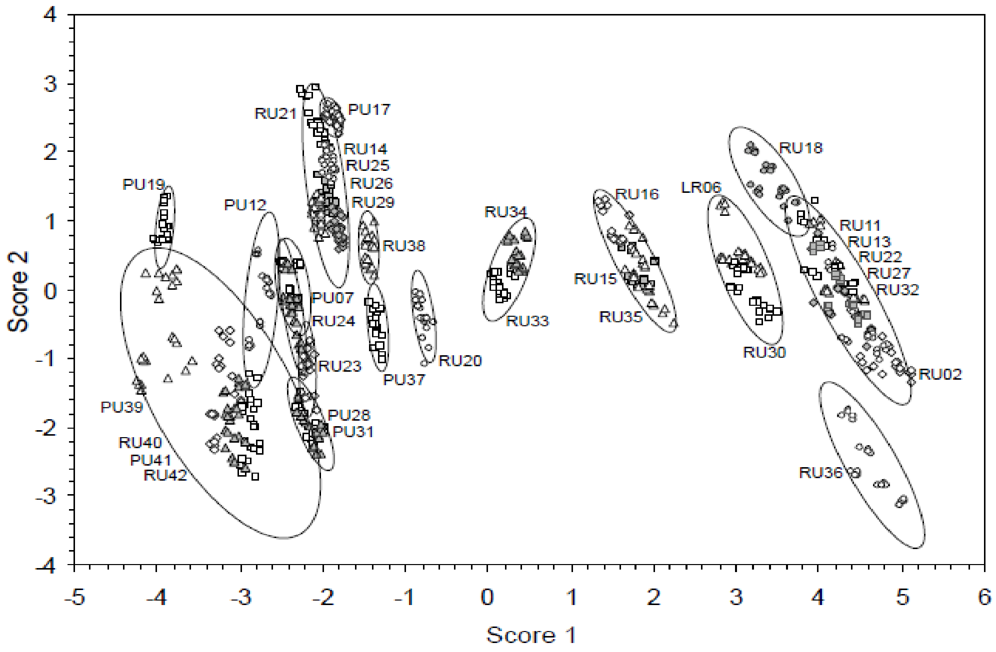


**Figure 1.17. PCA score plot of 35 petrol samples at five different levels of evaporation (0, 25, 50, 75 and 90% by weight). The 35 samples were divided into 18 groups by LDA (LR-lead replacement, PU-premium and RU-regular and numbers designate sampling stations). Reproduced from Sandercock and Du Pasquier [116].**

Sandercock and Du Pasquier also compared petrol samples from Australia and New Zealand using the same techniques as previously reported [117]. Using PCA and LDA analysis, the variation of PAH profiles from the two countries was clearly displayed and is reproduced in figure 1.18.

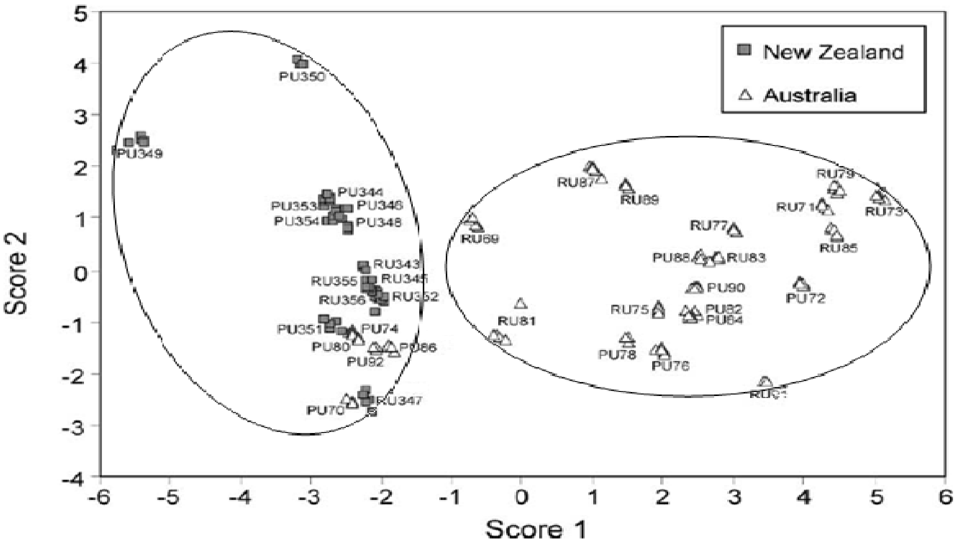


**Figure 1.18. PCA score plot of petrol samples collected New Zealand compared to samples collected in Australia. Most of the petrol was clearly segregated based on their sampling location. Reproduced from Sandercock and Du Pasquier[117].**

In the New Zealand sample pool, 14 summer samples and 14 winter samples were collected and analysed in five replicates. Overall, groupings (figure 1.19) with some misclassification of summer samples segregated the winter and summer petrol successfully suggesting that chemical variation in similar samples could be exploited when assisted by multivariate pattern recognition analysis.

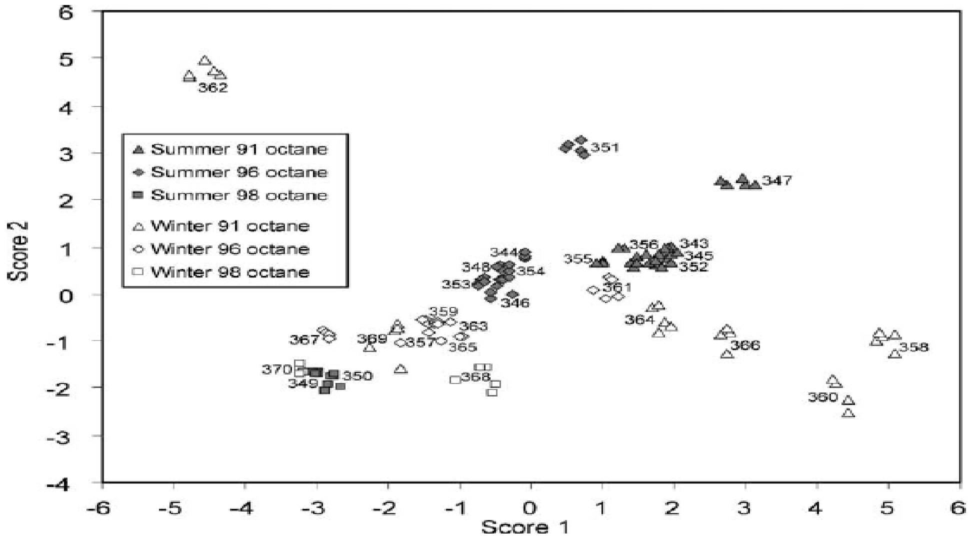


**Figure 1.19 PCA score plot of New Zealand petrol samples collected during summer and winter time. Numbers designated sampling petrol stations. Reproduced from Sandercock and Du Pasquier[117].**

Borusiewicz and co-workers attempted to distinguish between kerosene and diesel using the PCA and a likelihood ratio (LR) approach [52]. A wide range of volatile hydrocarbon compounds of diesel and kerosene samples were analysed and the chromatograms compared manually, particularly in the region of the $C_{11}$ and $C_{12}$ n-alkanes. Results from PCA analysis easily distinguished evaporated samples within diesel and kerosene and between the two ignitable liquid classes.

Based on previous and current ASTM accelerant classification systems, Bodle and Hardy used HCA, PCA and SIMCA to assess the effectiveness of these chemometric procedures for the discrimination of ignitable liquids, analysed using GC-FID [35]. Overlapping of the gasoline, kerosene and diesel classes was shown in the HCA results. Better classification was achieved when the data sets were subjected to PCA while the SIMCA model provided 98.5% and 97.2% classification accuracy for sample class prediction for the previous and current ASTM systems respectively.

The association of evaporated ignitable liquid to its source has also generated much interest in fire debris analysis. To achieve this, earlier work employed the peak area ratio of the prominent peaks in the selected region of the ignitable chromatogram to compare with the reference samples [78-79, 118]. Mann suggested that the region n-pentane to n-decane was useful to manually investigate variation between petrol of different sources [78]. The author also address the limitations of the techniques including the reproducibility from extracted samples and the distortion of the chromatogram due to evaporation and by-product presence with real case examples [79]. Similar studies conducted by Barnes *et al.* but using headspace samples of unevaporated and evaporated petrol concluded that peak ratio comparison to discriminate petrol is applicable to samples up to 75% evaporated[118].

In recent years, Sigman and Williams proposed covariance mapping to identify ignitable liquid in a database [119]. Using this mathematical approach, an absolute value of a particular compound is computed from retention time–ion abundance data, producing a simplified graph to represent each sample. Based on numerical comparison of distance matrices, the difference in the magnitude of the computed value is used to determine if the sample can be distinguished from other samples by doing pairwise comparison. Discrimination between petroleum distillates, isoparaffinic products, de-aromatized distillates, oxygenated solvents, naphthenic paraffinic products, and petrol was apparent while discrimination between petroleum distillate sub-classes (*i.e.* between MPD and HPD) was less distinctive.

Sigman *et al*. further refined their work by using covariance mapping combined with t-tests to discriminate 10 unevaporated petrol samples [120]. Each sample was analysed in triplicate to demonstrate inter-sample and intra-sample variation. Covariance mapping was computed for each sample and then the distance between samples was calculated. These values were then subjected to a t-test to statistically differentiate between samples. It was reported that triplicate analysis of two samples was shown to be sufficient to discriminate the samples at a significance level of 95%. Discrimination was only demonstrated for unevaporated samples [143].

Petraco *et al*. demonstrated the use of statistical methods to differentiate the origin of 20 petrol residues identified in casework samples [121]. Target compounds ranging from C2 alkylbenzenes to C4 alkylbenzenes were identified and chosen as the test variables. Numerical datasets of selected compounds were processed by PCA, Canonical Variate Analysis (CVA) and Orthogonal Canonical Variate Analysis (OCVA) coupled with LDA for discrimination. Misclassifications of petrol were reported to occur at very low levels and sample prediction using PCA (83% correct classification) did not produce a well-define cluster when visualised in a two and three dimensional plot. In comparison, CVA and OCVA performed better, reflected by a higher percentage of correct classification (88% and 92% respectively). Problems with the prediction of highly evaporated petrol samples (i.e more than 80 percent evaporated) were also acknowledged. Nonetheless, the authors suggested that procedures for the application of multivariate analysis to fire debris casework, even though still at initial stages, demonstrated potential applications in the future [121].

Using PCA and discriminant analysis (DA), Monfreda and Gregori studied the differentiation of unevaporated petrol samples by brand [122]. Fresh petrol samples from different refineries in different countries were extracted using SPME and analysed using GC-MS. A data matrix based on the chromatographic profiles of the aromatic compounds was used. PCA was performed using sixteen aromatic compounds and demonstrated that the untreated and unstandardised dataset gave the best clustering by brand. Prediction carried out by discriminate analysis (DA) using loadings from the principal components suggested in PCA subsequently gave 100% classification of the samples.

While most published work has focused on the discrimination of petrol, a few studies have been published investigating multivariate analyses of the analytical results from diesel fuel [123-125]. Four datasets of the full TIC, EICs of alkanes, alkyl benzenes and alkyl naphthalene profile from 25 unevaporated diesel samples were tested to determine the best grouping using PCA [146]. Datasets were subjected to numerous statistical evaluations such as peak alignment algorithms, various data pre processing, Pearson Product Moment Correlation (PPMC), *t*-tests and PCA. PCA failed to produce meaningful groupings while PPMC coefficient values did demonstrate associations between unevaporated samples from the same and from different sources. The authors concluded that a strong association was indicated by a 0.8-1.00 coefficient and EIC of aromatic compounds (m/z 91) proved to be the most useful for diesel discrimination.

In related research, PPMC and PCA procedures were applied to study the effect of the GC temperature program on the association and discrimination of 5 diesel samples [124]. It was postulated that shorter analysis times could possibly result in the loss of discriminatory information, leading to sample misclassification. In fact, the study proved that irrespective of GC analysis time, the chemometric analyses were still able to establish associations and discriminations between the samples, provided that the data matrix was built from well separated and highly resolved chromatographic pattern.

Marshall *et al*. also investigated the potential to link evaporated and unevaporated diesel samples [123, 125]. Using TIC and EIP profiles of aliphatic (m/z 57, 71, 85, 99) and aromatic data (m/z 91, 105, 119, 113), PPMC coefficients were calculated to reveal the correlation between the samples, while PCA was used to reveal associations or discriminations between the samples. This model was tested using a burnt diesel sample. Pairwise comparison yielded a PPMC coefficient of 0.976, and indicated a strong correlation between the test sample and one of the diesel samples (diesel 1). In contrast, the PCA result was not very encouraging as illustrated in figure 1.20. Consequently, the authors concluded that the limitations in their work were because of the reproducibility of the burning and extraction procedures as well as restrictions in the retention time alignment algorithm.

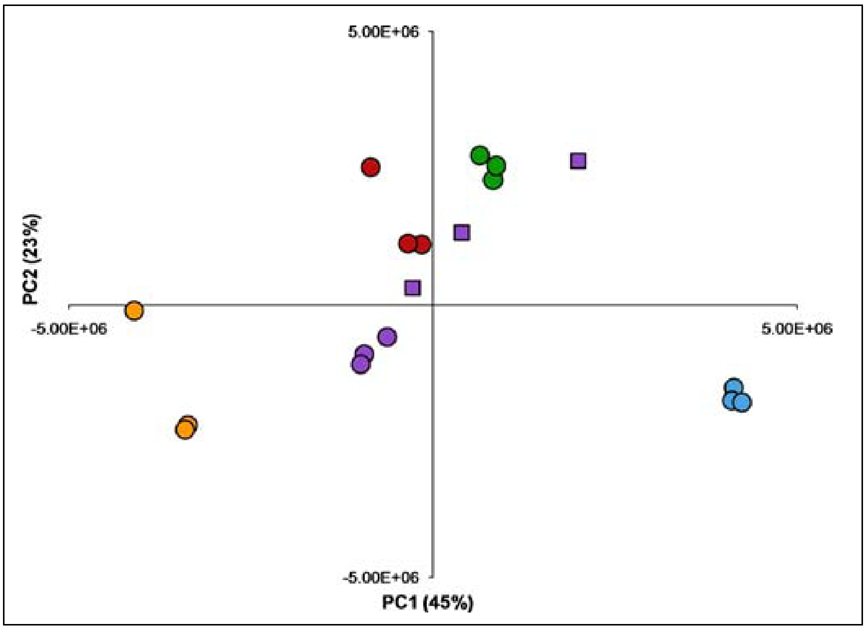


**Figure 1.20 PCA scores plot of five neat diesels (each colour represent one brand) and the burnt test sample (purple squares). Reproduced from Marshall *et al.* [148].**

Baerncopf *et al*. adopted the PPMC and PCA approach in an effort to associate ignitable liquid residues to their unevaporated counterparts [126-127]. Two samples, from the petrol, petroleum distillate, alkane, aromatic, iso-paraffinic and naphthenic paraffinic classes were studied. The ignitable liquids were spiked onto a carpet matrix and burnt to create simulated fire debris samples. These samples were extracted, analysed and compared to data derived from an ignitable liquid reference collection generated from the unevaporated samples and extracted in similar manner. Full TIC profiles were used as the data matrix.

Visual grouping of the residues from the burnt samples to the corresponding unevaporated ignitable liquid was not obvious from the PCA analysis. The PPMC coefficient however suggested either a strong or moderate correlation.

The application of more advanced multivariate pattern recognition such as Artificial Neural Networks (ANN) has gained interest in the past two decades in the analysis of data of relevance to forensic science [128-132]. Long and co-workers demonstrated the use of ANN to classify neat jet fuels [133]. Chromatographic data from seven different classes of jet fuels were translated into a binary pattern prior to ANN classification. The network used was optimised and trained to recognise pattern trends before being tested for prediction abilities. The results of the ANN classification are also benchmarked against two other chemometric models, K-Nearest Neighbour (KNN) and SIMCA. The ANN clearly outperformed the other two methods when it successfully classified all jet fuels in the training set and the test set. Good predictive ability was demonstrated by the ANN model with 100% accuracy while the KNN and SIMCA prediction accuracy were 96% and 65% respectively.

Back propagation ANN was used by Andrews and Lieberman in the identification of petrol, diesel fuels and oils[134]. Experimental data was obtained using laser induced fluorescent spectroscopy. Spectral patterns were used to train the ANN model and classification was achieved with a 96% success rate compared to 90% for PCA.

PCA and ANN procedures were also investigated by Doble *et al* [108]. They focused on the classification and discrimination of premium and regular grades of petrol. For each grade, samples were further divided into summer or winter petrol. The network was trained to recognise 44 characteristic compounds, known as matrix variables, chosen from the full chromatographic pattern. Both PCA and ANN procedures demonstrated correct grouping of the premium and regular petrol. The ANN model managed to correctly classified winter/summer petrol with 97% accuracy in comparison to only 48-62% accuracy obtained with PCA–LDA procedures. The authors concluded that for sample classification and prediction work, ANN would be a very valuable tool to consider.

Vona reported the development of a Neural Network Chromatogram Retrieval System (NNCRS) [135]. According to the author, “neural networks were explored because of their ability to match patterns despite a large amount of actual difference and signal noise”. The NNCRS would learn patterns of target ignitable liquid and related samples so that when challenged with an unknown sample could alert the analyst to the potential classification. Preliminary studies have been undertaken using kerosene as test samples with promising results. However, to date only the analysis of unevaporated samples has been reported using this system.

Other techniques include the use of advanced artificial intelligent model such as Fuzzy Logic and Fuzzy Rule Building Expert System (FuRES) procedures on classifying ignitable liquid chromatographic profiles have also been reported [136-138]. Both techniques are reported to predict sample class for unevaporated ignitable liquids with 100% accuracy and it is suggested that the identification of ignitable liquids in fire debris samples using these prediction models is worthy of further exploration.

## 1.10 Research Aims

In the interpretation of fire debris samples, manual comparison by visual assessment of chromatographic profiles for ignitable liquid identification from fire debris samples is widely practised although it is acknowledged that this can be difficult at times and may be highly subjective. Problems with visual assessment have two major issues; the weathering of the ignitable liquid and the presence of interfering substance from the fire debris matrix, both of which can lead to dramatic changes and differences in the resultant chromatogram when compared to a reference standard. In general, this study aims to propose, investigate and develop a less subjective method for the interrogation of chromatographic data using multivariate pattern recognition techniques.

The first stage of this study was the generation of a GC-MS database including petrol and various petroleum distillate products both unevaporated and systematically evaporated as well as various reference substrates commonly encountered in fire debris. The second stage of the study involved the investigation of the ability of various mathematical techniques to link evaporated samples to their source by brand. The final area explored was the ability of the mathematical approaches to discriminate various ignitable liquids from common burnt matrices.

## 1.11 References

1. *Arson Control Forum: Annual Report 2006*. 2006, Department for Communities and Local Government: London.

2. *Fire Statistics Great Britain 2010 - 2011*. 2011, Department for Communities and Local Government: London.

3. *Statistical Bulletin Crime and Justice Series: Fires in Scotland 2010-2011*. 2011, The Scottish Government: Edinburgh.

4. *Fire Research Report 2/2011 - The economic cost of fire: estimates for 2006*. 2011, Department for Communities and Local Government: London.

5. Young, N., and Cooper, D.A., *Detecting and convicting the arsonist: Lessons from the United States*. 2003, Arson Prevention Bureau: UK.

6. Stauffer, E., Dolan, J.A., and Newman, R., *Fire Debris Analysis*. 2008, Burlington: Academic Press.

7. Nowlan, M., Stuart, A.W., Basara, G., and Sandercock, P.M.L., *Use of a solid adsorbent and an accelerant detection canine for the detection of ignitable liquids burned in a structure fire.* Journal of Forensic Sciences, 2007. **52**(3).

8. Conner, L., Chin, S., and Furton, K.G., *Evaluation of field sampling techniques including electronic noses and a dynamic headspace sampler for use in fire investigations.* Sensors and Actuators B 2006. **116**(1-2): p. 121-129.

9. *Sampling debris at the fire scene; available from http://www.tcforensic.com.au/docs/article2.html*. [accessed on 23/05/2010].

10. Kwon, M., Hong, S., and Choi, H., *Sampling of highly volatile accelerants at the fire scene.* Canadian Society of Forensic Science Journal, 2003. **36**(4): p. 197-205.

11. Borusiewicz, R., Zie-Palus, J., and Zadora, G., *The influence of the type of accelerant, type of burned material, time of burning and availability of air on the possibility of detection of accelerants traces.* Forensic Science International, 2006. **160**(2-3): p. 115-126.

12. Bertsch, W., and Zhang, Q.W., *Sample preparation for the chemical analysis of debris in suspect arson cases.* Analytica Chimica Acta, 1990. **236**: p. 183-195.

13. Lennard, C., *Fire cause and fire debris analysis - A review: 1998 to 2001*, in *13th International Forensic Science Symposium*. 2001, INTERPOL: Lyon, France p. 71-96.

14. Carlsson, G., Johnson, S., Kopp, I., and Wistedt, I., *Conserving samples of fire debris suspected of containing accelerants.* Advances in Forensic Sciences, 1995. **3**: p. 187-190.

15. Mann, D.C., *In search of the perfect container for fire debris evidence.* Fire & Arson Investigator, 2000. **50**(3): p. 21-25.

16. Williams, M.R., and Sigman, M., *Performance testing of commercial containers for collection and storage of fire debris evidence.* Journal of Forensic Sciences, 2007. **5**(3): p. 1033-1049.

17. Wistedt, I., and Delemont, O., *Survey of packaging devices used by ENFSI forensic laboratories for the sampling of fire debris (Abstract and Presentation handouts)* in *2nd European Academic of Forensic Science (EAFS) Meeting*. 2000, ENFSI: Crakow, Poland.

18. Pert, A.D., Baron, M.G., and Birkett, J.W., *Review of analytical techniques for arson residues.* Journal of Forensic Sciences, 2006. **51**(5): p. 1033-1049.

19. Lang, T., *A study of contamination in fire debris containers.* Canadian Society of Forensic Science Journal, 1999. **23**(2&3): p. 75-83.

20. DeHaan, J.D., *Kirk's Fire Investigation*. 6 ed. 2007, New York: Brady Press.

21. Demer-Kohls, J.F., Ouderkirk, S.L., Buckle, J.L., Norman, E.W., Cartwright, N.S., and Dagenais, C., *An evaluation of different evidence bags used for sampling and storage of fire debris.* Canadian Society of Forensic Science Journal, 1994. **27**(3): p. 143-169.

22. Tontarski, R.E., *Evaluation of polyethylene containers used to collect evidence for aceelerant detection.* Journal of Forensic Sciences, 1983. **28**(2): p. 440-445.

23. Kinnard, W.D., and Midkiff, C.M., *Arson evidence container evaluation: II "New generation" KAPAK bags.* Journal of Forensic Sciences, 1991. **36**(6): p. 1714-1721.

24. Kocisko, M.J., *Absorption of ignitable liquids into polyethelene/polyvinylidene dichloride bags.* Journal of Forensic Sciences, 2001. **46**(2): p. 356-362.

25. Stryjnik, A., and Hong-You, R. *Evaluation of the effectiveness of Nylon bags as packaging for fire debris*. in *56th Annual Meeting of the American Academy of Forensic Sciences*. 2004. Texas, Dallas.

26. Lentini, J.J., *Scientific Protocols for Fire Investigation*. Protocols in Forensic Science. 2006, Boca Raton: Taylor & Francis Gp, CRC Press.

27. Adams, D.L., *The extraction and identification of small amounts of accelerants from arson evidence.* J. Crim. L. Criminology & Police Science., 1956. **47**(5): p. 593-596.

28. Midkiff, C.R., *Arson and explosive investigation*. Forensic Science Handbook, ed. R. Saferstein. Vol. 1. 1982, Prentice Hall: Eaglewood Cliff. 225.

29. Ettling, B.V., and Adams, M.F., *The study of accelerant residues in fire remains.* Journal of Forensic Sciences, 1968. **13**(1): p. 76-89.

30. *ASTM Annual Book of Standards*. Vol. 14.02. 2002, West Conshohocken: ASTM International.

31. *Standard Practice for Preservation of Ignitable Liquid Residues in Extracts from Fire Debris Samples and Questioned Liquid Samples Submitted for Ignitable Liquid Analysis*. Technical and Scientific Working Group For Fire and Explosions 2002 [accesssed on 15/07/2010]; Available from: http://www.swissforensic.org/publications/documents/assets/twgfexpreservation.pdf.

32. *Fire and Explosion Investigation; available at http://www.enfsi.eu/page.php?uid=61*. [accessed on 25/6/2009].

33. *ENFSI Guidance on best practice for the recovery and analysis of ignitable liquid residues in fire debris*, in *Fire and Explosion Investigation Working Group (FEIWG)*. 2011, European Network of Forensic Science Institutes..

34. Stauffer, E., and Lentini, J.J., *ASTM standards for fire debris analysis: a review.* Forensic Science International, 2003. **132**(1): p. 63-67.

35. Bodle, E.S., and Hardy, J.K., *Multivariate pattern recognition of petroleum-based accelerants by solid-phase microextraction gas chromatography with flame ionization detection.* Analytica Chimica Acta, 2007. **589**(2): p. 247-254.

36. DeHaan, J., *Our changing world. 2. Ignitable liquids: Petroleum distillates, petroleum products, and other stuff.* Fire & Arson Investigator, 2002. **52**(3): p. 46-47.

37. NicDaeid, N., *Fire Investigation*. 2004, Boca Raton: CRC Press.

38. *ASTM E1385 -95; available at* http://www.astm.org/DATABASE.CART/HISTORICAL/E1385-95.htm. [accsessed on 05/06/2011].

39. Almirall, J.R., and Furton, K.G., *Analysis and interpretation of fire scene evidence*. Forensic Science Techniques Series. 2004, Boca Raton: CRC Press. 255.

40. *ASTM Designation: E 1386 – 00 Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction*. 2000, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-2.

41. Bertsh, W., and Ren, Q., *The chemical analysis of fire debris for potential accelerants*. Forensic Science-Handbook of Analytical Separation. Vol. 2. 2000, Amsterdam: Elsevier Science B.V.

42. Lentini, J.J., and Armstrong, A.T., *Comparison of the eluting efficiency of carbon disulfide with diethyl ether: The case for laboratory safety*. Journal of Forensic Sciences, 1997. **42**(2): p. 307-311.

43. *ASTM Designation: E 1388 – 00 Standard Practice for Sampling of Headspace Vapors from Fire Debris Samples*. 2000, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-2.

44. *ASTM Designation: E 1413 – 00 Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Dynamic Headspace Concentration*. 2000, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-3.

45. Karkkainen, M., Seppala, I., and Himberg, K., *Detection of trace levels of gasoline in arson cases by Gas Chromatography-Mass Spectrometry with an automatic on-line thermal desorber*. Journal of Forensic Sciences, 1994. **39**(1): p. 186-193.

46. *Adsorbent resin for trapping volatiles; available at* http://www.sisweb.com/index/referenc/tenaxgrm.htm [accessed on 30/06/2008].

47. Borusiewicz, R., and Ziˌeba-Palus, J., *Comparison of the effectiveness of Tenax TAs and Carbotrap 300s in concentration of flammable liquids compounds.* Journal of Forensic Sciences, 2007. **52**(1): p. 70-74.

48. Newman, R., *Modern laboratory techniques involved in the analysis of fire debris samples*. Fire Investigation, ed. N.Nic Daeid. 2004, Boca Raton: CRC Press.

49. Jones, G., *Evaluation of a fully automated thermal desorption device for the headspace screening of fire debris.* Canada Society of Forensic Science Journal, 1986. **19**(2): p. 141-148.

50. Twibell, J.D., and Home, J.M., *Novel method for direct analysis of hydrocarbons in crime and air polution studies.* Nature, 1977. **268**(5622): p. 711-713.

51. Dietz, W.R., *Improved charcoal packaging for accelerant recovery by passive diffusion.* Journal of Forensic Sciences, 1991. **36**(1): p. 111-121.

52. Borusiewicz, R., Zadora, G., and Zie˛ba-Palus, J., *Application of head-space analysis with passive adsorption for forensic purposes in the automated thermal desorption gas chromatography-mass spectrometry system.* Journal Chromatographia (Supplement) 2004. **60**(S1): p. S133-S142.

53. Frontela, L., Pozas, J.A., and Picabea, L., *A comparison of extraction and adsorption methods for the recovery of accelerants from arson debris.* Forensic Science International, 1995. **75**(1): p. 11-23.

54. Kelly, R.L., and Martz, R.M., *Accelerant Identification in fire debris by Gas Chromatography/Mass Spectrometry techniques.* Journal of Forensic Sciences, 1984. **29**(3): p. 714-722.

55. Massey, D., Du-Pasquier, E., and Lennard, C., *Solvent desorption of charcoal strips (DFLEX) in the analysis of fire debris samples: Replacement of carbon disulfide.* Canadian Society of Forensic Science Journal, 2002. **35**(4): p. 195-207.

56. Marsh, H., and Rodríguez-Reinoso, F., *Activated Carbon*. 2006, Amsterdam: Elsevier.

57. *ASTM Designation E 1412 – 07 Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration With Activated Charcoal*. 2007, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-3.

58. Demers-Kohls, J.F., Ouderkirk, S.L., Buckle, J.L., Norman, W.E., Cartwright, N.S., and Dagenais, C., *Evaluation of the DFLEX device for fire debris analysis.* Canadian Society of Forensic Sciences Journal, 1994. **27**(3).

59. Newman, R.T., Dietz, W.R., and Lothridge, K., *The use of activated charcoal strips for fire debris extractions by passive diffusion. Part 1: The effects of time,temperature, strip size, and sample concentration.* Journal of Forensic sciences, 1996. **41**(3): p. 361-370.

60. Dolan, J.A., and Newman, R.R., *Solvent options for the desorption of activated charcoal in fire debris analysis*, in *55th Annual Meeting of the American Academy of Forensic Sciences*. 2001: Seattle.

61. Waters, L.V., and Palmer, L.A., *Multiple Analysis of Fire Debris Samples Using Passive Headspace Concentration.* Journal of Forensic Sciences, 1993. **38**(1): p. 165-183.

62. Pawliszyn, J., *Solid phase Microextraction: Theory and practice*. 1998, New York: John Wiley & Sons.

63. Almirall, J.R., Bruna, J., and Furton, K.G., *The recovery of accelerants in aqueous samples from fire debris using solid-phase microextraction (SPME).* Science & Justice, 1996. **36**(4): p. 283-287.

64. *ASTM Designation E 2154 – 01 (Reapproved 2008) Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Solid Phase Microextraction (SPME)*. 2008, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-3.

65. Furton, K.G., Almirall, J.R., and Bruna, J.C., *A novel method for the analysis of gasoline from fire debris using headspace solid-phase microextraction.* Journal of Forensic Sciences, 1996. **41**(1): p. 12-22.

66. Lloyd, J.A., and Edmiston, P.L., *Preferential extraction of hydrocarbons from fire debris samples by Solid Phase Microextraction.* Journal of Forensic Sciences, 2003. **48**(1): p. 1-5.

67. Yoshida, H., Kaneko, T., and Suzuki, S., *A solid-phase microextraction method for the detection of ignitable liquids in fire debris.* Journal of Forensic Sciences, 2008. **53**(3): p. 668-676.

68. Furton, K.G., Almirall, J.R., Bi, M., Wang, J., and Wu, L., *Application of solid-phase microextraction to the recovery of explosives and ignitable liquid residues from forensic specimens.* Journal of Chromatography A, 2000. **885**(1-2): p. 419-432.

69. Harris, A.C., and Wheeler, J.F., *GC-MS of ignitable liquids using solvent-desorbed SPME for automated analysis.* Journal of Forensic Sciences, 2003. **48**(1): p. 1-6.

70. *ASTM Designation: E 1618 – 06 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry*. 2006, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-11.

71. *ASTM Designation: E 1387 – 01 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography*. 2001, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-10.

72. McNair, H.M., and Miller, J.M., *Basic Gas Chromatography*. 1998, New York: John Wiley and Sons.

73. Etire, L.S., *Nomenclature for chromatography (IUPAC Recommendations 1993).* Journal of Pure & Applied Chemistry, 1993. **65**(4): p. 819-872.

74. Braithwaite, A., and Smith, F.J., *Chromatographic Methods*. 5th Edition ed. 1996, Dordrecht: Kluwer Academic Publishers.

75. *Gas Chromatography-Mass Spectrometry; available at www.chemistry.mcmaster.ca*. [accessed on 14/6/2008].

76. Handley, A.J., and Adlard, E.R., *Gas Chromatographic Techniques and Applications*, ed. J.M. Chalmers and Handley, A.J. 2001, Sheffield: Sheffield Academic Press.

77. Ettling, B.V., *Determination of hydrocarbon in fire remains*. Journal of Forensic Science, 1963. **8**: p. 261-267.

78. Mann, D.C., *Comparison of automotive gasolines using capillary gas chromatography I: Comparison methodology*. Journal of Forensic Sciences, 1987. **32**(3): p. 606-615.

79. Mann, D.C., *Comparison of automotive gasolines using capillary gas chromatography II: Limitations of automotive gasoline comparisons in casework*. Journal of Forensic Sciences, 1987. **32**(3): p. 616-628.

80. Tranthim-Fryer, D.J., and DeHaan, J.D., *Canine accelerant detectors and problems with carpet pyrolysis products*. Science & Justice, 1997. **37**(1): p. 39-46.

81. Hoffman, E.d., and Stroobant, V., *Mass Spectrometry: Principles and applications*. Third ed. 2007, Chichester: Wiley and Sons Ltd.

82. McMaster, M., and McMaster, C., *GC/MS A Practical User's Guide*. 1998, New York: Wiley-VCH. 167.

83. *Quadrupole and triple quadrupole mass analysis; available at http://www.chm.bris.ac.uk/ms/theory/quad-massspec.html*. [accessed on 15/6/2011].

84. Willard, H.H., Dean, J., Merritt, L., Settle, F.A., and Dean, J.A., *Instrumental methods of analysis*. 7th. ed. 1988, Belmont: Wadsworth Co.

85. Ekman, R., Silberring, J., Westman-Brinkmalm, A., and Kraj, A., *Mass Spectrometry: Instrumentation, interpretation and applications*. 2009, Hoboken: John Wiley and Sons Inc.

86. *Electron multipliers for mass spectrometry; available at http://www.chromspec.com/pdf/e/rk123.pdf*. [accessed on 14/06/2011.

87. *Toulene mass-spectrum; available at http://webbook.nist.gov/cgi/cbook.cgi?Name=toluene&Units=SI&cMS=on*. [accessed on 15/06/2011].

88. Mach, M.H., *Gas Chromatography-Mass Spectrometry of simulated arson residue using gasoline as an accelerant.* Journal of Forensic Sciences, 1977. **22**(2): p. 348-357.

89. Smith, R.M., *Arson analysis by mass chromatography.* Analytical Chemistry, 1982. **54**(13): p. 1399A-1409A.

90. Smith, R.M., *Mass chromatographic analysis of arson accelerants.* Journal of Forensic Sciences, 1983. **28**(2): p. 318-329.

91. Bertsch, W., and Seller, C.S., *Limits in arson debris analysis by capillary column gas chromatography/mass spectrometry.* Journal of High Resolution Chromatography & Chromatography Communications, 1986. **9**(11): p. 657-661.

92. Bertsch, W., Sellers, C.S., Babin, K., and Holzer, G., *Automation in the chemical analysis of suspect arson samples by GC/MS. A systematic approach.* Journal of High Resolution Chromatography & Chromatography Communications, 1988. **11**(11): p. 815-819.

93. Wallace, J.R.J., *GC/MS data from fire debris samples: Interpretation and applications.* Journal of Forensic Sciences, 1999. **44**(5): p. 996-1012.

94. Nowicki, J., *An accelerant classification scheme based on analysis by gas chromatography/Mass Spectrometry (GC-MS).* Journal of Forensic Sciences, 1990. **35**(5): p. 1064-1086.

95. Nowicki, J., *Analysis of fire debris sample by Gas Chromatography/Mass Spectrometry (GC-MS): Case studies.* Journal of Forensic Sciences, 1991. **36**(5): p. 1536-1550.

96. Lennard, C., Rochaix, V.T., Margot, P., and Huber, K., *A GC-MS database of target compound chromatograms for the identification of arson accelerants.* Science & Justice, 1995. **35**(1): p. 19-30.

97. Keto, R., and Wineman, P.L., *Detection of petroleum-based accelerants in fire debris by target compound gas chromatograph- mass spectrometry.* Analytical Chemistry, 1991. **63**(18): p. 1964-1971.

98. Vella, A.J., *Arson investigation using the ion trap detector.* Journal of the Forensic Science Society 1992. **32**(2): p. 131-142.

99. Newman, R., Gilbert, M., and Lothridge, K., eds. *GC-MS Guide to Ignitable Liquids*. 1998, CRC Press: Boca Raton.

100. Keto, R.O., *GC/MS data interpretation for petroleum distillate identification in contaminated arson debris.* Journal of Forensic Sciences, 1995. **40**(3): p. 412-423.

101. Gilbert, M.W., *The use of individual extracted ion profiles versus summed extracted ion profiles in fire debris analysis.* Journal of Forensic Sciences, 1998. **43**(4): p. 871-876.

102. Bertsch, W., *Chemical analysis of fire debris: Was it arson?* Analytical Chemistry News & Features, 1996. **68**(1): p. 541A-545A.

103. Fernandes, M.S., Lau, C.M., and Wong, W.C., *The effect of volatile residues in burnt household items on the detection of fire accelerants.* Science & Justice 2002. **42**(1): p. 7 - 15.

104. Bertsch, W., *Volatiles from carpet: A source of frequent misinterpretation in arson analysis.* Journal of Chromatography A, 1994. **674**(1-2): p. 329-333.

105. Stauffer, E., *Concept of pyrolysis for fire debris analysts.* Science & Justice 2003. **43**(1): p. 29 - 40.

106. Lentini, J.J., *Differentiation of asphalt and smoke condensates from liquid petroleum distillates using GC/MS.* Journal of Forensic Sciences, 1998. **43**(1): p. 97-113.

107. Cavanagh, K., Pasquier, E.D., and Lennard, C., *Background interference from car carpets - the evidential value of petrol residues in cases of suspected vehicle arson.* Forensic Science International, 2002. **125**(1): p. 22-36.

108. Doble, P., Sandercock, M., Pasquier, E.D., Petocz, P., Roux, C., and Dawson, M., *Classification of premium and regular gasoline by gas chromatography/mass spectrometry, principal component analysis and artificial neural networks.* Forensic Science International, 2003. **132**(1): p. 26-39.

109. Adams, M.J., *Chemometrics In Analytical Spectroscopy*, ed. N.W. Barnett. 1995, Cambridge: The Royal Society of Chemistry.

110. Tan, B., Hardy, J.K., and Snavely, R.E., *Accelerant classification by gas chromatography/mass spectrometry and multivariate pattern recognition.* Analytica Chimica Acta, 2000. **422**(1): p. 37-46.

111. Cserhati, T., *Multivariate method in Chromatography - A practical guide*. 2009, Chichester: John Wiley and Son.

112. Berrueta, L.A., Alonso-Saalces, R.M., and Heberger, K., *Supervise pattern recognition in food analysis.* Journal of Chromatography A, 2007. **1158**(1-2): p. 196-214.

113. Ichikawa, M., Nonaka, N., Takada, I., and Ishimori, S., *Mass spectrometric analysis for distinction between regular and premium motor gasolines.* Analytical Sciences, 1993. **9**(2): p. 261-267.

114. Sandercock, P.M.L., and Pasquier, E.D., *Chemical fingerprinting of unevaporated automotive gasoline samples.* Forensic Science International, 2003. **134**(1): p. 1-10.

115. Wang, Z., and Fingas, M., *Differentiation of the source of spilled oil and monitoring of the oil weathering process using GC-MS.* Journal Chromatography A, 1995. **712**(2): p. 321-343.

116. Sandercock, P.M.L., and Pasquier, E.D., *Chemical fingerprinting of gasoline 2. Comparison of unevaporated and evaporated automotive gasoline samples.* Forensic Science International, 2004. **140**(1): p. 43-59.

117. Sandercock, P.M.L., and Pasquier, E.D., *Chemical fingerprinting of gasoline Part 3. Comparison of unevaporated automotive gasoline samples from Australia and New Zealand.* Forensic Science International, 2004. **140**(1): p. 71-77.

118. Barnes, A.T., Dolan, J.A., Kuk, R.J., and Siegel, J.A., *Comparison of gasolines using gas chromatography-mass spectrometry and target ion response.* Journal of Forensic Sciences, 2004. **49**(5): p. 1018-1023.

119. Sigman, M.E., and Williams, M.R., *Covariance mapping in the analysis of ignitable liquids by Gas Chromatography/Mass Spectrometry.* Analytical Chemistry, 2006. **78**(5): p. 1713-1718.

120. Sigman, M.E., Williams, M.R., and Ivy, R.G., *Individualization of gasoline samples by covariance mapping and Gas Chromatography/Mass Spectrometry.* Analytical Chemistry, 2007. **79**(9): p. 3462-3468.

121. Petraco, N.D.K., Gil, M., Pizzola, P.A., and Kubic, T.A., *Statistical discrimination of Liquid gasoline samples from casework.* Journal of Forensic Sciences, 2008. **53**(5): p. 1092-1101.

122. Monfreda, M., and Gregori, A., *Differentiation of unevaporataed gasoline samples according to their brands, by SPME-GCMS and multivariate statistical analysis.* Journal of Forensic Sciences, 2011. **56**(2): p. 372-380.

123. Hupp, A.M., Marshall, L.J., Campbell, D.I., Smith, R.W., and McGuffin, V.L., *Chemometric analysis of diesel fuel for forensic and environmental applications.* Anal Chim Acta, 2008. **606**(2): p. 159-171.

124. Baerncopf, J.M., McGuffin, V.L., and Smith, R.W., *Effect of gas chromatography temperature program on the association and discrimination of diesel samples.* Journal of Forensic Sciences, 2010. **55**(1): p. 185-191.

125. Marshall, L.J., McIlroy, J.W., McGuffin, V.L., and Smith, R.W., *Association and discrimination of diesel fuels using chemometric procedures.* Analytical and Bioanalytical Chemistry, 2009. **394**: p. 2049-2059.

126. Baerncopf, J.M., McGuffin, V.L., and Smith, R.W., *Discrimination of Ignitable liquids from matrix interferences using chemometric procedures*, in *Proceedings of the 61st Annual Scientific Meeting of the American Academy of Forensic Science*. 2009, American Academy of Forensic Sciences: Denver. p. 124-125.

127. Baerncopf, J.M., McGuffin, V.L., and Smith, R.W., *Association of ignitable liquid residues to neat ignitable liquids in the presence of matrix interferences using chemometric procedures.* Journal of Forensic Sciences, 2011. **56**(1): p. 70-81.

128. Casale, J.F., and Watterson, J.W., *A computerized neural network method for pattern recognition of cocaine signatures.* Journal of Forensic Sciences, 1993. **38**(2): p. 292-301.

129. Verma, M.S., Pratt, L., Ganesh, C., and Medina, C., *Hair-MAP: a prototype automated system for forensic hair comparison and analysis.* Forensic Science International, 2002. **129**(3): p. 168-186.

130. Banno, A., *Estimation of bullet striation similarity using Neural Networks.* Journal of Forensic Sciences, 2004. **49**(3): p. 1-5.

131. Waddell, R.J., NicDaéid, N., and Littlejohn, D., *Classification of ecstasy tablets using trace metal analysis with the application of chemometric procedures and artificial neural network algorithms.* Analyst, 2004. **129**(3): p. 235-240.

132. Esseiva, P., Anglada, F., Dujourdy, L., Taroni, F., Margot, P., Pasquier, E.D., Dawson, M., Roux, C., and Doble, P., *Chemical profiling and classification of illicit heroin by principal component analysis, calculation of inter sample correlation and artificial neural networks.* Talanta, 2005. **67**(2): p. 360-367.

133. Long, J.R., Mayfield, H.T., Henley, M.V., and Kromann, P.R., *Pattern recognition of jet fuel chromatographic data by artificial neural networks with back-propagation of error.* Analytical Chemistry, 1991. **63**(13): p. 1256-1261.

134. Andrews, J.M., and Lieberman, S.H., *Neural network approach to qualitative identification of fuels and oils from laser induced fluorescence spectra.* Analytica Chimica Acta, 1994. **285**(1-2): p. 237-246.

135. Vona, M., *Neural Networks: Classifying Patterns*, in *Investigative data mining for security and criminal detection* J. Mena, Editor. 2003, Butterworth / Heinemann: Amsterdam.

136. Rearden, P., Harrington, P.B., Karnes, J.J., and Bunker, C.E., *Fuzzy Rule-Building Expert System Classification of Fuel Using Solid-Phase Microextraction Two-Way Gas Chromatography Differential Mobility Spectrometric Data.* Analytical Chemistry, 2007. **79**(4): p. 1485-1491.

137. Lu, Y., and Harrington, P.B., *Forensic Application of Gas Chromatography-Differential Mobility Spectrometry with Two-Way Classification of Ignitable Liquids from Fire Debris.* Journal of Analytical Chemistry, 2007. **79**(17): p. 6752-6759.

138. Lu, Y., Chen, P., and Harrington, P.B., *Comparison of differential mobility spectrometry and mass spectrometry for gas chromatographic detection of ignitable liquids from fire debris using projected difference resolution.* Analytical and Bioanalytical Chemistry, 2009. **394**(2): p. 2061-2067.

# CHAPTER 2: GAS CHROMATOGRAPHY MASS SPECTROMETRY (GC-MS) METHOD VALIDATION

## 2.1 Introduction

Before the actual sample is analysed, the instrument of choice needs to be validated in order to verify performance and efficiency. This is achieved using commercial or in-house standard mixtures to determine parameters such as repeatability, peak asymmetry, compound retention, selectivity, sensitivity and peak resolution [1-2].

The peak response (peak area or peak height) of each component in a test mixture used to validate an instrument is recorded and analysed using simple statistical calculations such as mean, standard deviation(s) and relative standard deviation (equations 2.1 to 2.3). Relative Standard Deviation (RSD), sometimes called the coefficient of variation, is a computation of the standard deviation relative to the mean or average of a given dataset and calculated using equation 2.3 [3]. Normally expressed in percentage i.e. % RSD, it measures the repeatability, which according to Miller, is the precision between duplicate runs or analysis [3]. Analytical variations of 5% RSD or lower are accepted as a standard practise and is considered as a value that signify good precision for chromatographic analysis [4].

$$Mean = \frac{\sum X_1 + X_2 + X_3 + ...... + X_n}{n} \text{ ..................Equation 2.1}$$

where, $Xi$=data value (measurement)

n= total number of data measurement (sample size)

$$s = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n - 1}}$$ .....................................Equation 2.2

where, $x_i$= each value in the sample

$\bar{x}$ = the mean of x values

n = total number of data (sample size)

$$\% \, RSD = \frac{s}{\bar{x}} \times 100$$ ..............................Equation 2.3

where, s= standard deviation

$\bar{x}$ = the mean of x values

According to the American Society for Testing and Measurement (ASTM) guidelines for fire debris analysis (E1378 and E1618), the instrument of choice, either GC-FID or GC-MS, should be able to detect and separate the standard mixture compounds at 0.005% vol/vol [5-6]. For the instrumental set-up, the same guidelines allow some changes on chromatographic parameters such as the temperature programming, split ratio and flow rate in order to achieve the desired separation within a reasonable analysis time.

## 2.2 Materials and Methodology

### 2.2.1 GC-MS Experimental Set-Up

Instrumental analysis was performed on a HP 6890 Gas chromatograph interfaced with HP 5973 Mass spectrometer detector. The column used was a DB1-MS capillary column (25.0 m x 0.20 mm diameter with film thickness 0.33 µm). Helium was used as the carrier gas with a constant flow rate of 1.0 mL/min. The oven temperature was held at 40 ºC for 5 minutes and ramped at 15 ºC/min to 280 ºC, and then held for 2 minutes at the final temperature. For heavy petroleum distillation samples (i.e. diesel) the final temperature time was prolonged for 4 minutes for complete higher hydrocarbon elution. Injection was by split mode with a split ratio of 1:20 involving 1µL of sample at 250 ºC. The scanning range was 35-500 amu. The ion source and the quadrupole temperatures of the MS were set at 150 ºC and 280 ºC respectively. Solvent delay was set at 2 minutes.

### 2.2.2 Solvent Study

Various non-polar solvents have been investigated and suggested for use in ignitable liquid dilution and extractions [7-9]. Each solvent has advantages and disadvantages to their use. Characteristics such as low boiling point, suitability for desorption of the substrate, high extraction efficiency, polarity, and safety were evaluated.

According to standard practise, a non-polar volatile solvent such as carbon disulfide ($CS_2$), dichloromethane (DCM), diethyl ether, hexane, pentane and others can be used as long as they do not interfere with the analysis or the sample itself [6, 9]. Recommended solvents are listed in table 2.1.

**Table 2.1 Physical and chemical properties of suitable solvents for ignitable liquid dilution and extraction of ILR from fire debris sample [10-11].**

| **Solvent** | **Hazards** | **Polarity Index** | **Density ($g/cm^3$)** | **Boiling point (ºC)** | **Solubility in water (%)** |
|---|---|---|---|---|---|
| n-Pentane | Highly flammable<br>Harmful | 0.0 | 0.626 | 36.1 | 0.0041 |
| Carbon disulfide | Highly flammable<br>Toxic | 1.0 | 1.26 | 46 | 0.210 |
| Diethyl ether | Highly flammable<br>Harmful | 2.9 | 0.713 | 34.6 | 6.04 |
| Di-chloromethane | Harmful | 3.4 | 1.325 | 40.0 | 1.73 |

One µL of each solvent was analysed using GC-MS as described in section 2.2.1 without solvent delay and the chromatographic results were visually compared and evaluated.

### 2.2.3 Preparation of Ignitable Liquid Test Mixtures

A test mixture containing aliphatic and aromatic compounds (table 2.2) was prepared. All chemicals were of high purity, 99% analytical grade and were obtained from BDH Chemicals (Poole, England) or Sigma-Aldrich (St. Louis, USA).

Each standard hydrocarbon compound was prepared as a 100 mg/mL stock solution in pentane (HPLC grade, WVR International, Leicestershire, UK). A 0.1 mL of each stock solution was transferred into a volumetric flask and diluted with pentane to prepare a 1mg/mL combined standard mixture.

**Table 2.2 Hydrocarbon compounds used in test mixtures.**

| **Hydrocarbon compounds** | **Formula** |
|---|---|
| Octane (C8) | $CH_3(CH_2)_6CH_3$ |
| Decane (C10), | $CH_3(CH_2)_8CH_3$ |
| Undecane (C11), | $CH_3(CH_2)_9CH_3$ |
| Hexadecane (C12), | $CH_3(CH_2)_{10}CH_3$ |
| Tetradecane (C14), | $CH_3(CH_2)_{12}CH_3$ |
| Pentadecane(C15), | $CH_3(CH_2)_{13}CH_3$ |
| Dodecane (C16), | $CH_3(CH_2)_{14}CH_3$ |
| Octadecane (C18), | $CH_3(CH_2)_{16}CH_3$ |
| Eicosane (C20), | $CH_3(CH_2)_{18}CH_3$ |
| Toluene | $C_6H_5CH_3$ |
| 1,4, Dimethylbenzene (p-Xylene) | $C_8H_{10}$ |
| o-Ethyltoluene | $C_9H_{12}$ |
| m-Ethyltoluene | $C_9H_{12}$ |
| 1,2,4-Trimethylbenzene (1,2,4 TMB). | $C_9H_{12}$ |

### 2.2.4 Instrumental Precision

Injection variation and instrumental precision were assessed based on the response of the test mixture compounds from six repetitive injections from a single and from multiple sample vials. Standard deviations and relative standard deviations of each component were calculated from the gas chromatographic response.

### 2.2.5 Peak Shape Evaluation (Resolution and Asymmetry)

Peak resolution measures the degree to which adjacent peaks are separated [1]. Peak resolution and asymmetry were calculated to determine compound resolution. The asymmetry ratio of a peak (asymmetry factor), A, was calculated according to the following equation:

$$A=b/a \quad \text{.....................................Equation 2.4}$$

Where, a and b are the left and right halves of the peak width at 10% peak height.

Peak resolution values were obtained manually from the chromatograms using the following equation[1]:

$$\mathrm{Rs} = \frac{trB - trA}{\frac{[(wb)\,B + (wa)A]}{2}} \ldots\ldots\ldots\ldots \text{Equation 2.5}$$

where tr A =retention time of the first peak

tr B =retention time of the second peak

$w_b$ A= peak width of the first peak

$w_b$ B= peak width of the second peak

### 2.2.6 Limit of Detection

#### *2.2.6.1 Preparation of Calibration Curve Standard Solution*

A commercial standard mixture (E1618-97 Test mixture, 0.05% vol/vol) consisting of 12 aliphatic and aromatic hydrocarbons compounds (listed in table 2.3) of 99% purity was purchased from Restek Inc. (Bellefonte, USA).

**Table 2.3 Hydrocarbon compounds comprised in the commercial standard mixtures.**

| **Hydrocarbon compounds** | **Formula** |
|---|---|
| Octane (C8) | $CH_3(CH_2)_6CH_3$ |
| Decane (C10), | $CH_3(CH_2)_8CH_3$ |
| Hexadecane (C12), | $CH_3(CH_2)_{10}CH_3$ |
| Tetradecane (C14), | $CH_3(CH_2)_{12}CH_3$ |
| Dodecane (C16), | $CH_3(CH_2)_{14}CH_3$ |
| Octadecane (C18), | $CH_3(CH_2)_{16}CH_3$ |
| Eicosane (C20), | $CH_3(CH_2)_{18}CH_3$ |
| Toluene | $C_6H_5CH_3$ |
| 1,4, Dimethylbenzene (p-Xylene) | $C_8H_{10}$ |
| o-Ethyltoluene | $C_9H_{12}$ |
| m-Ethyltoluene | $C_9H_{12}$ |
| 1,2,4-Trimethylbenzene (1,2,4 TMB). | $C_9H_{12}$ |

A series of standard solutions (at concentrations 0.05%, 0.025%, 0.01%, 0.005% and 0.001% vol/vol) were prepared in pentane and analysed as described previously. The equations of the standard curves were calculated using linear regression analysis and the limits of detection for each compound were assessed using statistical methods [3]. No results were obtained for the 0.001% standard.

### 2.2.7 Inter and Intra Ignitable Liquid Sample Variations

Analyses were performed using lighter fluid samples. A two percent lighter fluid solution was prepared by diluting 20 µL of the sample fluid with 1000 µL pentane. 0.5 mg/mL Tetrachloroethylene was added as an internal standard.

Six repetitive injections of one brand of lighter fuel (Zippo) and samples from six different containers of Zippo lighter fluid were analysed to determine the instrumental variation for an ignitable liquid sample (intra-batch variation) and the between brand variation (inter-batch variation)

## 2.6 Results and Discussions

### 2.6.1 Solvent Study

The total ion chromatograms (TICs) of each of the solvents analysed are presented in figure 2.1. Pentane and diethyl ether appear to elute close to each other (RT 1.381 min and RT 1.360 min respectively) while dichloromethame (DCM) (RT 1.459 min) and carbon disulfide ($CS_2$) (RT 1.523 min) elute slightly later. Apart from this slight variation in elution time, no other significant difference in terms of the chromatogram was observed. For ease of use and safety, pentane was chosen as the solvent for all phases throughout this work.

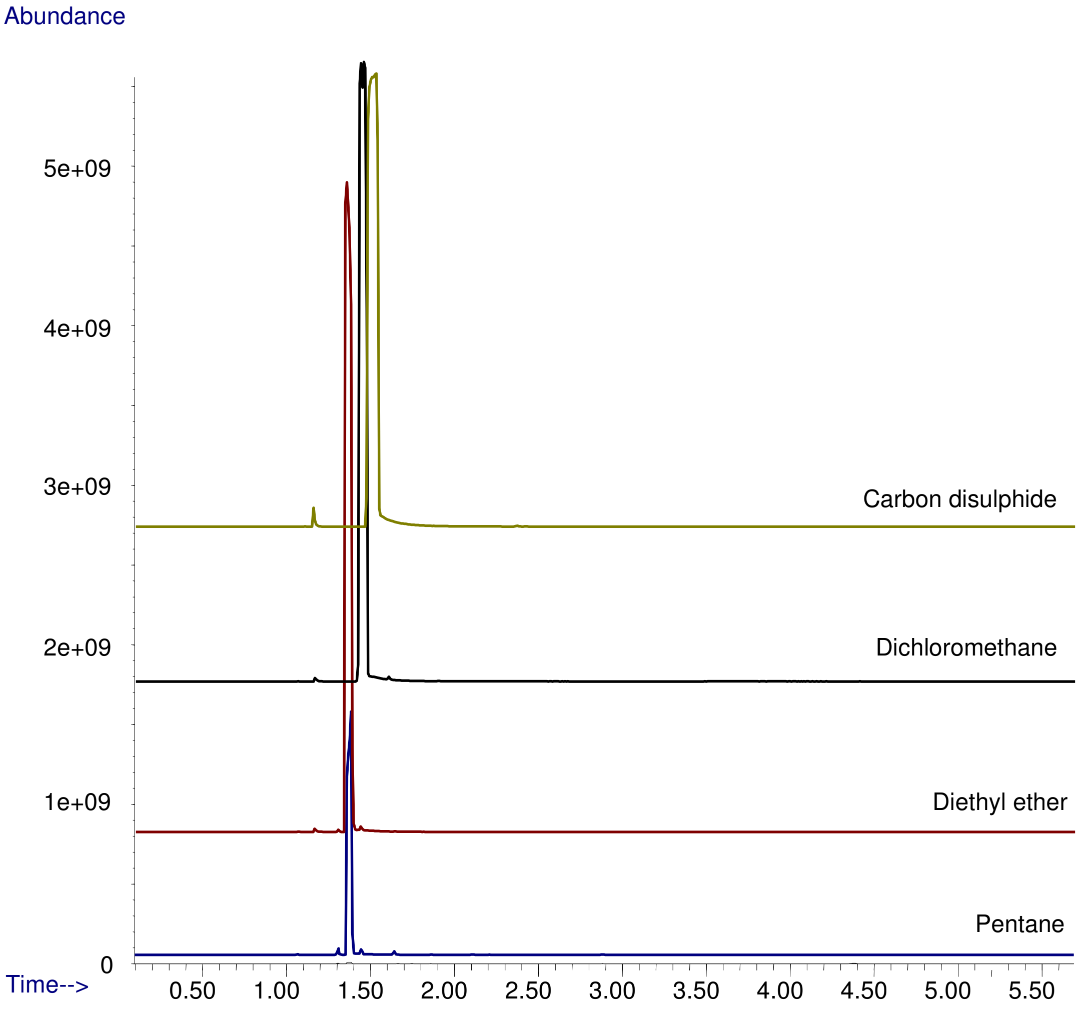


**Figure 2.1 Partial TICs showing chromatographic profile of blank solvents.**

### 2.6.2 Assessment of Instrumental Performance

Repeatability of the GC system was determined by interrogating the peak area response of six replicate analysis of the standard mixture for both a single sample and between six separate samples. A sample total ion chromatogram is presented in figure 2.2.

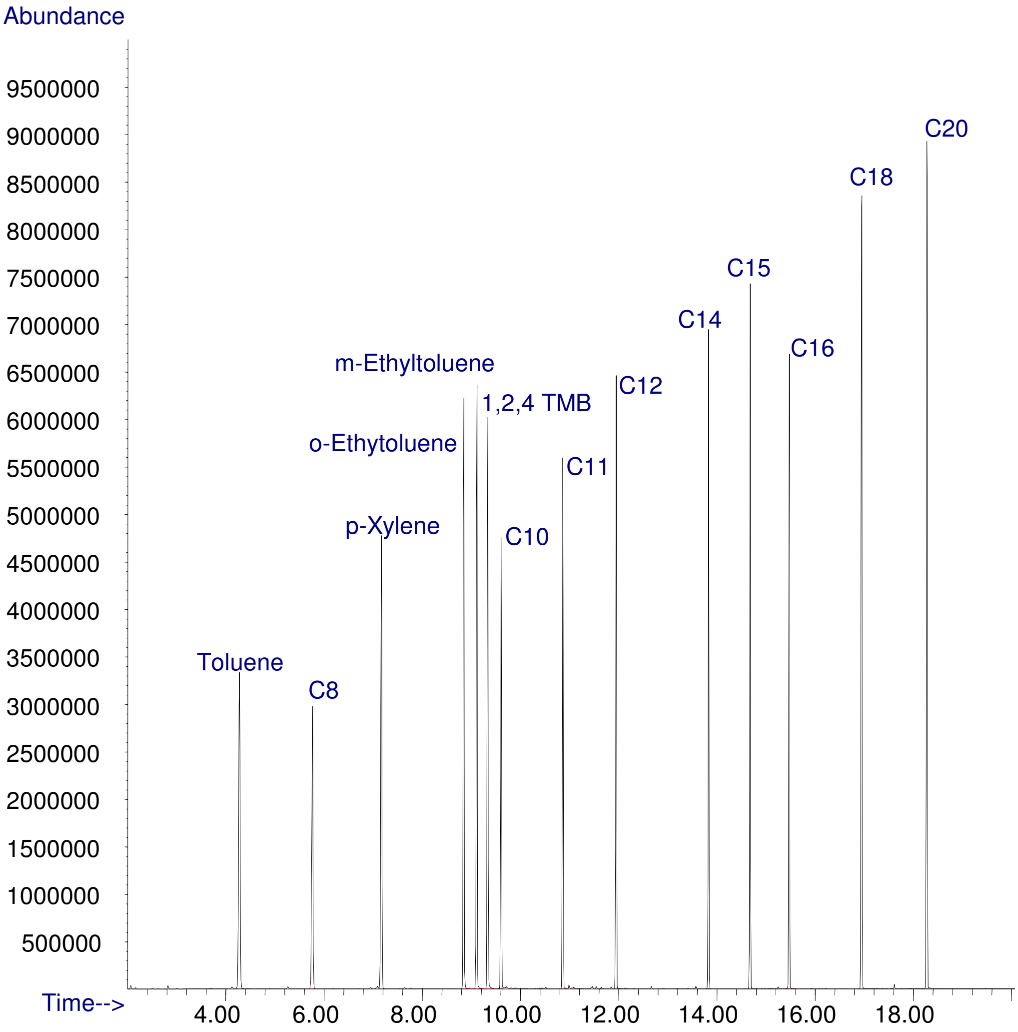


**Figure 2.2 TIC of 1 mg/mL standard test mixture in pentane.**

### 2.6.3 Peak Evaluation (Resolution and Asymmetry)

The ideal peak shape is associated with a symmetry factor value of one or close to one and a peak resolution (Rs) value of 1.5 is associated with baseline resolution between adjoining peaks [1-2, 12]. Qualitative examination based on figure 2.2, revealed that the GC-MS method chosen facilitated excellent separation of all compounds in the test mixture including closely eluting peaks such as the ethyltoluenes, 1,2,4 trimethylbenzene (TMB) and the C10 peak. This is confirmed by the results presented in table 2.4.

**Table 2.4 Percent Relative Standard Deviation (% RSD) of 14 compounds (normalised against total peak area) in ignitable liquid standard mixture.**

| **Peak No.** | **Compound** | **R.T** | **% RSD of peak area** | | **Peak Resolution, Rs** | **Peak asymmetry** |
|---|---|---|---|---|---|---|
| | | | **Injection variation (n=6)** | **Sample variation (n=6)** | | |
| 1 | Toluene | 4.375 | 2.08 | 3.69 | 4.2 | 1.02 |
| 2 | C8 | 5.859 | 2.24 | 4.02 | 6.6 | 1.00 |
| 3 | p-Xylene | 7.239 | 1.75 | 3.65 | 6.1 | 1.00 |
| 4 | o-Ethyltoluene | 8.901 | 2.00 | 3.36 | 7.4 | 0.98 |
| 5 | m-Ethyltoluene | 9.164 | 1.90 | 3.68 | 1.2 | 0.98 |
| 6 | 1,2,4-TMB | 9.389 | 1.78 | 3.45 | 1.0 | 0.92 |
| 7 | C10 | 9.662 | 1.95 | 4.06 | 1.2 | 1.02 |
| 8 | C11 | 10.911 | 1.99 | 4.08 | 5.6 | 1.04 |
| 9 | C12 | 11.99 | 2.13 | 3.42 | 4.8 | 0.97 |
| 10 | C15 | 13.868 | 1.85 | 3.54 | 8.3 | 1.02 |
| 11 | C14 | 14.714 | 1.74 | 4.22 | 3.7 | 1.00 |
| 12 | C16 | 15.512 | 2.09 | 3.51 | 3.5 | 0.97 |
| 13 | C18 | 16.977 | 1.79 | 3.79 | 6.5 | 0.98 |
| 14 | C20 | 18.301 | 1.90 | 3.48 | 5.9 | 1.02 |

### 2.6.4 Limit of Detection

The sensitivity of the instrument was evaluated by determining the limit of detection (LOD) of the compounds within a series of commercial test mixtures. LOD is the measure of the smallest concentration that the instrument can detect with reasonable certainty (commonly a 90% confidence limit) for a given analytical procedure [13]. According to IUPAC, the LOD is determined based on the standard deviation of the blank i.e;

$$xL= x_{bi} + ks_{bi} \text{...........................Equation 2.6}$$

where, $x_{bi}$= mean of blank measures

$s_{bi}$= standard deviation of the blank measures

k = numerical factor chosen from the confidence level

The LOD can also be extrapolated from statistical calculations of the regression lines/calibration curves of the analyte [3-4]. An example of the calculations using toluene is provided in appendix section. In this work, the confidence limit was set at 95%.

The linearity of the 12 analysed compounds (concentrations 0.005% to 0.05% vol/vol) are presented in figures 2.3 and 2.4. Based on the $R^2$ values in table 2.5, the linearity of each compound shows a good fit to the corresponding concentration. The detection limits are between 0.0038% to 0.0057% vol/vol, which satisfies the ASTM requirement for instrument sensitivity intended for ignitable liquid analysis.

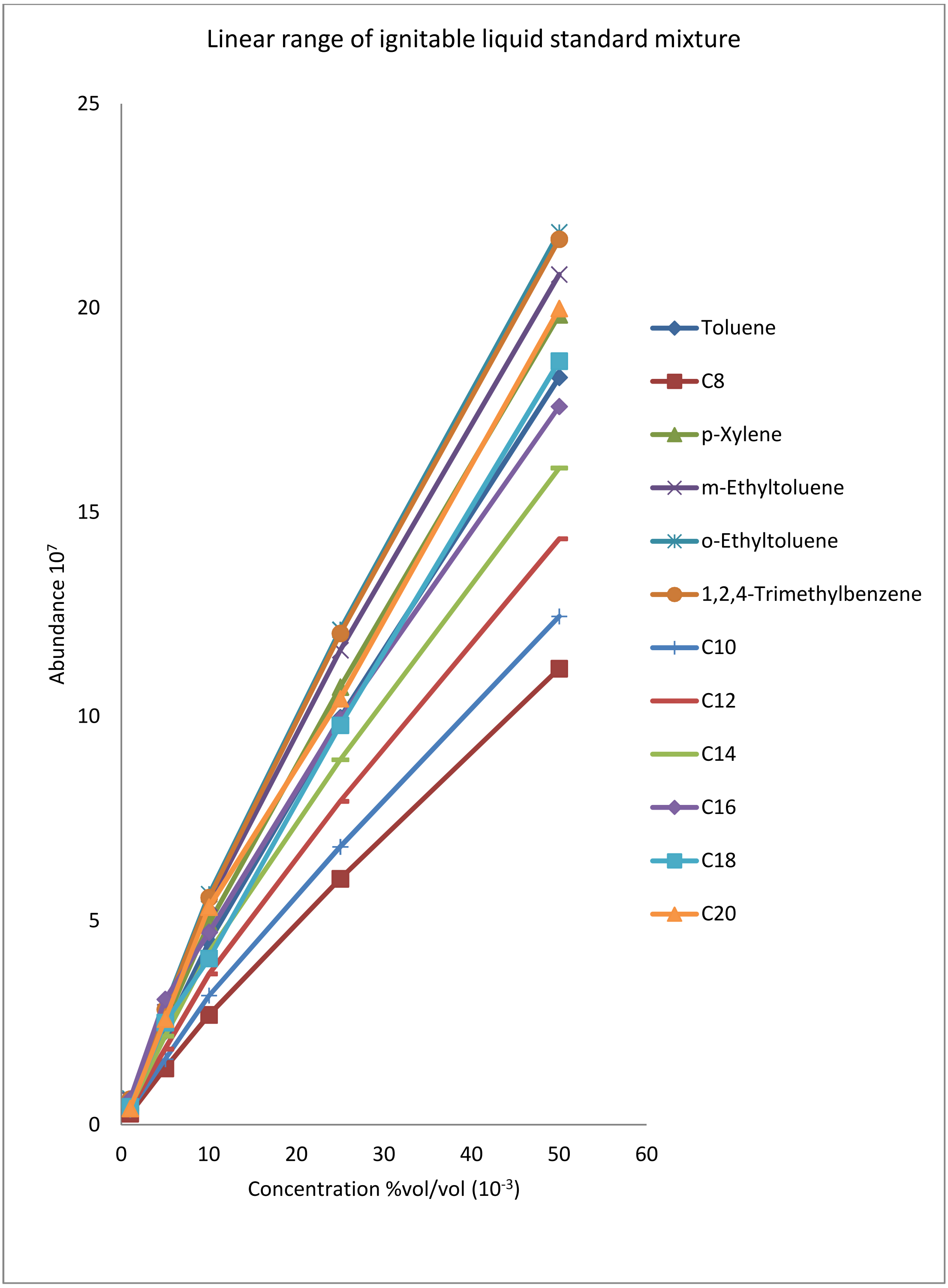


**Figure 2.3 shows a linear relationship between the peak area and commercial test mixtures (concentration 0.005% to 0.05% vol/vol).**

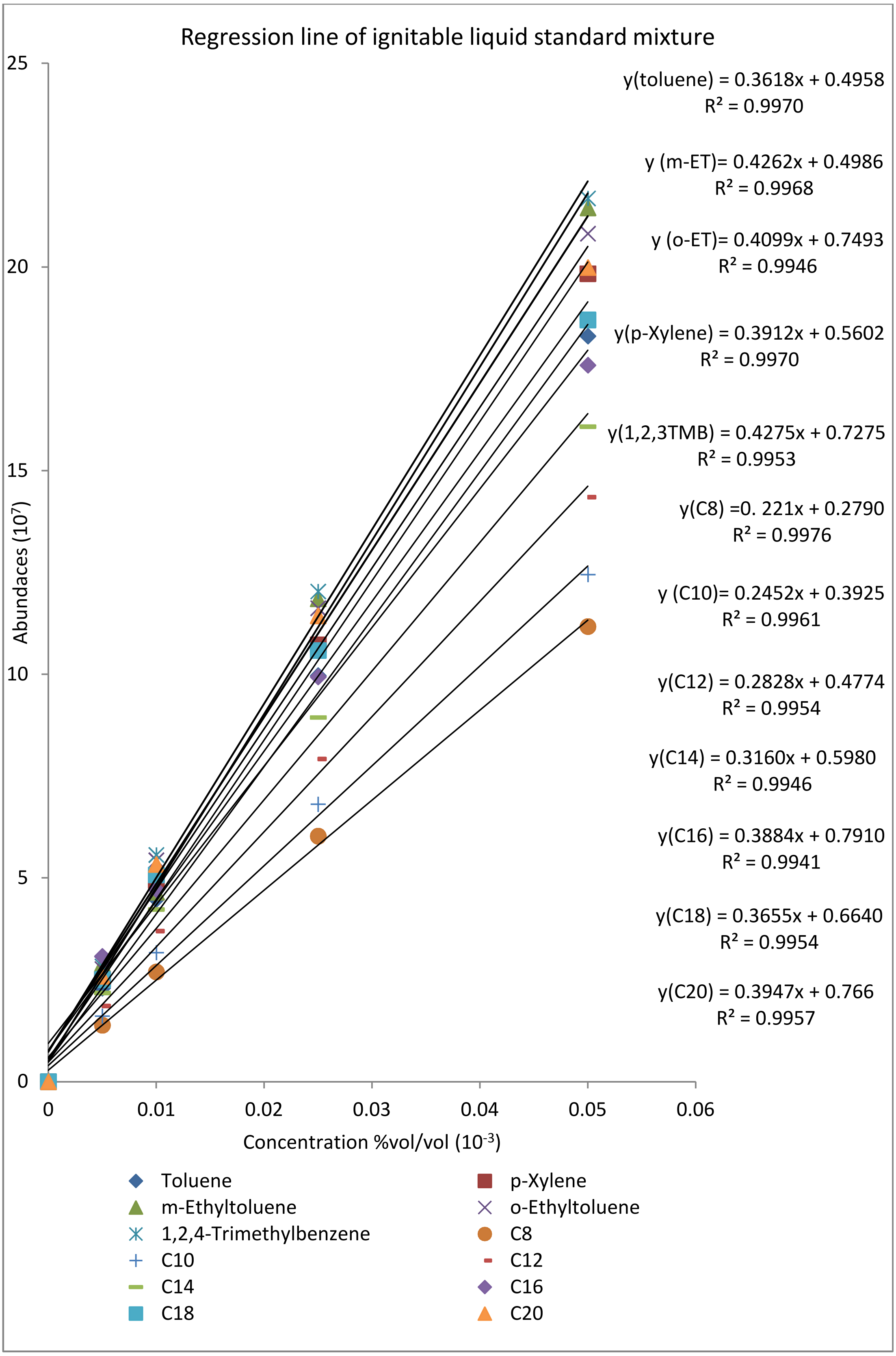


**Figure 2.4 presents the regression lines of 12 compounds from the commercial standard mixture at concentrations up to 0.05% vol/vol.**

**Table 2.5 Instrumental or method LOD obtained from linear equation of IL standard mixture (0.005% vol/vol - 0.05% vol/vol).**

| Compound | Linear equation | $R^2$ | LOD ($10^{-3}$) %vol/vol |
|---|---|---|---|
| Toluene | y = (0.3618±0.0364)x + (0.4958± 0.9292) | $R^2 = 0.9970$ | 3.8371±0.1215 |
| C8 | y = (0.2210±0.0331)x + (0.2791± 0.8427) | $R^2 = 0.9976$ | 5.6969±0.2679 |
| p-Xylene | y = (0.3912±0.0378)x + (0.5602± 0.8432) | $R^2 = 0.9970$ | 3.6834±0.8432 |
| m-Ethyltoluene | y = (0.4099±0.0531)x + (0.7493± 1.1827) | $R^2 = 0.9946$ | 4.9306±0.2007 |
| o-Ethyltoluene | y = (0.4262±0.0471)x + (0.4986± 1.0499) | $R^2 = 0.9968$ | 4.2096±0.1463 |
| 1,2,4-TMB | y = (0.4275±0.0516)x + (0.7275± 1.1499) | $R^2 = 0.9953$ | 4.5965±0.1744 |
| C10 | y = (0.2453±0.0267)x + (0.3925± 0.5956) | $R^2 = 0.9961$ | 4.1492±0.1421 |
| C12 | y = (0.2828±0.0354)x + (0.4774± 0.7883) | $R^2 = 0.9954$ | 4.7632±0.1563 |
| C14 | y = (0.3160±0.0408)x + (0.5980± 0.9114) | $R^2 = 0.9946$ | 4.9290±0.2006 |
| C16 | y = (0.3884±0.0486)x + (0.7910± 1.0831) | $R^2 = 0.9941$ | 5.4697±0.2470 |
| C18 | y = (0.3655±0.0519)x + (0.6640± 1.1568) | $R^2 = 0.9954$ | 5.4087±0.2415 |
| C20 | y = (0.3947±0.0556)x + (0.7660± 1.2399) | $R^2 = 0.9957$ | 5.3684±0.2379 |

### 2.6.5 Within and Between Sample Variations

Variations of the compounds in Zippo lighter fluid within the same container and between different containers were also investigated in order to validate the analytical method for application to ignitable liquid analysis. An example of the resultant chromatogram is presented in figure 2.5 with the associated peak area data presented in table 2.6.

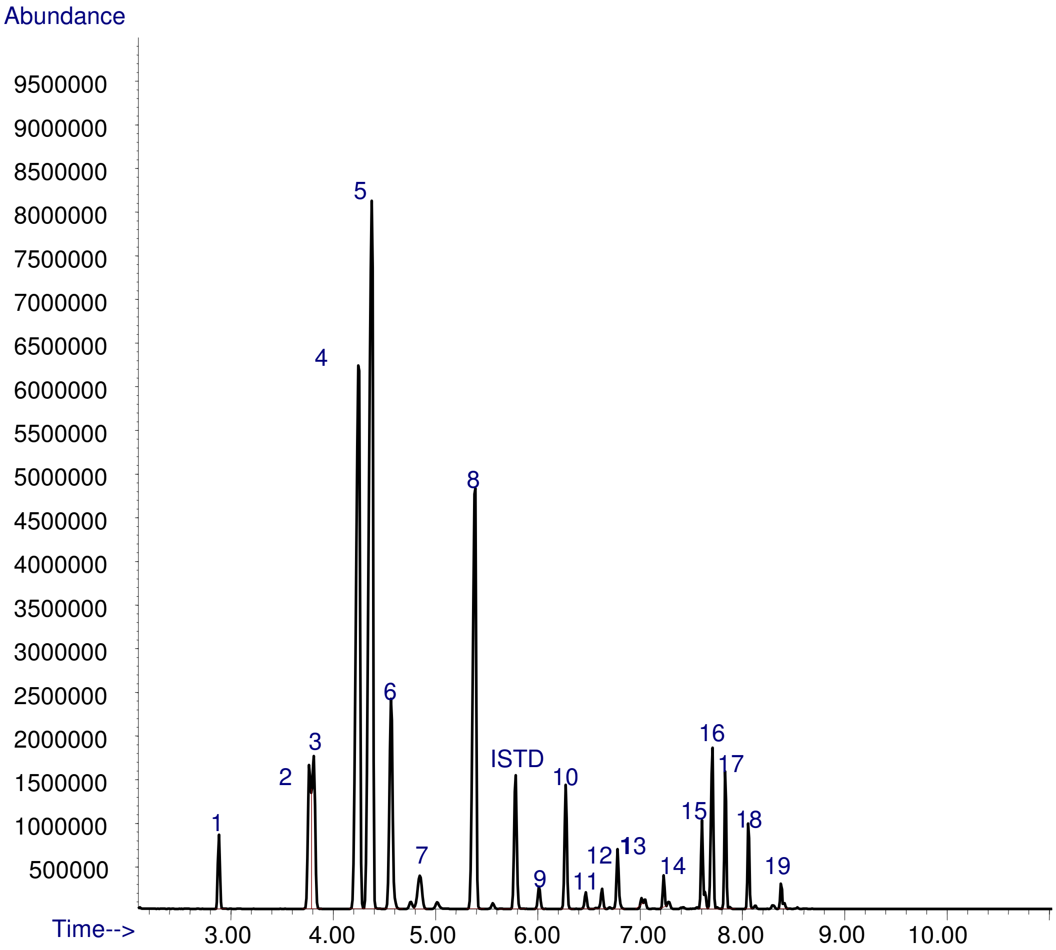


Figure 2.5 Chromatogram of Zippo lighter fluid at 2% dilution in pentane.

Peak areas of the compounds were normalised using the peak area of the internal standard (Tetrachloroethylene). Excellent instrumental precision is reflected by the results of repeated injections from a single vial (injection variation) giving %RSD values of between 0.35 - 3.75. Similar excellent %RSD values were obtained for both the between Zippo lighter fluid samples.

**Table 2.6 % RSD of 19 peaks detected from Zippo lighter fluid sample.**

| Peak | RT (min) | %RSD of peak areas normalised to the internal standard | | |
|---|---|---|---|---|
| | | InjectionVariation n=6 | Within sample n=6 | Between sample n=6 |
| 1 | 2.88 | 0.36 | 1.69 | 1.46 |
| 2 | 3.77 | 0.83 | 1.31 | 1.28 |
| 3 | 3.81 | 0.61 | 2.14 | 0.57 |
| 4 | 4.25 | 0.89 | 1.48 | 0.92 |
| 5 | 4.39 | 1.21 | 1.30 | 1.55 |
| 6 | 4.57 | 0.42 | 1.50 | 1.09 |
| 7 | 4.85 | 0.26 | 1.21 | 1.17 |
| 8 | 5.39 | 0.79 | 1.31 | 0.88 |
| 9 | 6.02 | 0.72 | 1.25 | 1.71 |
| 10 | 6.27 | 0.27 | 1.14 | 1.07 |
| 11 | 6.47 | 0.41 | 1.56 | 1.59 |
| 12 | 6.63 | 0.56 | 1.49 | 1.43 |
| 13 | 6.79 | 0.21 | 1.18 | 0.92 |
| 14 | 7.24 | 3.75 | 3.83 | 0.89 |
| 15 | 7.61 | 0.60 | 1.56 | 1.30 |
| 16 | 7.71 | 0.36 | 1.20 | 0.89 |
| 17 | 7.84 | 0.48 | 1.06 | 0.84 |
| 18 | 8.07 | 0.35 | 1.25 | 1.08 |
| 19 | 8.39 | 0.35 | 1.11 | 1.51 |

## 2.7 Conclusions

A series of validation studies to determine the solvent, column performance, instrumental precision and the repeatability of chromatography has demonstrated that the GC-MS method chosen was appropriate for carrying out the experimental analysis required for this work. The detector response for the standard compounds was shown to be of excellent linearity and satisfied the lowest limit of detection for ignitable liquid and ignitable liquid residue analysis according to the ASTM standard method E1618.

## 2.8 References

1. McNair, H.M., and Miller, J.M., *Basic Gas Chromatography*. 1998, New York: John Wiley and Sons.

2. Rod, D., *The Troubleshooting and Maintenance Guide for Gas Chromatographers*. 4th ed. 2007, Weinhem: Wiley-VCH.

3. Miller, J.C., and Miller, J.N., *Statistics for Analytical Chemistry*. 3rd Edition ed. 1993, London: Ellis Harwood.

4. Owens, R., *Validation of analytical procedures: Methodology*. 1999,: U.S. Department of Health and Human Services, Food and Drug Administration Center for Veterinary Medicine, Rockville.

5. *ASTM Designation: E 1387 – 01 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography*. 2001, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-10.

6. *ASTM Designation: E 1618 – 06 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry*. 2006, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-11.

7. Lentini, J.J., and Armstrong, A.T., *Comparison of the eluting efficiency of carbon disulfide with diethyl ether: The case for laboratory safety.* Journal of Forensic Sciences, 1997. **42**(2): p. 307-311

8. Dolan, J.A., and Newman, R.R., *Solvent options for the desorption of activated charcoal in fire debris analysis*, in *55th Annual Meeting of the American Academy of Forensic Sciences*. 2001: Seattle.

9. Massey, D., Du-Pasquier, E., and Lennard, C., *Solvent desorption of charcoal strips (DFLEX) in the analysis of fire debris samples: Replacement of carbon disulfide.* Canadian Society of Forensic Science Journal, 2002. **35**(4): p. 195-207.

10. *Material safety data sheet; available at http://msds.chem.ox.ac.uk/.* [accessed on 23/04/2009].

11. Stauffer, E., Dolan, J.A., and Newman, R., *Fire Debris Analysis*. 2008, Burlington: Academic Press.

12. Braithwaite, A., and Smith, F.J., *Chromatographic Methods*. 5th Edition ed. 1996, Dordrecht: Kluwer Academic Publishers.

13. *IUPAC Compendium of Chemical Terminology 2nd Edition (1997); available at http://old.iupac.org/goldbook/L03540.pdf* [accessed on 04/02/2011].

# CHAPTER 3: PREPARATION AND ANALYSIS OF IGNITABLE LIQUIDS, EVAPORATED IGNITABLE LIQUIDS, BURNT SUBSTRATES AND IGNITABLE LIQUID SPIKED BURNT SUBSTRATES

## 3.1 Introduction

This chapter outlines the methodology used in the preparation of samples of both ignitable liquids (IL) and evaporated ignitable liquid residues (ILR) used in this work. This included optimisation and validation of sample preparation procedures and the preparation of samples of the four sub-classes of petroleum distillate products investigated which were petrol, light petroleum distillate product (LPD), medium petroleum distillate product (MPD) and heavy petroleum distillate product (HPD). Each sub-class was represented by a range of commercial brands within that sub-class obtained from local sources (petrol stations and hardware retail outlets around Glasgow). A range of common materials were also used to generate a reference collection for burnt interfering products (IPs).

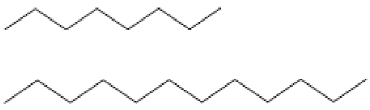
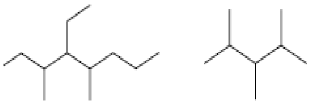
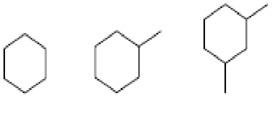
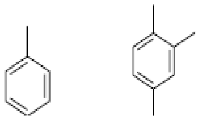
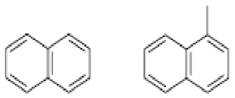
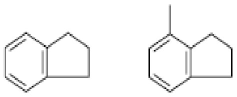
The ignitable liquid samples together with evaporated (sometimes called 'weathered') samples produced under controlled conditions, were used to generate a reference collection and to form subsequent multivariate analysis. Multivariate analytical techniques were used to investigate the variability of chromatographic patterns of samples of the same sub-class and within and between brands of products. These results are presented in chapter 4. The influence of interfering products on the discrimination of ignitable liquids and residues are discussed in more detail and presented in chapter 5.

### 3.1.1 Ignitable Liquids (IL)

Ignitable liquids are the most common liquid accelerants used to deliberately start and promote the development of a fire. Ignitable liquids can be described as "any liquid or the liquid phase of any material that is capable of fueling a fire, including a flammable liquid, combustible liquid, or any other material that can be liquefied and burned" [1]. From an analytical perspective, ignitable liquids are categorised based on the raw material from which they are derived and can be divided into petroleum and non-petroleum based products.

According to the ASTM standards in fire debris analysis, the classification scheme of hydrocarbon compounds in ignitable products as outlined earlier (chapter 1) is focused more on the presence of aliphatic and aromatic hydrocarbons [2]. Aliphatic hydrocarbons are referred to as alkanes, commonly designated by normal alkanes, isoalkanes or cycloalkanes. Aromatic hydrocarbons are hydrocarbon compounds with a benzene ring structure and the groups that are commonly associated with ignitable liquids include alkylbenzenes, polynuclear aromatics and indanes as presented in table 3.1.

**Table 3.1 Characteristics of hydrocarbon compounds commonly associated with petroleum based ignitable liquid composition [3].**

| Type of compound | Specific structure | Description | Examples |
|---|---|---|---|
| Alkane | Normal alkanes (n-alkanes) | Straight-chain hydrocarbons ($C_nH_{2n+2}$) |  |
| | Isoalkanes (isoparaffins) | Branched-chain hydrocarbons ($C_nH_{2n+2}$) |  |
| | Cycloalkanes (cycloparaffins, naphthenics) | Cyclic hydrocarbons ($C_nH_{2n}$) |  |
| Aromatic | Simple | Alkyl-substituted benzenes |  |
| | Polynuclear (naphthalenes) | Multiple fused benzene ring compounds |  |
| | Indane | Benzene ring fused to cyclopentane |  |

Petroleum based ignitable liquids are derived from crude oil while non-petroleum based products are derived from sources such as natural solvents (for example turpentine from pine) or other oxygenated solvent. Non petroleum based ignitable liquids such as acetone, ethyl alcohol, diethyl ether and turpentine oil have been listed among common fire accelerants[4]. Nonetheless, records have shown that petroleum based ignitable liquids are the most common liquid accelerants of choice because of their high combustibility, ready availability and low cost [5-7]. As a consequence this study has focused on petroleum based ignitable liquids only.

### 3.1.2 Petroleum Based Ignitable Liquid: Production and Process

Crude oil, also known as petroleum, is a complex mixture of primarily hydrocarbon material (85% wt% of carbon and 12% of hydrogen) and also containing some nitrogen, sulphur, oxygen and some metals (e.g. nickel, vanadium and chromium)[8]. Major groups of hydrocarbon compounds derived from crude oil include alkanes and isoalkanes (paraffins and isoparrafins), cycloalkanes including polycyclic compounds such as naphthenes and aromatic compounds. In its natural form, crude oil is barely usable and thus needs to be refined to convert the crude material into more desirable products ready for consumer consumption. These include petrol, solvents, diesel and kerosene.

Crude oil refining is a high-technology industry, involving complicated chemical and physical processes. These processes are applied under designed engineering systems where crucial parameters such as heat, pressure, the use of catalysts, and other operating conditions are strictly monitored. In general, the production of the final consumer products from crude oil can be simplified into five sequential stages involving fractional distillation, conversion, treatment, blending and additional post-refining operations [9]. A simple explanation of these stages is presented below and in table 3.2.

**Stage 1:** Fractional distillation (by utilising the differences in boiling points) in atmospheric or vacuum distillation columns for separation of hydrocarbon compounds according to their molecular size and boiling point ranges. This process generates a certain amount of finished (straight run) product for example liquid petroleum gas (LPG), straight run petrol and lighter fuel gas. The remaining product is used as intermediates (feedstock) for subsequent refinement processes.

**Stage 2:** Conversion is carried out to change the size of the hydrocarbon molecular structure either by cracking (decomposing larger molecules into smaller molecules), polymerisation and alkylation (building large molecules from smaller molecules) or rearrangement (altering the hydrocarbon molecular structure by isomerisation and other catalytic reforming process).

**Stage 3:** Treatment processes are used to 'clean' and remove contaminants to produce better quality distilled products. Treatment methods include desalting, hydro-sulfurisation, solvent refining, 'sweetening', solvent extraction and de-waxing.

**Stage 4:** Blending and combining of hydrocarbon fractions, with other derivatives, detergents, additives, colouring and other chemical enhancers is undertaken to meet product or regulating body specifications. Consequently, multiple grades of finished products such as premium, regular and super petrol, kerosene and jet fuel or diesel and heating oil are available.

**Stage 5:** Post-refining operations include storage and handling, light end recovery and by product management for sulphur recovery, solid waste and waste water treatments.

A broader scheme of the refinery flow process and plant operations are shown in figures 3.1 and 3.2 respectively.

**Table 3.2 Petroleum refining operation process terminologies [9].**

| Process name | Purpose |
|---|---|
| Thermal cracking | Increase petrol production |
| Hydrocracking | Improve fuel quality and remove sulphur |
| Fluid catalytic cracking | Increase petrol yield and octane |
| Catalytic polymerisation | Improve petrol yield and octane number |
| Catalytic cracking | Higher octane petrol |
| Coking | Produce petrol base stock |
| Thermal reforming | Improve octane number |
| Residual hydrocracking | Increase petrol yield from residual |
| Alkylation | Increase petrol yield and octane |
| Isomerisation | Produce alkylation feedstock |
| Deasphalting | Produce alkylation feedstock |
| Catalytic isomerisation | Convert to molecules with high octane numbers |
| Catalytic reforming | Convert low-quality naphtha |
| Hydrogenation | Remove sulphur |
| Hydro-sulpherisation | Remove sulphur |
| Sweetening | Reduce sulphur and odour |
| Inhibitor sweetening | Remove mercaptans (sulphur containing organic compounds) |
| Solvent extraction | Improve pour point |
| Catalytic de-waxing | Improve pour point |
| Visbreaking | Reduce viscosity |

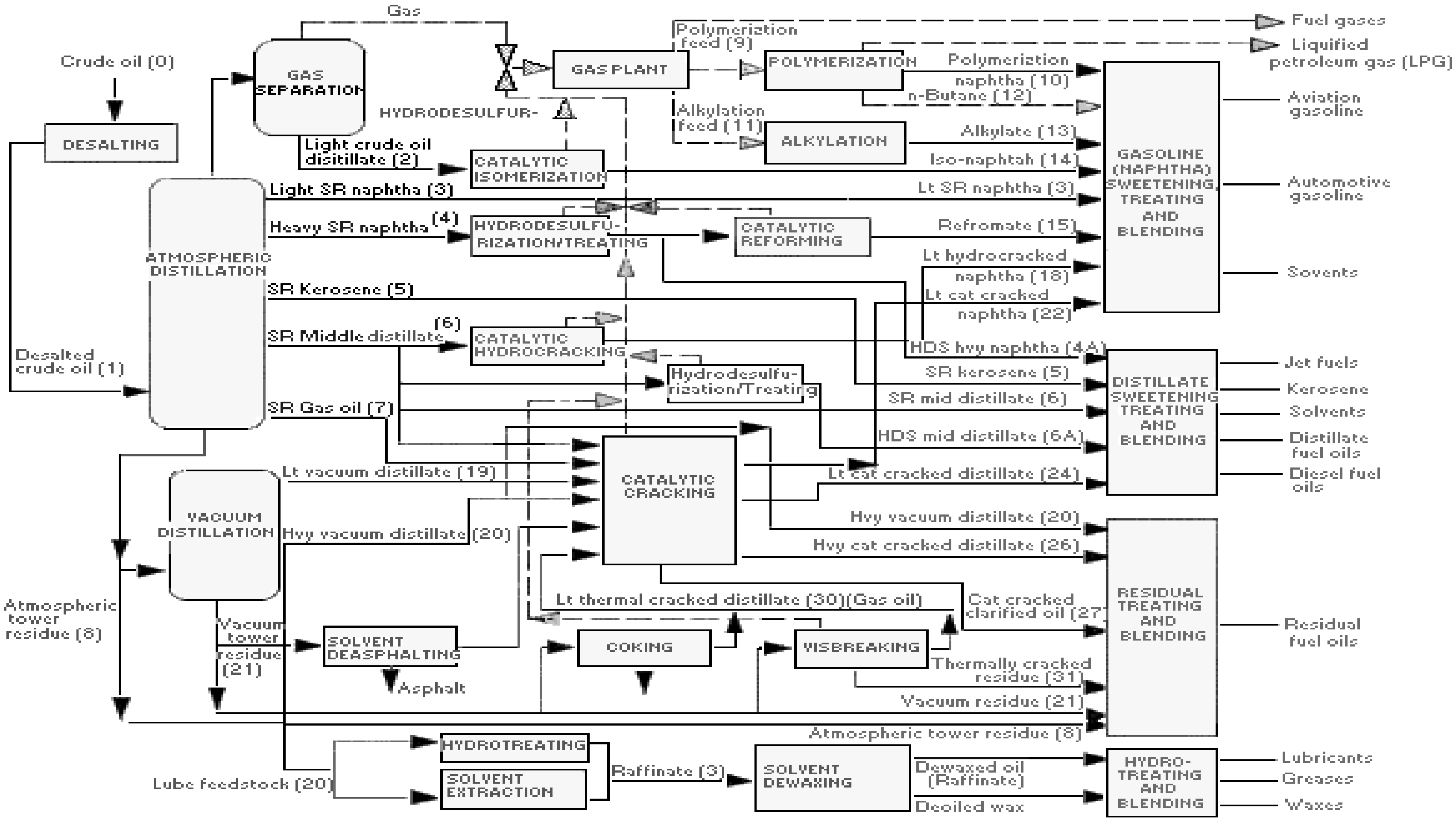


**Figure** 3.1 Crude oil refinery process flow diagram [10].

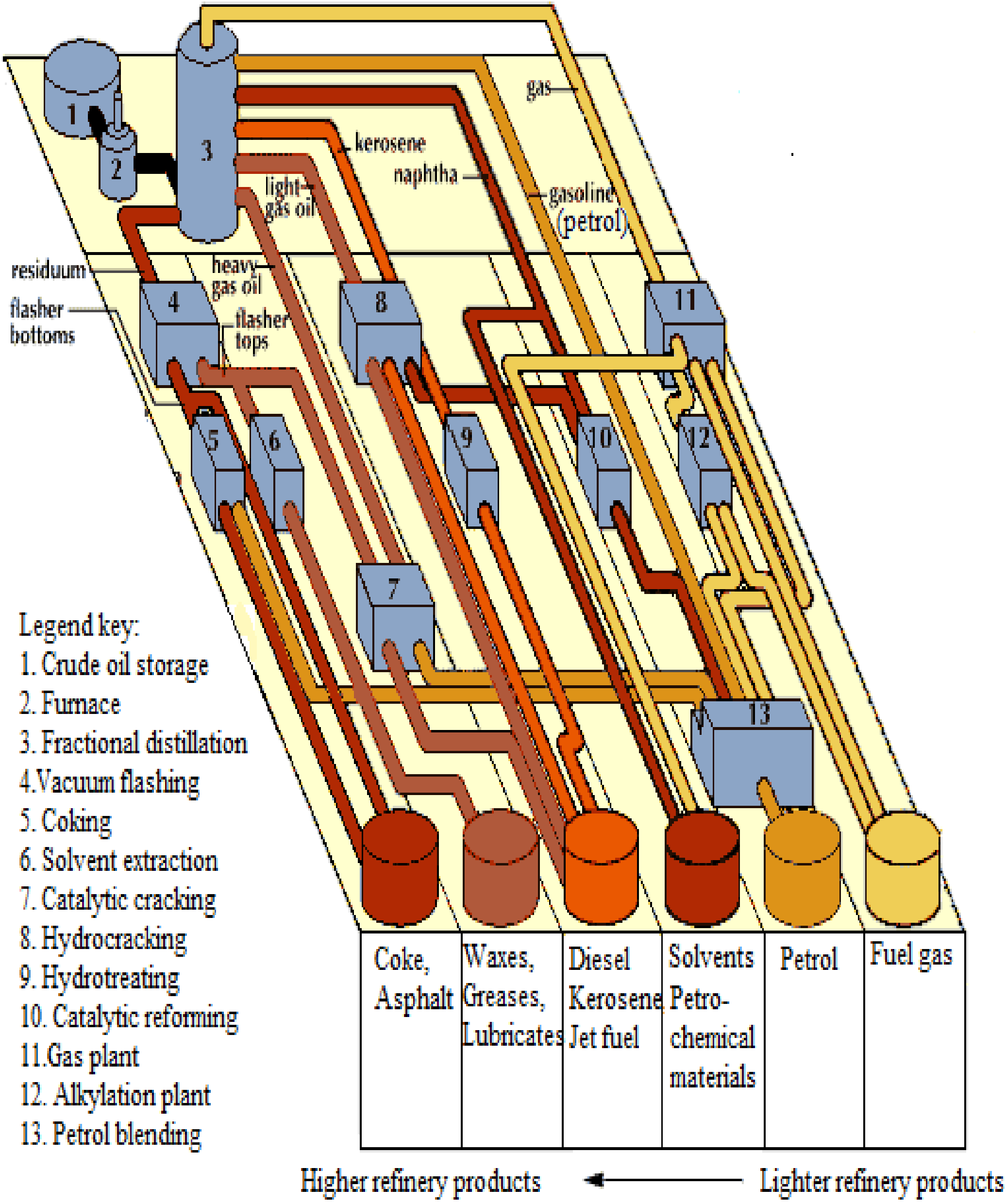
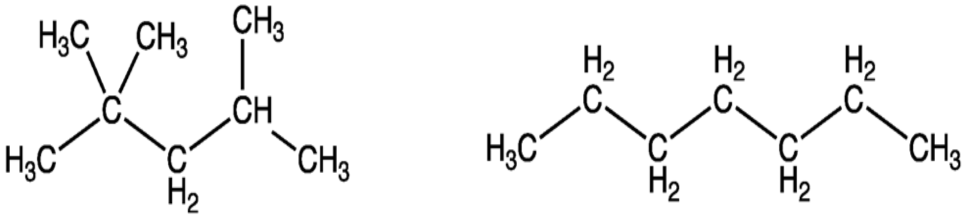


**Figure 3.2 Illustration of typical refinery plant process and produce from crude oil [11].**

### *3.1.2.1 Petrol*

Petroleum fuel has come a long way since the use of petrol light fuel in the spark-ignition engine carriage in 1885 by Benz [12]. Today, the production of petrol as a fuel accounts for almost half of all of the crude oil distillation products generated [13-14]. Petrol from fractional distillation is further processed and reformulated to modify the fuel to meet physical and chemical specifications of the final product and improve the octane rating of the fuel (by increasing the amount of aromatic compounds and reducing the amount of alicyclic compounds present). Upon distribution of petrol to storage terminals, additives and detergents are finally blended in by the individual petrol companies. Consequently, petrol is a complex mixture of hundreds of components [12]. The final product consists primarily of hydrocarbon from $C_4$-$C_{12}$, and is dominated by alkyl-benzene based compounds.

Advancement in modern and more powerful automotive engines demanded petroleum fuel to be sufficiently volatile, clean (engine wise and environmentally) economical and most importantly to have good octane quality. The octane number measures the ability of the fuel to resist 'knocking' in the engine, where the higher the octane quality, the greater the resistance to 'knocking'[12]. Fuel with a low octane number leads to a low compression ratio in the engine's compression chamber, resulting in premature ignition and an audible 'knock' sound which directly affects the engine's performance, lessens fuel efficiency and can damage the engine. The octane rating of petrol is determined by comparing the fuel's performance to iso-octane and n-heptane (figure 3.3).



Isooctane or 2,24-trimethylpentane
Octane rating is 100

n-Heptane
Octane rating is 0

**Figure 3.3 Molecular structure of octane rating compounds.**

Iso-octane burns smoothly and is given an index of 100 while n-heptane is given an index of 0 as it has relatively poor knocking properties. The octane number of petrol describes the same performance as a specific iso-octane-heptane mixture. For example, petrol with the same knocking characteristics as a mixture of 90% iso-octane and 10% heptane would have an octane rating of 90. As such, petrol fuels are graded and marketed according to their octane numbers symbolised by RON 95, RON 97 and RON 99 which are regular, premium and super unleaded petrol respectively. Improving the octane number in unleaded petrol is achieved by incorporating oxygenated compounds such as ethyl tertiary butyl ether (ETBE), methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME) and other oxygenated compounds into the blend [15].

Up until the 1990's, lead additives, mostly tetra-ethyl lead (TEL) or tetra methyl lead (TML) were added to petrol as 'anti knock' agents [12]. In the UK the use of leaded petrol has been withdrawn entirely however, concessions on the supply of limited leaded petrol, known as four star petrol for specialised historic vehicles is permitted and available under strict regulations [16].

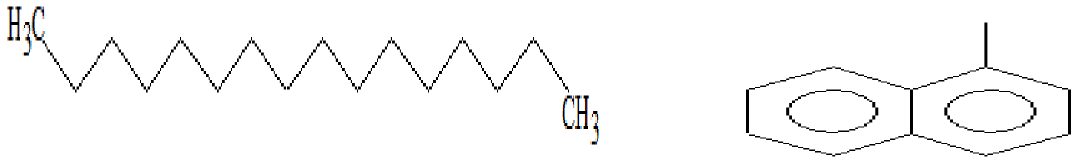
#### *3.1.2.2 Light and Medium Petroleum Distillates (LPD and MPD)*

Light and medium petroleum products are obtained from the distillation of naphta which consists of mixtures of paraffin, naphthenes and aromatic hydrocarbons of $C_5$–$C_{12}$ (with 30°C -200°C boiling point range) [17]. LPD and MPD undergo relatively little refining but some hydro-sulpherisation and hydrogenation processes may also be undertaken. The $C_5$-$C_6$ light and medium aliphatic distillation products include cigarette lighter fuels and camping stove fuels while heavy naphta ($C_6$-$C_{12}$ mononaphthalenes and monoaromatics) include cleaning solvents such as paint brush cleaners, petroleum white spirits, turpentine substitute and other products[17-18].

#### *3.1.2.3 Heavy PetroleumDistillates (HPD)*

Diesel fuel, jet fuel, kerosene and lubricating oil are classified as the "middle distillates" of crude oil and are also classified as heavy petroleum distillates (as mentioned previously section 1.5.1) by the ASTM E 1618[2]. These products consist of hydrocarbon compounds containing $C_8$-$C_{20}$ or above and have relatively higher boiling temperatures (200°C -350°C) and lower evaporation rates.

Automotive diesel fuel (usually 2D type) generally undergoes hydro-cracking or hydro-sulphurisation before it is reformulated in order to satisfy the requirements for successful engine combustion [9]. Diesel consists primarily of aliphatic and aromatic hydrocarbon compounds with the aliphatic compounds far in excess. Similar to the octane number for petrol, the performance of a diesel fuel is measured using a cetane number (figure 3.4) where the higher the rating, the easier the engine will start and the smoother the combustion process [20].



Cetane or hexadecane, $C_{16}H_{34}$
Cetane number is 100
( high ignition quality)

1-Methylnaphtalene
Cetane number is 0
(low ignition quality)

**Figure 3.4 Molecular structures of cetane rating compounds.**

Diesel fuel is graded into three types, based mainly on properties such as volatility, viscosity, pour point and sulphur content, and are classified as types 1D, 2D and 4D [19-20]. Regular and premium diesel grades are associated as 48 and 55 cetane number respectively. Blending between these diesel types are sometimes carried out to improve the fuels performance in cold temperature conditions.

## 3.2 Materials and Methods

### 3.2.1 Ignitable Liquid Collection

Petrol and diesel samples were collected directly from public fuelling stations using an appropriate clean fuel can. The various samples were then returned to the laboratory and 100 mL's decanted into a clean double sealed screw-top 125 mL aluminium can as soon as practical after initial collection. These samples were labelled as neat samples (zero percent evaporated) and given a code letter for subsequent ease of identification. The remaining samples were used to prepare the appropriate evaporated samples for each ignitable liquid collected.

The source of each petrol and diesel sample is provided in tables 3.3 and 3.4 and their location indicated in figure 3.5.

**Table 3.3 List of petrol samples collected.**

| No | Sample Class | Brand | Code |
|---|---|---|---|
| 1 | Unleaded premium grade | BP | A |
| 2 | Unleaded premium grade | Esso | B |
| 3 | Unleaded super grade | Tesco | C |
| 4 | Unleaded premium grade | Sainsbury | D |
| 5 | Unleaded premium grade | Shell | E |
| 6 | Leaded gasoline - 4 Star | Bayford & Co | F |
| 7 | Unleaded regular grade | BP | G |
| 8 | Unleaded regular grade | Esso | H |
| 9 | Unleaded regular grade | Sainsbury | J |
| 10 | Unleaded regular grade | Shell | K |
| 11 | Unleaded regular grade | Jet | L |
| 12 | Unleaded regular grade | Tesco | M |
| 13 | Unleaded regular grade | Asda | N |
| 14 | Unleaded regular grade | Morrison | P |

**Table 3.4 List of diesel samples collected.**

| No. | Sample Class | Brand | Code |
|---|---|---|---|
| 1 | Diesel | Asda | DA |
| 2 | Diesel | Esso | DB |
| 3 | Diesel | Jet | DC |
| 4 | Diesel | Sainsbury | DD |
| 5 | Diesel | Shell | DE |
| 6 | Diesel | Morrison | DF |
| 7 | Diesel | BP | DG |
| 8 | Diesel | Tesco | DH |

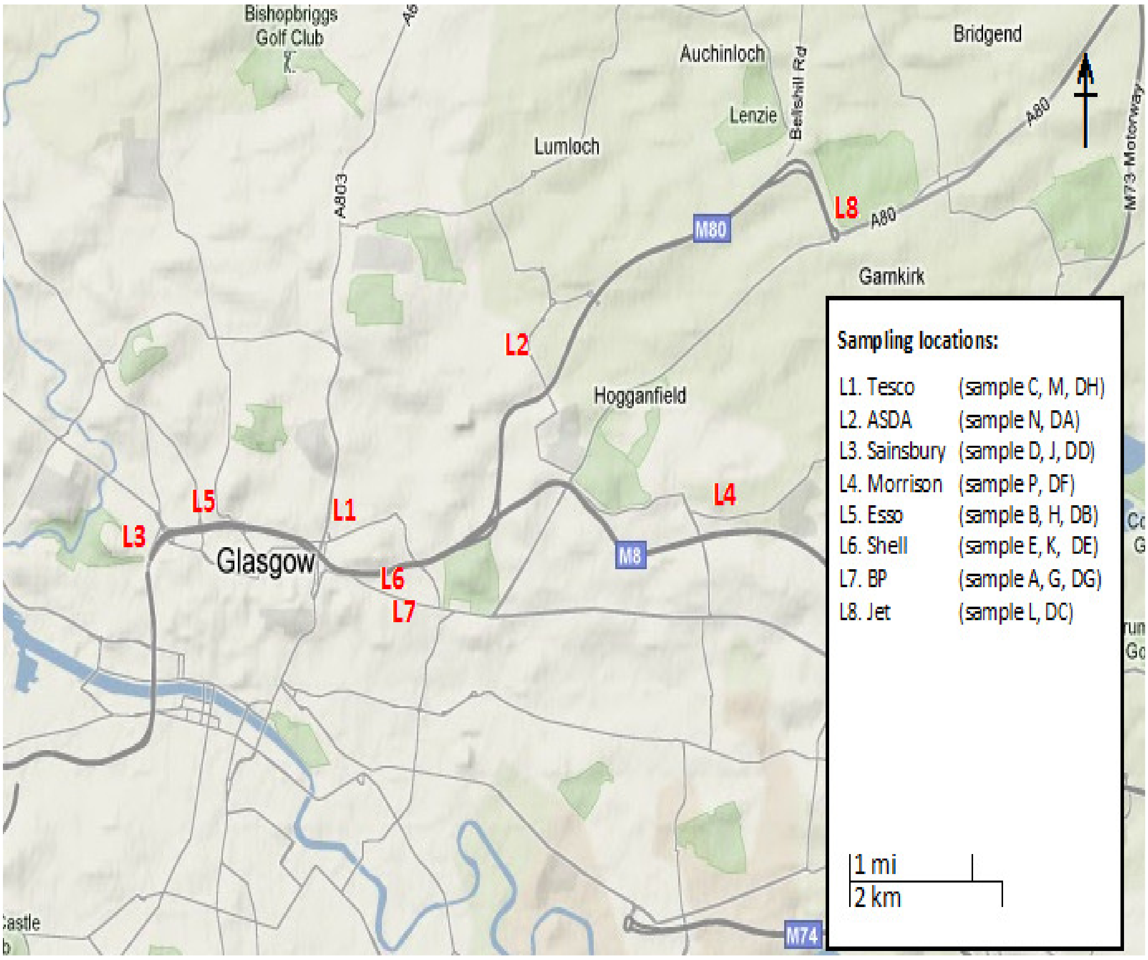


**Figure 3.5 Location map showing fuelling station where petrol and diesel samples were obtained. Sample F (leaded petrol) was obtained from regulated garage in England.**

Lighter fuel was chosen to represent the light petroleum distillate (LPD) class. Compared to other products in LPD range, for example camping fuel or petroleum ether, lighter fluid is readily available from local stores at a relatively cheap price. More importantly, numerous lighter fluid brands are available, facilitating interbrand comparisons.

A wider range of product types were selected to represent the MPD samples which included white spirits, paint brush cleaners and lamp oils.

The various light and medium petroleum distillate products were purchased from commercial stores in Glasgow, the locations of which are indicated in figure 3.6. The list of samples and their respective codes are presented in table 3.5 and 3.6.

**Table 3.5 List of LPD samples.**

| No. | Sample Class | Brand | Code |
|---|---|---|---|
| 1 | Ligher fuel | Zippo | ZIPPO |
| 2 | Ligher fuel | Ronsonol | RON |
| 3 | Ligher fuel | Swan | SWAN |
| 4 | Ligher fuel | Perma Fluid | PERMA |
| 5 | Ligher fuel | Dunhill | DUN |

**Table 3.6 List of MPD samples.**

| No. | Sample Class | Brand | Code |
|---|---|---|---|
| 1 | White spirit | B&Q own brand | BQWS |
| 2 | White spirit | Tesco own brand | TWS |
| 3 | White spirit | Homebase own brand | HBWS |
| 4 | White spirit premium low odour | Bartoline | BWS |
| 5 | Brush cleaner | Homebase own brand | HBC |
| 6 | Brush cleaner | Polycell | PBC |
| 7 | Lamp oil | Bartoline | BLO |
| 8 | Lamp oil ultra pure low odour | After dark | ADLO |

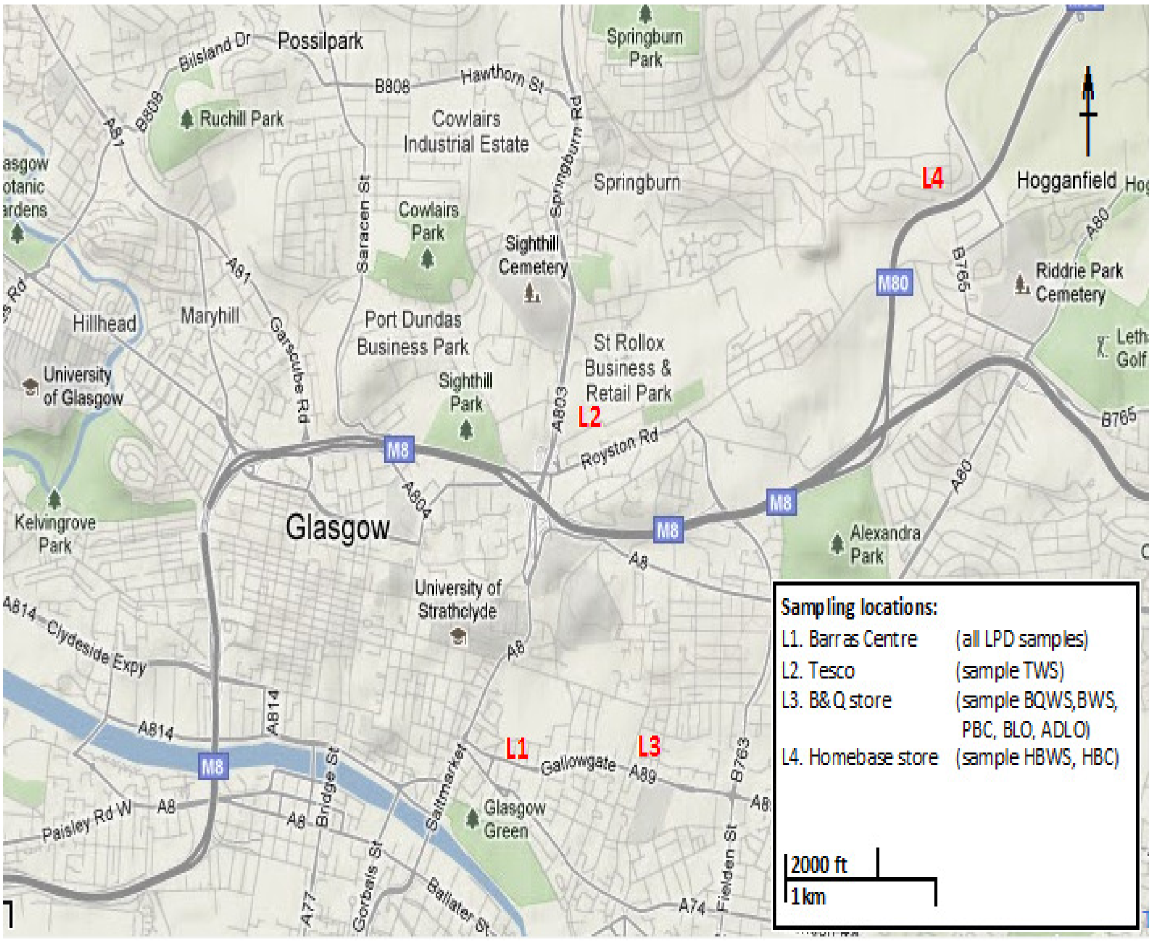


Figure 3.6 Location map showing local stores in Glasgow where LPD and MPD samples were obtained.

### 3.2.2 Preparation of Evaporated Petrol Samples

For each petrol sample collected, a set of evaporated samples was generated. The fresh petrol sample (100mL) was placed in graduated cylinder and allowed to evaporate over time. Samples were collected when the original volume had been reduced by 10, 25, 50, 75, 90 and 95 mL respectively. This produced a set of partially evaporated samples at approximately 10, 25, 50, 75, 90 and 95 percent evaporation for each petrol brand and type.

Approximately 1mL of each evaporated sample was removed once the desired volume had been reached and transferred into glass vials, labelled and capped using aluminium foil and tightly sealed with screw caps. All samples were stored in darkness at room temperature prior to analysis.

### 3.2.3 Preparation of Evaporated Ignitable Liquids (LPD, MPD and HPD)

Evaporated samples were prepared from each LPD, MPD and diesel sample as follows: each ignitable liquid (100 mL) was placed into a clean round bottom flask which was attached to a distillation apparatus as illustrated in figure 3.7. The round bottom flask was gently heated and once the desired volume of distillate had been recovered in the graduated receiving flask a sub sample, approximately 1mL of the ignitable liquid remaining in the round bottom flask was removed. For each ignitable liquid, sub samples were recovered when the original liquid had been reduced by approximately 10, 25, 50, 75, 90 and 95 mLs in volume. This produced a set of partially evaporated samples for each lighter fluid liquid at approximately 10, 25, 50, 75, 90 and 95 percent evaporation. Samples were transferred into glass vials, labelled and capped using aluminium foil and tightly sealed with screw caps. All samples were stored in darkness at room temperature prior to analysis.

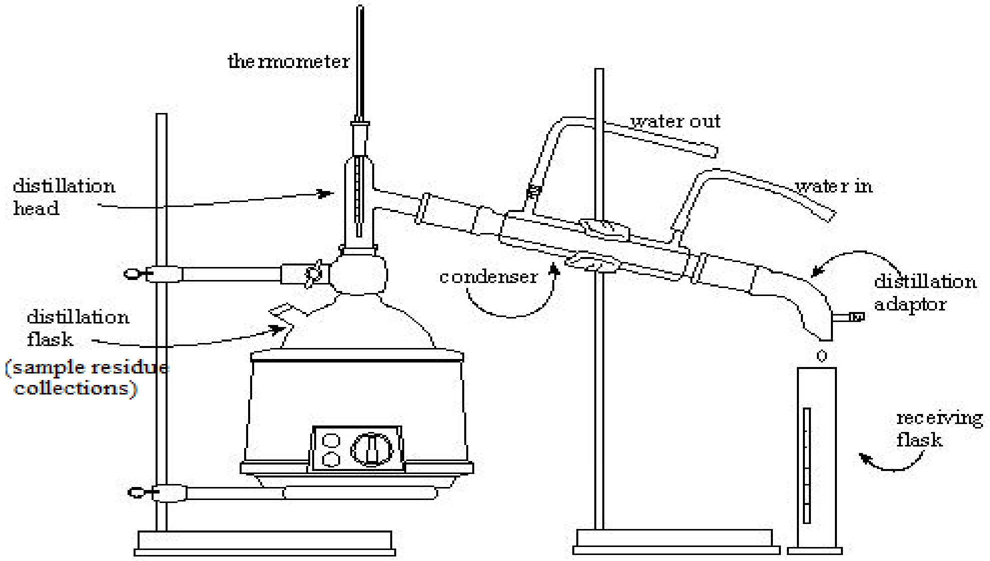


**Figure 3.7 Fractional distillation set-up for evaporation of ignitable liquids, adapted from [21].**

### 3.2.4 GC-MS Analysis of Unevaporated and Evaporated Ignitable Liquid Samples

Prior to instrumental analyses, each sample (unevaporated and evaporated) was diluted to 2% in pentane (HPLC grade, WVR International, Leicestershire, UK) with 0.5 mg/mL tetrachloroethylene (Sigma Aldrich, > 99%, St. Louis USA) as internal standard

[22]. Instrumental analysis was performed using the instrumental method outlined in chapter 2 (section 2.2.1).

### 3.2.5 Reproducibility of the Ignitable Liquid Evaporation Technique

Six replicates of the 50% evaporated petrol sample derived from unleaded premium grade BP and six replicates of the 50% evaporated Zippo lighter fluid were prepared according to the method described in section 3.2.2 and 3.2.3 respectively. The samples were diluted and analysed and the percentage relative standard deviation of the peak areas from the resultant chromatogram were determined as raw data, data normalised to the peak area of the relevant internal standard and data normalised to the relevant total peak area to provide an assessment of reproducibility of the preparation method.

## 3.3 Optimisation

### 3.3.1 Optimisation of Passive Headspace Methods for the Recovery of Volatile Materials from Substrates.

Volatile organic compounds from the various substrates investigated were recovered using a passive headspace concentration technique. This involved adsorption of the volatile materials onto an activated charcoal strip (ACS, Plastech Corporation, Minneapolis USA) following the ASTM E1412 standard [23]. This technique was chosen because of its ease of use, applicability to the samples under study and efficiency in hydrocarbon capture [24-29].

After adsorption, the tin was removed from the oven (GenLab D3A, Widnes, England) and allowed to cool to room temperature. The activated carbon strip from was removed from the tin and placed into a 2 mL clear glass GCMS vial (Agilent Technologies UK, Cheshire, England) and 1 mL pentane (1 mL containing 0.5 mg/mL Tetrachloroethylene (Sigma Aldrich, >99%) as internal standard) was added and the sample analysed using the previously described GC-MS method.

### 3.3.2 Optimisation of Carbon Strip Size for Passive Headspace Extraction

The ACS used can be varied in size and as such the ACS size was optimised for use in the experimental set up described. A range of ACS strips were prepared as detailed in table 3.7. An unevaporated petrol sample was used as a test sample for ACS size optimisation because of the wide range and variety of hydrocarbon compounds contained within the sample matrix.

**Table 3.7 ACS sizes tested for the passive headspace adsorption technique.**

| Activated carbon strip | Dimensions | | |
|---|---|---|---|
| | **Width (mm)** | **Length (mm)** | **Total area ($mm^2$)** |
| A | 5 | 10 | 50 |
| B | 5 | 15 | 75 |
| C | 5 | 20 | 100 |
| D | 5 | 25 | 125 |
| E | 7 | 20 | 140 |
| F | 7 | 25 | 175 |

A clean white cotton square (2.0 cm x 2.0 cm) was spiked with petrol (10 µL and placed inside a tin can (125 mL, WA Products, Essex, England). Using a magnet and paper clip, an activated carbon strip was suspended inside the tin can containing the cotton substrate as illustrated in figure 3.8. The tin can was sealed with a metal lid and heated in an oven (GenLab D3A, Widnes, England) for 16 hrs at 80 ºC [30]. Six replicates were performed for each size of ACS.

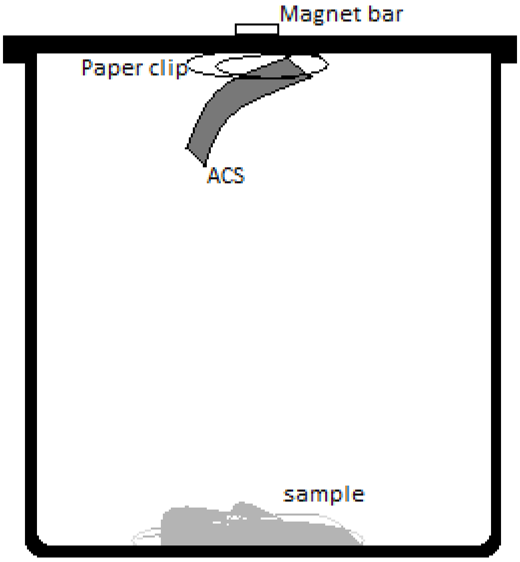


**Figure 3.8 Illustration of the experimental set up for the passive adsorption phase.**

A tin containing the ACS with a sample of white cotton (2.0 cm x 2.0 cm) without the petrol spike and a tin containing only the ACS were also prepared as control samples.

### 3.3.3 Reproducibility of ACS Sample Recovery

The reproducibility of the optimised method for ACS recovery was evaluated using an ignitable liquid test mixture prepared from 50% evaporated petrol and 50% evaporated diesel (1:1). Samples were prepared as previously described (section 3.3.1-3.3.3) using ACS of two sizes, 20 mm x 5 mm (C) and 25 mm x 5 mm (D). In each case 10 µL of the test sample was used and six replicates of each sample set were prepared. The relative standard deviations of the peak areas from the resultant chromatograms were determined as data normalised to the peak area of the relevant internal standard.

### 3.3.4 Optimisation of the Volume of Ignitable Liquid Spiked onto the Substrate.

To determine the volume of ignitable liquid required to generate an observable chromatographic pattern using the experimental set up described, the volume of petrol spiked onto the cotton substrate was varied and petrol spikes of 10, 15, 20, 25 and 30 µL were used. The samples were spiked onto the cotton support as previously described using the optimised size of ACS. Six replicate samples were generated for each volume of petrol.

## 3.4 Preparation of Substrate Materials.

### 3.4.1 Collection of Substrate Materials

Pure polymer samples (BDH Chemicals, Boodle, England), wood samples and various common household products made of natural and synthetic polymeric material were used to generate a reference collection of chromatographic interference products. A full list of materials is listed in tables 3.8 to 3.10. The supplier of these substrates materials are listed in these tables accordingly. In total 45 different substrates were analysed.

**Table 3.8 Polymers resin used to generate interfering pyrolysis products (n=14).**

| **Polymer** | **Supplier** |
|---|---|
| Low Density Poly ethylene (LDPE) | BDH Chemicals, Boodle, England |
| High Density Poly ethylene (HDPE) | BDH Chemicals, Boodle, England |
| Polyethylene oxide (PEO) | BDH Chemicals, Boodle, England |
| Polyvinyl alcohol (PVOH) | BDH Chemicals, Boodle, England |
| Polyvinyl chloride(PVC) | BDH Chemicals, Boodle, England |
| Polypropylene (PP)PP | BDH Chemicals, Boodle, England |
| Polymethyl methacrylate (PMMA) | BDH Chemicals, Boodle, England |
| Polyvinyl acetate (PVA) | BDH Chemicals, Boodle, England |
| Polyethylene glycol (PEG) | BDH Chemicals, Boodle, England |
| Polyethylene terephthalate (PET) | Chemistry Dept.,University of Strathclyde |
| Nylon 6 | Chemistry Dept.,University of Strathclyde |
| Cellulose acetate | Chemistry Dept.,University of Strathclyde |
| Polystyrene(PS) | Chemistry Dept.,University of Strathclyde |
| Polyurethane (PU )foam | Chemistry Dept.,University of Strathclyde |

**Table 3.9 Wood used to generate interfering pyrolysis products (n=10).**

| Wood sample | Supplier |
|---|---|
| Birch | East End Sawmill, Glasgow |
| Maple | East End Sawmill, Glasgow |
| Sycamore | East End Sawmill, Glasgow |
| Pine | East End Sawmill, Glasgow |
| MDF | East End Sawmill, Glasgow |
| Plywood | East End Sawmill, Glasgow |
| White Oak | East End Sawmill, Glasgow |
| Red Oak | East End Sawmill, Glasgow |
| Cedar | East End Sawmill, Glasgow |
| Douglas fir | East End Sawmill, Glasgow |

**Table 3.10 House hold items used to generate interfering pyrolysis products. Floorings(n=9), fabrics(n=8) and others(n=4).**

| Items | Supplier |
|---|---|
| Vinyl tile (with adhesive) | J&W Carpet, Glasgow |
| Vinyl sheet (without adhesive) | J&W Carpet, Glasgow |
| Carpet 100% wool | Stevens & Graham Tartan Carpet Specialist, Glasgow |
| Carpet 80%w, 20%nylon | Stevens & Graham Tartan Carpet Specialist, Glasgow |
| Carpet 80%w, 10%nylon, 10%polyester | Stevens & Graham Tartan Carpet Specialist, Glasgow |
| Carpet 100%polypropylene (rubber backing) | Stevens & Graham Tartan Carpet Specialist, Glasgow |
| Carpet 100%polypropylene (woven backing) | Stevens & Graham Tartan Carpet Specialist, Glsgow |
| Door mat | Bonny Pack Wholesale Ltd., Glasgow |
| Car mat | Bonny Pack Wholesale Ltd, Glasgow |
| Polyester | WBL Whaleys Bradford Ltd. |
| Nylon | WBL Whaleys Bradford Ltd. |
| Cotton | WBL Whaleys Bradford Ltd. |
| Acrylic 100% | WBL Whaleys Bradford Ltd. |
| Denim | Mandors, Glasgow, UK |

***Table 3.10 continued***

| | |
|---|---|
| Brown bovine leather | The Clyde Leather Co., Glasgow, UK |
| Brown leatherette synthetic fabric covered with a soft PVC layer | www.fabricuk.com |
| Microfibre (70%PE,30%polyamide) | Bonny Pack Wholesale Ltd., Glasgow |
| CD casing | Bonny Pack Wholesale Ltd., Glasgow |
| Magazine paper | Tesco store, Glasgow,UK |
| Newspaper | Tesco store, Glasgow, UK |
| Carrier bag | Tesco store, Glasgow, UK |

### 3.4.2 Preparation of Burnt Substrate Samples

Approximately 1.0 g of each substrate was placed into a tin can (125 mL, WA Products, Essex, England). The tin can was suspended approximately 20 cm above a retort stand. The tin was heated by the direct application of a flame from a Bunsen burner placed underneath the tin as illustrated in figure 3.9. The flame was kept in contact with the bottom of the tin for 60 seconds. After this time, the flame was removed and the sample was left to cool to room temperature before the tin lid was secured in place. A K-thermocouple (Pico Technology, Cambrideshire, UK) probe was inserted into the tin to monitor the temperature during the heating process. Burnt sample was generated in triplicate for each substrate.

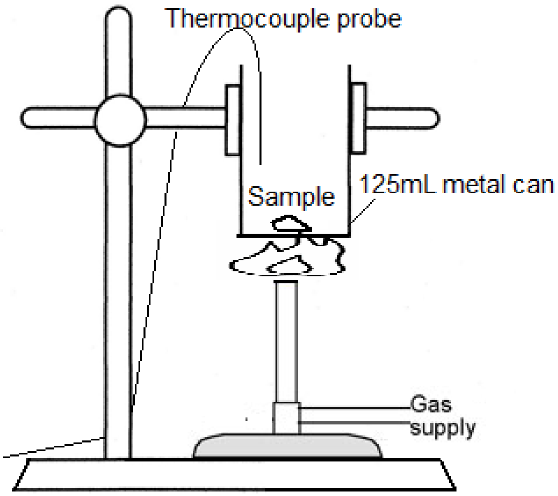


**Figure 3.9 Illustration of burnt substrate sample preparation.**

The HDPE polymer beads (BDH Chemicals, Boodle, UK) were used to investigate the reproducibility of the sample preparation technique. One gram of sample of HDPE (1 g) was weighed into six individual tins and the substrate samples prepared as previously described. The percent relative standard deviations of the peak areas from the resultant chromatograms were determined using data normalised to the peak area of the relevant internal standard.

### 3.4.3 Preparation of Burnt Substrates Spiked with Ignitable Liquid.

Eleven substrates out of the original 45 were chosen for the substrate study because they produced relatively strong chromatographic signals on initial analysis. The samples chosen are listed in table 3.11.

**Table 3.11 Materials chosen for substrate study.**

| Substrate | Code |
|---|---|
| 100% Polypropylene carpet with rubber backing | S1 |
| 100% Polypropylene carpet with woven jute backing | S2 |
| Lino sheet | S3 |
| Lino tile | S4 |
| PVC casing | S5 |
| Polyurethane foam | S6 |
| Carrier bag (Polyethylene bag) | S7 |
| Red Pine | S8 |
| MDF | S9 |
| Plywood | S10 |
| Newspaper | S11 |

Approximately 1.0 g of each substrate was placed into a tin can (125 mL, WA Products, Essex, England). Each substrate sample was spiked with the optimised volume of unevaporated ignitable liquids to produce simulated fire debris samples. Samples were heated using the same method previously described. Each substrate and ignitable liquid sample was generated only once as the reproducibility of the interfering product technique had been previously established and the focus of the experiment was to generate a set on interfering products in tandem with the ignitable liquid residues. In total, 385 test samples (35 ignitable liquids x 11 substrates) were prepared.

### 3.4.4 Passive Headspace Extraction of Burnt Substrates and Ignitable Liquid Spiked Burnt Substrates.

The passive headspace adsorption process outlined in the optimisation stage (section 3.3.1.and section 3.3.5) was followed for the recovery of the volatile components derived from the heated substrate samples with and without the ignitable liquid spike.

## 3.5 Results and Discussions

### 3.5.1 Ignitable Liquid Reference Collection

In total, 245 samples of ignitable liquids from the LPD, MPD, HPD and petrol classes were collected or prepared. Examples of the total ion chromatograms (TICs) of fresh and evaporated samples are included in the following sections. These data were used in the application of the various multivariate chemometric methods discussed in later chapters.

### 3.5.2 Chromatographic Patterns of Fresh and Evaporated Petrol Samples

In order to capture the full range of compounds contained within the petrol samples under study, the samples were analysed without solvent delay on the GC-MS. The resultant total ion chromatograms of each of the petrol brand analysed are presented in figure 3.10. Initial observations suggest minimal, if any, differences across the chromatographic pattern. No obvious differences were observed between leaded and unleaded petrol or between premium and regular unleaded petrol. The TIC pattern of diagnostic compounds for petrol which include the C2 alkylbenzenes (retention times 7.00 - 8.00 minutes), C3 alkylbenzenes (retention times 8.50 - 9.50 minutes) and C4 alkylbenzenes group (retention times 9.50 -11.00 minutes) are consistent across all samples.

The effect of evaporation of petrol can be observed in figure 3.11. In general, lighter boiling point hydrocarbon compounds are more volatile and thus evaporate at a faster rate. As the evaporation process progresses, these compounds diminish in relative concentration while the higher boiling point hydrocarbon compounds are present with increased relative abundance. It was observed in each case, that the chromatographic pattern presented a significant change once the petrol had experienced evaporation at

75% or more, with the loss of the majority of compounds with retention time less than that of toluene (retention time ~4.4 minutes).

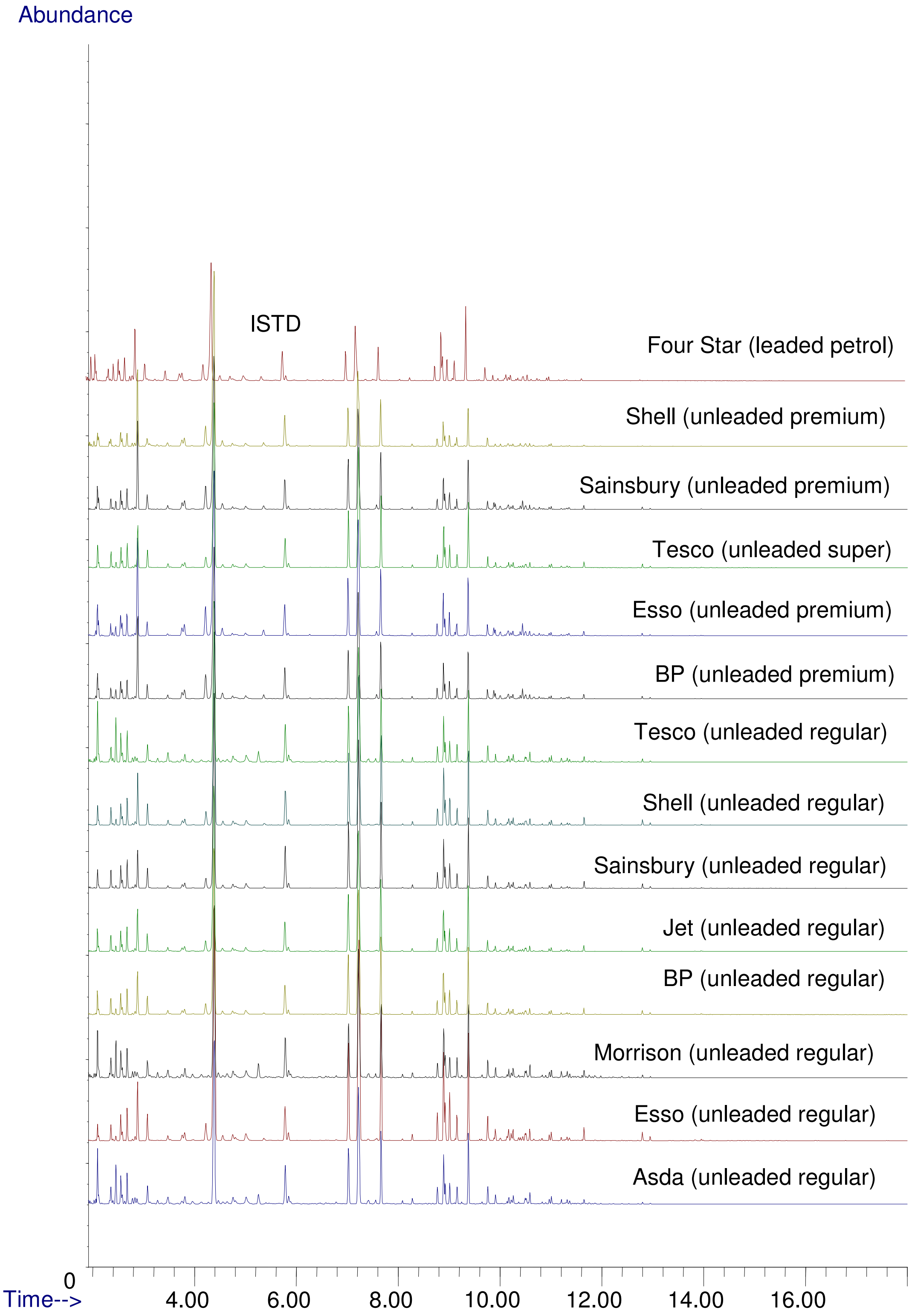


**Figure 3.10 TICs of unevaporated petrol from regular unleaded petrol, premium unleaded petrol and leaded petrol. Coding of the samples corresponds to the brands and type in table 3.3.**

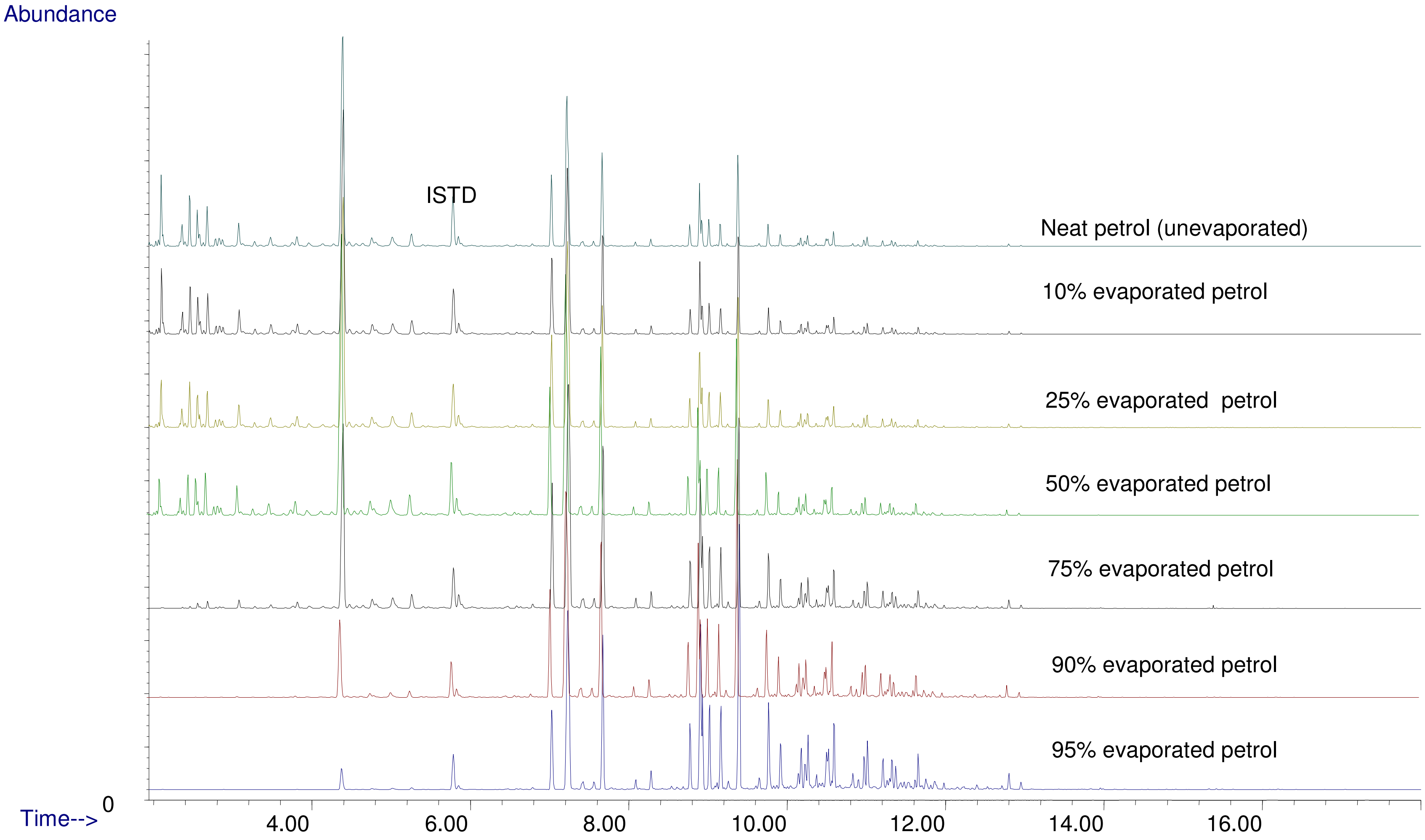


**Figure 3.11 An example of unevaporated to highly evaporated chromatographic pattern of petrol sample (BP unleaded premium grade). TICs of other samples are included in appendix section.**

### 3.5.3 Chromatographic Pattern of Fresh and Evaporated LPD Samples

The chromatographic patterns derived from the five lighter fuels are presented in figure 3.12. Initial examination revealed compositional differences for Swan, Dunhill and Zippo samples, however Perma and Ronsonol displayed very similar chromatographic patterns to each other.

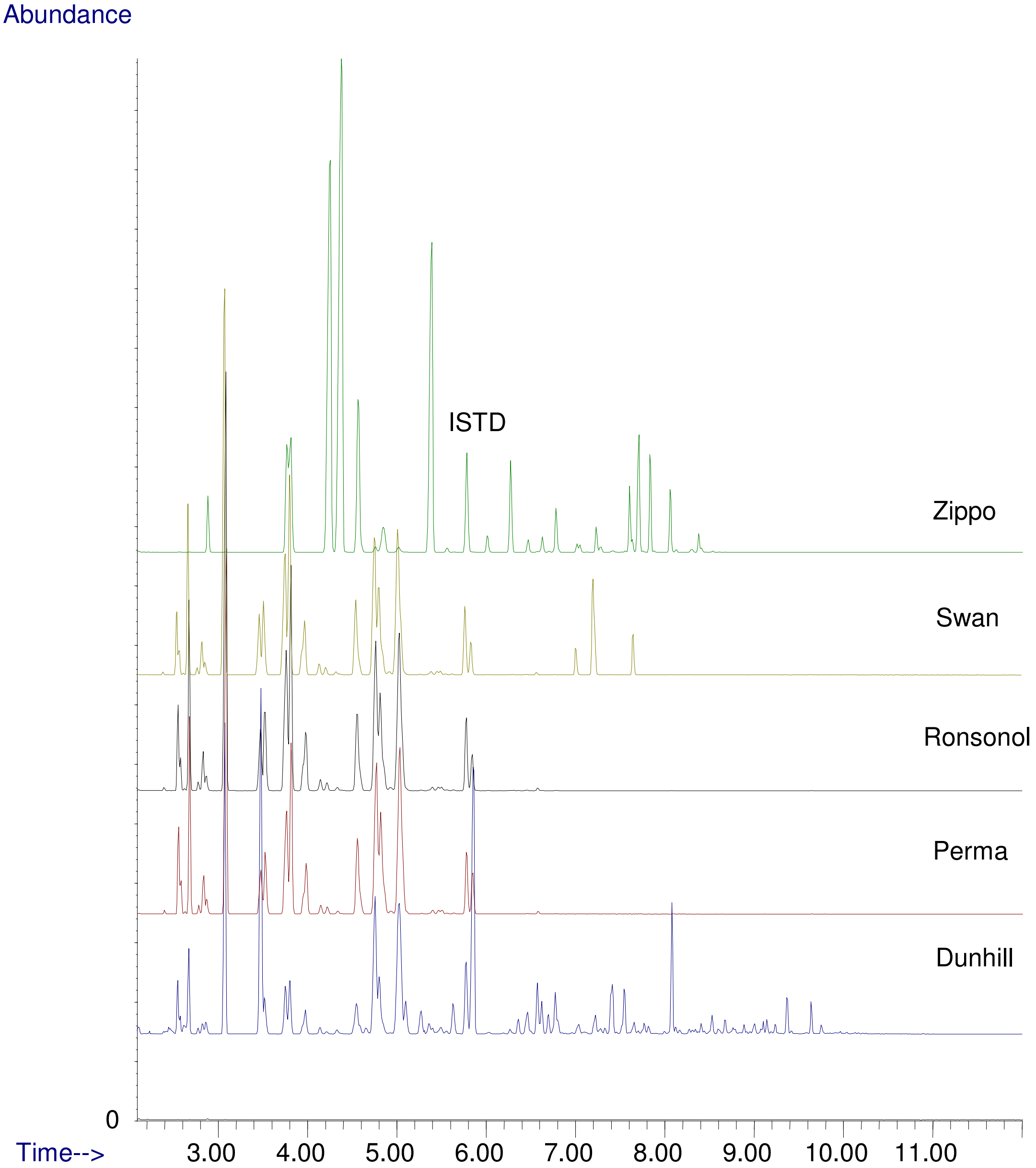


**Figure 3.12 TICs of unevaporated LPD (lighter fluid) samples from 5 different brands.**

An exemplar of the chromatogram from unevaporated lighter fluid to the most highly evaporated is presented in figure 3.13 and while these do not show a major shift in term of chromatographic pattern as peak compounds from unevaporated and evaporated samples were consistent throughout, they clearly demonstrate substantial changes in peak abundance especially the lower and higher boiling compounds at both ends. This is common in narrow boiling point light petroleum distillate products such as lighter fluids which contain $C_4$ to $C_9$ alkanes when compared to petrol ($C_4$-$C_{12}$) or other classes of petroleum distillate products [22, 31].

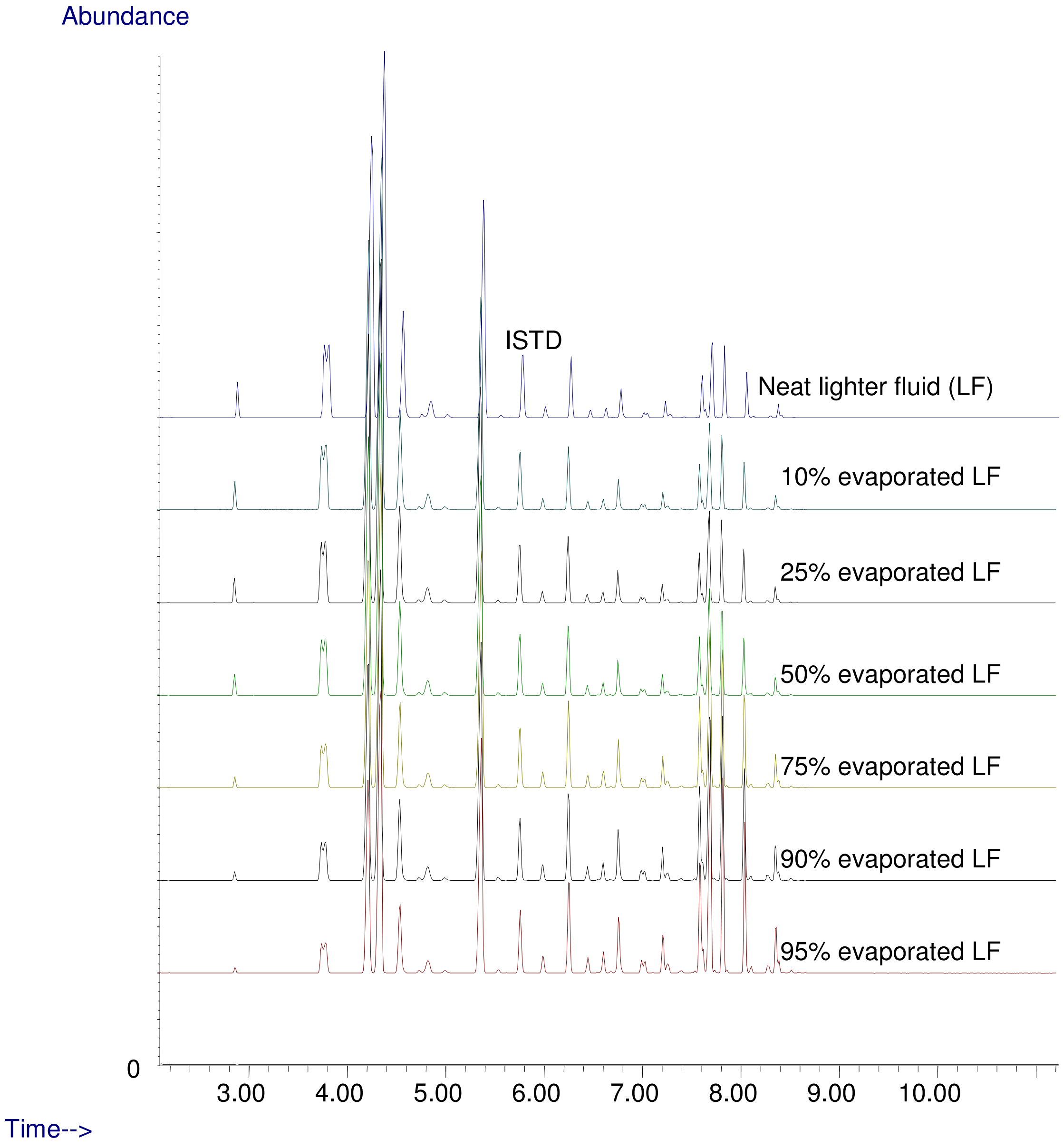


**Figure 3.13 An example of unevaporated to highly evaporated chromatographic pattern of LPD sample (Zippo lighter fluid).**

### 3.5.4 Chromatographic Pattern of Unevaporated and Evaporated MPD Samples

The chromatographic profiles for white spirit, paint brush cleaner and lamp oil as representatives of the medium petroleum distillate classification are presented in figure 3.14.

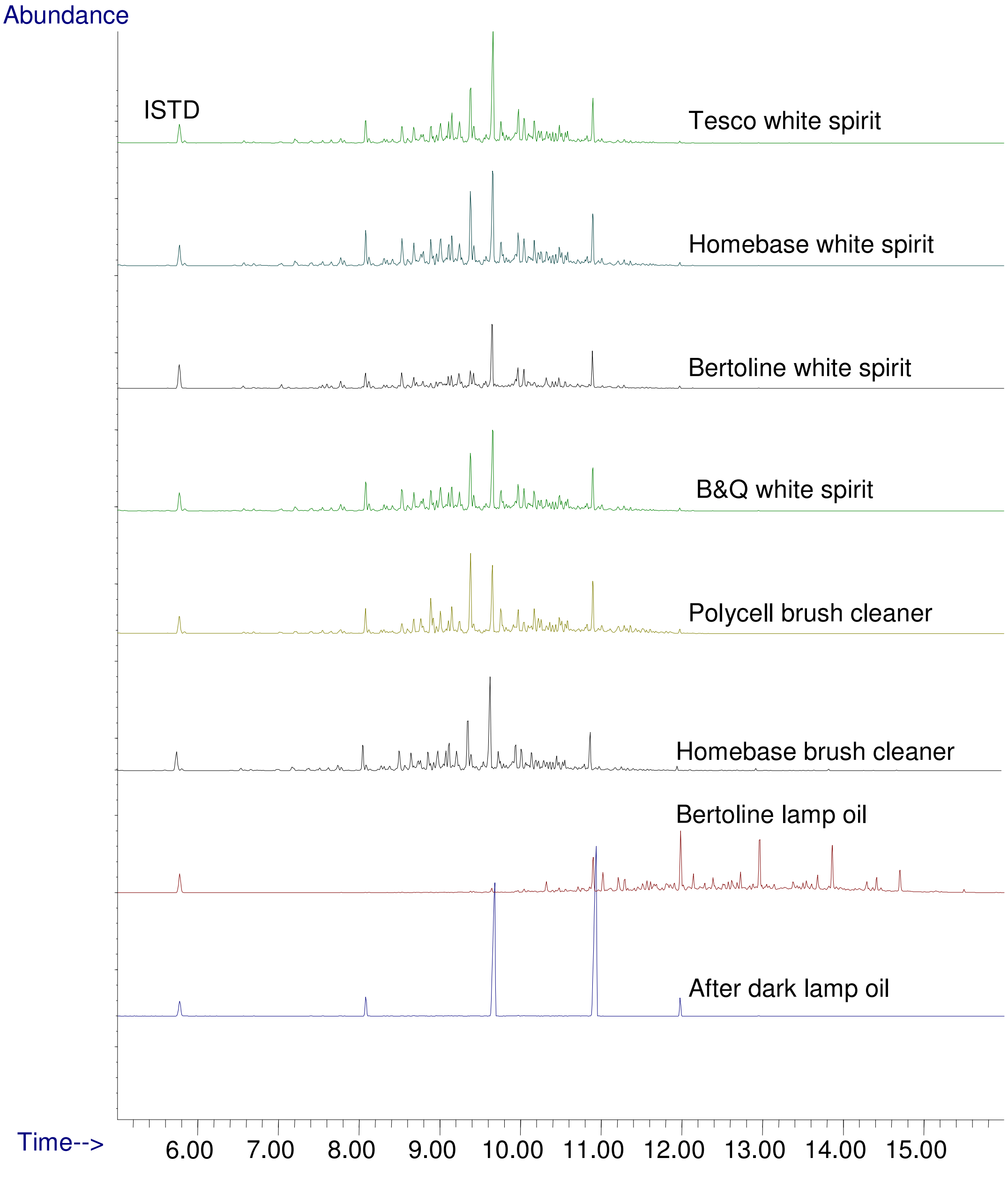


**Figure 3.14 TICs of unevaporated MPD samples from 3 types of MPD (white spirit, paint brush cleaner and lamp oil) from various brands.**

The aliphatic peaks, mainly normal alkanes, can be observed as a Gaussian distribution pattern. Apart from ADLO and BLO samples, both of which were lamp oils, similar chromatographic profiles are evident between paint brush cleaner and white spirit. The total ion chromatogram patterns also demonstrate a high degree of similarity among samples within the sub-class. According to peak identification based on mass spectrum profiles (shown in section 4.8.3), Bertoline lamp oil range between C8-C14 thus can be described as a medium to heavy petroleum distillate product. Nonetheles, within the United Kingdom, lamp oils were widely regarded as members of the MPD class even though their chromatographic patterns are very different. The effect of evaporation of MPD is illustrated in figure 3.15. The gradual change in chromatographic pattern is similar to other petroleum distillate products such that when the evaporation progresses, lower boiling compounds diminish, while higher boiling point compounds begin to predominate with a higher relative abundance.

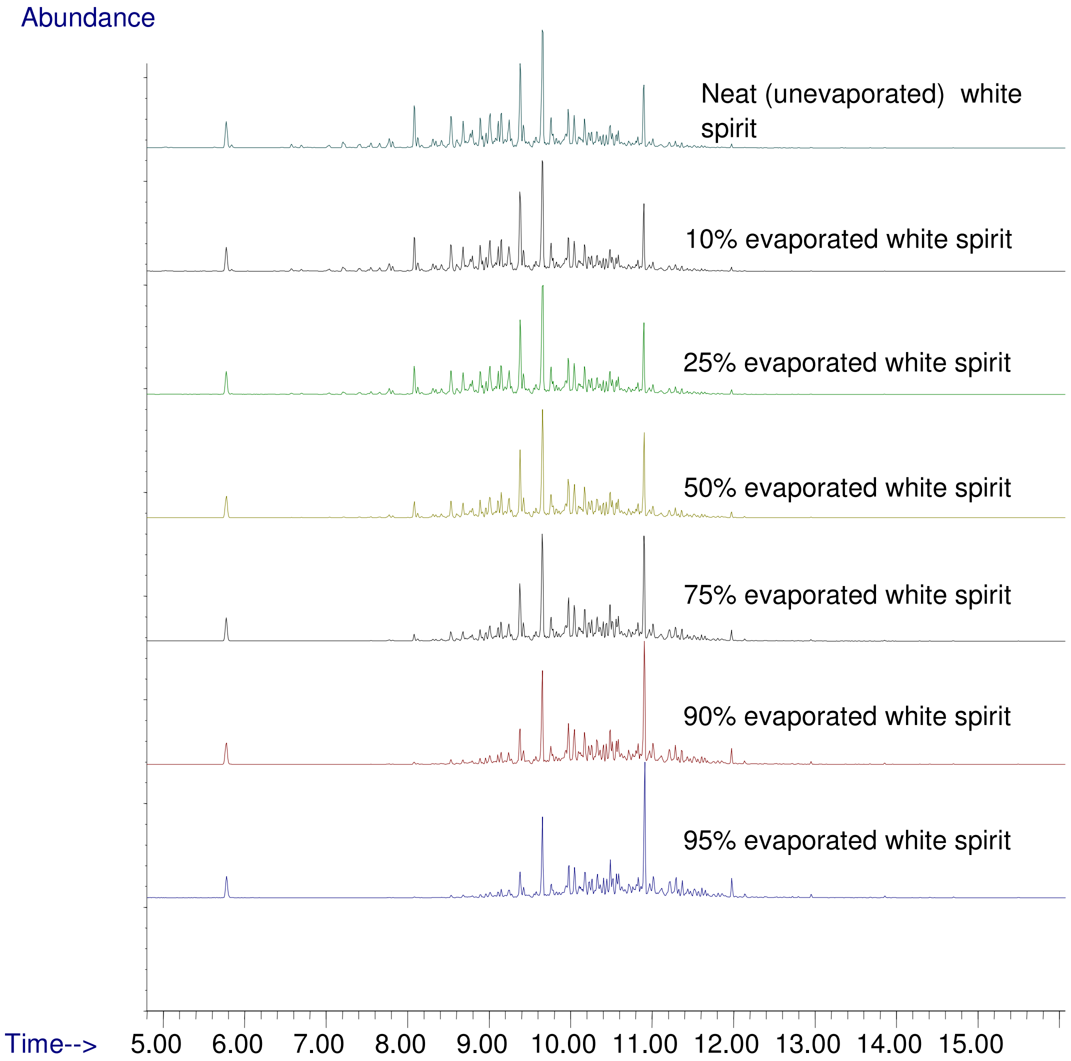


**Figure 3.15 An example of unevaporated to highly evaporated chromatographic pattern of MPD sample (B&Q white spirit).**

### 3.5.5 Chromatographic Pattern of Unevaporated and Evaporated HPD Samples

Diesel is the dominant member of the heavy petroleum distillate class of ignitable liquids. The total ion chromatograms of all unevaporated diesel samples from the various brands under study are presented in figure 3.16 and display very similar chromatographic patterns.

In comparison to medium petroleum distillates, diesel encompasses a broader hydrocarbon compound range normally from $C_8$-$C_{20}$ and contains predominantly alkanes, aromatic compounds and naphthalenes.

The presence of aliphatic peaks, mainly the normal alkanes appear as high abundance peaks in a very obvious Gaussian distribution which dominates the chromatogram of this ignitable liquid. A diagnostic feature of diesel fuel derived from the petroleum industry is the presence of pristine ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$), the consecutive peaks that emerge after the long chain alkanes $C_{17}$ and $C_{18}$ respectively. Molecular structure of these compounds is referred to table 1.5(in chapter1).

Differences in the peak abundances are noticeable most probably due to natural variants of crude oil, chemical and reformulation product processing, blending and storage [9, 32]. Evaporated diesel patterns are presented in figure 3.17 and display similar trends to those observed in previous samples.

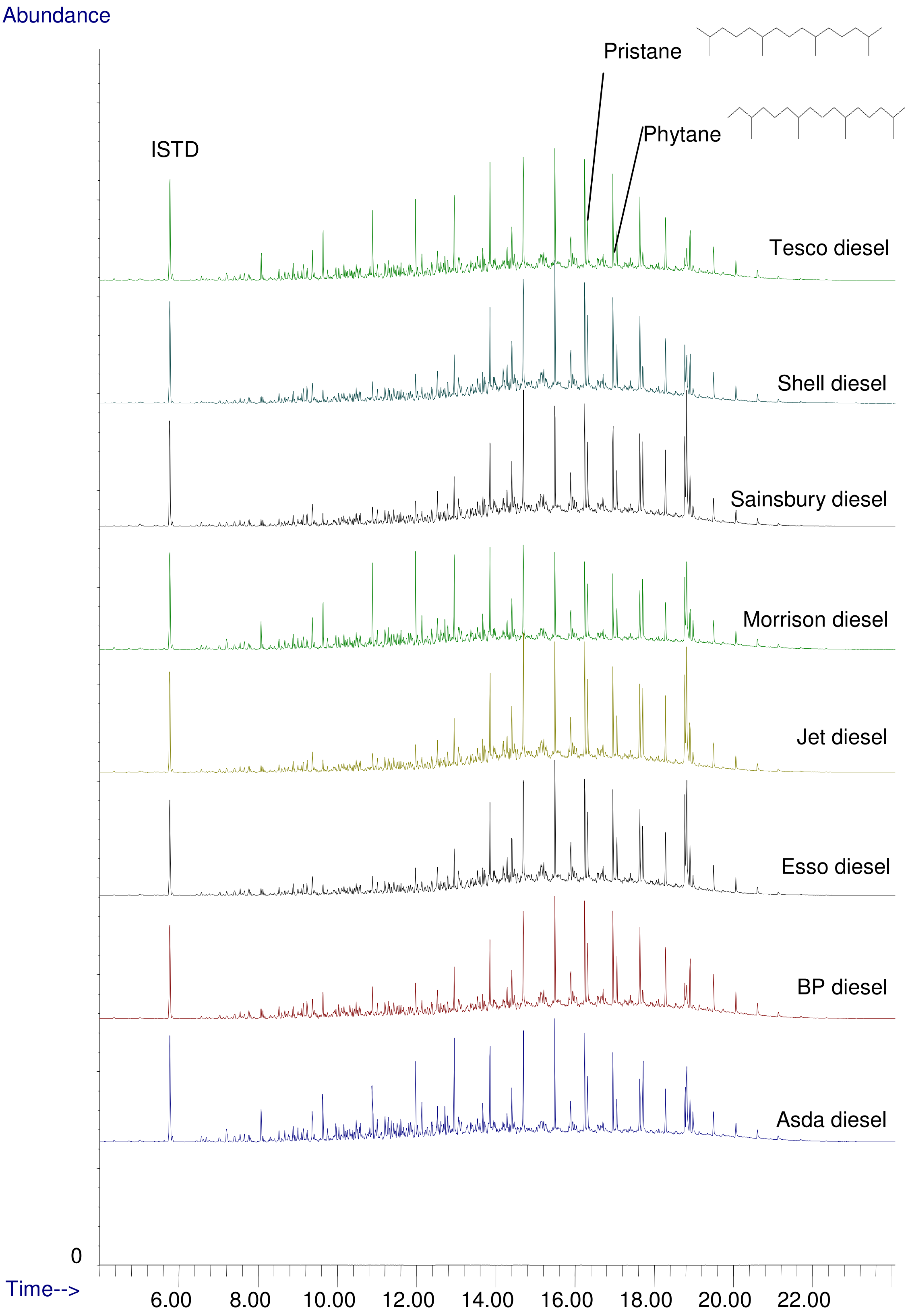


**Figure 3.16 Representative TICs of some of unevaporated HPD samples (i.e. diesel) from different brands.**

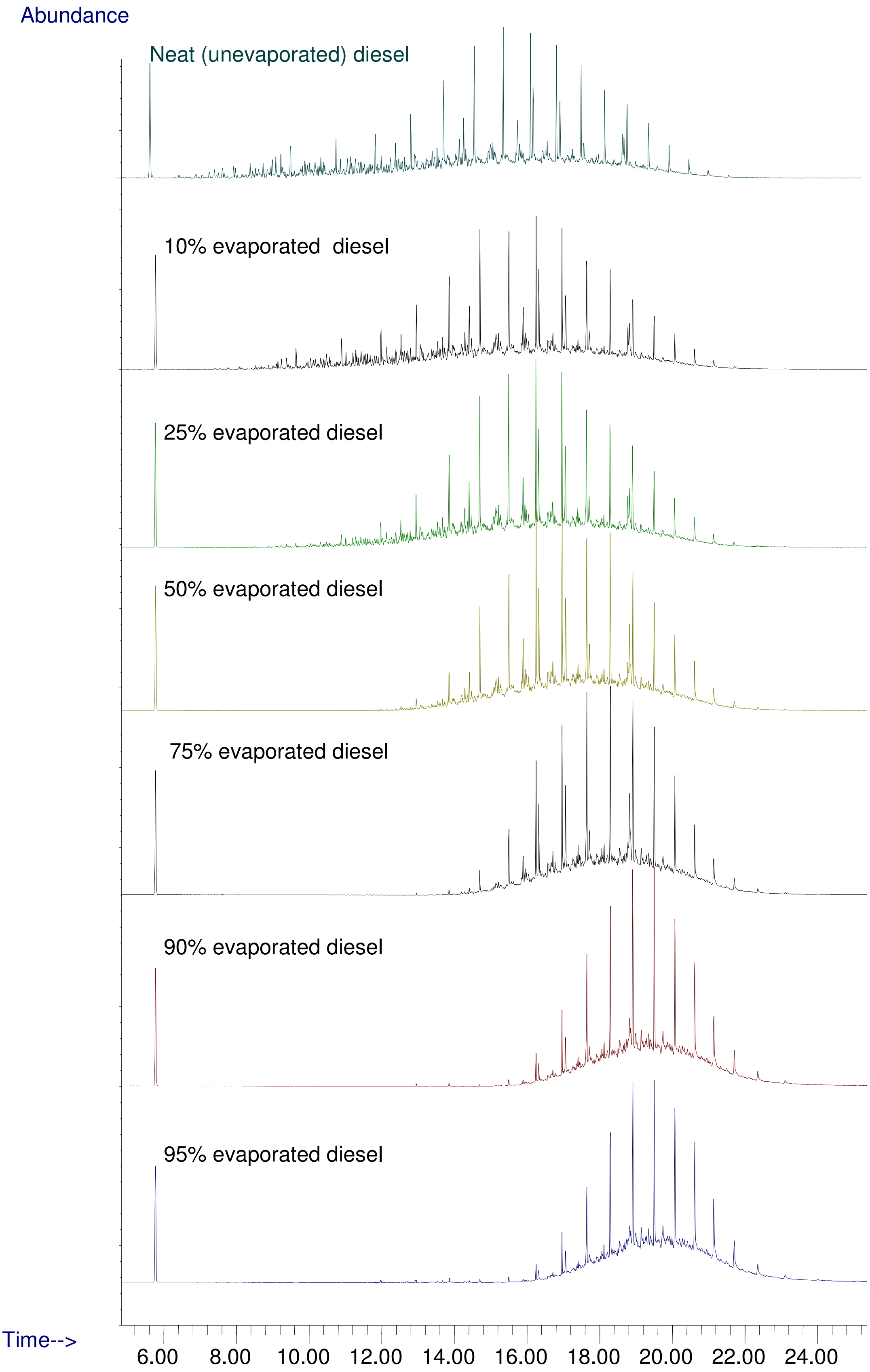


**Figure 3.17 An example of unevaporated to highly evaporated chromatographic pattern of diesel sample (Tesco diesel).**

### 3.5.6 Reproducibility of the Ignitable Liquid Evaporation Technique

Determining the reproducibility of the evaporated liquid sample preparation technique was critical in order to have confidence that any observed differences between ignitable liquid sample brands were due to compositional differences rather than artefacts of sample preparation.

The reproducibility of the evaporation technique was evaluated using six separately extracted samples of 50% evaporated lighter fluid and 50% evaporated petrol. The reproducibility of peak areas of selected compounds within each chromatogram was obtained from the percentage relative standard deviation of data normalised to the internal standard and to the total peak area, both produced %RSD values which were better than those for the raw data as would be expected. The results are presented in figure 3.18 and table 3.12 for petrol and figure 3.19 and table 3.13 for lighter fluid.

Overall, the percentage RSD for six samples of 50% evaporated petrol was between 3.09% - 6.96% (normalised to the internal standard) and 2.33% – 6.85% (normalised to the total peak area). In comparison, the % RSD values for the 50% evaporated lighter fluids were 3.73%-5.24% (normalised to the internal standard) and 2.81%-5.90% (normalised to the total peak area).

The results obtained from the data normalised to total peak area in both cases demonstrated marginally better reproducibility to those standardised to the internal standard. This has demonstrated excellent reproducibility of both evaporation methods employed in the sample preparation throughout the study.

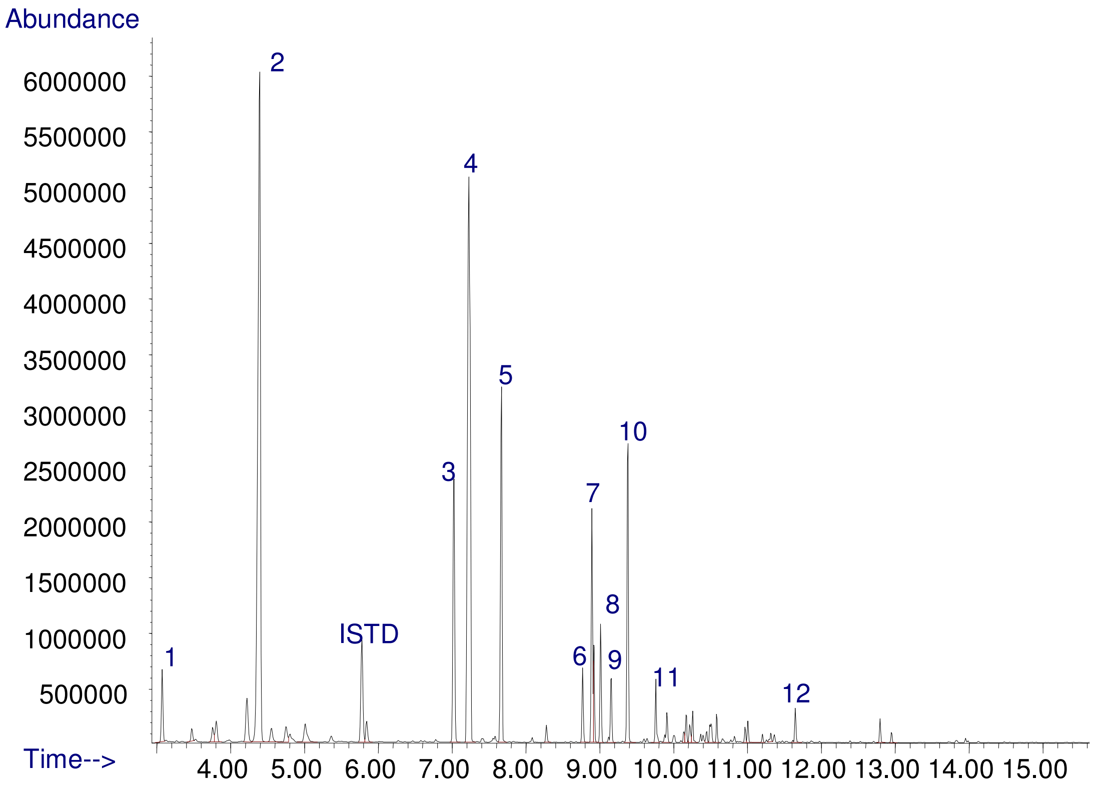


**Figure 3.18 TIC of 50% evaporated petrol sample (BP unleadedregular).**

**Table 3.12 reproducibility of compounds in 50% evaporated BP unleadedregular petrol. (ISTD= internal standard and TPA=total peak area).**

| **Peak no** | **RT** | **Compound** | **%RSD** | | |
|---|---|---|---|---|---|
| | | | **A (raw)** | **B (to ISTD)** | **C (to TPA)** |
| 1 | 2.85 | Isooctane | 4.83 | 3.23 | 2.36 |
| 2 | 4.40 | Toluene | 4.75 | 4.07 | 2.91 |
| 3 | 7.03 | Ethylbenzene | 5.68 | 4.73 | 2.73 |
| 4 | 7.23 | m-Xylene, p-Xylene | 4.67 | 3.10 | 2.33 |
| 5 | 7.67 | o-Xylene | 6.41 | 4.53 | 3.94 |
| 6 | 8.77 | Propylbenzene | 7.80 | 6.52 | 4.52 |
| 7 | 8.90 | 3-Ethyltoluene | 8.63 | 6.97 | 6.85 |
| 8 | 9.01 | 1,3,5 TMB | 5.43 | 3.90 | 1.84 |
| 9 | 9.19 | 2-Ethyltoluene | 6.67 | 5.22 | 3.39 |
| 10 | 9.38 | 1,2,4 TMB | 7.12 | 5.16 | 4.12 |
| 11 | 9.76 | 1,2,3 TMB | 5.58 | 3.56 | 2.54 |
| 12 | 11.65 | Naphthalene | 6.25 | 4.56 | 3.30 |

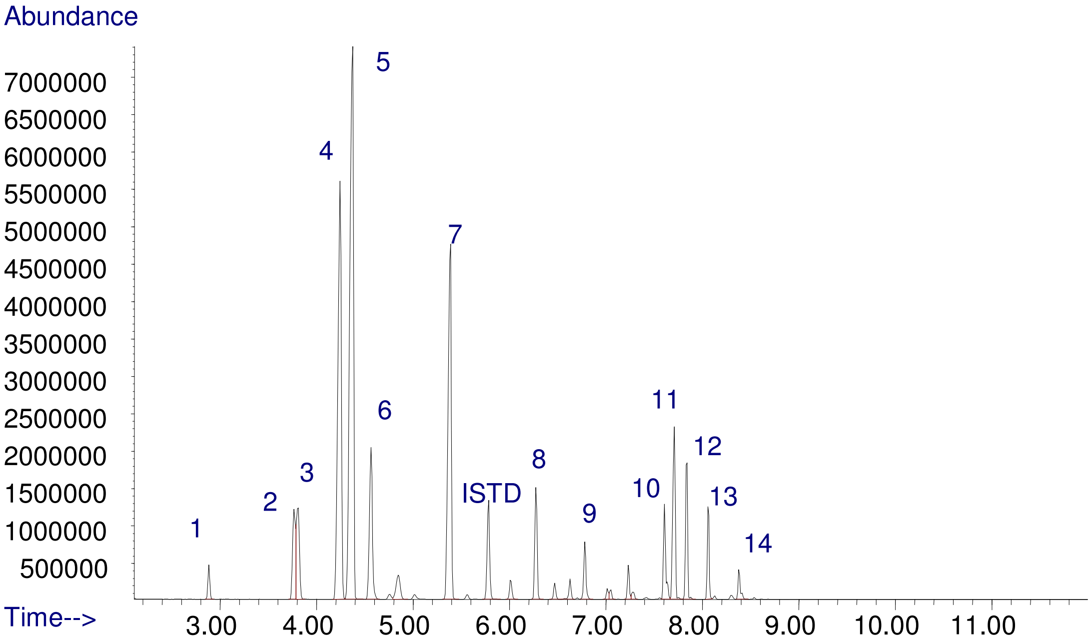


**Figure 3.19 TIC of 50% evaporated Zippo lighter fluid sample.**

**Table 3.13 Compounds reproducibility from 50% evaporated Zippo lighter fluid (ISTD= internal standard and TPA=total peak area).**

| Peak no | RT | Compound | %RSD | | |
|---|---|---|---|---|---|
| | | | A (raw) | B (to ISTD) | C (to TPA) |
| 1 | 2.89 | Tetramethylbutane | 6.50 | 4.42 | 3.70 |
| 2 | 3.81 | 2,5-Dimethylhexane | 8.52 | 5.24 | 4.51 |
| 3 | 3.92 | 2,4-Dimethylhexane | 5.24 | 3.73 | 4.04 |
| 4 | 4.25 | 2,3,4-Trimethylpentane | 5.41 | 4.10 | 2.81 |
| 5 | 4.38 | 2,3,3-Trimethylpentane | 5.07 | 4.01 | 3.36 |
| 6 | 4.57 | 2,3-Dimethylhexane | 5.59 | 4.37 | 3.43 |
| 7 | 5.39 | 2,2,4-Trimethylhexane | 6.10 | 4.21 | 5.90 |
| 8 | 6.29 | 2,3,5-Trimethylhexane | 6.90 | 4.50 | 3.06 |
| 9 | 6.79 | 2,5-Dimethylheptane | 7.02 | 4.36 | 3.83 |
| 10 | 7.62 | 2,3-Dimethylheptane | 6.42 | 4.97 | 3.52 |
| 11 | 7.74 | 2,2,4-Trimethylheptane | 6.18 | 4.51 | 3.45 |
| 12 | 7.84 | 2,2-Dimethyloctane | 7.44 | 4.35 | 3.48 |
| 13 | 8.06 | unknown | 6.67 | 4.42 | 4.88 |
| 14 | 8.38 | 3,3,5-Trimethylheptane | 7.15 | 4.44 | 3.94 |

### 3.5.7 Optimisation of Carbon Strip Size for Passive Headspace Extraction

The determination of the appropriate size of activated carbon strip used for passive headspace analysis requires a balance between good reproducibility and good sensitivity within the resultant chromatogram. Petrol was used as a test sample and various sizes of ACS investigated. Seven target compounds were identified within the petrol chromatogram and used for the comparison and are illustrated in figures 3.20. Variations in the peak area across replicate extractions for each ACS were determined after normalisation with the internal standard and the results are presented in table 3.14.

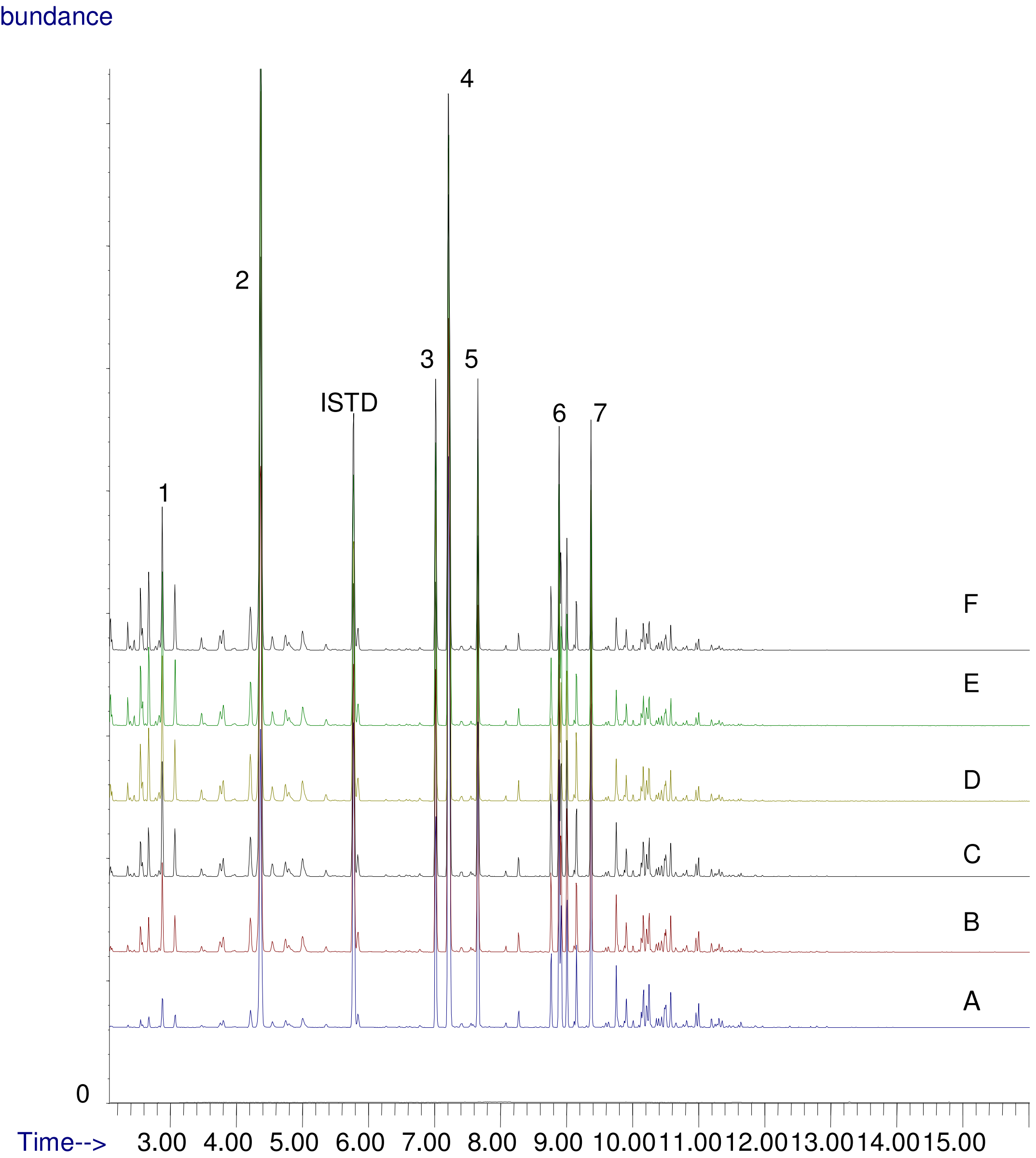


**Figure 3.20 An example of chromatogram section obtained from ACS passive headspace concentration of petrol sample (BP unleaded regular). Identification of targeted peaks is referred to table 3.7.**

**Table 3.14 Variations (%RSD) of hydrocarbon compounds extracted from ACS of different sizes.**

| No | Compound | Area of activated charcoal strip | | | | | |
|---|---|---|---|---|---|---|---|
| | | A ($50mm^2$) | B ($75mm^2$) | C ($100mm^2$) | D ($125mm^2$) | E ($140mm^2$) | F ($175mm^2$) |
| 1 | Isooctane | 0.47 | 0.76 | 0.67 | 0.33 | 0.19 | 0.41 |
| 2 | Toluene | 0.45 | 0.56 | 0.45 | 0.20 | 0.47 | 0.38 |
| 3 | Ethylbenzene | 0.18 | 0.53 | 0.14 | 0.32 | 0.34 | 0.21 |
| 4 | m-Xylene,<br>p-Xylene | 0.33 | 0.41 | 0.23 | 0.29 | 0.46 | 0.12 |
| 5 | o-Xylene | 0.34 | 0.38 | 0.16 | 0.38 | 0.63 | 0.51 |
| 6 | Ethyltoluene | 2.19 | 0.67 | 1.61 | 0.47 | 1.06 | 3.48 |
| 7 | 123 TMB | 0.09 | 0.11 | 0.34 | 0.55 | 1.68 | 0.36 |

The efficiency of the ACS adsorption in term of its size was evaluated (where incubation time and temperature were kept constant). From the results in table 3.14, all activated charcoal strips demonstrated good reproducibility of the target volatile compounds with low peak area variations. Nevertheless, despite their low % RSD values, ACS samples A and B demonstrated relatively low signal responses to the sample. The relevant literature suggest that smaller activated carbon strip became saturated relatively quickly and as such may encourage compound displacement [28-29]. Theoretically, in cases where the concentration of vapour exceeds the available adsorption sites on the carbon strip, compounds having a higher affinity (aromatics) will be more favourably adsorbed. Consequently, a disproportionate representation of volatile compounds within the actual sample can occur due to this displacement effect [29]. According to ASTM E1412, the minimum recommended activated charcoal strip size is 100 $mm^2$ [23].

The effect of the activated carbon strip size is illustrated in figure 3.21 where a plot of the ACS size against the normalised peak area for each of the target compounds reveals that ACS size D (5 mm x 25 mm) provided the best chromatographic result overall. In terms of practicality, ACS size C (5 mm x 20 mm) was a better fit for the GC-MS vial where sample desorption took place. As a consequence of these results, both ACS sizes D (5 mm x 25 mm) and C (5 mm x 20 mm) were further investigated.

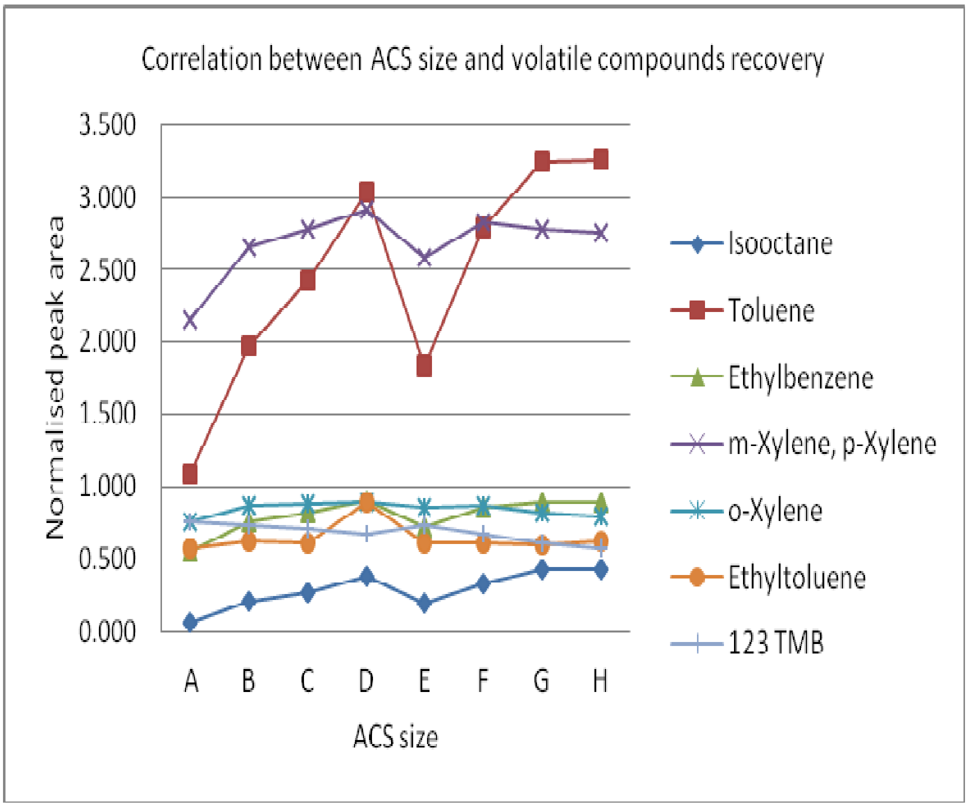


**Figure 3.21: Graph showing volatile compounds recovery (10µL petrol sample) by headspace passive extraction in closed container.**

### 3.5.8 Reproducibility of ACS Sample Recovery

Both activated charcoal strips C and D were further investigated using a mixture of 50% evaporated petrol and diesel (of the BP brand) at 1:1 ratio in order to ensure that the ACS extraction method provided a good chromatographic result for the wide range of hydrocarbons under test.

The total ion chromatograms for both ACS sizes are presented in figure 3.22. Qualitatively, both activated charcoal strips demonstrate the ability to produce similar patterns for all replicate samples clearly illustrating the recovery of both lighter and heavier hydrocarbon compounds.

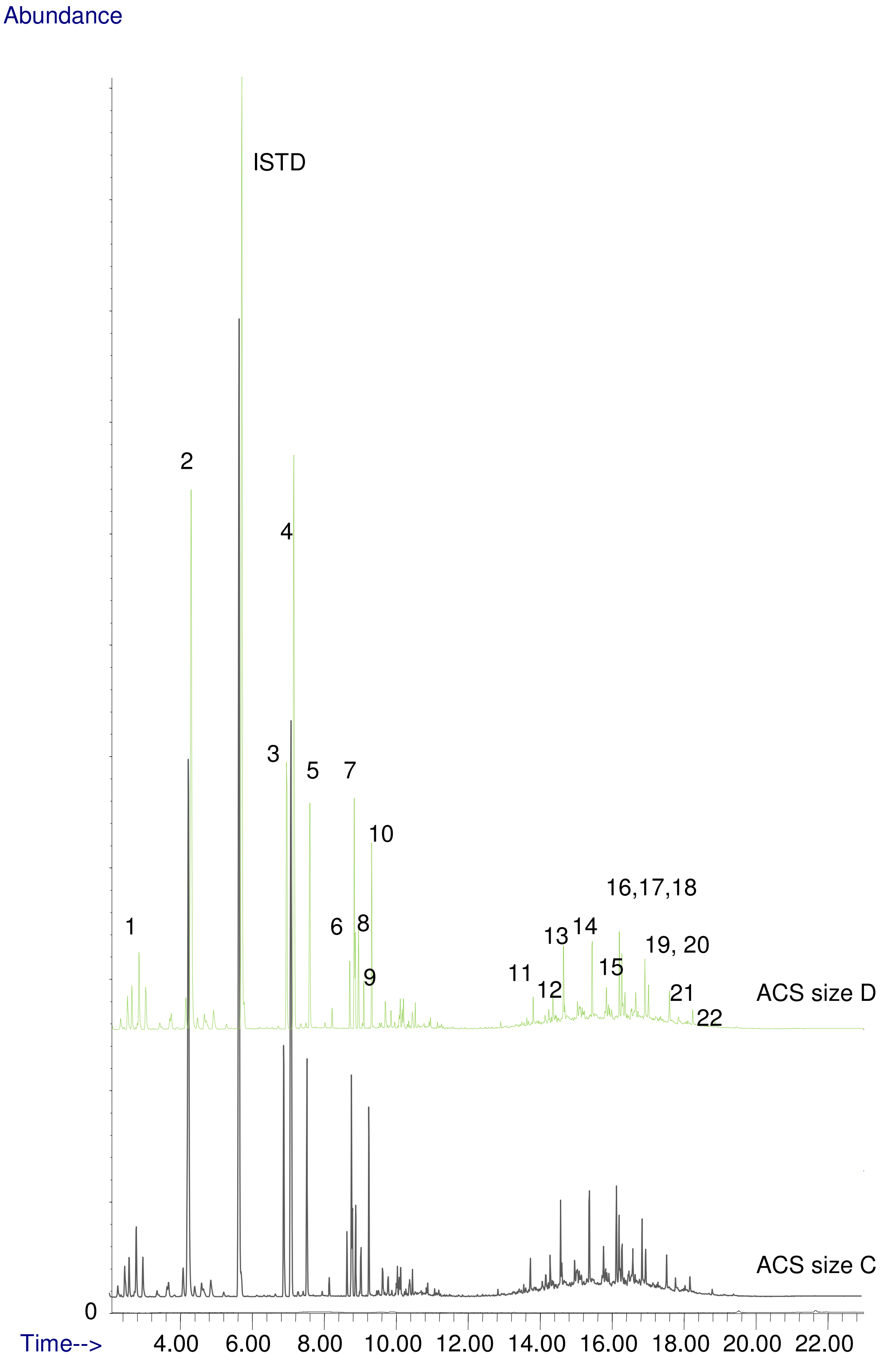


**Figure 3.22 TIC profile obtained from 50% evaporated petrol (BP unleaded regular) and 50% evaporated diesel (BP brand) at 1:1 ratio extracted using passive headspace with ACS C (5 mm x 20 mm) and ACS D (5 mm x 25)**

The % RSD of the prominent peaks (normalised to the internal standard) are presented in table 3.15. The results clearly indicate that overall, the recovery from ACS size C (5mm x 20mm) has slightly lower variation (5.10 - 34.72 % RSD) compared to that of ACS size D (5 mm x 25 mm) with 8.86 - 40.26 % RSD. The activated charcoal strip size C also had the advantage of fitting comfortably into the GC-MS vial used in the desorption phase and was thus chosen as the optimised ACS for all substrate recovery studies.

**Table 3.15 % RSD of vapour compounds from 50% petrol (BP unleaded regular) and 50% BP diesel (1:1 ratio).**

| Peak no. | Rt | Components | C Strips | D Strips |
|---|---|---|---|---|
| 1 | 2.844 | Isooctane | 7.92 | 11.35 |
| 2 | 4.289 | Toluene | 5.10 | 9.30 |
| 3 | 6.945 | Ethylbenzene | 5.40 | 8.86 |
| 4 | 7.14 | m-Xylene, p-Xylene | 5.93 | 9.76 |
| 5 | 7.588 | o-Xylene | 6.69 | 11.06 |
| 6 | 8.701 | Propylbenzene | 6.28 | 10.36 |
| 7 | 8.825 | 3-Ethyltoluene | 6.31 | 9.19 |
| 8 | 8.943 | 1,3,5 TMB | 6.27 | 11.09 |
| 9 | 9.08 | 2-Ethyltoluene | 5.73 | 12.22 |
| 10 | 9.31 | 1,2,4 TMB | 6.44 | 12.89 |
| 11 | 13.798 | Tetradecane C14 | 26.37 | 20.50 |
| 12 | 14.352 | Unknown | 25.08 | 28.83 |
| 13 | 14.642 | Pentadecane C15 | 26.49 | 26.15 |
| 14 | 15.438 | Hexadecane C16 | 25.84 | 28.67 |
| 15 | 15.836 | Unknown | 34.72 | 40.26 |
| 16 | 16.191 | Heptadecane C17 | 20.45 | 27.14 |
| 17 | 16.265 | Pristane | 19.73 | 26.48 |
| 18 | 16.347 | Unknown | 29.20 | 36.23 |
| 19 | 16.649 | Unknown | 33.79 | 35.89 |
| 20 | 16.905 | Octadecane C18 | 25.17 | 30.93 |
| 21 | 17.004 | Phytane | 21.07 | 29.45 |
| 22 | 17.586 | Nonadecane C19 | 28.70 | 32.69 |

### 3.5.9 Optimisation of the Volume of Ignitable Liquid Spiked onto the Substrate.

Five different volumes of ignitable liquid spike were investigated. The objective was to determine the volume of ignitable liquid which could be added to the polymer substrate such that the resultant chromatogram would display the features of both the ignitable liquid and the interfering products evolving from the substrate.

The effect of the spike drop size is illustrated in figure 3.23 using unleaded petrol (BP unleaded regular) on a carpet substrate. Visual observation of the chromatograms reveals that the interfering product signal is obscured when 30 μL of petrol spike was added.

In order to refine the spike volume further, four pyrolysis peaks within the chromatogram of the carpet substrate were selected and ratioed to six individual compounds present in the petrol sample. The selected peaks are illustrated in figure 3.24. The values of these selected ratios signify the magnitude of the peak abundance from the two sources and are illustrated in figure 3.25.

Figure 3.25 illustrates that a petrol spike volume of 20 μL or greater generally suppress the chromatographic pattern of the substrate while a spike volume of 5 or 10 μL facilitates a general predominance of the chromatographic pattern of the substrate. A petrol spike volume of 15 μL provides more balanced ignitable liquid and substrate peak abundances.

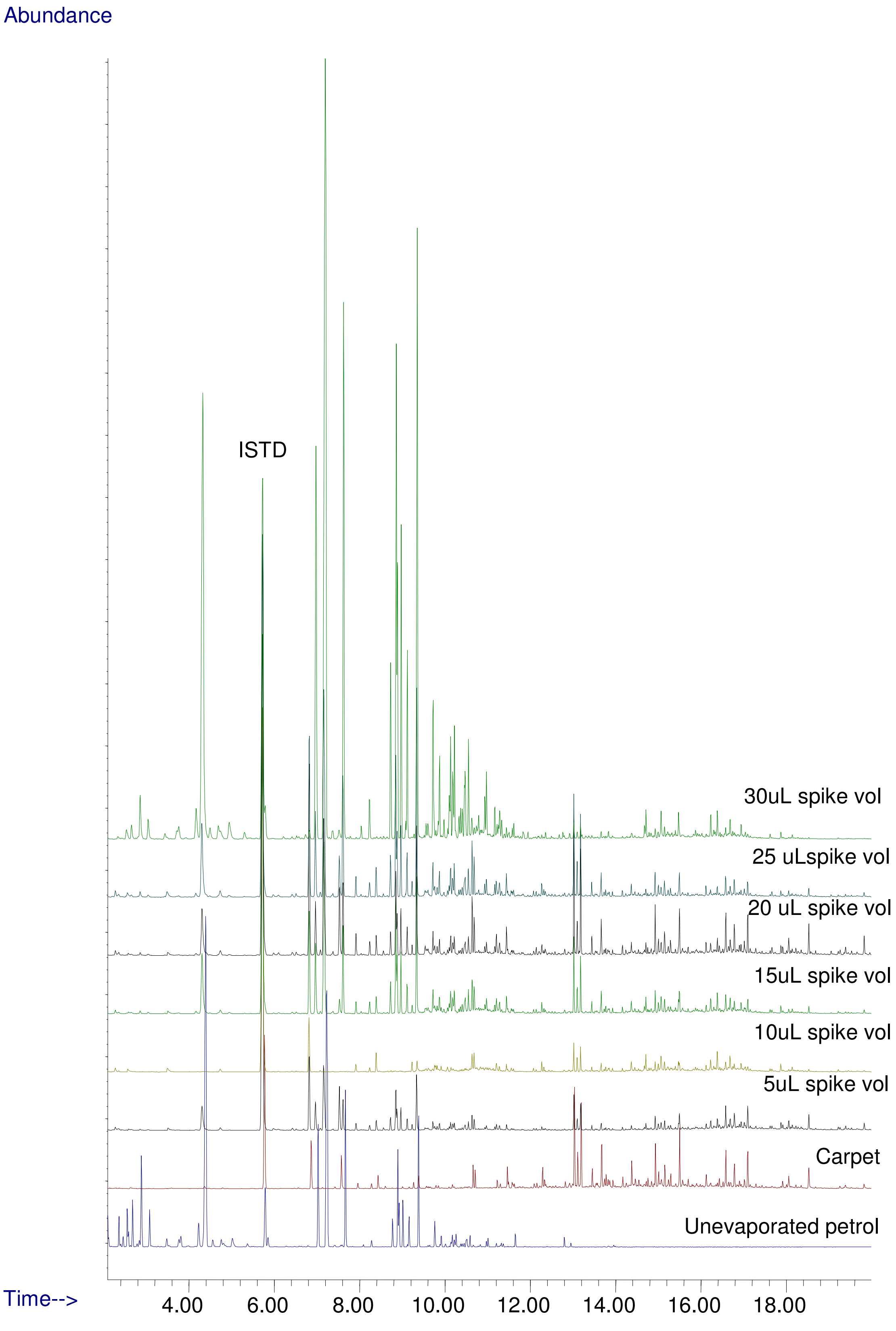


**Figure 3.23 A comparisons of TICs profiles obtained from ACS extracts of unevaporated petrol (BP unleaded regular), burnt carpet substrate and simulated fire debris samples (carpet and petrol) at 80°C for 16hrs.**

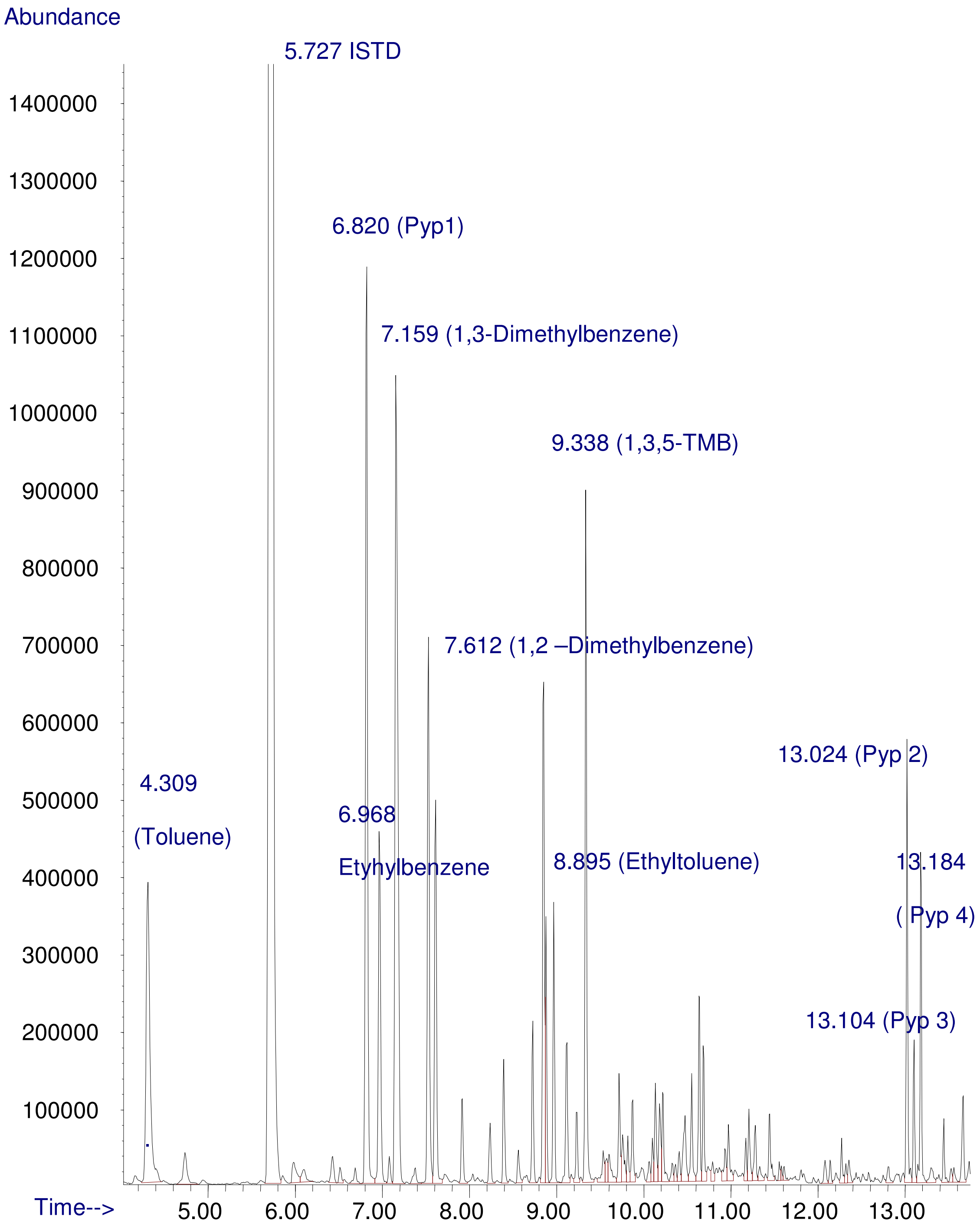


**Figure 3.24 Zoomed section to enhance detail in chromatographic profile from simulated fire debris sample (carpet burnt with petrol). Peaks Pyp 1-4 were chosen for ratio analysis.**

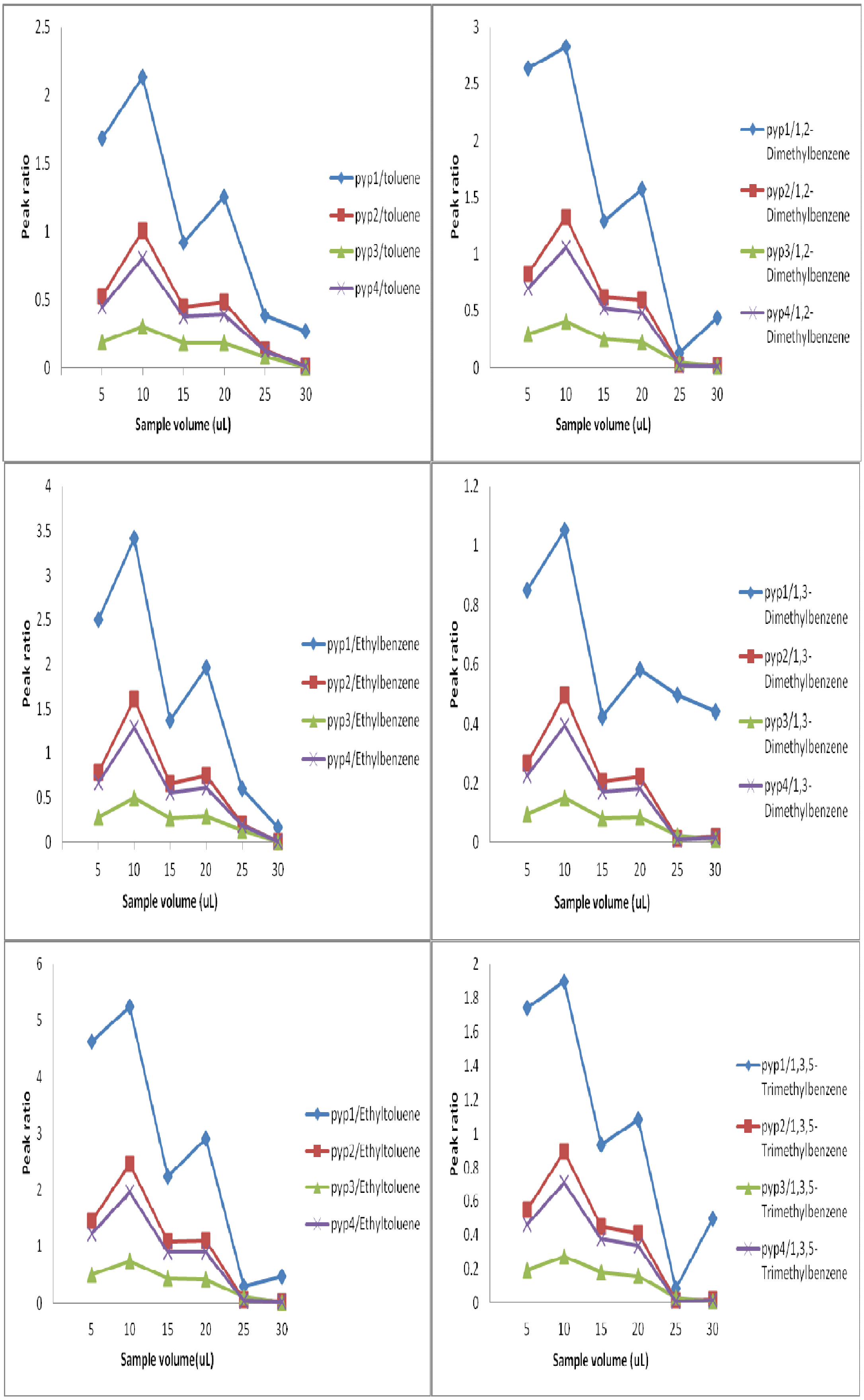


**Figure 3.25 Peak area ratio calculated from the simulated fire debris sample with various petrol drop sizes.**

### 3.5.10 Preparation of Burnt Substrate Samples and Burnt Substrate Samples Spiked with Ignitable Liquids

The temperature during the production of background pyrolysis products was maintained below 300°C following initial experiments which demonstrated that at higher temperatures, the materials were completely consumed and no chromatographic profile was obtained. Moldeveanu [14] reported that pyrolysis occurred at different levels with thermal degradation occurring at temperatures between 100°C and 300°C, mild pyrolysis occurring between 300°C and 500°C and vigorous pyrolysis occurring at 800°C and higher.

Stauffer also proposed a mechanism for differentiating pyrolysis products using GC-MS and pyrolysis gas chromatography, however he reported that the comparison of the chromatographic profiles of the interfering products (a mixture of background substrate, pyrolyis products and combustion products) were not feasible due to limitations of the sample preparation, inconsistent chromatographic patterns and chromatographic shifts between instruments [33].

No distinction has been made between the nature of the pyrolysis and combustion products produced in this study and as such the general term interfering products has been used to describe the pyrolysis/combustion products generated. Of the 45 samples of polymer products investigated, 11 produced identifiable chromatographic profiles and these are presented and discussed further in chapter 5. Chromatograms of the burnt substrate samples spiked with the appropriate ignitable liquid samples were also analysed and are discussed in detail in chapter 5.

### 3.5.11 Reproducibility of Interfering Products Sampling

A sample of high density polyethylene (HDPE) was used to investigate the reproducibility of the interfering product preparative method. In total, three samples were prepared and the sample preparation was refined in order to achieve a maximum temperature range (249.28 ºC - 267.52 ºC) which was kept as consistent as possible across the samples and is represented in figure 3.26.

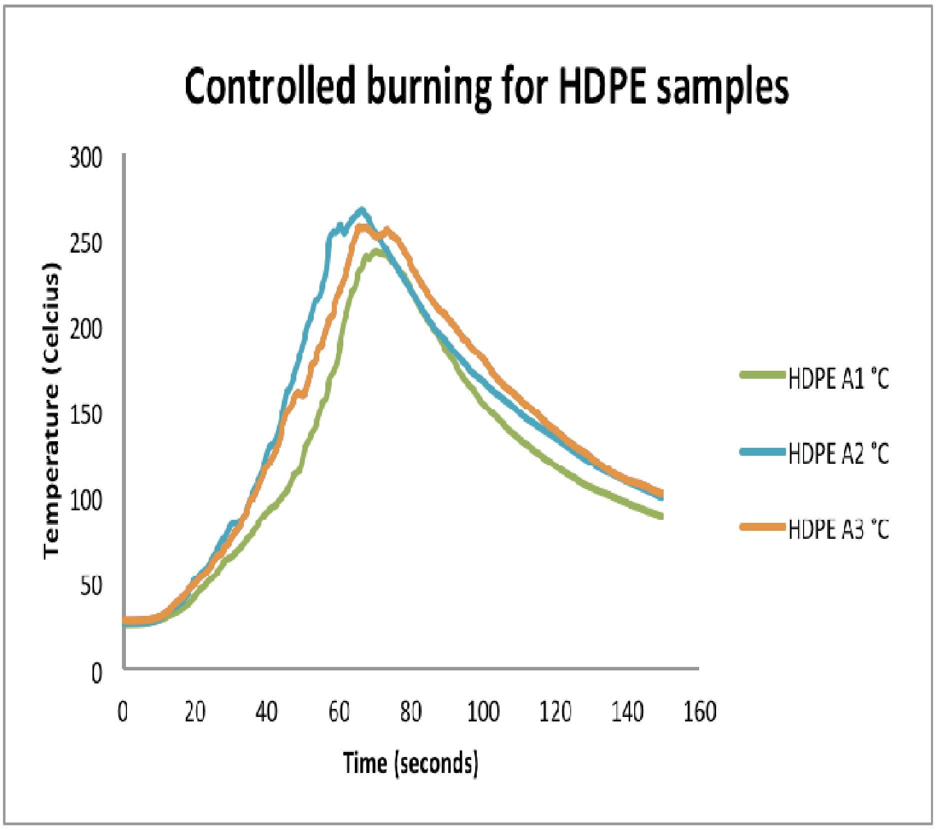


**Figure 3.26 Recorded temperatures during the burning of high density polyethylene (HDPE) showing the temperature range between replicates sample preparations.**

Notwithstanding this temperature variation, visual comparisons of the overall chromatographic patterns derived from the three samples demonstrated a consistency of interfering products recovered and is illustrated in figure 3.27.

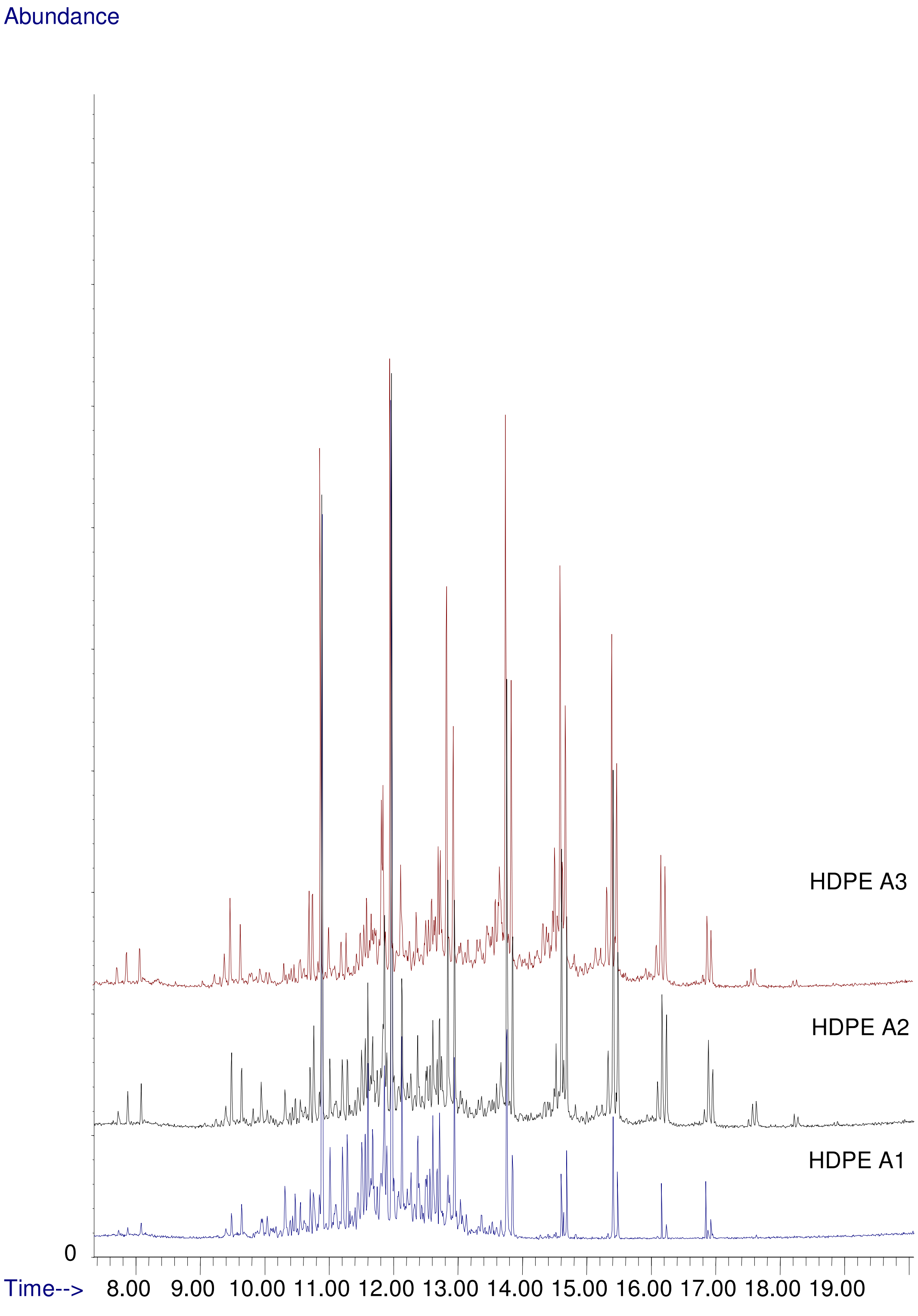


**Figure 3.27 TIC patterns of volatiles extracted using passive headspace concentration technique from HDPE polymer sample burnt with a maximum temperature in the range of 249.28°C - 267.52°C.**

Within the HDPE chromatogram, eleven compounds were identified from the chromatographic pattern and the peak area variations were determined. The peaks chosen are illustrated in figure 3.28. Reproducibility of the peak areas of the selected peaks are presented in table 3.16.

Temperature is not the only factor that influences the variability of interfering product production from burnt substrates and factors such as heat intensity, type of substrate, quantity of material, availability and type of oxidiser, method of extinguishment and air flow during the burning will also have influence [33-34].

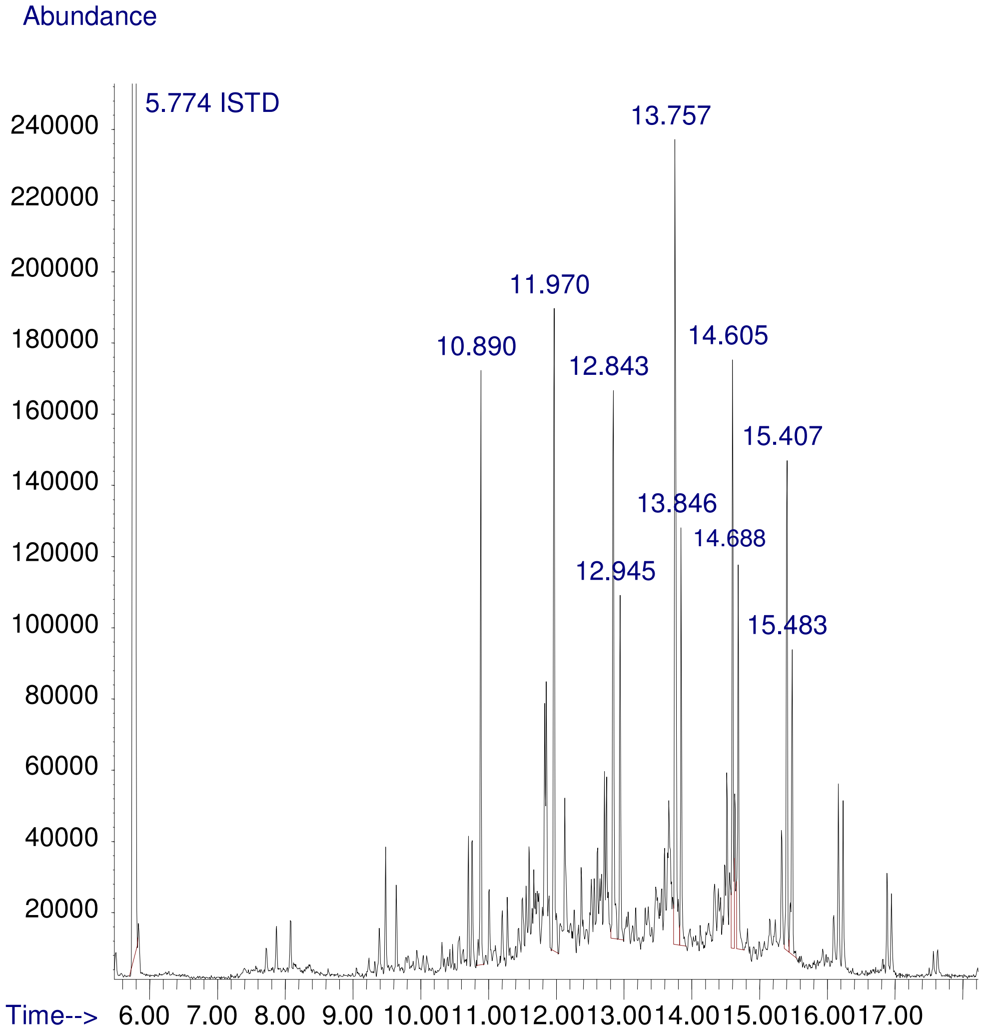


**Figure 3.28 Volatiles extracted using passive headspace concentration technique from a high density polyethylene (HDPE) polymer sample.**

**Table 3.16 calculated RSD values of prominent peaks from triplicate analysis of HDPE pyrolysis product.**

| Peak No. | RT | Compound | %RSD |
|---|---|---|---|
| 1 | 10.889 | Undecane $C_{11}$ | 26.51 |
| 2 | 11.852 | Dodecene | 23.39 |
| 3 | 11.97 | Dodecane $C_{12}$ | 29.89 |
| 4 | 12.843 | Tridecene | 24.59 |
| 5 | 12.945 | Tridecane $C_{13}$ | 29.92 |
| 6 | 13.753 | Tetradecene | 25.58 |
| 7 | 13.843 | Tetradecane $C_{14}$ | 11.76 |
| 8 | 14.603 | Pentadecene | 11.41 |
| 9 | 14.686 | Pentadecane $C_{15}$ | 35.64 |
| 10 | 15.404 | Hexadecene | 14.12 |
| 11 | 15.483 | Hexadecane $C_{16}$ | 18.44 |

Although many parameters were controlled during the process used to generate the interfering products, the results have demonstrated that the presence and abundance of the volatile compounds were not always constant. This is in agreement with previous work done by Stauffer who also discussed other influencing factors and the resultant poor chromatographic reproducibility for interfering product signals [33]. These results would mimic closely the variability from operational fire debris samples.

## 3.6 Conclusions

The process of establishing an ignitable liquid reference collection for unevaporated and evaporated samples is straight forward and was obtained with excellent reproducibility. For the evaporated samples, within and between sample variation was minimal facilitating, with confidence, direct brand to brand sample comparison across the range of unevaporated and evaporated samples.

The recovery method used for passive headspace analysis of burnt substrates and burnt substrates spiked with ignitable liquids using activated charcoal strips was optimised and validated in terms of reproducibility and sensitivity to the test matrix. Chromatographic profiles were also obtained for various substrates and the reproducibility of the interference patterns within sample replicates, in line with previous literature, was more problematic.

## 3.7 References

1. *Common Terms Used in Fire Investigation; available at http://advancedinvestigativesolutions.ca/glossary/ [accessed on 24/11/2011].*

2. *ASTM Designation: E 1618 – 06 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry*. 2006, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-11.

3. NicDaeid, N., *Fire Investigation*. 2004, Boca Raton: CRC Press.

4. *Fire and Arson Accelerants; available at www.interfire.org/res_file/aec_20ig.asp*. [accessed on 23/01/2012].

5. Tranthim-Fryer, D.J., *The application of a simple and inexpensive modified carbon wire adsorption/solvent extraction technique to the analysis of accelerants and volatile organic compounds in arson debris.* Journal of Forensic Sciences, 1990. **35**(2): p. 271-280.

6. Jackowski, J.P., *The incidence of ignitable liquid residues in fire debris as determined by a sensitive and comprehensive analytical scheme.* Journal of Forensic Sciences, 1997. **42**(5): p. 828-832.

7. *Hamilton County Coroner's Office Annual report (arson) 2006; available at http://www.hamilton-co.org/coroner/ARSON%202006.htm*. [accessed on 01/05/2010].

8. Lucas, A.G., *Modern Petroleum Technology, Downstream, 6th. Edition*. Vol. 2. 2000, Chichester: John Wiley & Sons Ltd.

9. Gary, J.H., E.Handwerk, G., and Kaiser, M.J., *Petroleum Refining Technology and Economics,5th Ed.* 2007, CRC Press: Boca Raton.

10. *Petroleum Refining Processes; available at http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html*. [accessed on 26/11/2011].

11. *Petroleum Refining; available at http://kids.britannica.com/comptons/art-53784/The-petroleum-refining-process-begins-in-the-distilling-column-with*. [accessed on 26/11/11].

12. *Petrol in Profile*, in *Shell Education Service*. 1996, Shell U.K. Limited, Caldwell Prince Limited: London.

13. *What a barrel of crude oil makes; available at http://www.txoga.org/categories/Resources/*. [accessed on 28/11/2011].

14. *Crude oil; available at* http://www.window.state.tx.us/specialrpt/energy/nonrenewable/crude.php. [accessed on 27/11/2011].

15. *The Petroleum Handbook : Shell* Sixth Edition, Research Department Shell Group of Companies, 1983, Elsevier: Amsterdam.

16. *The Motor Fuel (Composition and Content) Regulations No. 3107 PART III.* 1999, The National Archives: London.

17. Antos, G.J., and Aitani, A.M., *Catalytic Naphtha Reforming*. 2004,: Marcel Dekker Inc. New York

18. *Environmental Health Criteria 187 (White Spirit); available at* http://www.inchem.org/documents/ehc/ehc/ehc187.htm. [accessed on 28/05/2009].

19. Irwin, R.J., VanMouwerik, M., Steven, L., Seese, M.D., and Bashamn, W., *Environmental Contaminants Encyclopedia* 1997, National Park Service,Water Resources Division: Colorado.

20. Marcus, A., *Diesel Fuel Basics, What is diesel fuel and where does it comes from?* 1999, Passage Maker Magazines, Inc.,Annappolis

21. *Fractional Distillation of Binary Mixture; available at* http://www.pharmainfo.net/reviews/fractional-distillation-binary-solvent-mixture. [accessed on 21/03/2009].

22. Newman, R., Gilbert, M., and Lothridge, K., *GC-MS Guide to Ignitable Liquids*. 1998, CRC Press: Boca Raton.

23. *ASTM Designation E 1412 – 07 Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration With Activated Charcoal.* 2007, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-3.

24. Dietz, W.R., *Improved charcoal packaging for accelerant recovery by passive diffusion.* Journal of Forensic Sciences, 1991. **36**(1): p. 111-121.

25. Demers-Kohls, J.F., Ouderkirk, S.L., Buckle, J.L., Norman, W.E., Cartwright, N.S., and Dagenais, C., *Evaluation of the DFLEX device for fire debris analysis.* Canadian Society of Forensic Sciences Journal, 1994. **27**(3).

26. Bertsch, W., and Zhang, Q.W., *Sample preparation for the chemical analysis of debris in suspect arson cases.* Analytica Chimica Acta, 1990. **236**: p. 183-195.

27. Borusiewicz, R., Zadora, G., and Zie˛ba-Palus, J., *Application of head-space analysis with passive adsorption for forensic purposes in the automated thermal desorption gas chromatography-mass spectrometry system.* Journal Chromatographia (Supplement) 2004. **60**(S1): p. S133-S142.

28. Newman, R.T., Dietz, W.R., and Lothridge, K., *The use of activated charcoal strips for fire debris extractions by passive diffusion. Part 1: The effects of time,temperature, strip size, and sample concentration.* Journal of Forensic Sciences, 1996. **41**(3): p. 361-370.

29. Williams, M., Fernandes, D., Bridge, C., Dorrien, D., Elliott, S., and Sigman, M., *Adsorption saturation and chromatographic distortion effects on passive headspace sampling with activated charcoal in fire debris analysis.* Journal of Forensic Sciences, 2005. **50**(2).

30. Lentini, J.J., and Armstrong, A.T., *Comparison of the eluting efficiency of carbon disulfide with diethyl ether: The case for laboratory safety.* Journal of Forensic Sciences, 1997. **42**(2): p. 307-311.

31. Newman, R., *Modern Laboratory Techniques Involved in the Analysis of Fire Debris Samples*. Fire Investigation, ed. N.N. Daeid. 2004, Boca Raton: CRC Press.

32. Sandercock, P.M.L., and Pasquier, E.D., *Chemical fingerprinting of gasoline 2. Comparison of unevaporated and evaporated automotive gasoline samples.* Forensic Science International, 2004. **140**(1): p. 43-59.

33. Stauffer, E., *Identification and characterization of interfering products in fire debris analysis*, Thesis, *Chemistry Department*. 2001, Florida International University: Florida. p. 268

34. Drysdale, D., *An Introduction to Fire Dynamics*. 1998, Chicester: John Wiley and Sons Ltd.

# CHAPTER 4: MATHEMATICAL ANALYSIS OF CHROMATOGRAPHIC DATA DERIVED FROM UNEVAPORATED AND EVAPORATED IGNITABLE LIQUIDS

This chapter focuses on the assessment of various multivariate analytical and artificial neural network methods to provide an objective measure of the subjective pattern recognition techniques predominantly used in the comparison of chromatographic data derived from ignitable liquid residues. Chromatographic data derived from various brands of unevaporated and sequentially evaporated petroleum distillate samples were subjected to multivariate analytical techniques using unsupervised methods (principal component analysis and hierarchical cluster analysis) and a self organising feature mapping (SOFM) artificial neural network analytical method.

This work also examined various data pre-processing mechanisms to ascertain which of these facilitated the best overall discrimination across the range of samples within a given classification of ignitable liquid expected in the evaluation of such samples. The possibility of linking samples that have undergone compositional change (through evaporation) back to their unevaporated source was also examined. The use of an artificial neural network system also facilitated the assessment of the predictive rather than simple clustering or grouping abilities of this method.

## 4.1 Introduction

Analysis of ignitable liquids and fire debris, and the subjective comparison of the derived chromatographic patterns with those from a series of ignitable liquid standards is an established technique in the field [1-3]. Subjective comparison of data and the challenges pertaining to it has been discussed in the literature [4-12] and the consensus that such methods can be difficult, time consuming, highly subjective and rely heavily on the skill and experience of the analyst have been highlighted. More recently, multivariate analytical methods have been suggested to objectively compare, classify or discriminate ignitable liquid and ignitable liquid residue samples [4, 13-25].

The distribution of ignitable liquids, such as petrol or diesel, involves major refiners such as British Petroleum (BP), Esso and Shell sending their products directly to branded service stations or distributors [26-28]. For economic reasons, “sharing agreements” also facilitate refineries supplying petrol or diesel to other service stations outside of their own brand. As a consequence, the true origin of a sample may not be known without the relevant distribution information being available. This is particularly the case for ignitable liquids (petrol and diesel) distributed at supermarket filling stations. Furthermore, compositional changes can also occur with the addition of detergents, fuel performance enhancers and other additives either at the refinery or during the distribution network. The composition of the ignitable liquid may also alter as the sample resides within the storage tanks of the filling station. Individualisation of petrol and diesel samples is therefore very challenging due to their ‘dynamic’ nature and the complexity of the matrices involved.

## 4.2 Multivariate Analysis for Pattern Recognition

To date, Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA), the two most common unsupervised multivariate techniques, have been used in the interpretation of various datasets of forensic interest including those derived from the analysis of drug profiles, paint analysis, ink analysis and ignitable liquid analysis [17, 29-34]. HCA and PCA are regarded as conventional multivariate methods when compared to the Self Organising Feature Mapping (SOFM) artificial neural network technique. SOFM is an accepted technique in machine learning and, has been reported as a powerful method of pattern recognition for data in areas such as environmental science and food technology [35-38]. For forensically related data, recent publications have indicated an increasing interest in the application of SOFM as a pattern recognition tool [39-43].

Depending on the nature of the sample, analysis usually will produce data with patterns involving high dimensionality. The measurement and interpretation of these patterns can be simplified using multivariate pattern recognition techniques. In chemistry, such chemometric analysis are defined as “techniques applied to describe the operations associated with the mathematical manipulation and interpretation of chemical data” [44].

In general, multivariate analysis transforms a multidimensional dataset into a two dimensional form (known as dimensionality reduction), facilitating the representation of the results in a simpler graphical form. In the context of the present study multivariate analysis uses numerical values from a particular ‘pattern’ as the dataset which can be examined to determine underlying connections within or between samples using mathematical or statistical algorithms. Secondly, multivariate analysis facilitates the extraction of underlying information from within the dataset in order to reveal relationships (if present), compare, and estimate the classification of the sample or possibly link samples by common characteristics. Multivariate analysis can be carried out either by [46]:

i. **a supervised scheme**, where the model learning requires the introduction of training sets of known categories as exemplars upon which the subsequent classification is based,

ii. **an unsupervised scheme** where the model learning is based on methods which do not require a training set of known categories to derive the classification model. Instead the given data is used to establish grouping structures within the dataset.

For an effective multivariate analysis model to develop, it is suggested that the model is built using a structured staged approach although not each step is essential for every single case [45-48]:

1. The problems or the need for multivariate investigation is identified and understood allowing clear objectives for the analysis to be set. Selection of the training set, calibration set and the test set of the samples is undertaken.
2. Data collection, using either continuous or discrete data is recorded.

3. The data is examined to identify any obvious features. Appropriate variables are selected (feature extraction) and noise eliminated. Pre-processing of data is crucial at this stage.
4. Construction of a chemometric model that demonstrates classification based on the compiled data set is undertaken. Output results demonstrate clustering, if present, in a graphical form as well as through numerical results. As a consequence, the identification of compound classifiers is possible for example in techniques like PCA and SOFM. Usually for unsupervised chemometric analysis, the study can be successfully concluded at this stage.
5. The classification model is validated using a related test data set.
6. The validated model is used to predict the classification of unknown samples. At this stage, further validation may be useful to provide further confidence of the predicted values.

The process may be prolonged when supervised multivariate analysis is undertaken [48]. Commonly, multivariate analysis requires measured data to be presented in the form of rows and columns in a matrix represented in figure 4.1. The row data represents measurements recorded within a particular sample while the column data represents the measurements made for a particular variable. Once the data matrix is prepared, it is common for the dataset to undergo pre-processing and transformation.

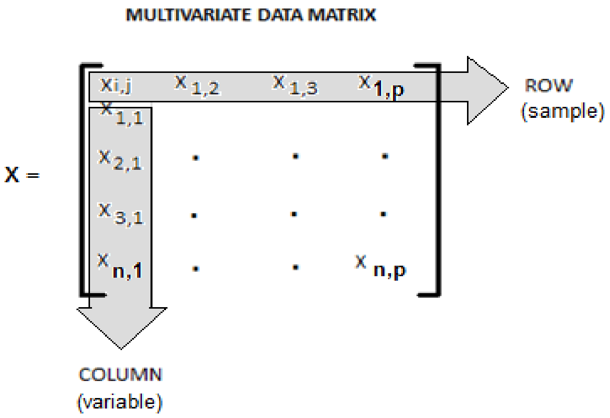


**Figure 4.1 Representation of typical multivariate data matrix arrangements. Adapted from Everitt [49].**

### 4.2.1 Data Pre-processing and Pre-treatment

The terms ‘data pre-processing’ and ‘data pre-treatment’ are generally used interchangeably to explain how original data are prepared prior to the application of multivariate analysis. It is necessary to consider how analytical data is prepared since it can directly affect the outcome of data analysis [47, 50]. The methodology for multivariate analysis is presented in figure 4.2.

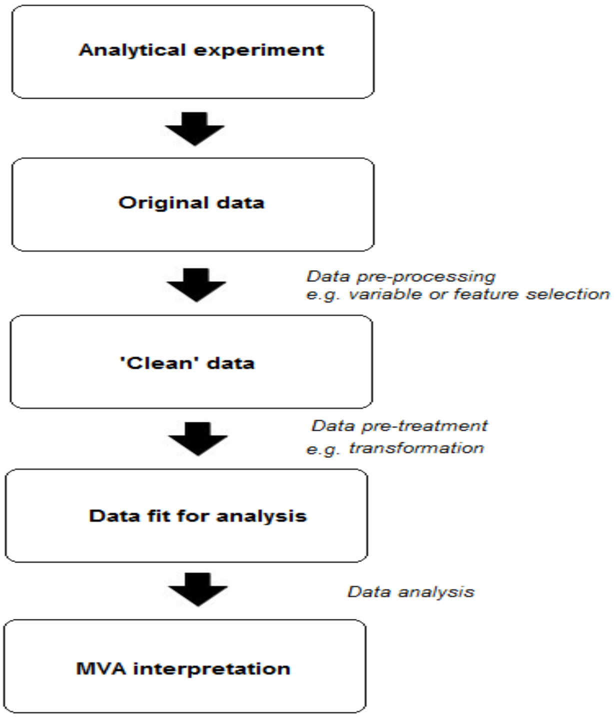


**Figure 4.2 Multivariate analysis scheme (adapted from Van den Berg *et al*) [50].**

Previous work by Van den Berg *et al.* explains data pre-processing as a means to generate ‘clean’ information from original data [50]. Data pre-treatment converts the ‘clean’ data to a different scale or order of magnitude in order to reduce or eliminate the influence of factors such as large discrepancies between component peaks within a chromatogram. Most multivariate analysis works best when distributions are symmetric rather than skew and data pre processing and pre-treatment facilitates this [47, 50]. Numerous data pre-treatment strategies include the scaling methods, centring methods, transformation methods or combinations of those have been reported [46-47].

The pre-processing of data sets, for example through normalisation of the variables, depends entirely on the preference of the analyst [14, 17, 51-53]. Studies by Bodle and Hardy investigated two sets of summation interval (also known as binning techniques) from chromatographic profiles of accelerant datasets which were normalised for PCA and SIMCA analyses [18]. Other methods reported the normalisation of datasets using power or natural logarithmic transformations prior to the application of multivariate analysis [47-48].

### 4.2.1.1 Power Transformation

The main goal of power transformations is to effectively reduce the differences in the magnitude of data points to provide a more symmetrical dataset (in term of the scale of the dataset). This method is particularly useful for handling datasets with zero values representing missing data. Studies using this method on chromatographic data have been previously reported [29, 47, 50, 54]. In power transformation, each data point is replaced by its *n*th root value, mathematically denoted as:

$$x_{ij} \text{ to } (x_{ij})^{1/n} \text{ ................................................Equation 4.1}$$

where a common default value of n=2 (square root power transformation) is used.

The effects of power transformation are twofold; it reduces the influence of large values while at the same time, slightly increasing the values for small data points. These effects can be highlighted using an example of randomly generated data points presented in table 4.1 [55]. It is apparent that the spread of raw data spanning 0.51-18.6 is reduced to 0.71-4.31 once the square root power transformation has been applied. Further reduction of the data range can be observed for fourth and sixteenth root power transformations respectively. Reduction in the scale or magnitude of these data points is illustrated in figure 4.3a. Comparison between data point distribution from the raw (original) data and power transformed data is illustrated in figure 4.3b, showing that power transformation effectively reduced the spread of the data points thus providing a more symmetric data distribution.

Table 4.1The effect of power transformation on randomly generated data.

| | Raw | Sq root | 4th root | 16th root |
|---|---|---|---|---|
| **Point 1** | 0.68 | 0.82 | 0.91 | 0.98 |
| **Point 2** | 5.90 | 2.43 | 1.56 | 1.12 |
| **Point 3** | 0.51 | 0.71 | 0.85 | 0.96 |
| **Point 4** | 1.30 | 1.14 | 1.07 | 1.02 |
| **Point 5** | 6.30 | 2.51 | 1.58 | 1.12 |
| **Point 6** | 4.80 | 2.19 | 1.48 | 1.10 |
| **Point 7** | 0.70 | 0.84 | 0.91 | 0.98 |
| **Point 8** | 18.60 | 4.31 | 2.08 | 1.20 |
| **Point 9** | 2.50 | 1.58 | 1.26 | 1.06 |

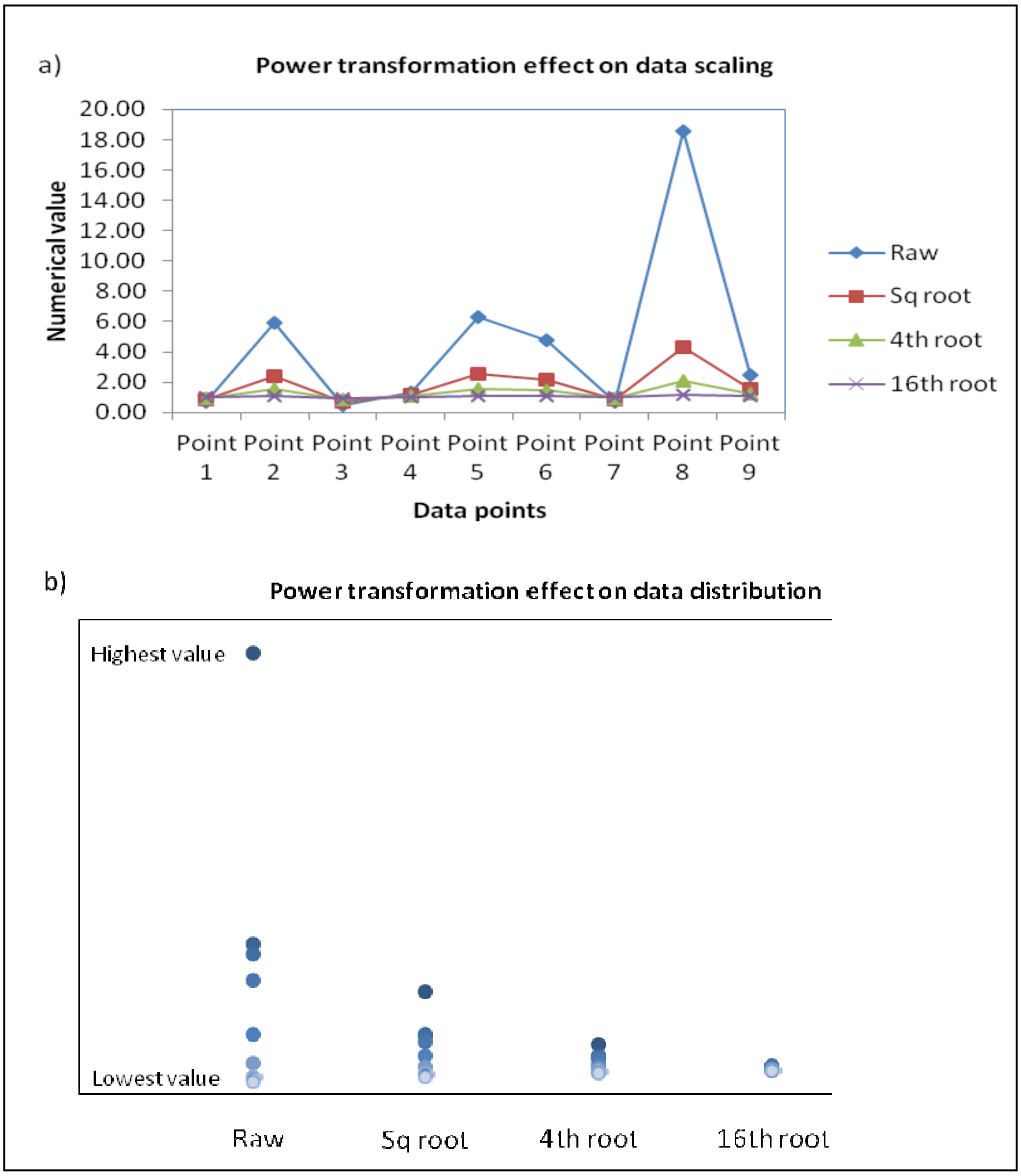


Figure 4.3 The effect of power transformation illustrates a) the reduction in scale or magnitude and b) comparison in data distribution of raw data and power transformed for data in table 4.1 [47,55].

### *4.2.1.2 Row Scaling*

Scaling of data matrix is usually carried out to normalise measurements where the concentration of the compounds of interest are unknown [54, 56]. Numerous scaling techniques are possible but in this work, row scaling to constant peak area was used. The process is carried out by dividing each data point (or each variable) by the sum of all variables for that particular row.

## 4.3 Cluster Analysis

Massart and Kaufman defined cluster analysis as "the classification into groups of objects, characterised by their qualitative or quantitative properties" [57]. Cluster analysis aims to group samples within a large data populations (multi-dimensional datasets) according to similarities or dissimilarities between the elements in the dataset.

## 4.4 Principal Component Analysis (PCA).

PCA is the oldest and probably the most widely used chemometric technique to provide a visualised classification of a given dataset [49]. Within the scope of this study, PCA is used as a means of identifying patterns in data which highlight similarities and differences. PCA can also identify outliers, within a dataset and identify variables that best describe the structure of that dataset.

PCA defines a linear algorithm of an original high dimensional dataset which is used to transform and reduce the original dataset into a more manageable form facilitating interpretation. The full dataset is explained by new and reduced variables known as principal components (PCs). Mathematically, PCs are derived from linear combinations of the original variables perpendicular to latent variable axes, creating specific loadings for each principal component as presented in equation 4.2;

$$PC_n=\alpha_{n1}X_1+\alpha_{n2}X_2+\alpha_{n3}X_3+\ldots\ldots\ldots\ldots+\alpha_{nP}Xp\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{Equation 4.2}$$

Where $\alpha_{ni}$ = the loading for each variable and

$Xi$ = is the standardised value of the original variable.

Each PC is associated with a value known as an eigenvalue that measures the overall variance from the dataset. The larger the eigenvalues, the more significant the PC is. PCs are arranged in order such that the first PC accounts for the largest variance in the data set presented, sequentially followed by the remaining PCs. Usually, the first few PCs represent cumulative eigenvalues accounting for 80% or above of the variation within the data set and are sufficient to describe or explain most of the variability in the given dataset thus reducing the dimensionality [45] .

A score plot of the first two PCs is used to graphically display the clustered outcomes. Figure 4.4 demonstrates the score plot from randomly generated data. This plot provides an important means of visualising and summarising the original dataset and often reveals patterns that were previously elusive. The score plot shows the relative position of the samples where samples having similar scores are positioned closely together, and clustered into one group.

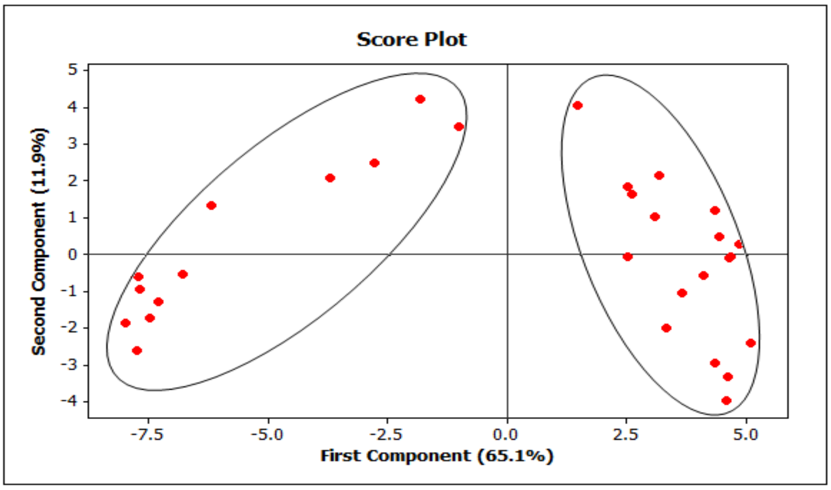


**Figure 4.4 An example of PCA score plot to illustrate sample clustering in two dimensional spaces. Overall, samples are clustered in two big groups.**

PC loading is another useful measurement which defines a direction (positive or negative) in space associated with a degree of magnitude (figure 4.5). The magnitude of the loading indicates the strength of the correlation where a magnitude close to zero indicates weak correlation and vice versa. The combination of score and loading plots generates a bi-plot (figure 4.6) which can be used to study the influence of variables on sample clustering. Interpreting bi-plots however, can be challenging and may seem impractical if one is dealing with too many variables[45].

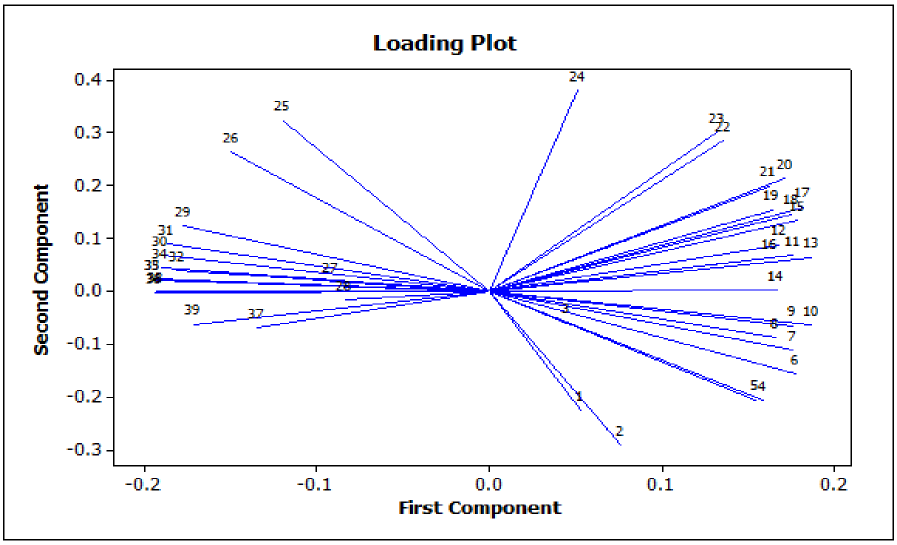


**Figure 4.5 Loading plot for PC 1 and PC2,that convey correlation among the variables.**

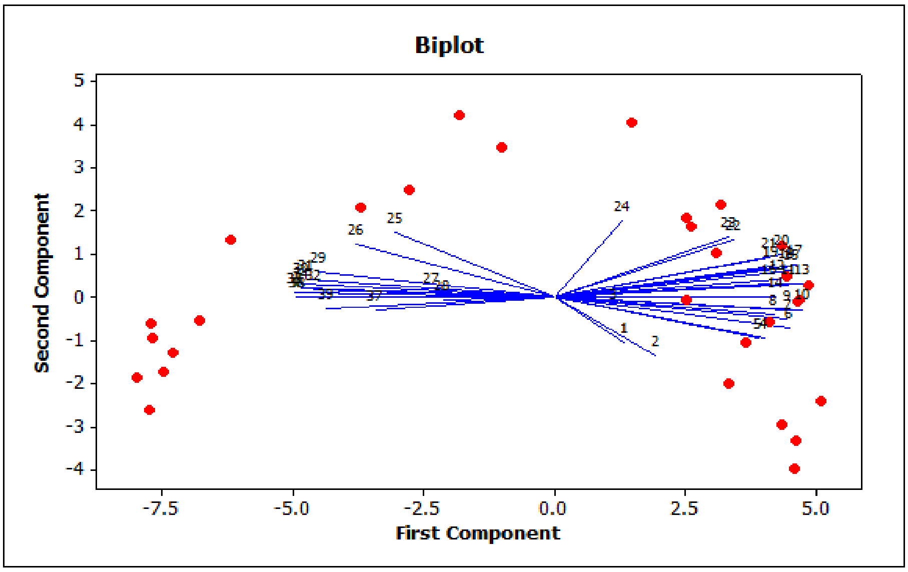


**Figure 4.6 Biplot for PC 1 and PC2 representing information about variables and their relationship with sample clustering as indicated by their distances.**

### 4.4.1 Issues with PCA

A major disadvantage of PCA is its inability to deal with non-linear datasets. The PCA framework is based upon a linear transformation and is greatly influenced by the directionality of the variance axis. As such, this procedure becomes ill defined when dealing with data sets which are not governed by linear relationships. Hiden and co-workers used non-linear chemical refinery data to demonstrate this issue and proposed a non-linear modification PCA (with integration of a neural network framework) as a solution [58]. A similar approach is also discussed in other literature [59].

### 4.5 Hierarchical Cluster Analysis

Hierarchical cluster analysis (HCA) is a commonly used data clustering method often used with large data sets and increasingly used in data sets with forensic science relevance. The method uses a number of approaches for elucidating clusters in a given dataset [49, 60-61]:

i. **Agglomerative methods**. Clustering starts with all elements or points considered as individual separated clusters. The two most similar elements (based on a proximity/distance measurement[1]) are joined together followed sequentially by the next nearest element. The merging of clusters continues until all clusters are joined into one large group as illustrated in figure 4.7.

ii. **Divisive method**, all elements are considered as one large cluster and successively split into smaller groups until each group contains only one element.

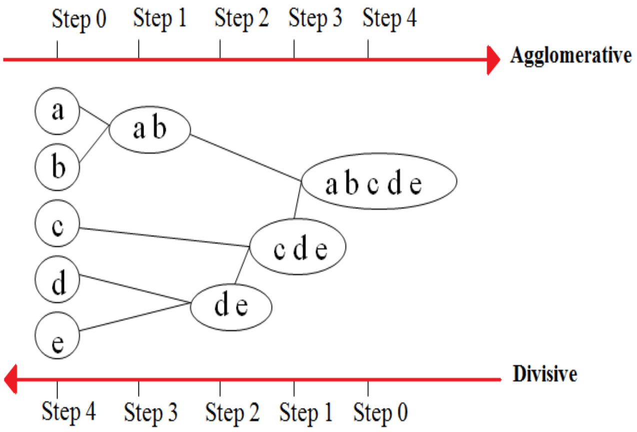


**Figure 4.7 Illustration of cluster analysis scheme by agglomerative and divisive methods [49].**

---

[1] Measure the closeness between two objects. The lower the measure, the closer the objects are.

Agglomerative methods are probably the most commonly used in the application of HCA to chemical data [57, 60].

### 4.5.1 Proximity/Distance measurement

A distance measure is normally employed to decide the closeness of two elements within the data set. Various distance measures can be employed for cluster analysis such as Euclidean, Canberra, Mahalanobis (quadratic) and Manhattan (city-block) distance [48-49, 60]. However, Euclidean distance is most widely used due to simplicity and eases of understanding and was applied for both the HCA and SOFM analysis in this study.

The Euclidean distance is a straight line distance between two points that exist in more than two dimensions and is illustrated in figures 4.5 to 4.7 [62]. Clustering is performed using various linkage strategies known as single, complete and average linkage. The simplest procedure is single linkage, also known as nearest neighbour or minimum distance. Here, the distance between two clusters is measured by the smallest distance between the two nearest elements from adjacent clusters (figure 4.8).

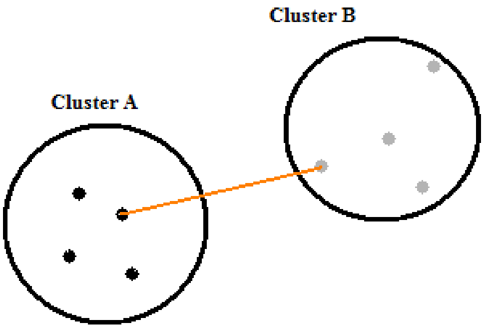


**Figure 4.8 Illustration of single linkage (nearest neighbour or minimum distance).**

In contrast, the complete linkage (furthest neighbour or maximum distance) works by measuring the greatest distance between two elements from different clusters. Finally, the average linkage uses the average distance between all element pairs from each cluster. These linkages strategies are illustrated in figure 4.9 and figure 4.10.

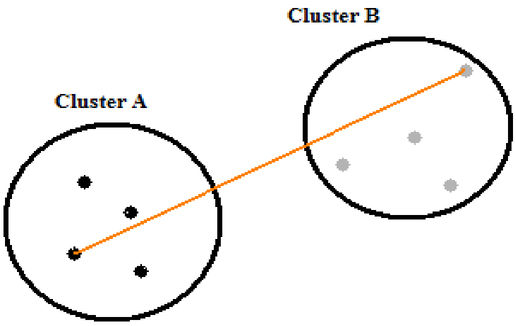


**Figure 4.9 Illustration of complete linkage (furthest neighbour or maximum distance).**

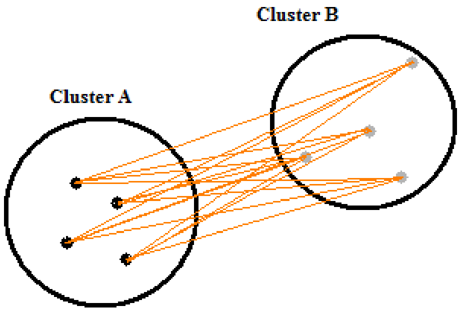


**Figure 4.10 Illustration of average linkage (average distance).**

The outcomes of hierarchical cluster analysis (HCA) are visualised graphically by a two-dimensional tree diagram known as a dendrogram which graphically represents the connections made at each stage of the clustering process. An example of a dendrogram is presented in figure 4.11. In the dendrogram, elements or objects that are similar are positioned and linked close together. The construction of the dendrogram is directly influenced by the distance measure algorithms and linkage methods.

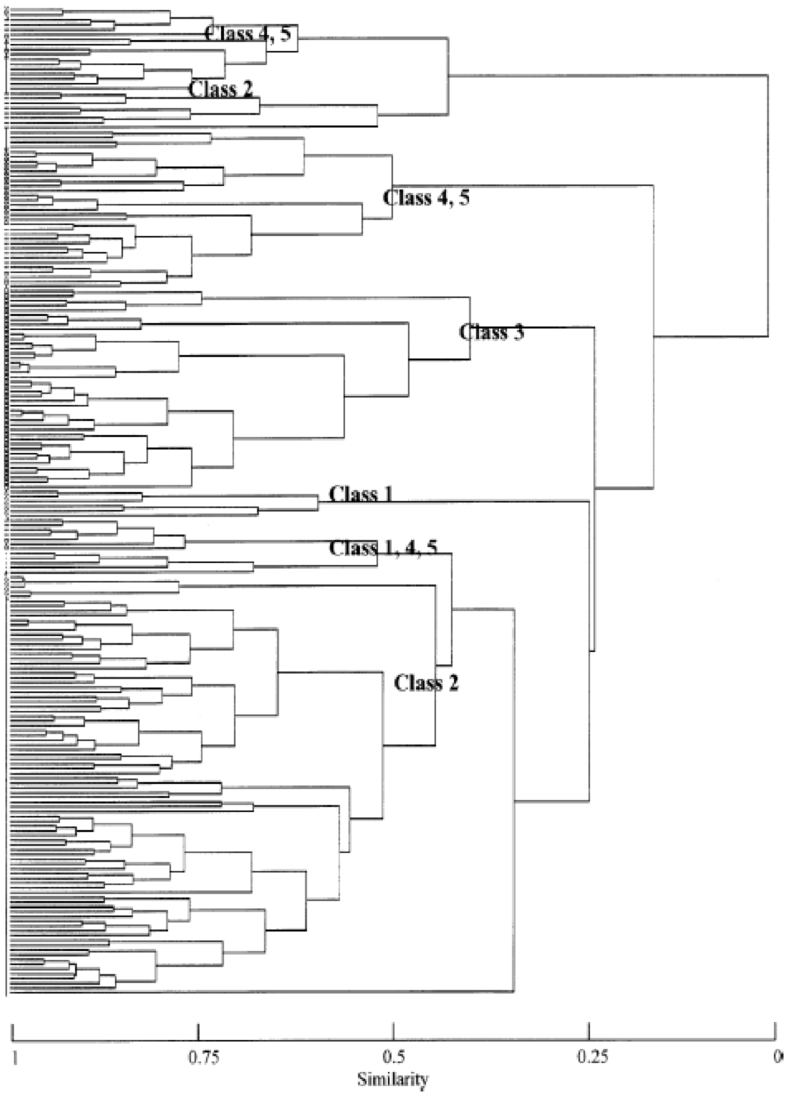


**Figure 4.11 Dendrogram from HCA of ignitable liquid samples clustered based on previous ASTM ignitable liquid classification scheme. Reproduced from Bodle and Hardy[18].**

### 4.5.2 Issues with Hierarchical Cluster Analysis

When the clusters are not well resolved, their interpretation can become confusing or subjective and the loss of information becomes unavoidable. Despite a simpler and more straight forward interpretation relative to PCA, the HCA procedure does not provide a means to investigate the influencing variables within a dataset. Furthermore, one obvious limitation of HCA is that a range of clustering strategies need to be explored to determine the method which provided the most meaningful outcome.

## 4.6 Self Organising Feature Map (SOFM)

SOFM, sometimes referred as Kohonen network was introduced by Kohonen for speech recognition studies in the early 1980's [47]. It is an unsupervised artificial neural network scheme that generally aims to achieve similar objectives to PCA and HCA, hence is suggested as an alternative or complementary mathematical technique to the conventional multivariate analysis. Typical applications for SOFM include data mining for clustering and high dimensional data visualisation. In addition, SOFM has been reported to work with both linear and nonlinear datasets [35, 47, 63-64].

### 4.6.1 SOFM Algorithm

SOFM is arranged as a two-layer form consisting of an input and an output layer. The input layer represents the 'input neurons' which are the variables (elements or object) from the dataset. The output layer is described as a two-dimensional platform equipped with a number of map units (neurons or pixels) for the input patterns to be mapped onto. A typical architecture of SOFM is illustrated in figure 4.12.

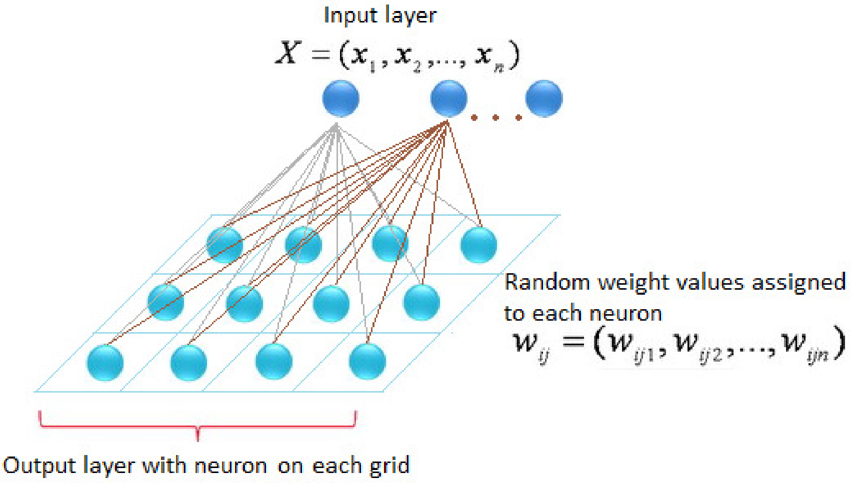


**Figure 4.12 Two layer structure of SOFM neural network. Each input variable is connected to all neurons on the platform. Adapted from [65].**

The mapping process starts with initialisation of the model where each map unit or node on the output layer is given a random weight value. The next stage is the training or the learning process. At this stage, input vectors are introduced to the network iteratively so that all the neurons will be stimulated by the input vectors until the best matching unit (BMU) is identified. The BMU is chosen based on the similarity of the output vector to the input vector whereby similarities between the two vectors are measured using Euclidean distances.

Next, the weights of the BMU's are corrected so that they become closer to the input vectors in the next iteration of the algorithm. The neighbouring neurons of the BMU undergo weight adjustment in proportion to their distance to the BMU such that the further they are, the less the adjustment is made. As the iterative process continues, the SOFM organises into a state whereby similar input vectors are mapped onto similar neurons on the output layer. When the process ends, the output neuron is labelled according to the input or object that has stimulated or mapped onto it to reveal if clustering has emerged from the training. The SOFM matrix is trained to correctly classify the members of the chosen training set. Once trained, the ability of the specific SOFM algorithm to correctly classify novel samples can be revealed and validated by using a test set of known data.

### 4.6.2. SOFM Visualisation

The output layer or output map is a powerful means of visualising complex multidimensional data with a clever use of spatial arrangement and colour coding that presents general clustering inherent within the dataset. Apart from the output map, there are other multiple visualisation methods offered depending on the information acquired, for example, various types of distance matrix maps, and two and three dimensional projections of hit histograms [66-67]. Multiple visualisation techniques allow the analyst to view the results from a variety of perspectives increasing the interpretative value of the data.

Individual component maps (associated with each input variable) can be particularly useful as they facilitate the examination of the characteristics of the clusters and explore the association between the variables within the dataset [67-68].

### 4.6.3 SOFM Classification on Sample Dataset

The application of SOFM in forensic science is a relatively a new concept and the specific mode of application can be explained using a relatively trivial example presented by Kohonen [66]. If we consider a small group of animals (n=16) classified on the basis of 13 morphological attributes where each attribute was scored either 1 if present or 0 if absent. This produces a 16 x 13 data matrix. The output map obtained is presented in figure 4.13. Obvious groupings can be identified from the map. A 'bird family' is grouped on the left side of the map while the 'cat family' is positioned on the right side. Within each cluster, a further grouping of 'hunter' or 'peaceful' can be identified.

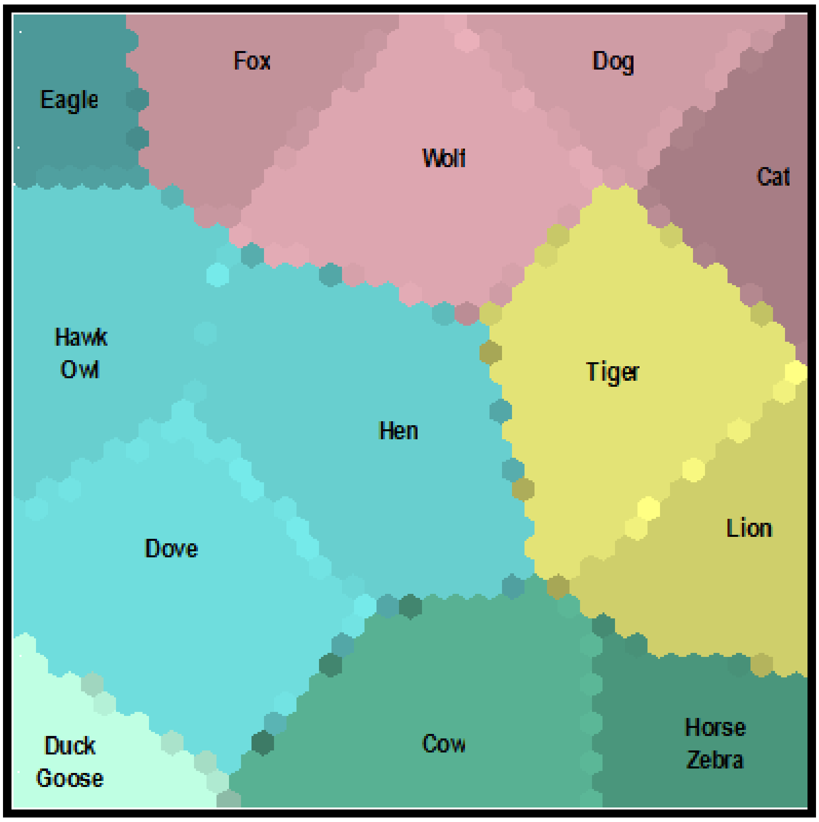
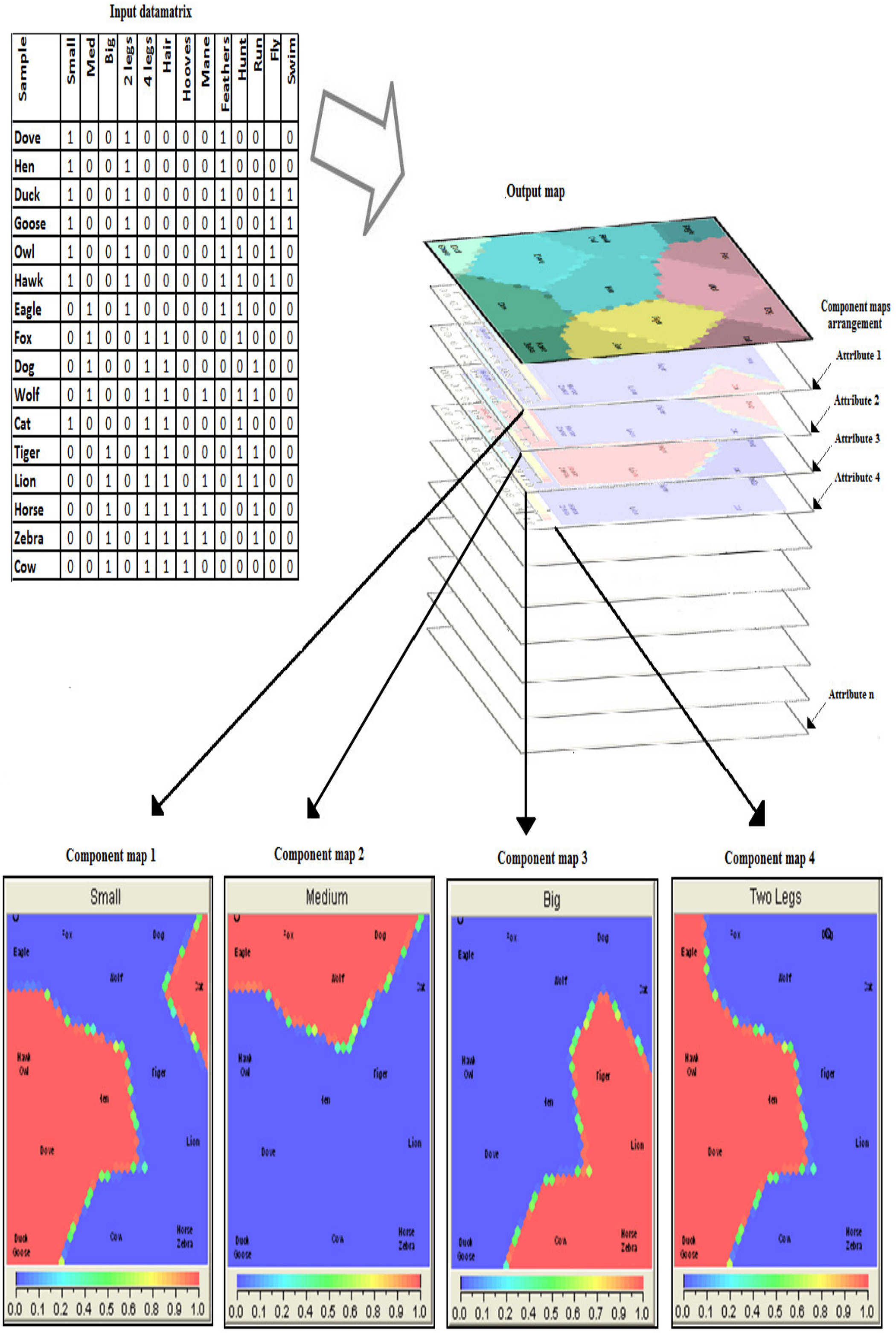


**Figure 4.13 Output map shows similarities within the animal dataset.**

Underlying structures associated with the output map can be investigated using component maps. In this example, 13 component maps (one for each attribute) were built to facilitate visualisation of a particular attribute across the sample. Four of the 13 component maps are presented in figure 4.14 as examples.



Input datamatrix

| Sample | Small | Med | Big | 2 legs | 4 legs | Hair | Hooves | Mane | Feathers | Hunt | Run | Fly | Swim |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Dove | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |  | 0 |
| Hen | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| Duck | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 1 | 1 |
| Goose | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 1 | 1 |
| Owl | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 1 | 0 |
| Hawk | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 1 | 0 |
| Eagle | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 |
| Fox | 0 | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 |
| Dog | 0 | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| Wolf | 0 | 1 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 1 | 0 | 0 |
| Cat | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 |
| Tiger | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 |
| Lion | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 1 | 0 | 0 |
| Horse | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 0 |
| Zebra | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 0 |
| Cow | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |

**Figure 4.14 Simplified schematic presentations that illustrate the framework of component maps in SOFM. Each component map correlates to a single attribute which clearly show, for example the distinction between animals in term of physical attributes (e.g size).**

Because these maps are presented in two dimensions and are colour coded, the interpretation is relatively straight forward, for this data set, but may become impractical when dealing with large numbers of variables. The colour bar at the bottom of each component map enables us to study the qualitative and quantitative features of the map. Blue (or value 0.0) would indicate the absence of the feature and red (value 1.0) would indicate the presence of the feature.

### 4.6.4 Limitations of SOFM

SOFM is proposed as a mathematical technique which can complement the existing and established methods using HCA and PCA. Despite its proven performance, the method is computationally complex and remains to be universally accepted in the interpretation of forensic science data. A major obstacle in the application of SOFM, is that it requires extra computation time as the network learns and becomes optimised. Parameters such as the numbers of nodes and the number of iterations in the learning process are carried out largely by trial and error.

## 4.7 Experimental Methodology

### 4.7.1. Chromatographic Pattern Examination and Identification

Data acquisitions were performed using MS Chemstation (version B.00.01 Hewlet Packard, Agilent technologies). During GC-MS analysis, the method was retention locked to Tetrachloroethylene (ISTD) retention time (5.778) to minimise retention time drift between injections. Chromatographic profiles were examined using mass spectrometer and target compound analysis, as outlined in ASTM method and other work [1, 12, 69-71] .

Datasets were produced from the chromatographic profiles of the ignitable liquid samples generated previously and outlined in chapter 3. Total ion chromatograms of samples were manually aligned and components of similar retention time and with relative standards deviation of less than 5% on triplicate analysis were selected. Identification of compounds which had undergone small retention time shifts was confirmed by examination of the respective mass spectral profile. Peak area response data was acquired as comma separated values (CSV) files and converted into an Excel (version 10.0) spread-sheet for ease of use. As the composition of the samples differed by brands, and lower volatile compounds diminish as evaporation progresses, any missing components in any individual sample were given a zero value.

For practicality, peak integration was automated using Chemsation software version (E02.00.493) and set to a threshold value of 15, in order to account for smaller peaks especially when the chromatographic profiles changed as a result of evaporation [72]. Identification of peak compounds were carried out using mass spectral search program NIST/EPA/NIH Mass spectral library (NIST 08) (version 2.0f, Gaithersburg, MD distributed by The National Institute of Standards and Technology(NIST)© 1987-2008, United States of America) [73].

### 4.7.2 Data Pre-treatment

The peak area response in all datasets were normalised to the response of the internal standard (tetrachloroethylene 0.5mg/mL). Further data pre-processing was undertaken by applying power transformations, then row scaling (each data point i.e. peak area in the respective row is divided by the row's total sum of the peak areas) to these datasets to minimise the influence of larger peak areas over smaller peaks in line with previous studies [47, 74]. Various degrees of power transformation (square root, fourth root and sixteenth root) were applied to the normalised data in order to reveal the most appropriate pre-processing methods.

The data sets prepared are listed in table 4.2. Because of the nature of the samples, especially petrol samples, multiple data sets were examined in order to demonstrate the effect of variable selection on the changing chromatograms encountered as the samples evaporate. Three data matrices were generated for petrol samples as indicated in table 4.2:

**Table 4.2 List of ignitable liquid datasets subjected to multivariate analyses.**

| No | Sample class (samples x variables) | Data description | Data pre-processing |
|---|---|---|---|
| 1 | LPD data matrix (35x51) | Full chromatograms | Raw data |
| | | Full chromatograms | Normalised, row scaled |
| | | Full chromatograms | Normalised, Square root, row scaled |
| | | Full chromatograms | Normalised, Fourth root, row scaled |
| 2 | MPD data matrix ( 56 x 85) | Partial chromatograms | Raw data |
| | | Partial chromatograms | Normalised, row scaled |
| | | Partial chromatograms | Normalised, Square root, row scaled |
| | | Partial chromatograms | Normalised, Fourth root, row scaled |
| | | Partial chromatograms | Normalised, Sixteenth root, row scaled |
| 3. | HPD data matrix ( 56 x 19) | Partial chromatograms | Raw data |
| | | Partial chromatograms | Normalised, row scaled |
| | | Partial chromatograms | Normalised, Square root, row scaled |
| | | Partial chromatograms | Normalised, Fourth root, row scaled |
| | | Partial chromatograms | Normalised, Sixteenth root, row scaled |
| 4. | Petrol<br>i.- Data matrix 1 [a](98 x 62) | Full chromatograms | Raw data |
| | | Full chromatograms | Normalised, row scaled |
| | | Full chromatograms | Normalised, Square root, row scaled |
| | | Full chromatograms | Normalised, Fourth root, row scaled |
| | | Full chromatograms | Normalised, Sixteenth root, row scaled |
| | ii-Data matrix 2[b] (98x 31) | Partial chromatograms | Raw data |
| | | Partial chromatograms | Normalised, row scaled |
| | | Partial chromatograms | Normalised, Square root, row scaled |
| | | Partial chromatograms | Normalised, Fourth root, row scaled |
| | | Partial chromatograms | Normalised, Sixteenth root, row scaled |
| | ii-Data matrix 3[c] (98x 28) | Indane EIP profiles | Raw data |
| | | Indane EIP profiles | Normalised, row scaled |
| | | Indane EIP profiles | Normalised, Square root, row scaled |
| | | Indane EIP profiles | Normalised, Fourth root, row scaled |
| | | Indane EIP profiles | Normalised, Sixteenth root, row scaled |

Notes:[a] Data matrix 1 Full chromatogram comprising of lower (Isobutene) to higher hydrocarbon compound (Methylnaphthalenes)

[b] Data matrix 2 : Partial selection of higher hydrocarbon compound (from C2-alkylbenzenes to C4-alkylbenzenes)

[c] Data matrix 3 : Extracted indane profiles (m/z ions 117, 118,131, 1320)

Finally, in order to ascertain the classification of unevaporated and evaporated ignitable liquid samples, chromatographic data from all petroleum distillate classes (LPD, MPD, HPD and petrol) were combined together and pre-processed according to the appropriate method determined from initial results. Overall, the combined data matrices encompassed 245 samples each with 151 variables (245 x 151).

### 4.7.3 Data Analysis

Various mathematical tools were used to assess the classification facilitated by these data sets, if any, and the potential to discriminate samples by brand as well as link evaporated samples to their original brands. HCA, PCA and SOFM were applied to each dataset generated. HCA was performed using the Euclidean distance measure on single, average, and complete linkage strategies to reveal the best clustering.

Raw and processed datasets were inputted to MATLAB® 2008a (version 7.6, Mathwork Inc., USA) and Minitab® (version 15.1.1, Minitab Inc.) where PCA and HCA were performed. SOFM-artificial neural network analysis was performed using Viscovery®SOMine (version 5.0.2, Viscovery Software GmbH). Dataset learning was carried out using the optimum specification set by the software whereby the number of iterations (epochs) in each case was 40 with 2000 map units (neurons). In order to test both the predictive nature of the SOFM approach as well as provide reassurance that unknown samples would indeed cluster within their source group, cross validation was performed where the overall dataset were split into two; a training and a test set. The training set was used to model the data while the test set was used to test the quality and predictive ability of the model. The training and test sets used are presented in table 4.3.

**Table 4.3 K-fold cross validation strategy devised to determine the predictive abilities of the SOFM network for ignitable liquid samples.**

| Set | Training set | Test set |
|---|---|---|
| V neat (unevaporated) | All samples except neat (unevaporated) | Neat (unevaporated) sample |
| V10 | All samples except 10% | 10% evaporated |
| V25 | All samples except 25% | 25% evaporated |
| V50 | All samples except 50% | 50% evaporated |
| V75 | All samples except 75% | 75% evaporated |
| V90 | All samples except 90% | 90% evaporated |
| V95 | All samples except 95% | 95% evaporated |

Initially, the SOFM network was introduced to the training dataset in order to facilitate correct sample clustering. The test set was then inputted into the trained network and classified into the output layer. This procedure was carried out for each of the training and test sets listed in table 4.3. A similar validation strategy was carried out for each ignitable liquid class separately in this work.

### 4.8 Results and Discussion

Multivariate analysis was performed on the raw data, normalised data, normalised square root data and normalised fourth root data) for each of the ignitable liquid samples to assess the effectiveness of the approach. Principal component analysis and hierarchical cluster analysis were compared with artificial neural networks in their ability to distinguish between the various ignitable liquids and to determine whether it was possible to establish a link between the unevaporated and evaporated samples of the ignitable liquid.

### 4.8.1 SOFM Model Validation

One of the critical issues in the use of neural networks as opposed to simple multivariate clustering techniques such as HCA and PCA, is the validation of the method. This is particularly important when utilising the technique for classification based upon pattern recognition. To estimate the general performance of the SOFM model to classify or predict a classification for a given test set, validation of the model was undertaken where the entire original dataset was partitioned into segments according to the evaporation level of the sample. Each segment was tested individually. This is an appropriate validation strategy suggested by previous literature for small datasets [47, 74-75].

Using unevaporated to highly evaporated ignitable liquid samples as the data sets, SOFM was validated for each ignitable liquid in this study (lighted fluid, medium petroleum distillates, petrol and diesel). The results from the trained and test output maps from the lighter fluid samples are revealed in figure 4.15 as an exemplar of the SOFM outputs and the remaining outputs for the other ignitable liquids classes are presented in appendix I, J and K.

Observations of the groupings demonstrate that the SOFM network was able to completely resolve light and medium petroleum distillate samples by brand and all test samples were correctly assigned to their respective clusters. Some misclassifications however, were recorded within the diesel and petrol samples.

The percentage of correct classification for each model is presented in table 4. 4. Despite some misclassification in the case of petrol and diesel SOFM models, performance values of above 85% in each case suggest that SOFM demonstrates a promising approach to providing an objective measurement in the interpretation of complex patterns for these samples.

**V Neat**

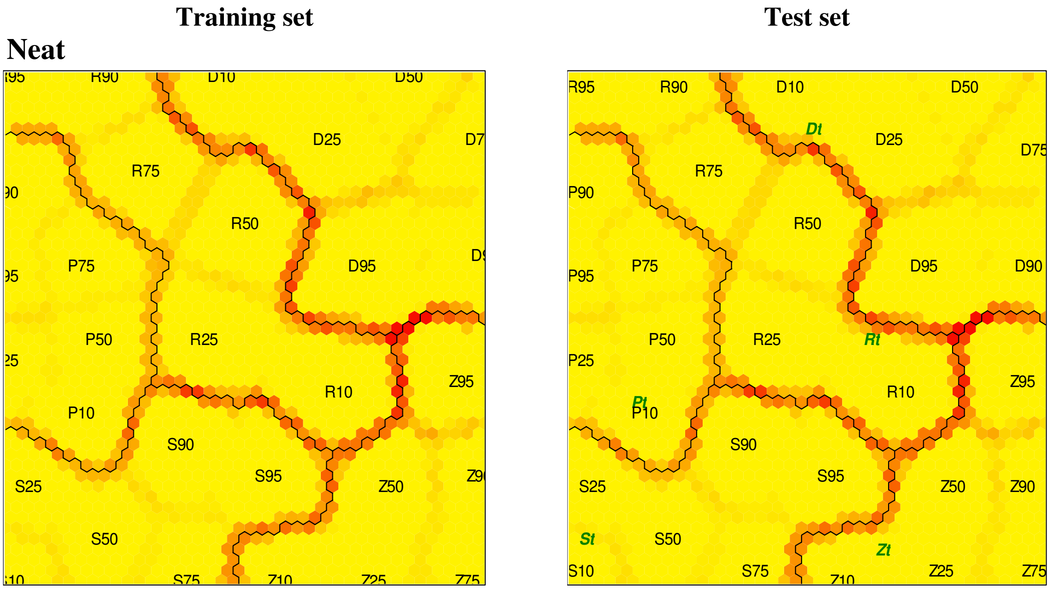
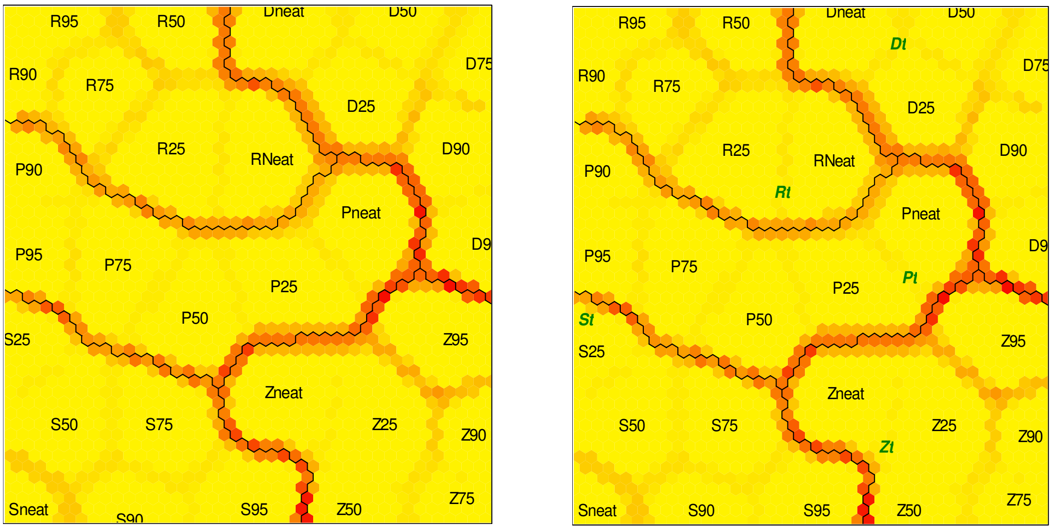
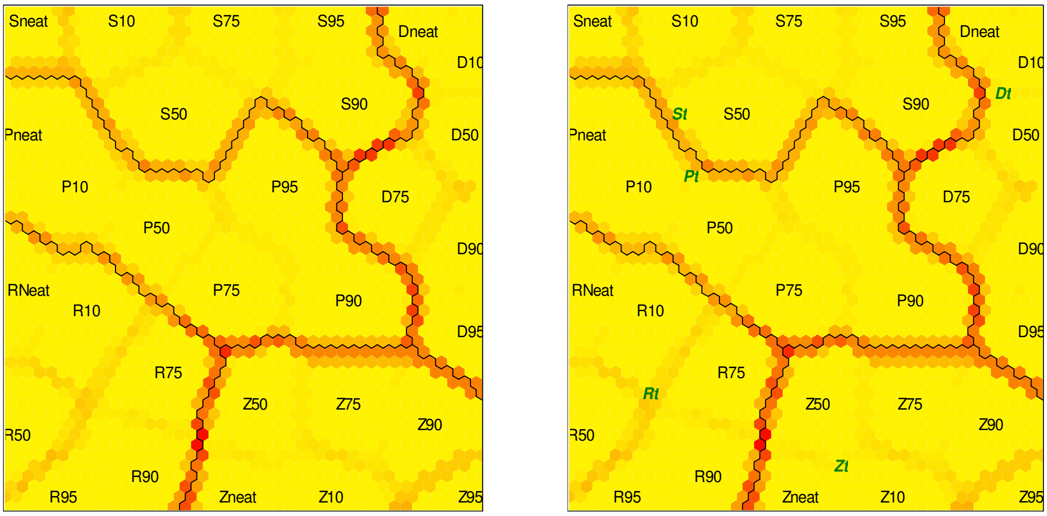


***Figure 4.15 continued***

**V 10**



**V 25**



**V50**

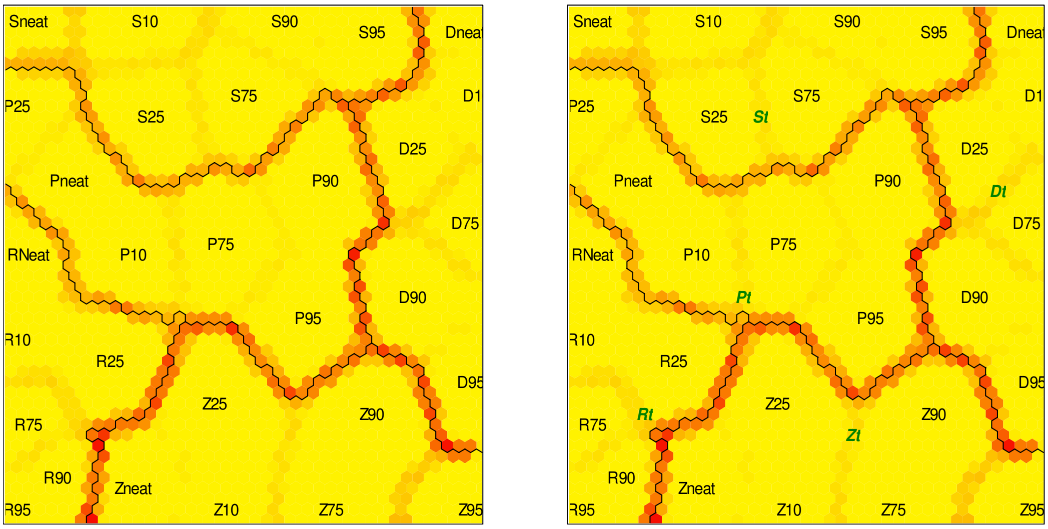
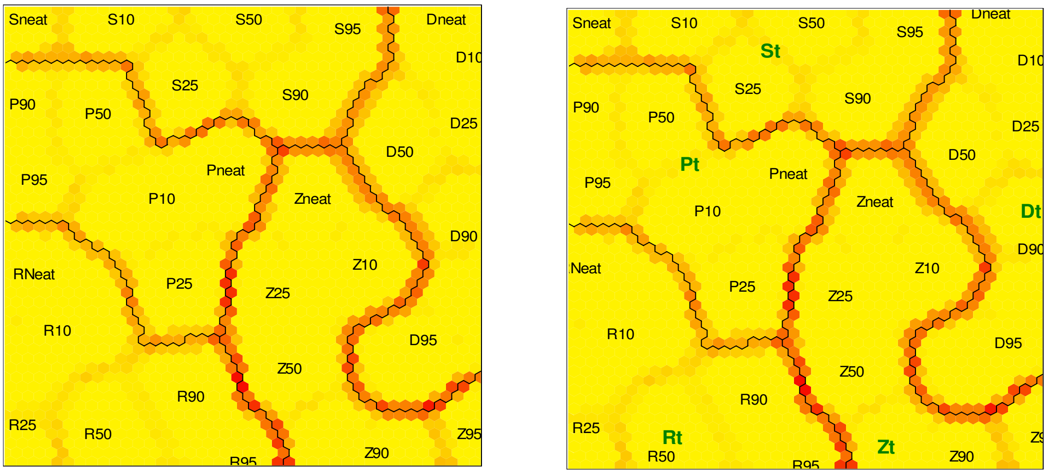
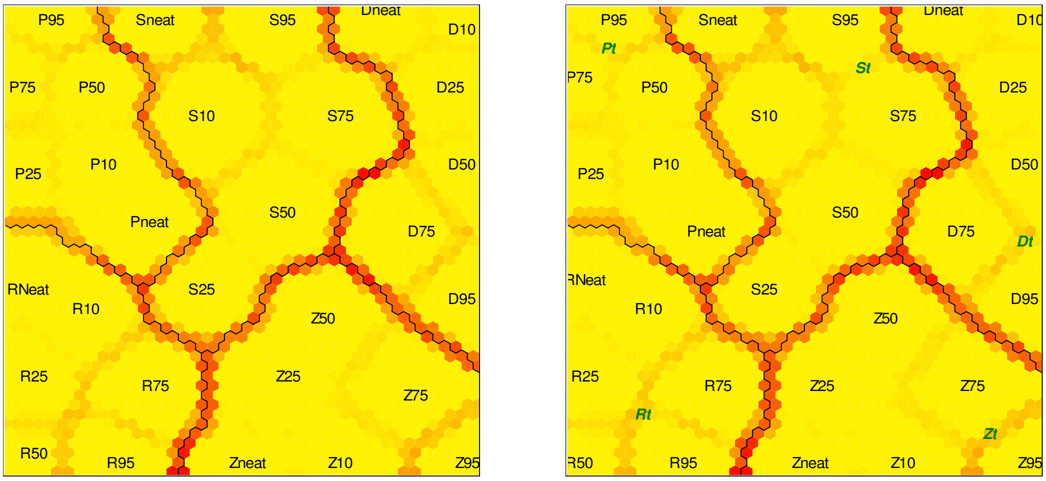


*Figure 4.15 continued*

**V75**



**V90**



**V95**

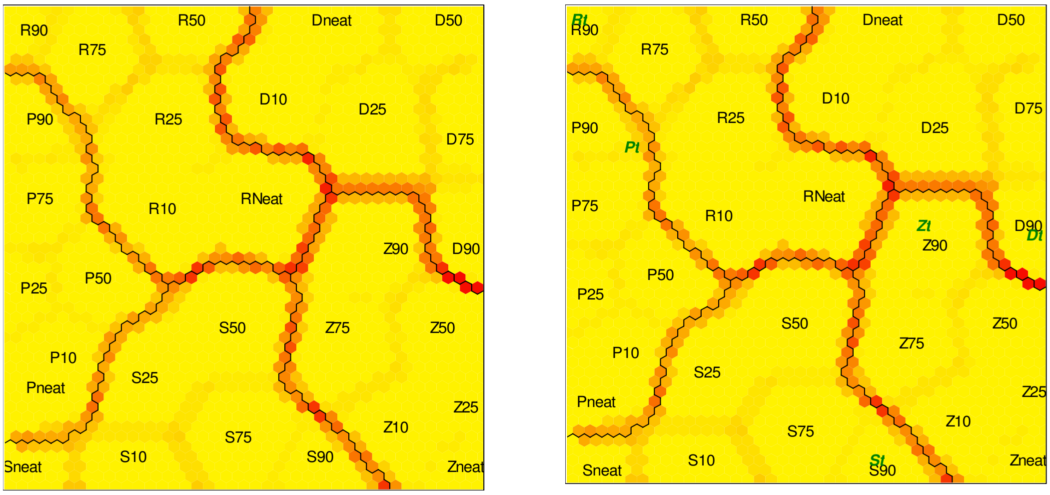


**Figure 4.15 Output map of the training (left) and test set (right) showing correct association of the unevaporated (neat),to highly (95%) evaporated LPD samples to their group by brand. Samples code are D=Dunhill, P=Perma, R=Ronsonol, S=Swan and Z=Zippo and numbers designated level of evaporation. Test samples were coded in green italic font.**

**Table 4.4 Evaluation table for training set and test set of SOFM model.**

| Validation set | LPD (Test samples = 5) | | MPD (Test samples = 8) | | HPD (Test samples = 8) | | Petrol (Test samples = 14) | |
|---|---|---|---|---|---|---|---|---|
| | Misclassified samples | Correct classification (%) | Misclassified samples | Correct classification (%) | Misclassified samples | Correct classification (%) | Misclassified samples | Correct classification (%) |
| Vneat | None | 100 | None | 100 | None | 100 | 1 | 92.8 |
| V10 | None | 100 | None | 100 | None | 100 | None | 100 |
| V25 | None | 100 | None | 100 | None | 100 | None | 100 |
| V50 | None | 100 | None | 100 | 2 | 75 | None | 100 |
| V75 | None | 100 | None | 100 | None | 100 | 2 | 85.7 |
| V90 | None | 100 | None | 100 | 3 | 62.5 | None | 100 |
| V95 | None | 100 | None | 100 | 3 | 62.5 | 1 | 92.8 |
| Overall performance (%) | 100 | | 100 | | 85.71 | | 95.90 | |

## 4.8.2 Light Petroleum Distillate

### *4.8.2.1Chromatographic Examination and Identification of Light Petroleum Distillates*

Light petroleum distillate consists of a narrow hydrocarbon range (C4-C9) and the changes in the chromatographic profile in terms of chemical composition of the samples are not particularly dramatic. However, during evaporation, substantial changes in peak height are apparent as lower boiling point compounds diminish or are lost completely while higher boiling point compounds increase in their abundance relative to neighbouring compounds.

The chromatographic examination and identification of each lighter fluid sample from each of the 5 brands revealed compositional differences for Swan, Dunhill and Zippo samples. By contrast Perma and Ronsonol revealed chromatographic patterns which were very similar to each other as shown in figure 4.16.

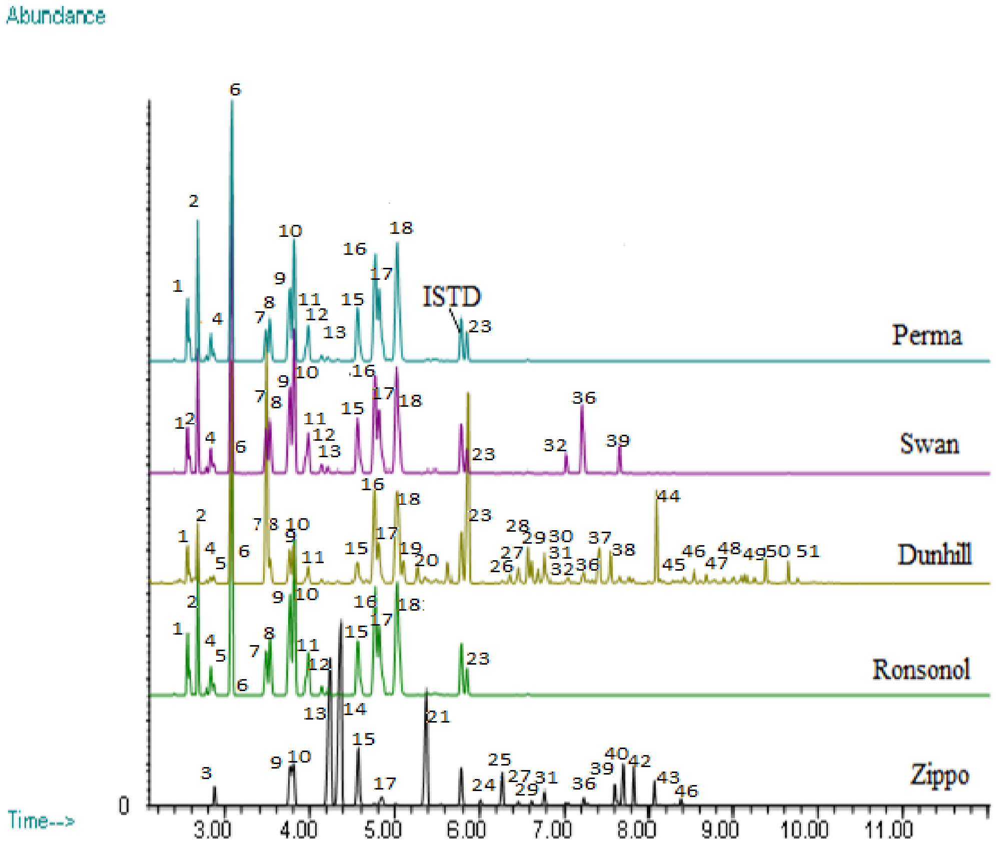


**Figure 4.16 Chromatograms of unevaporated lighter fluid samples (2% in pentane with 0.5mg/mL tetrachloroethylene ISTD). Numbered peaks correspond to identification in table 4.5.**

Identification of the components common to the various lighter fluid samples is presented in table 4.5.

**Table 4.5 Peaks from LPD samples identified using the NIST mass spectral library. Highlighted (in bold) are the target compounds as listed in ASTM 1618 and other literature[1, 5].**

| No | RT | Peak identification | No | RT | Peak identification |
|---|---|---|---|---|---|
| 1 | 2.55 | 2-Methylhexane | 27 | 6.47 | 2,4-Dimethylheptane |
| 2 | 2.68 | **3-Methylhexane** | 28 | 6.58 | **Ethylcyclohexane** |
| 3 | 2.84 | 3-Ethylpentane | 29 | 6.63 | 2,6-Dimethylheptane |
| 4 | 2.89 | 2,2,4-Trimethylpentane | 30 | 6.70 | 1,1,3-Trimethylcyclohexane |
| 5 | 3.08 | **Heptane** | 31 | 6.78 | 2,5-Dimethylheptane |
| 6 | 3.47 | 1,2-Dimethylcyclopentane | 32 | 7.02 | 2,3,4-Trimethylhexane |
| 7 | 3.48 | Cyclomethylhexane | 33 | 7.04 | 3-Methylheptane |
| 8 | 3.53 | 2,2-Dimethyl-3-hexene | 34 | 7.06 | 1,3,5-Trimethylcyclohexane |
| 9 | 3.77 | 2,5-Dimethylhexane | 35 | 7.21 | m-Xylene |
| 10 | 3.81 | 2,4-Dimethylhexane | 36 | 7.23 | 2,3-Dimethylheptane |
| 11 | 3.99 | 3,3-Dimethylhexane | 37 | 7.43 | 2-Methyl octane |
| 12 | 4.15 | 1,2,3-Trimethylcyclopentane | 38 | 7.56 | 3-Methyl octane |
| 13 | 4.23 | 2,3,4-Trimethylpentane | 39 | 7.66 | p-Xylene |
| 14 | 4.37 | 2,3,3-Trimethylpentane | 40 | 7.71 | 2,3,6-Trimethylheptane |
| 15 | 4.56 | 2,3-Dimethylhexane | 41 | 7.78 | 1-Ethyl-4-methylcyclohexane |
| 16 | 4.77 | **2-Methylheptane** | 42 | 7.83 | 2,2,4-Trimethylheptane |
| 17 | 4.82 | 4-Methylheptane | 43 | 8.07 | 3,3-Dimethyloctane |
| 18 | 5.03 | 3-Methylheptane | 44 | 8.09 | **Nonane** |
| 19 | 5.11 | 1,4-Dicyclohexane | 45 | 8.30 | 3,4-Dimethyloctane |
| 20 | 5.28 | 1,1-Dicyclohexane | 46 | 8.41 | 2,4-Dimethyl-3-ethylpentane |
| 21 | 5.37 | 2,2,4-Trimethylhexane | 47 | 8.54 | cis-1,1,3,5-Tetramethylcyclohexane |
| 22 | 5.64 | 1,2-Dicyclohexane | 48 | 8.69 | 2,6-Dimethyloctane |
| 23 | 5.85 | **Octane** | 49 | 9.12 | 1-ethyl-1,3-dimethylcyclohexane |
| 24 | 6.01 | 2,4,4-Trimethylhexane | 50 | 9.15 | Toluene |
| 25 | 6.28 | 2,3,5-Trimethylhexane | 51 | 9.65 | Decane |
| 26 | 6.36 | 2,2-Dimethylheptane | | | |

The full chromatographic profile (highlighted in boxed area in figure 4.17) was used as the lighter fluid data matrix because the compositional change in the samples was considered to be consistent throughout unevaporated to highly evaporated samples.

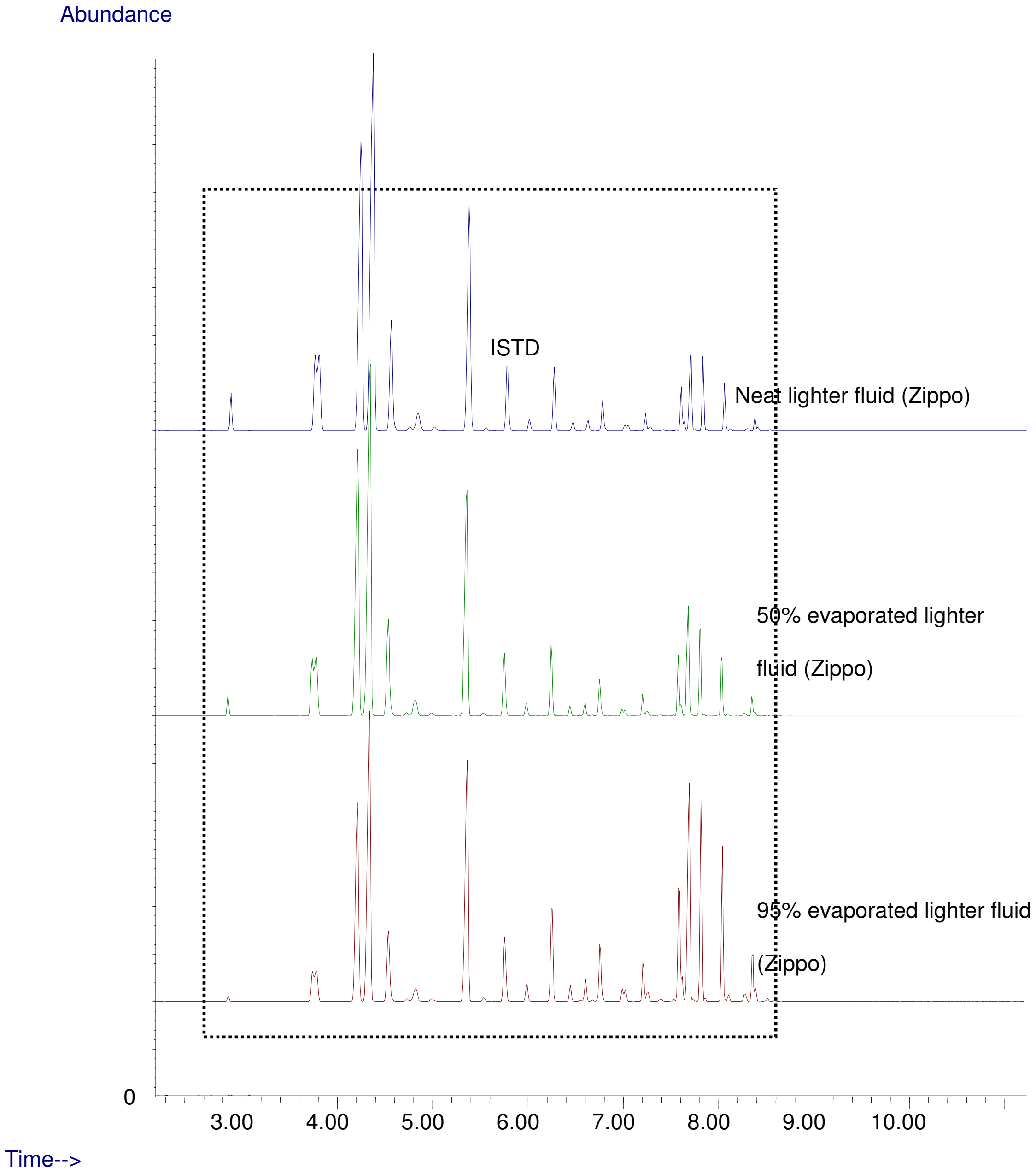


**Figure 4.17 Chromatographic pattern of neat (unevaporated) to highly evaporated LPD using Zippo brand as an example. Full chromatographic profile (in boxed area) illustrates the peaks selected for multivariate analysis. Chromatographic patterns of other LPD samples are included in appendix B.**

### *4.8.2. PCA Classification for LPD (Lighter Fluid) Samples*

Score plots obtained when all datasets were subjected to PCA analysis are presented in figure 4.18. Each score plot represents a series of principal components (PC) illustrating the variances within the data sets. For all of data sets analysed only two brands of lighter fluid (Zippo and Dunhill) were successfully resolved irrespective of the data pre-treatment method used.

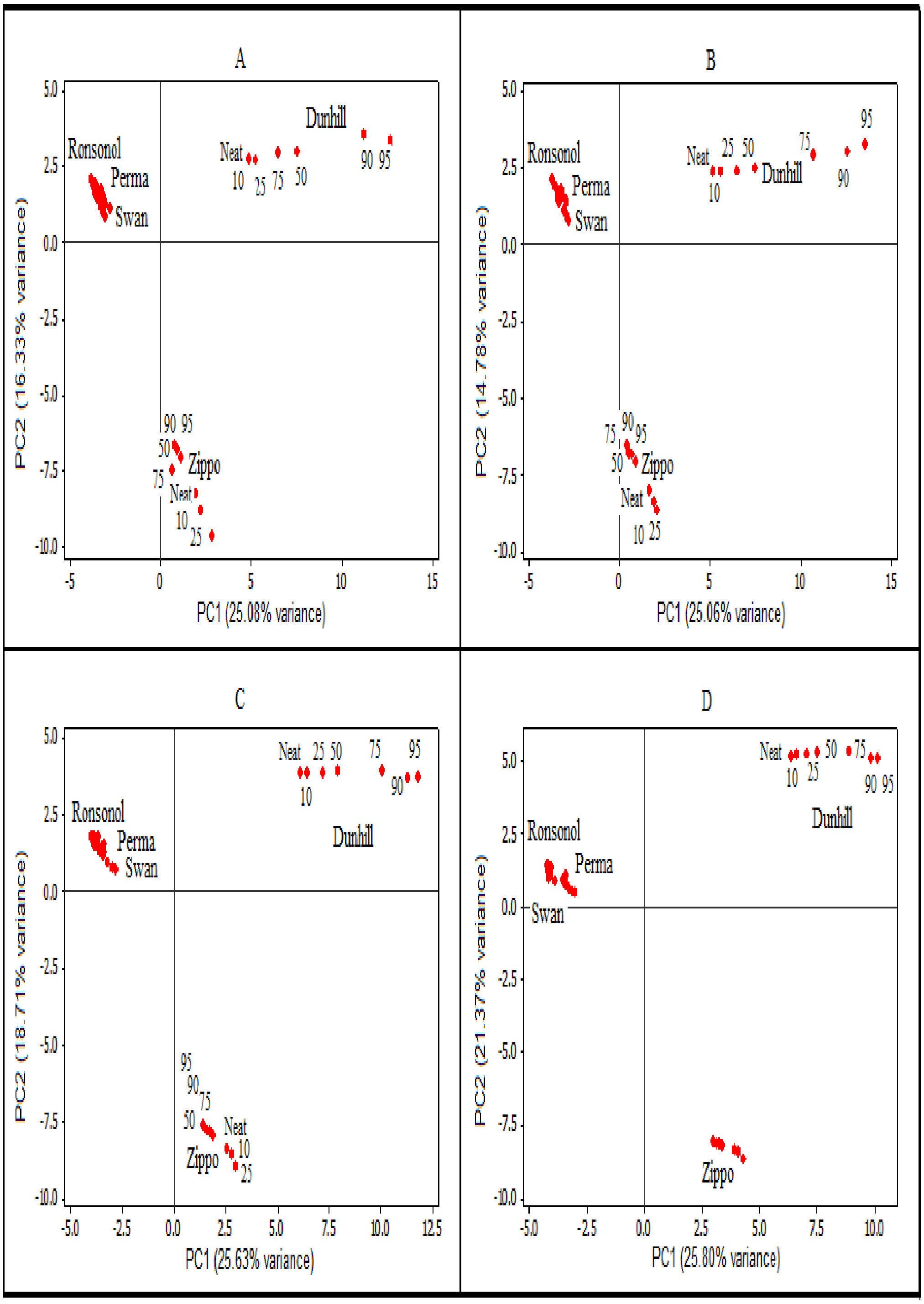


**Figure 4.18: Principal component score plots of pure and evaporated samples. A, B, C and D represent plots of raw data, normalised, normalised square root and normalised fourth root transformation datasets respectively.**

### *4.8.2.3 HCA Classification for LPD (Lighter Fluid) Samples*

HCA was performed using the same four datasets analysed using PCA. Euclidean distance measurement using single, average and complete linkage strategies were used to reveal the best clustering regime which in this case was complete linkage. The results are presented in figures 4.19.

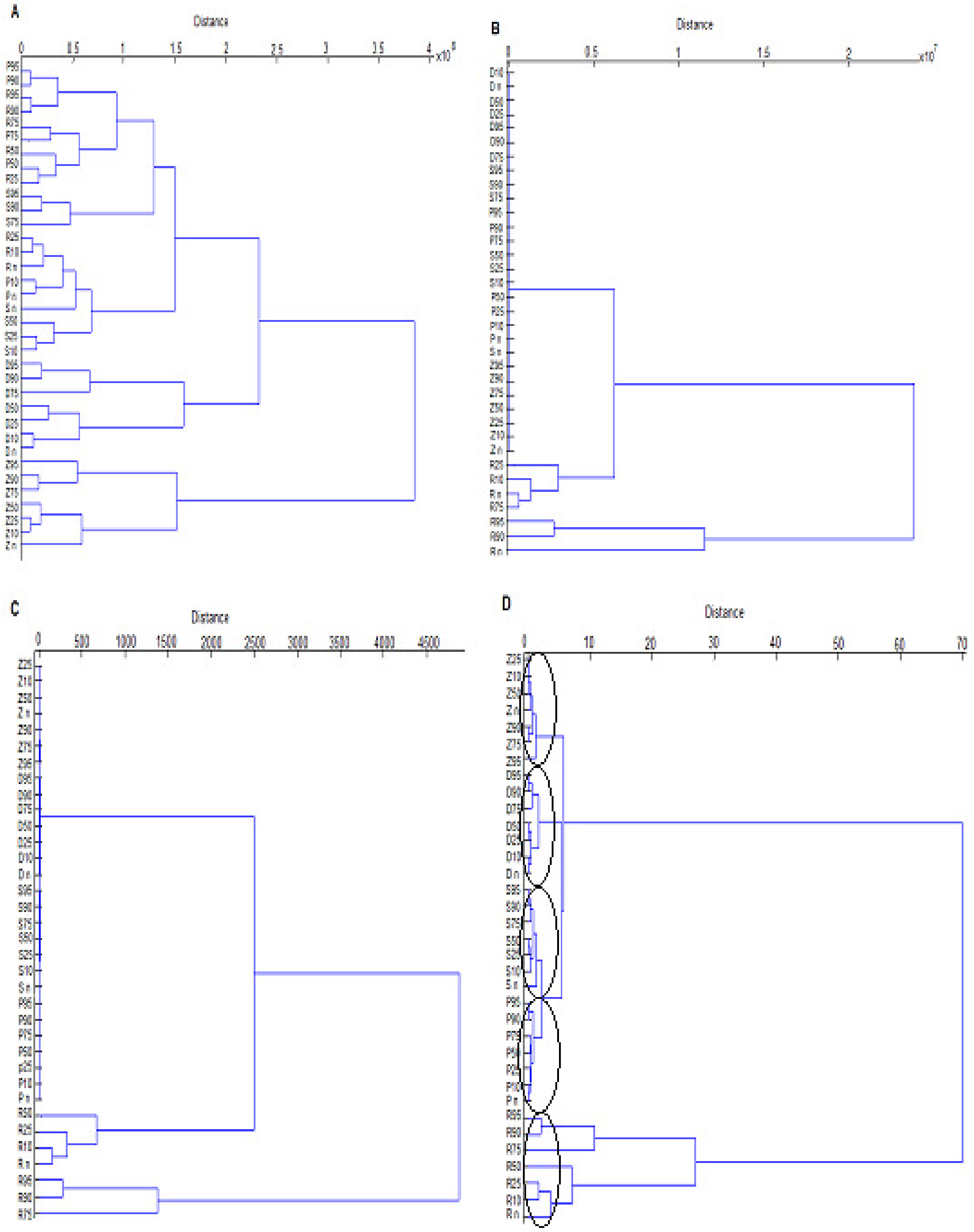


**Figure 4.19: Hierarchical clustering of pure and evaporated samples. A, B, C and D represent dendrogram of raw data, normalised, normalised square root and normalised fourth root transformation datasets respectively. (D=Dunhill, P=Perma, R=Ronsonol, S=Swan and Z=Zippo).**

Like PCA, HCA did not correctly classify the samples by brand when using the raw data, normalised or normalised square root data sets. However, in contrast to PCA, the normalised fourth root data set produced a HCA classification which was capable of separating all of the unevaporated and evaporated samples by brand and is shown in figure 4.19(D).

The HCA classification suggests similarities between Swan and Perma brand samples as well as similarities between both of these samples and those of the Dunhill and Zippo brands. This was not revealed in a visual comparison of the chromatographic profiles of these samples where clear differences were in evidence. The Ronsonol sample set was clustered away from all other sample sets including the Perma sample set even though their chromatographic profiles were visually similar.

#### *4.8.2.4 SOFM Classification for LPD (Lighter Fluid) Samples*

The ability of SOFM to cluster related samples using the four data sets is shown in figure 4.20. Data visualisation in SOFM can be accomplished by a number of techniques which can be a hit histogram, component planes and a Unified-Matrix (U-Matrix) map [47, 67]. In this study, a U-matrix map was employed because this visualisation technique shows similarity of a unit to its neighbour as well as exposing potential clusters. The groupings and the degree of dissimilarity between groupings are shown by a greater intensity of the coloured boundary lines and darker boundary lines reflect a greater distance between the adjoining samples while less intense lines mean a greater resemblance with neighbouring samples.

As a result of using the U-Matrix visualisation method, groupings within and between sample brands and the cluster presentation was straight forward and easy to understand. The effectiveness of SOFM over both PCA and HCA is demonstrated by its ability to correctly classify samples using the normalised and pre-treated data sets, although as with HCA the best result was observed with normalised forth root data. In addition, SOFM clearly illustrates samples that have similar chromatographic profiles (such as Ronsonol and Perma) by placing these sample clusters in close proximity with each other. This was not achievable using HCA.

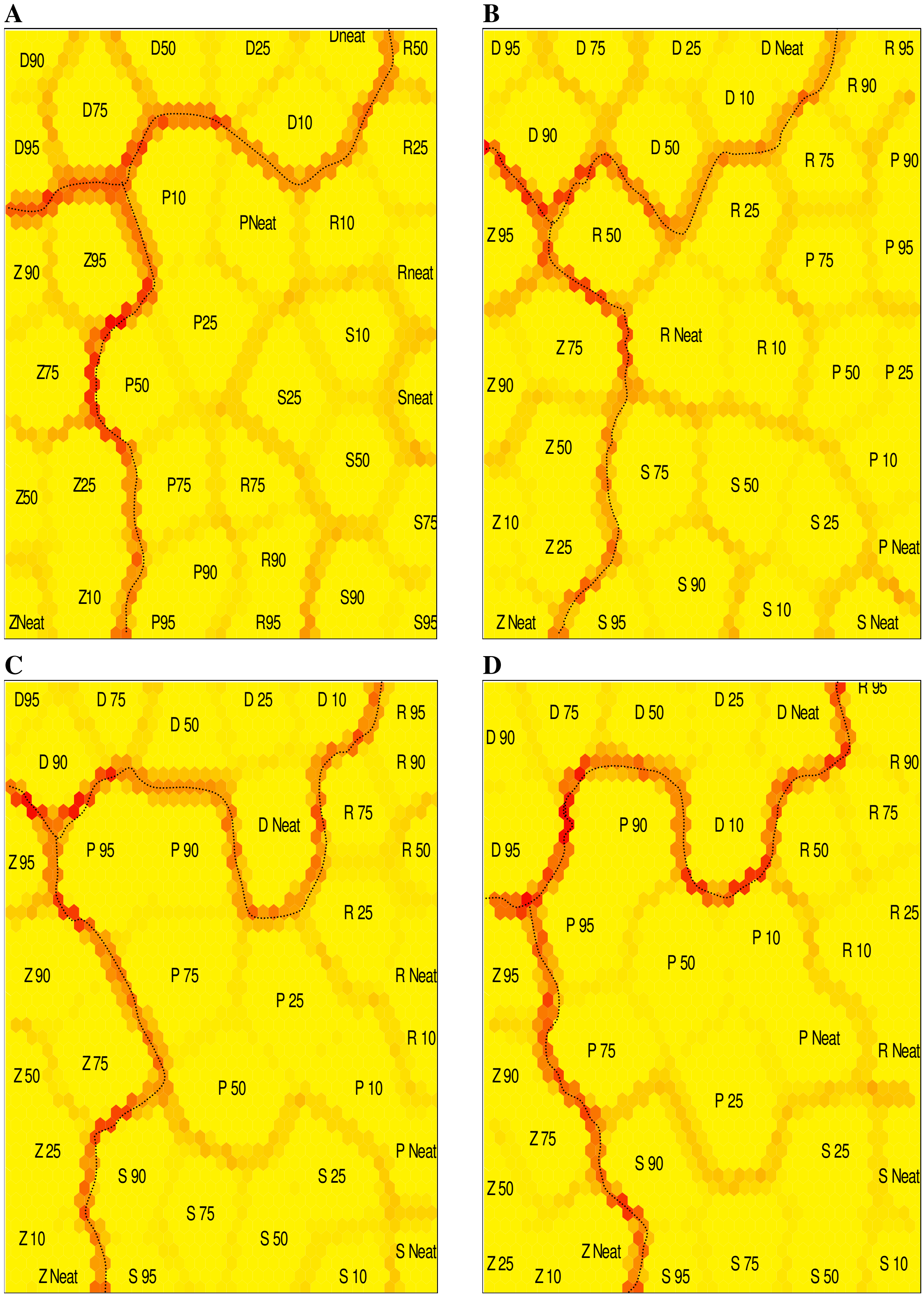


**Figure 4.20: SOFM topographic maps of pure and evaporated samples. A,B,C and D represent the maps of raw data, normalised, normalised square root and normalised fourth root transformation dataset respectively. (D=Dunhill, P=Perma, R=Ronsonol, S=Swan and Z=Zippo).**

Regardless of multivariate procedure used, the grouping of the chromatographic profiles of the lighter fluid samples are noticeably improved when the dataset is treated using a higher power transformation.

This finding may suggest that further power transformation could possibly be applied for more complex or ‘busy’ chromatographic profiles to achieve meaningful linkages.

### 4.8.3 Medium Petroleum Distillate

#### *4.8.3.1Chromatographic Examination and Identification of Medium Petroleum Distillates*

The chromatographic profiles of white spirit, paint brush cleaner and lamp oil are presented in figure 4.21 and all demonstrate a typical pattern for medium petroleum distillates products[13]. Peak identification is provided in table 4.6.

Apart from After Dark lamp oil and Bertoline lamp oil samples, (ADLO and BLO respectively), all other medium petroleum distillate samples demonstrated similar chromatographic profiles. Both lamp oils were included in the overall sample set as these liquids are widely regarded as members of the medium petroleum distillate class within the United Kingdom, even though they are predominantly only n-alkane products according to the ASTM E 1618-06 classification. The inclusion also provided a means of testing the clustering abilities of the statistical approaches employed.

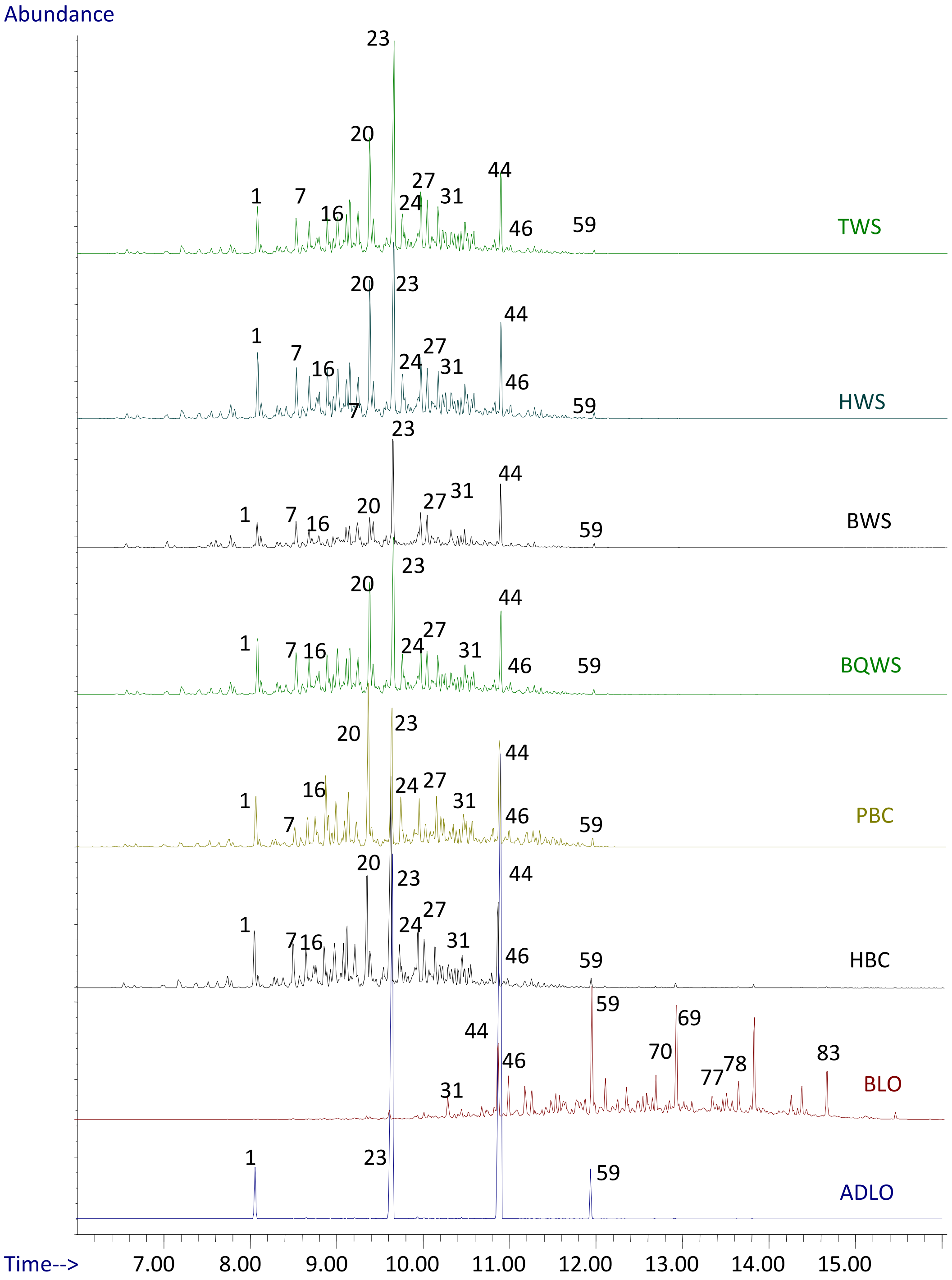


**Figure 4.21: TICs pattern from unevaporated MPD samples from eight different brands. Target compounds for MPD class are identified and numbered according to identification table 4.6. Keycode for the samples are BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO=After Dark lamp oil.**

**Table 4.6 Compound identification for MPD samples. Peaks were identified using the NIST mass spectral library. Highlighted (in bold) are the target compounds as listed in ASTM 1618 and other literature[1, 5].**

| **No** | **Rt** | **Peak Identification** | **No** | **Rt** | **Peak Identification** |
|---|---|---|---|---|---|
| 1 | 8.086 | **Nonane** | 43 | 10.857 | 1-(Cyclohexylmethyl)-2-methylcyclohexane |
| 2 | 8.127 | 1-Ethyl-2-Methylcyclohexane | 44 | 10.900 | **Undecane** |
| 3 | 8.175 | cis-1-Ethyl-4-Methylcyclohexane | 45 | 10.968 | 1,2-Dimethyl-3-ethylbenzene |
| 4 | 8.313 | 1-Methyl-1-cyclooctene | 46 | 11.011 | **1,2,3,5-Tetramethylbenzene** |
| 5 | 8.348 | Isopropylcyclohexane | 47 | 11.113 | 2,6-Dimethyldecane |
| 6 | 8.418 | 2,4,6-Trimethylheptane | 48 | 11.213 | 1-Methyldecahydronaphthalene |
| 7 | 8.536 | **Propylcyclohexane** | 49 | 11.288 | n-Heptyl cyclohexane |
| 8 | 8.606 | Unknown | 50 | 11.323 | 3,4-Dimethylstyrene |
| 9 | 8.683 | 2,6-Dimethyloctane | 51 | 11.366 | 1,3-Diethylbenzene |
| 10 | 8.715 | 1-Ethyl-2,3-dimethylcyclohexane | 52 | 11.434 | 1,2,3,4-Tetrahydronaphthalene |
| 11 | 8.771 | n-Propylbenzene | 53 | 11.468 | Unknown |
| 12 | 8.798 | 2-Methyl-3-ethylheptane | 54 | 11.518 | 6-Methyloctadecane |
| 13 | 8.845 | 1-Methyl-3-propylcyclooctane | 55 | 11.565 | 2,3-Dimethyldecane |
| 14 | 8.893 | m-Ethyltoluene | 56 | 11.611 | 2-Phenyl-2-methylbutane |
| 15 | 8.964 | 1,1,2,3-Tetramethylcyclohexane | 57 | 11.650 | Naphthalene |
| 16 | 9.012 | **1,3,5-Trimethylbenzene** | 58 | 11.908 | Cyclododecene |
| 17 | 9.113 | 4-Methylnonane | 59 | 11.977 | **Dodecane** |
| 18 | 9.152 | 2-Methylnonane | 60 | 12.085 | 1,6-Dimethyl decahydronaphthalene- |
| 19 | 9.248 | 4-Methyl-1-decene | 61 | 12.074 | 1-ethyl-4-(1-methylethyl)benzene, |
| 20 | 9.384 | **1,2,3-Trimethylbenzene** | 62 | 12.138 | 2,6-Dimethylundecane |
| 21 | 9.425 | 1-Isobutyl-3-methylcyclopentane | 63 | 12.284 | 1-Ethyldecahydronaphthalene |
| 22 | 9.578 | 1-methyl-2-propylcyclohexane | 64 | 12.386 | Hexylcyclohexane |
| 23 | 9.659 | **Decane** | 65 | 12.577 | 5-butyl-4-Nonene |
| 24 | 9.762 | **1,2,4-trimethylbenzene** | 66 | 12.621 | Unknown |
| 25 | 9.827 | 1-isopropyl-4-methylbenzene | 67 | 12.687 | Unknown |
| 26 | 9.974 | 2,6-dimethylnonane | 68 | 12.727 | 2,6,7-Trimethyldecane |
| 27 | 10.047 | **Butylcyclohexane** | 69 | 12.957 | Tridecane |
| 28 | 10.174 | 1-methyl-3-propylbenzene | 70 | 13.05 | Unknown |
| 29 | 10.226 | 1-methyl-4-propylbenzene | 71 | 13.144 | 2-Hexyl-1-octanol |
| 30 | 10.26 | 2,5-Dimethylethylbenzene | 72 | 13.38 | Heptylcyclohexane |
| 31 | 10.326 | **Transdecalin** | 73 | 13.501 | Unknown |
| 32 | 10.364 | 1-methyl-2-propylbenzene | 74 | 13.543 | Unknown |
| 33 | 10.402 | 5-Methyldecane | 75 | 13.609 | Unknown |
| 34 | 10.440 | 4-Methyldecane | 76 | 13.682 | Unknown |
| 35 | 10.485 | 2-Methyldecane | 77 | 13.864 | Tetradecane |
| 36 | 10.510 | Isopropyltoluene | 78 | 13.913 | Unknown |
| 37 | 10.561 | 3-Methyldecane | 79 | 13.964 | Unknown |
| 38 | 10.587 | p-Isopropyltoluene | 80 | 14.291 | Cyclotetradecane |
| 39 | 10.625 | 1,3,5-Trimethyl-2-octadecylcyclohexane | 81 | 14.413 | Unknown |
| 40 | 10.663 | Unknown | 82 | 14.468 | 3-Methyltetradecane |
| 41 | 10.714 | 1-Methyl-2-pentylcyclohexane | 83 | 14.704 | Pentadecane |
| 42 | 10.763 | 5-Undecene | 84 | 15.497 | Unknown |

Medium petroleum distillates generally undergo compositional changes when thermally degraded or evaporated. An example of this is presented in figure 4.22 for white spirit. As the evaporation progresses, lower boiling point hydrocarbon compounds diminish and higher boiling point hydrocarbon compounds begin to predominate with a higher relative abundance.

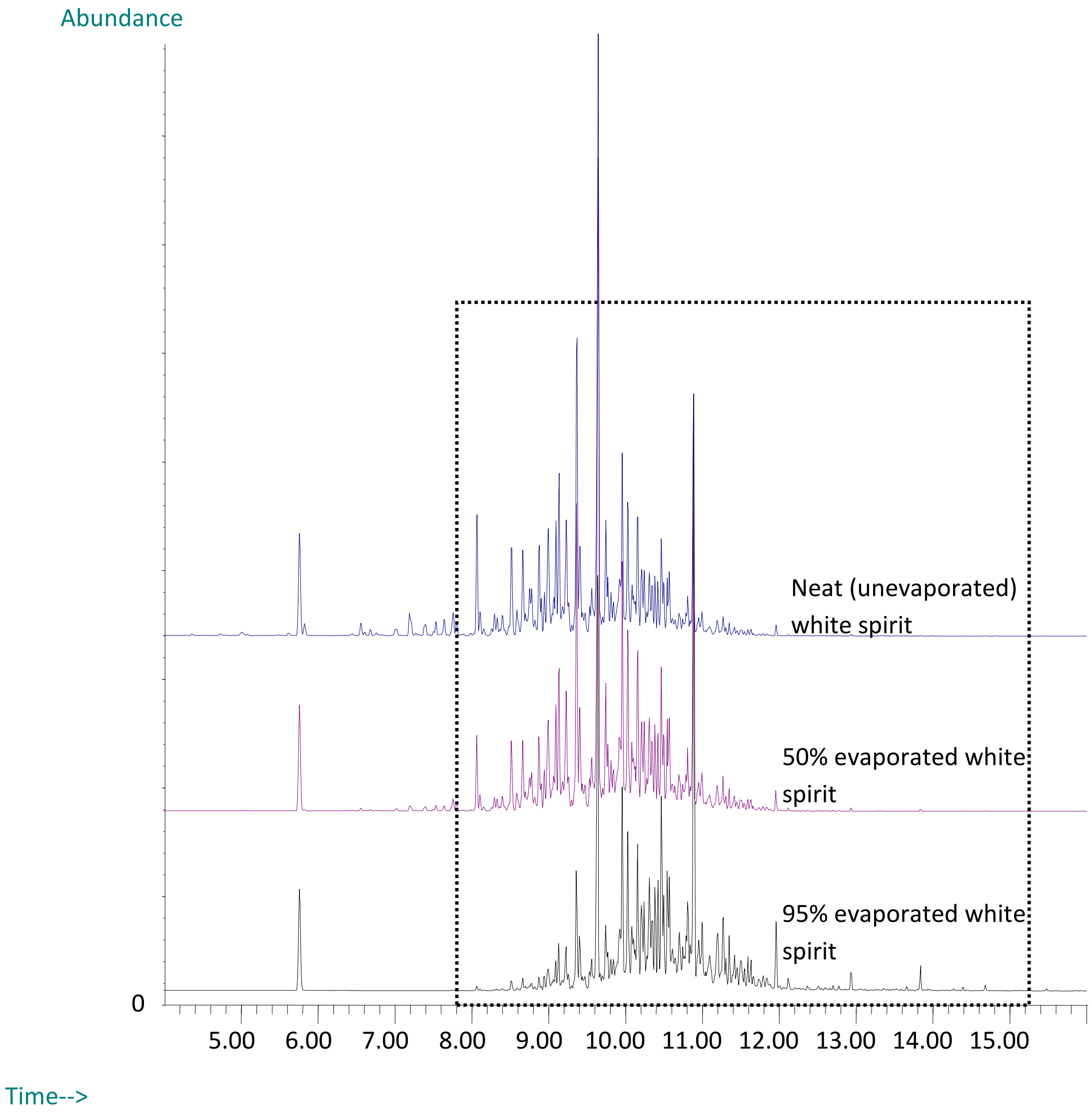


**Figure 4.22 Chromatographic pattern of neat (unevaporated) to highly evaporated MPD using white spirit as an example. Partial chromatographic profile (in boxed area) illustrates the peaks selected for multivariate analysis. Chromatographic patterns of other MPD samples are included in appendix C.**

The effect of gradual evaporation on sample grouping was examined by employing a partial selection of the chromatographic profiles (unevaporated samples through to the most evaporated sample) in order to reduce the number of zero values in the data matrix. This resulted in the selection of chromatographic peaks from 8.00 minutes and above, producing a data matrix of 56 x 84 variables corresponding to the selected area in figure 4.22. The higher boiling point hydrocarbon compounds were chosen for data analysis because they were more persistent and consistent in the evaporated samples.

Data pre-processing was applied to the data set as previously described however in each case for PCA, HCA and SOFM only the sixteenth-root pre-treatment provided any meaningful sample linkage.

#### *4.8.3.2 PCA Classification for MPD Samples*

The score plot for the principal components generated from the sixteenth root pre-treated medium petroleum distillate dataset is displayed in figure 4.23. The plot of the first and second principal component accounted for 55.49% of the total variance. Bertoline lamp oil, After Dark lamp oil and Homebase brush cleaner were successfully discriminated. However Tesco white spirit, Bertoline white spirit, B&Q white spirit, Homebase white spirit and Polycell brush cleaner were all combined into one larger convoluted cluster. Within the Bertoline lamp oil, After Dark lamp oil and Homebase brush cleaner cluster, samples were closely arranged according to their degree of weathering.

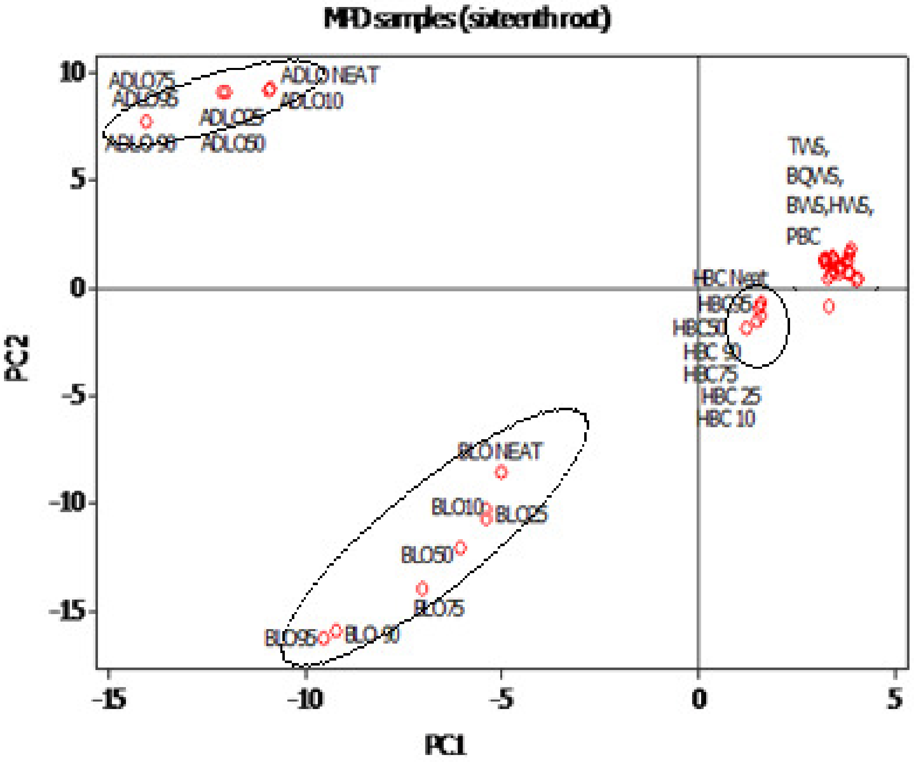


**Figure 4.23 PCA score plot of MPD samples from sixteenth root dataset. PC1 and PC2 explain 55.49% of total variance in the dataset. Keycode for the samples are BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO= After Dark lamp oil**.

### *4.8.3.3 HCA Classification for MPD samples*

Euclidean distance was used as the proximity measure and complete linkage as the amalgamation strategy in the HCA classification. The resulting dendrogram is revealed in figure 4.24.

Samples from the medium petroleum distillates B&Q white spirit, Bertoline white spirit, Bertoline lamp oil and After Dark lamp oil were all successfully grouped and linked close to each other. HCA however, failed to link all Homebase white spirit and Polycell brush cleaner samples and those with a higher degree of evaporation were linked to the Tesco white spirit and Homebase brush cleaner clusters respectively.

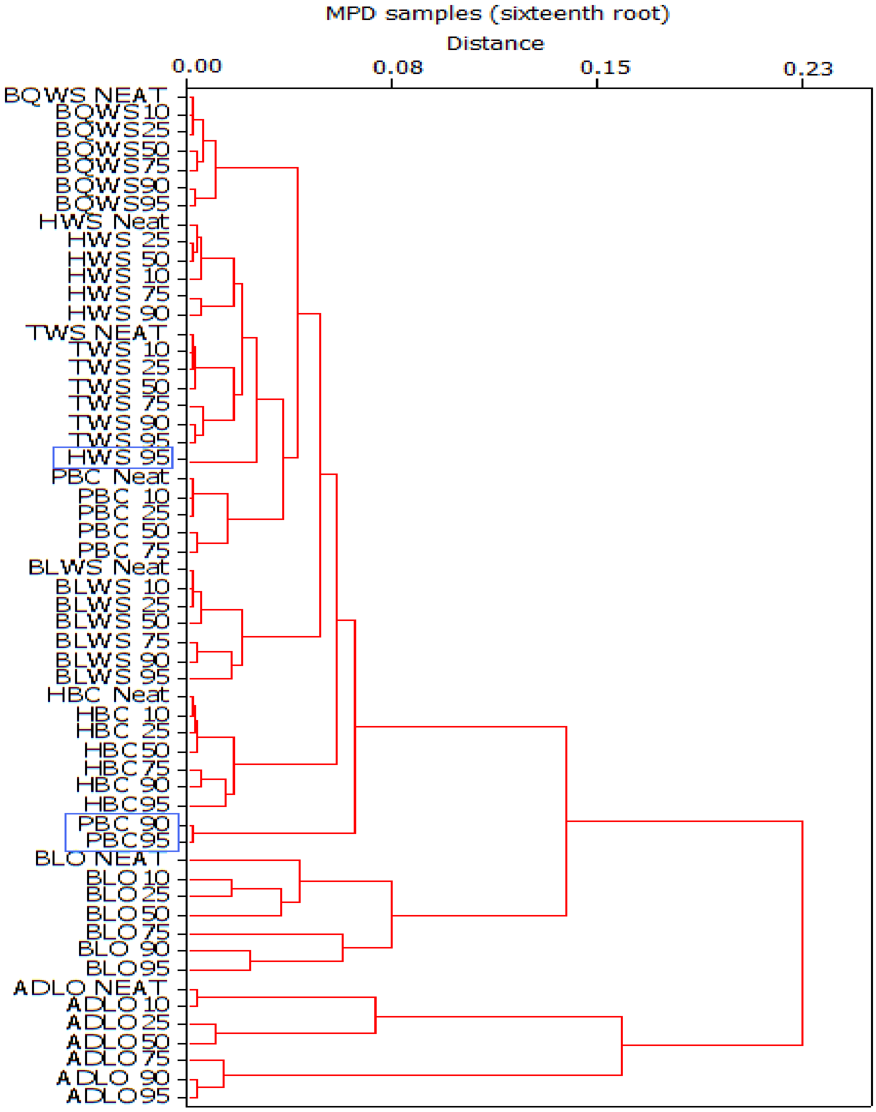


**Figure 4.24 Dendrogram of HCA for MPD classification from sixteenth root power transformed dataset. Misclassified samples are highlighted. Keycode for the samples are BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO= After Dark lamp oil**.

### *4.8.3.4 SOFM classification for MPD samples*

An output map utilising the distance matrix technique demonstrated the best clustering using SOFM. Figure 4.25 presents the U-matrix output map and reveals very distinctive clustering of the samples according to both type and brand in every case. The intensity of the borders between adjacent units signifies the level of similarity of the unit with its neighbour and is particularly obvious with the lamp oil samples (ADLO and BLO) as would be expected given that they both contain medium range normal alkane products.

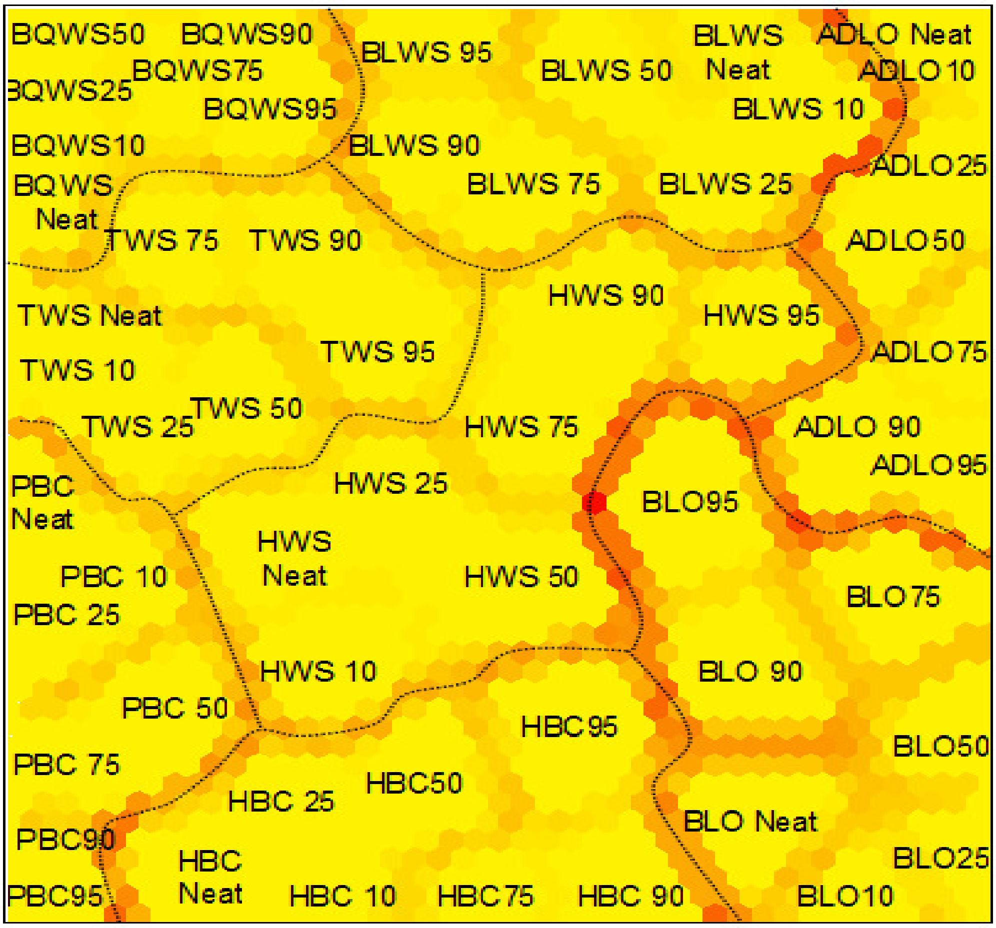


**Figure 4.25 U-matrix output map of MPD samples. Dotted lines are drawn to emphasise the boundaries between the samples. Keycode for the samples are BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO= After Dark lamp oil. Black lines emphasises sample groupings.**

The white spirits samples are clustered on the upper left and central part of the map whereas the paint brush cleaner samples are clustered together at the lower portion of the output map. Vague borders within the units from the same brand are inevitable and signify the compositional changes that have occurred as the sample has evaporated. The results also suggest that, even though there have been some substantial changes in the chromatographic pattern as the samples have evaporated, samples with a common origin still share sufficient features, and are consequently clustered together using SOFM without any misclassification.

### 4.8.4 Heavy Petroleum Distillate

#### *4.8.4.1Chromatographic Examination and Identification of Diesel Samples*

Diesel samples demonstrate very similar chromatographic patterns across all samples investigated and are presented in figure 4.26. The prominent peaks in diesel samples were identified as listed in table 4.7.

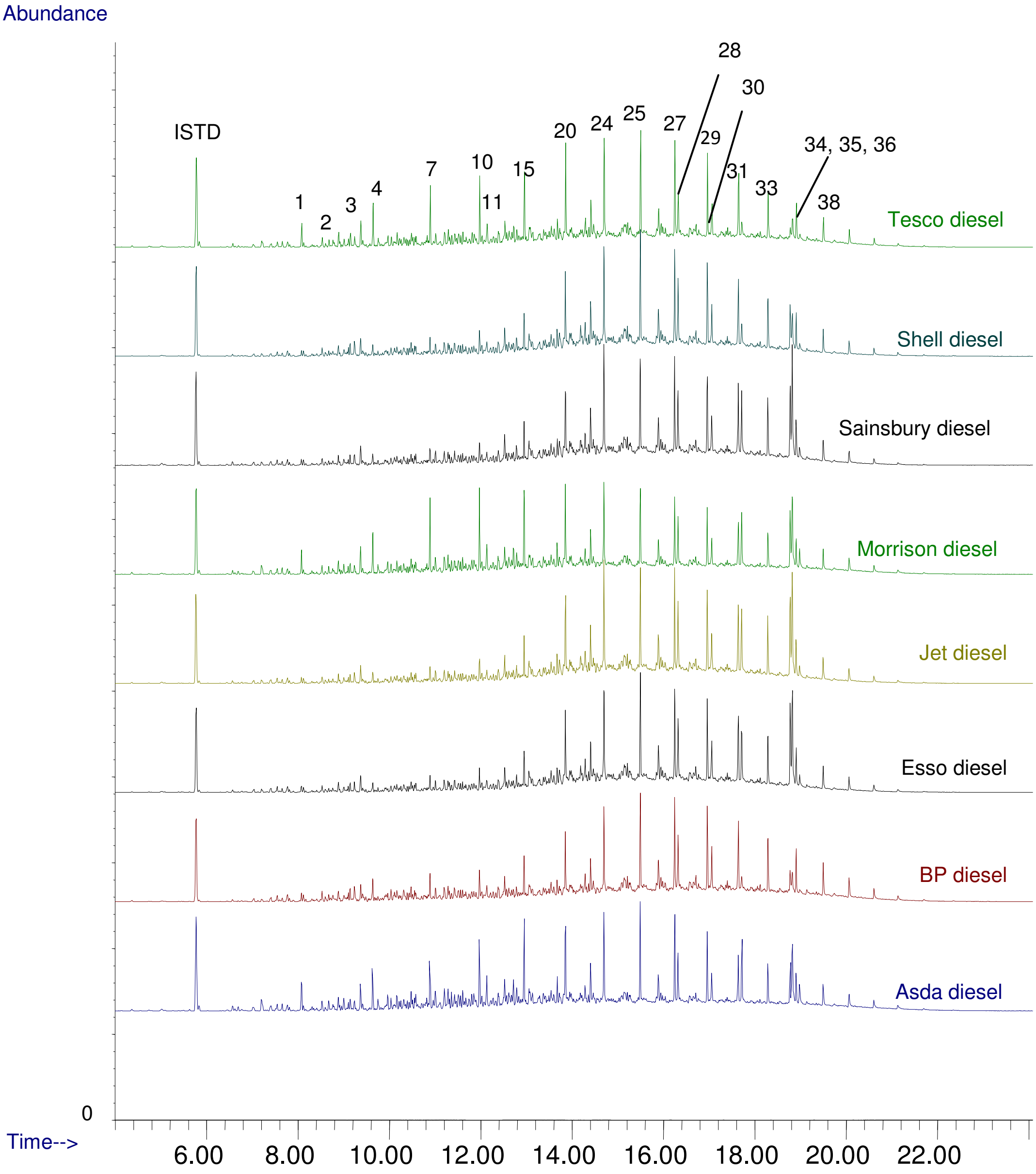


**Figure 4.26 Representative TICs of unevaporated diesel from different brands. For brevity, prominent peaks are numbered as identified in table 4.7 accordingly as similar pattern are observed in other samples.**

**Table 4.7 Compound identification for HPD (i.e diesel) samples identified using the NIST mass spectral library. Highlighted (in bold) are the target compounds as listed in ASTM 1618 and other literature[1, 5].**

| No | Rt | Peak Identification | No | Rt | Peak Identification |
|---|---|---|---|---|---|
| 1 | 8.078 | Nonane | 22 | 14.409 | 2,6,10-Trimethyltetradecane |
| 2 | 8.886 | m-Ethyltoluene | 23 | 14.467 | Unknown |
| 3 | 9.372 | 1,2,3 Trimethylbenzene | 24 | 14.700 | **n-Pentadecane** |
| 4 | 9.641 | **Decane** | 25 | 15.495 | **n-Hexadecane** |
| 5 | 10.165 | m-Propyltoluene | 26 | 15.893 | 2,6,10-Trimethylpentadecane |
| 6 | 10.315 | **Transdecalin** | 27 | 16.248 | **n-Heptadecane** |
| 7 | 10.893 | Undecane | 28 | 16.321 | **2,6,10,14-Tetramethylpentadecane or Pristane** |
| 8 | 11.012 | unknown | 29 | 16.962 | **n-Octadecane** |
| 9 | 11.206 | Unknown | 30 | 17.059 | **2,6,10,14-Tetramethylhexadecane or Phytane** |
| 10 | 11.97 | Dodecane | 31 | 17.641 | **Nonadecane** |
| 11 | 12.126 | 2,6-Dimethylundecane | 32 | 17.714 | Hexadecanoic methyl ester |
| 12 | 12.521 | 5-Methyl-1,2,3,4-tetrahydronaphthalene | 33 | 18.288 | **n-Eicosane** |
| 13 | 12.720 | Unknown | 34 | 18.776 | 8,11-Octadecadienoic acid methyl ester |
| 14 | 12.787 | 6-Methyl-1,2,3,4-tetrahydronaphthalene | 35 | 18.823 | 8-Octadecenoic acid, methyl ester |
| 15 | 12.953 | **Tridecane** | 36 | 18.908 | **n-Heneicosane** |
| 16 | 13.080 | Unknown | 37 | 18.983 | 16-methyl-Heptadecanoic acid methyl ester |
| 17 | 13.375 | unknown | 38 | 19.499 | n-Docosane |
| 18 | 13.541 | unknown | 39 | 20.066 | n-Tricosane |
| 19 | 13.677 | 2,6,10-Trimethyldodecane | 40 | 20.606 | n-Tetracosane |
| 20 | 13.856 | **Tetradecane** | 41 | 21.130 | n-Pentacosane |
| 21 | 14.287 | n-Eicosanol | 42 | 21.697 | unknown |

The loss of volatile compounds as a result of the evaporation process in diesel is illustrated in figure 4.27. The dataset for numerical analysis were built using an appropriate portion of the chromatogram by selecting prominent peaks consisting of relatively higher aliphatic and aromatic hydrocarbons. This selection excluding the initial peaks not only effectively minimised the zero values in the dataset but also reflected the nature of these ignitable liquids which would be expected to be encountered in fire debris samples.

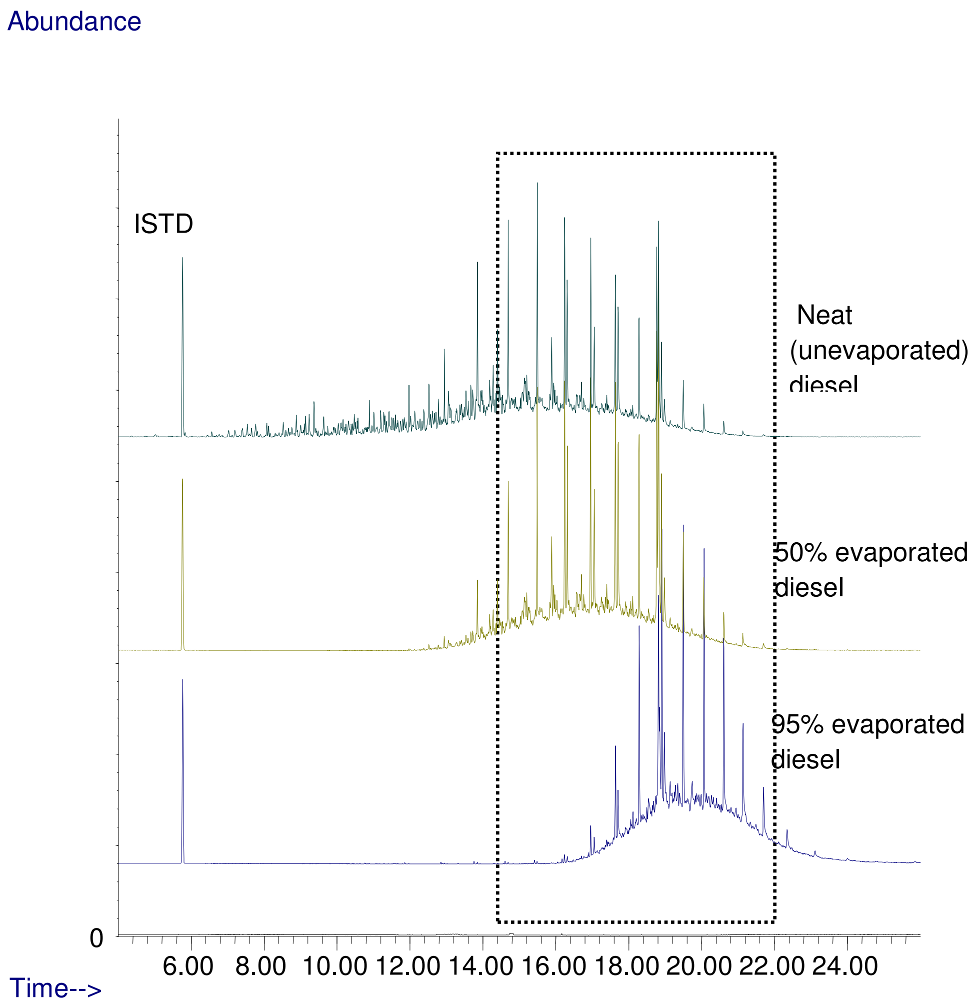


**Figure 4.27 Chromatographic pattern of neat (unevaporated) diesel and highly evaporated diesel. Partial chromatographic profile (in boxed area) showed the peaks included for multivariate analysis. Chromatographic patterns of other HPD samples are included in appendix D.**

To reveal the best grouping with regard to data pre-treatment methods, five datasets as outlined in previous sections were prepared and analysed. Of these, the sixteenth root power transformed datasets provided the best sample linkage and is discussed in the next sections. It is worth mentioning that an attempt was made to use diesel biomarkers to classify and associate the diesel samples by brand but with little success although this was suggested as a useful technique elsewhere [76-78]. Examination of chromatographic and mass spectral data for biomarkers such as adamantenes, sesquiterpanes, isomeric terpanes and monoaromatic stearenes all failed to identify their presence in the diesel samples studied.

### *4.8.4.2 PCA Classification for HPD (diesel) Samples*

The scores plot of PC1 versus PC2 for unevaporated to highly evaporated diesel samples is presented in 4.28. The two principal components described 80.73% of the variance in the dataset. Based on the score plot, PC 1 appear to described the samples based on their degree of evaporation where unevaporated or slightly evaporated samples were positioned on the negative side of PC1 and highly evaporated samples are positioned on the positive side. Although loosely scattered, two large groups are evident from the score plot, showing that PC2 is able to model diesel samples to some degree according to their brand. Tighter grouping of unevaporated to moderately evaporated diesel samples for diesel from Asda, Esso, Jet, Sainsbury and Morrison (DA, DB, DC, DD and DF respectively) are shown in negative side of PC2 (the lower left). Unevaporated to 50% evaporated Shell, Tesco and BP diesel (DE, DH and DG respectively) are loosely scattered on the upper left region of the score plot. No successful grouping or linking of highly evaporated to unevaporated diesel, in terms of its brand was achieved.

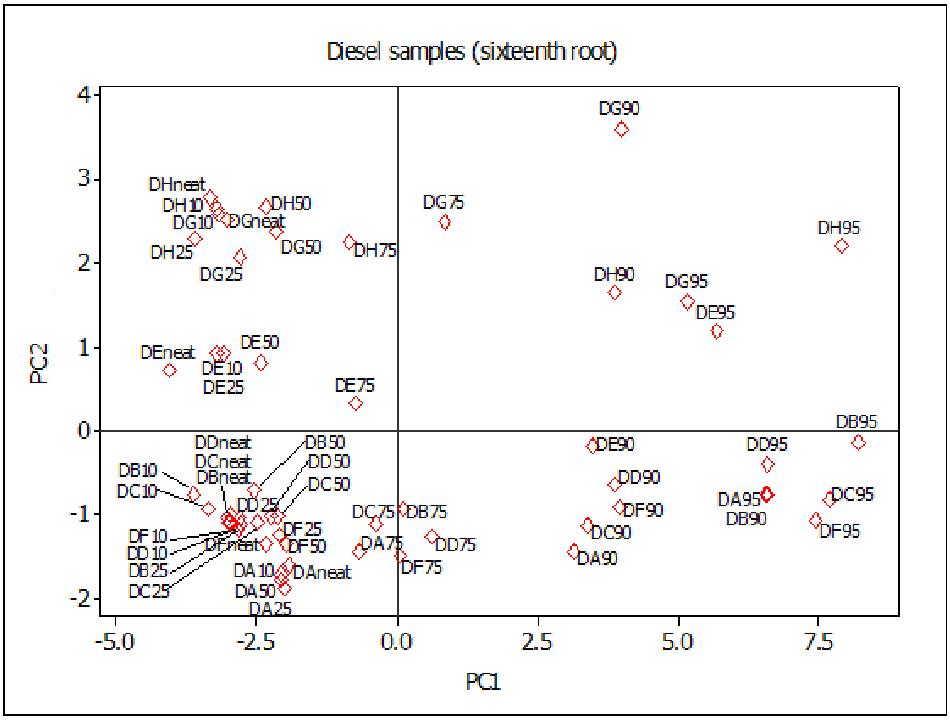


**Figure 4.28 Score plot (accounted for 72.1% and 8.63% variation in PC1 and PC2) showing the groupings of 8 diesel samples obtained from different stations. Sample codes are; DA=Diesel Asda, DB=Diesel Esso, DC=Diesel Jet, DD=Diesel Sainsbury, DE=Diesel Shell, DF=Diesel Morrison, DG=Diesel BP and DH=Diesel Tesco. The code numbering designates level of sample evaporation.**

### *4.8.4.3 HCA Classification for HPD (diesel) Samples*

The dendrogram from the sixteenth root dataset using Euclidean distance and average linkages is shown in figure 4.29. The results reveal a similar outcome to the PCA analysis. Fresh and moderately evaporated diesel samples are linked into two groups; the first group contains the ASDA (DA), Esso(DB), Jet(DC), Sainsbury (DD) and Morrison(DF) samples, and the second group contains the Shell(DE), BP(DG) and Tesco(DH) samples. When the samples were severely evaporated, all diesel samples were linked together, shown in the third level of dendrogram shown in figure 4.29.

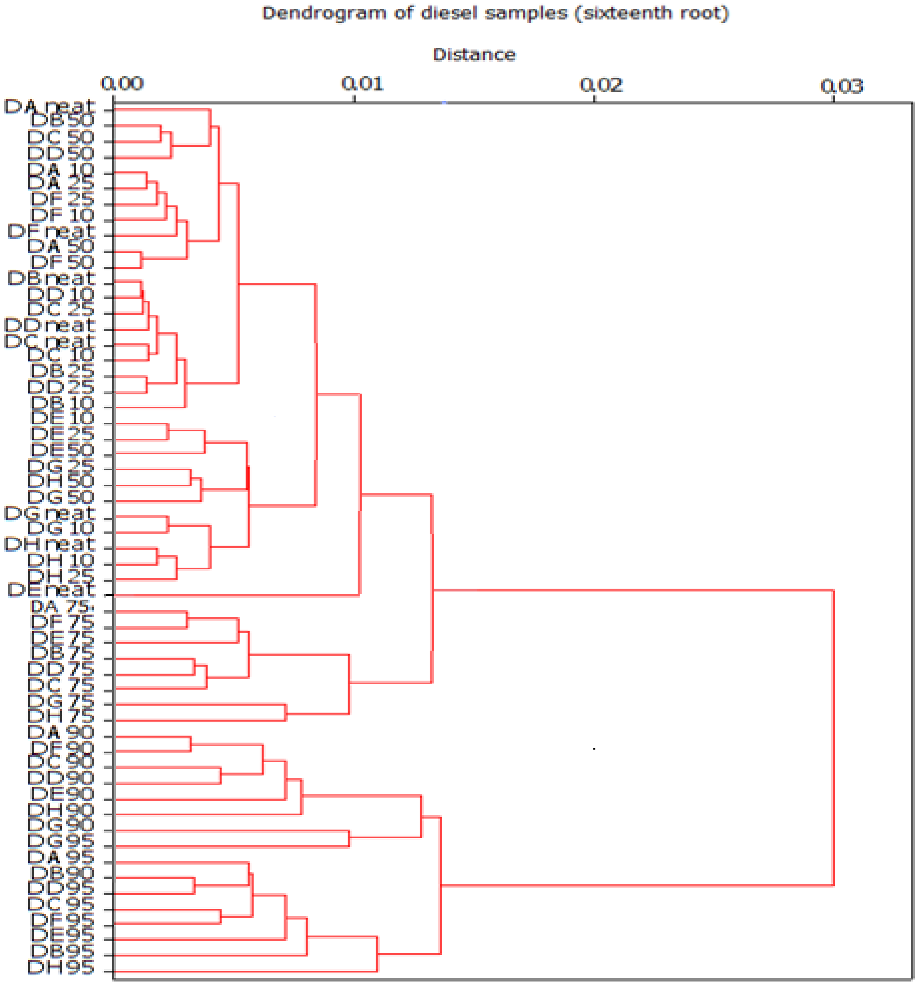


**Figure 4.29 Dendrograms showing the linking of unevaporated, moderately and severely evaporated diesel samples. Sample codes are; DA=Diesel Asda, DB=Diesel Esso, DC=Diesel Jet, DD=Diesel Sainsbury, DE=Diesel Shell, DF=Diesel Morrison, DG=Diesel BP and DH=Diesel Tesco. The code numbering designates level of sample evaporation.**

### *4.8.8.4 SOFM Classification for HPD (diesel) Samples*

In general, output maps generated from these datasets (raw to sixteenth root datasets) did not reveal any significant grouping. Results presented in figure 4.30 illustrate similar grouping patterns to those generated by PCA and HCA where the grouping in general, seemed to be made based on the degree of evaporation only. Highly evaporated samples are presented on the left side while fresh and moderately evaporated samples on the opposite side. Interestingly, evaporated and unevaporated Shell diesel (DE) is closely clustered together (highlighted in circles). Apart from that, no other meaningful or apparent clustering based on sample brands can be seen from the resulting output map.

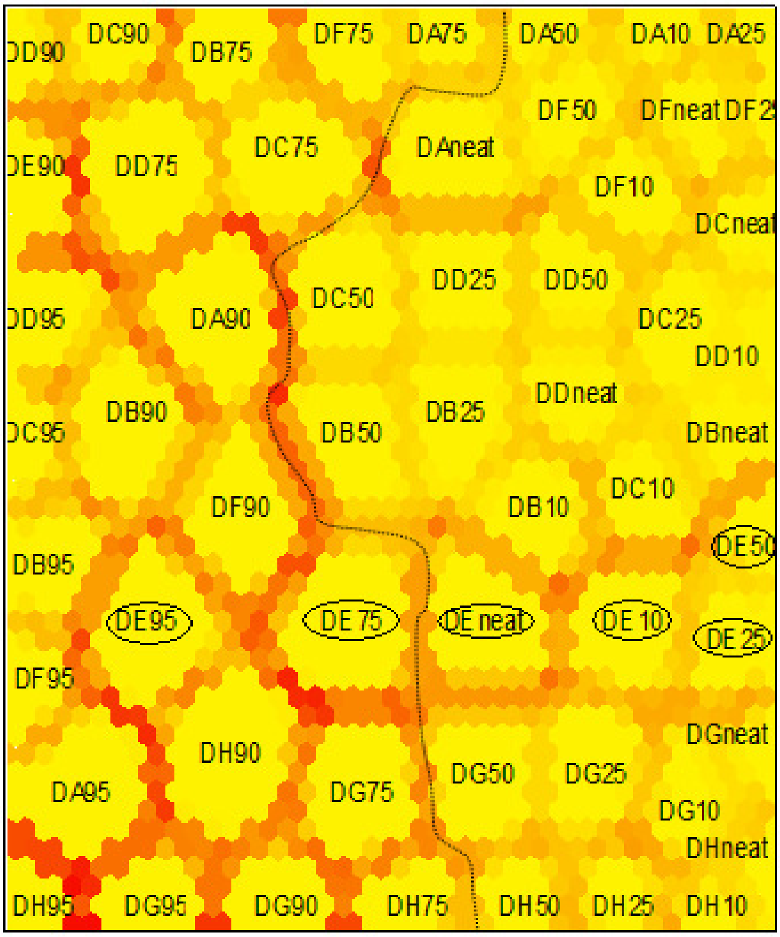


**Figure 4.30 SOFM Output map revealing no apparent groupings from neat (unevaporated) and evaporated diesel samples of different brands. Sample codes are; DA=Diesel Asda, DB= Diesel Esso, DC= Diesel Jet, DD= Diesel Sainsbury, DE= Diesel Shell, DF= Diesel Morrison, DG= Diesel BP and DH= Diesel Tesco. The code numbering designates level of sample evaporation.**

Overall, similar trends were obtained from all multivariate techniques (PCA, HCA and SOFM). These results suggest that partial chromatographic profiles consisting predominantly of aliphatic hydrocarbons are able to demonstrate some discrimination based on sample evaporation state but not sufficient to associate and individualise diesel samples according by brand. This result is in agreement with previous work carried out by Baerncopfl *et al.* in which the full total ion chromatograms and aliphatic and aromatic extracted ion profiles were examined in an attempt to associate and discriminate fresh diesel [79].

### 4.8.5 Petrol

#### *4.8.5.1Chromatographic Examination and Identification of Petrol*

The chemical composition of petrol includes compounds with a hydrocarbon range spanning C4 to C12 and are classified as an exclusive group using the current accepted classification systems [13, 80-81]. Petrol samples (figure 4.31) demonstrate very similar chromatographic pattern regardless of its grade or type, hence discrimination by grade, type or brand could be very challenging. Peak identification of petrol peaks are provided in table 4.8.

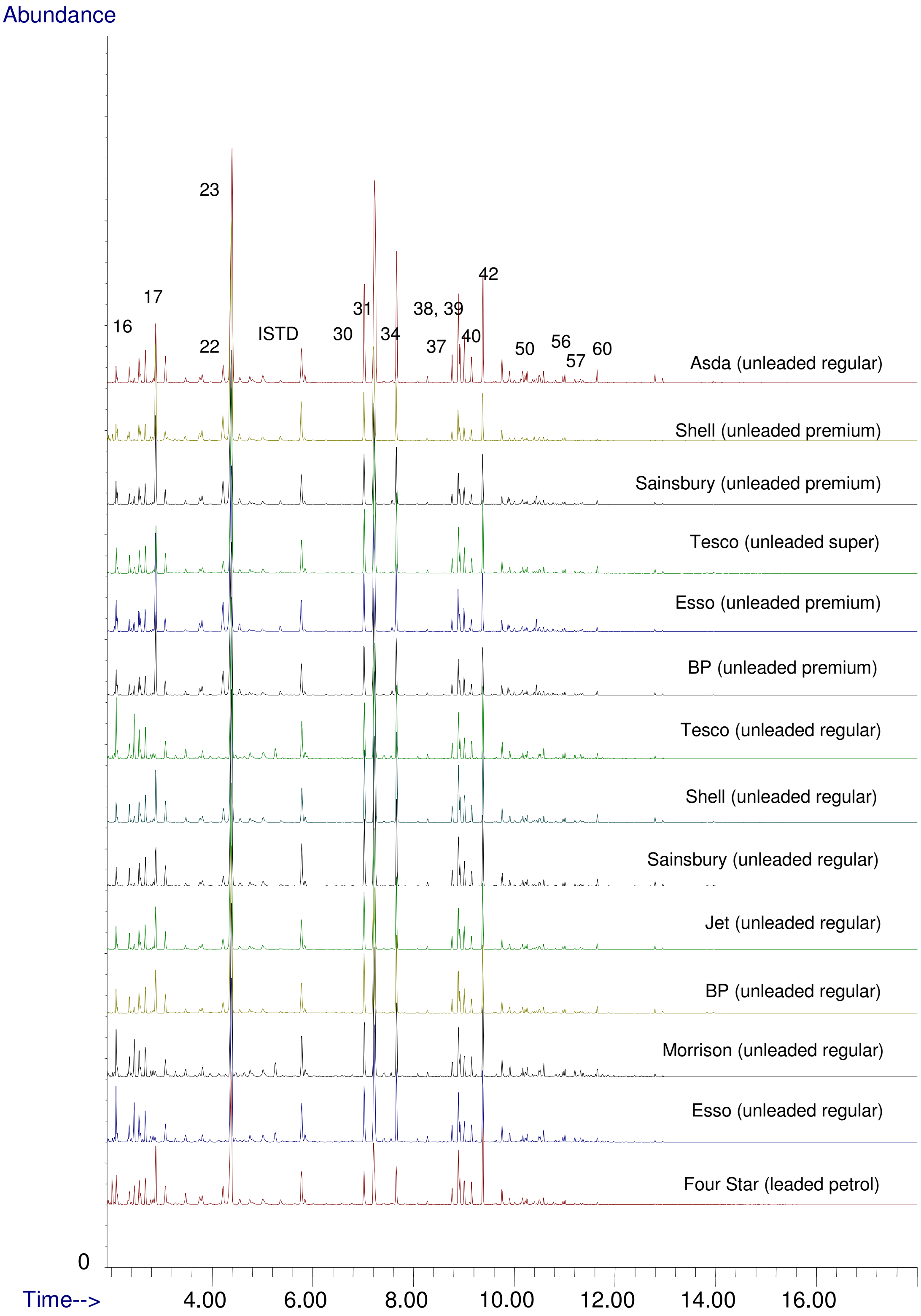


**Figure 4.31 TICs of unevaporated petrol from regular unleaded petrol, premium unleaded petrol and leaded petrol. For brevity, the prominent peaks are numbered as identified in table 4.8 accordingly as similar pattern are observed across all petrol samples.**

**Table 4.8 Peaks from petrol samples, identified using the NIST mass spectral library. Target compounds as listed in ASTM 1618 and other literature are highlighted in [1, 5].**

| No. | RT | Compound identification | No. | RT | Compound identification |
|---|---|---|---|---|---|
| 1 | 1.15 | Isobutane | 32 | 7.56 | 3-Methyloctane |
| 2 | 1.183 | Butane | 33 | 7.579 | Styrene |
| 3 | 1.249 | Ethanol | 34 | 7.662 | **o-Xylene** |
| 4 | 1.503 | 2,2-Dimethylpentane | 35 | 8.08 | Nonane |
| 5 | 1.588 | Cyclopentene | 36 | 8.277 | Isopropylbenzene |
| 6 | 1.664 | Methyl pentane | 37 | 8.768 | n-Propylbenzene |
| 7 | 1.749 | 3-Methylpentane | 38 | 8.891 | m-Ethyltoluene |
| 8 | 1.864 | Hexane | 39 | 8.921 | p-Ethyltoluene |
| 9 | 2.098 | Methylcyclopentane | 40 | 9.01 | **1,3,5-Trimethylbenzene** |
| 10 | 2.116 | 2,4-Dimethylpentane | 41 | 9.155 | o-Ethyltoluene |
| 11 | 2.358 | Benzene | 42 | 9.377 | **1,2,4-Trimethylbenzene** |
| 12 | 2.457 | Cyclohexane | 43 | 9.757 | **1,2,3-Trimethylbenzene** |
| 13 | 2.554 | 2-Methylhexane | 44 | 9.882 | 3a,4,7,7a-Tetrahydro-4,7-methanoindene |
| 14 | 2.581 | 2,3-Dimethylpentane | 45 | 9.91 | **Indane** |
| 15 | 2.677 | 3-Methylhexane | 46 | 10.009 | 2,2,4,6,6-Pentamethylheptane |
| 16 | 2.886 | 2,2,4-Trimethylpentane | 47 | 10.167 | m-Propyltoluene |
| 17 | 3.075 | Heptane | 48 | 10.218 | o-Propyltoluene |
| 18 | 3.478 | **Cyclohexylmethane** | 49 | 10.256 | 1,4-Dimethyl-2-ethylbenzene |
| 19 | 3.76 | 2,5-Dimethylhexane | 50 | 10.401 | 2,6,7-Trimethyldecane |
| 20 | 3.807 | 2,4-Dimethylhexane | 51 | 10.446 | Unknown |
| 21 | 4.222 | 2,3,4-Trimethylpentane | 52 | 10.506 | 1,3-Dimethyl-4-ethylbenzene |
| 22 | 4.277 | 4,4-Dimethylcyclopentane | 53 | 10.585 | m-Isopropyltoluene |
| 23 | 4.386 | **Toluene** | 54 | 10.661 | 5-Ethyldecane |
| 24 | 4.472 | 2,2,4-Trimethyl-3-pentane | 55 | 10.775 | Decahydro-2-naphthalenol |
| 25 | 4.551 | 2,3-Dimethylhexane | 56 | 10.968 | **1,2,4,5-Tetramethylbenzene** |
| 26 | 5.01 | 3-Methylheptane | 57 | 11.007 | **1,2,3,5-Tetramethylbenzene** |
| 27 | 5.26 | 2,3,4-Trimethyl-2-pentene | 58 | 11.205 | 3,4-Dimethylstyrene |
| 28 | 5.362 | 2,2,5-Trimethylhexane | 59 | 11.358 | Unknown |
| 29 | 5.844 | Octane | 60 | 11.649 | **Naphthalene** |
| 30 | 7.022 | Ethylbenzene | 61 | 12.797 | **2-Methylnaphthalene** |
| 31 | 7.226 | **m,p-Xylene** | 62 | 12.951 | **1-Methylnaphthalene** |

Changes in the petrol chromatogram can be quite dramatic, particularly after 50% evaporation (figure 4.32). This provides significant challenges to the selection of compounds for inclusion into a data matrix for subsequent multivariate analysis. Example of peaks that appeared consistently in the unevaporated samples through to the most unevaporated samples was chosen for inclusion in subsequent data analysis as shown by represented chromatograms in figure 4.32.

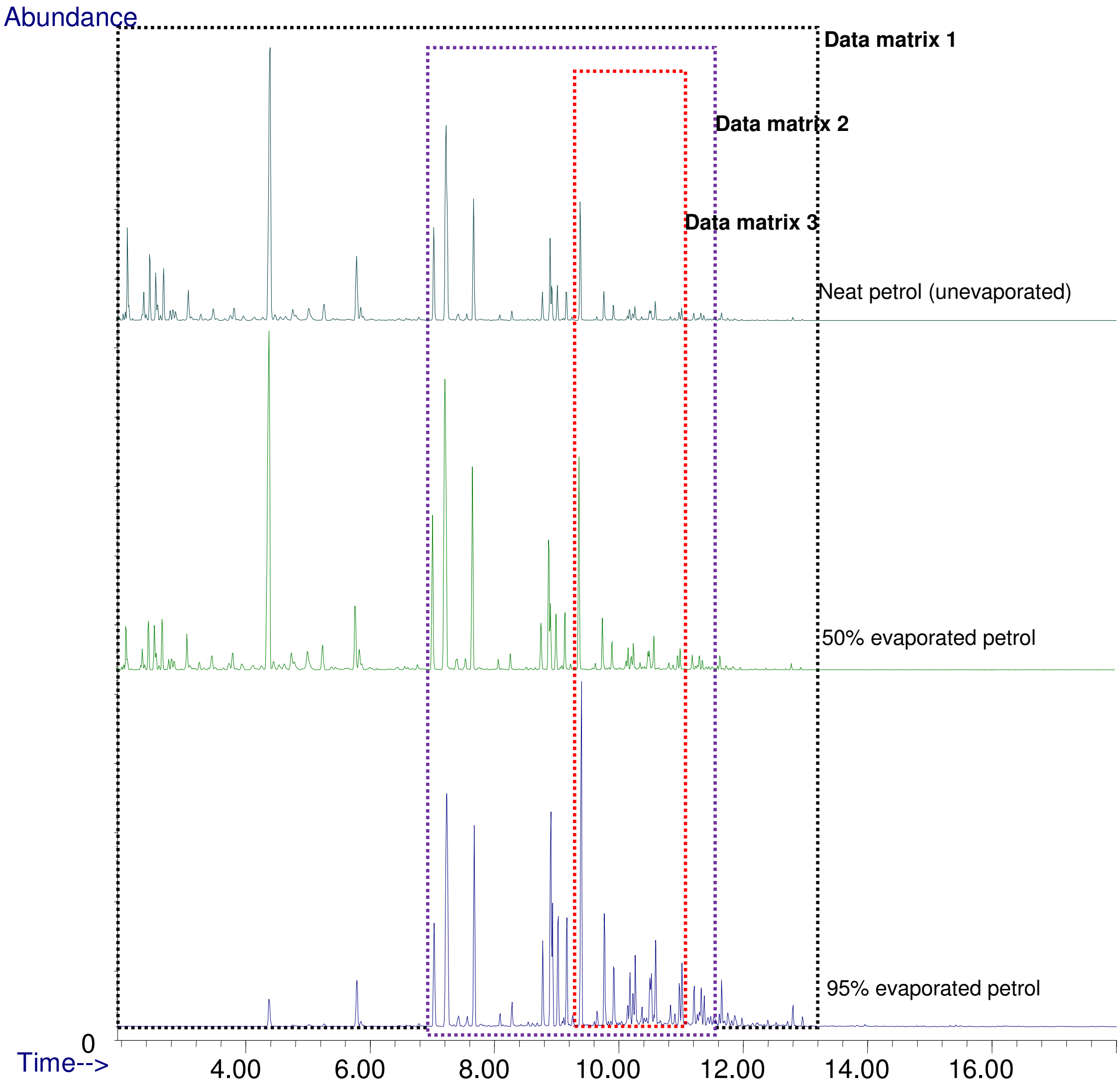


**Figure 4.32 Zoomed TICs showing an example of pattern shift as petrol gradually evaporates. Data matrices strategies are highlighted to illustrate full, partial and extracted ion chromatogram region for PCA, HCA and SOFM analysis.**

#### *4.8.5.2 Petrol Data Matrices*

Total ion chromatograms of 98 samples (all of the unevaporated and evaporated samples for each petrol brand) were manually aligned and visually compared for peak selection. As before, the best discrimination was obtained where the data was pre-processed using the sixteenth root power transformation.

Initially, a total of 62 components were selected from the full chromatographic profile of unevaporated and evaporated petrol for inclusion into the data matrices (labelled as data matrix 1 in figure 4.32).

A second data set (data matrix 2 in figure 4.32) consisting of compounds with peaks in the range of 7.00 to 12.00 minutes were selected because this region includes the C2-alkylbenzenes to C4-alkylbenzenes. This region has been reported as relatively more persistent when petrol evaporates and is often used for the identification of petrol in a sample [13, 51, 82]. Compound identification is provided in table 4.8.

A third data matrix (labelled as data matrix 3 in figure 4.32) was studied using the indane extracted ion chromatogram profile to assess if classification could be improved using more persistent compounds. Previous studies suggested using compounds such as poly aromatic hydrocarbons and diamondoid compounds to link petrol samples to source [51-53, 83-85]. Structurally, indanes are the unsaturated hydrocarbon compound of benzene fused with 5-membered ring compounds with high boiling points properties (181°C) thus, are relatively resistant to evaporation [86]. Investigating extracted ion profiles of indane compounds has previously been suggested [5, 87]. An example of the indanes extracted ion profile (m/z 117,118,131 and 132) and peak identification (with reference to mass spectral library) is shown in figure 4.33 [73]. In this study however, indane profile provided very limited variables and many of the compounds abundance were below 15 threshold limit.

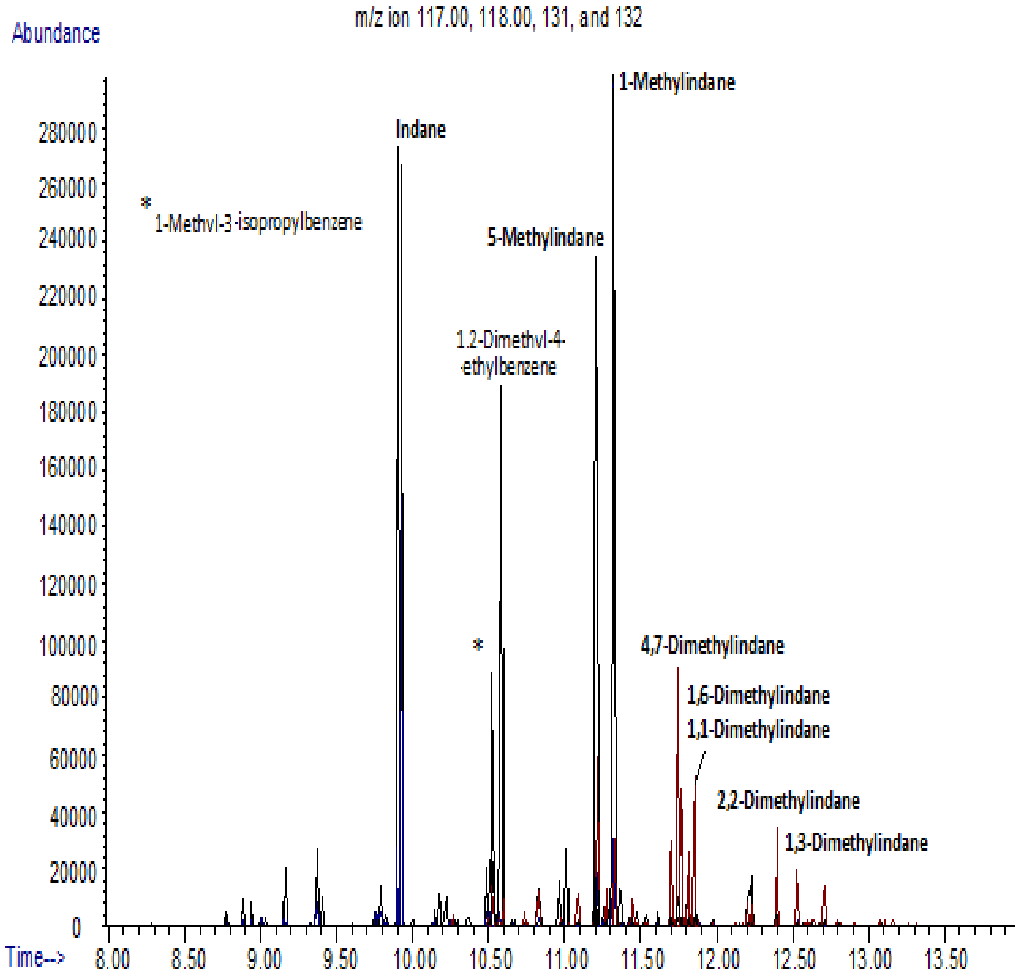


**Figure 4.33 EIP of indane from petrol sample.**

### *4.8.5.3 PCA Classification for Petrol Samples*

When PCA was applied to the sixteenth root power transformed data from data matrix 1 (98 samples x 62 compounds), no useful groupings or discrimination of leaded, regular and premium unleaded petrol were in evidence. PC1 described the positive and negative correlation of unevaporated and highly evaporated petrol samples respectively while PC 2 separates Tesco, Asda and Morrison (M, N and P) of regular grade from the rest of the petrol samples. The scores plot (figure 4.34) represents 71.0% of the variation in the dataset but did not show any clear groupings or discrimination of petrol samples based on individual brands.

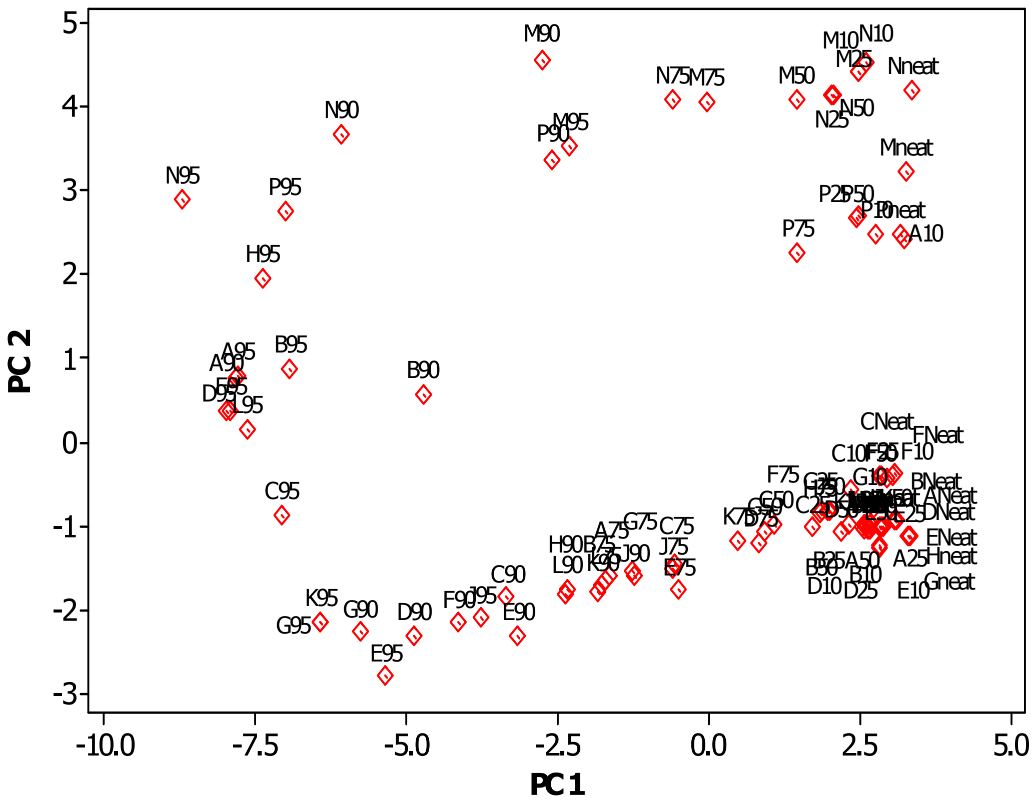


**Figure 4.34 Scores plot of full chromatographic profiles (data matrix 1) of unevaporated and evaporated samples from 14 petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation.**

Using data matrix 2 (the C2 to C4 alkylbenzene range – 98 samples x 31 compounds), improved sample grouping as shown in figure 4.35. In this case the score plot of the first two PCs accounted for 88% variation in the dataset. Discrimination of samples from Asda regular (N), Tesco regular (M), Sainsbury regular (J), Shell premium (E) and Tesco super (C) have all been achieved while Morrison regular (P) and Four star leaded (F) samples are grouped together. Two convoluted groups were observed containing seven petrol brands BP, Shell and Esso (G, K, and H respectively, all regular petrol) and BP, Esso, Sainsbury and Jet (A, B, D (all premium grade) and L (regular) respectively.

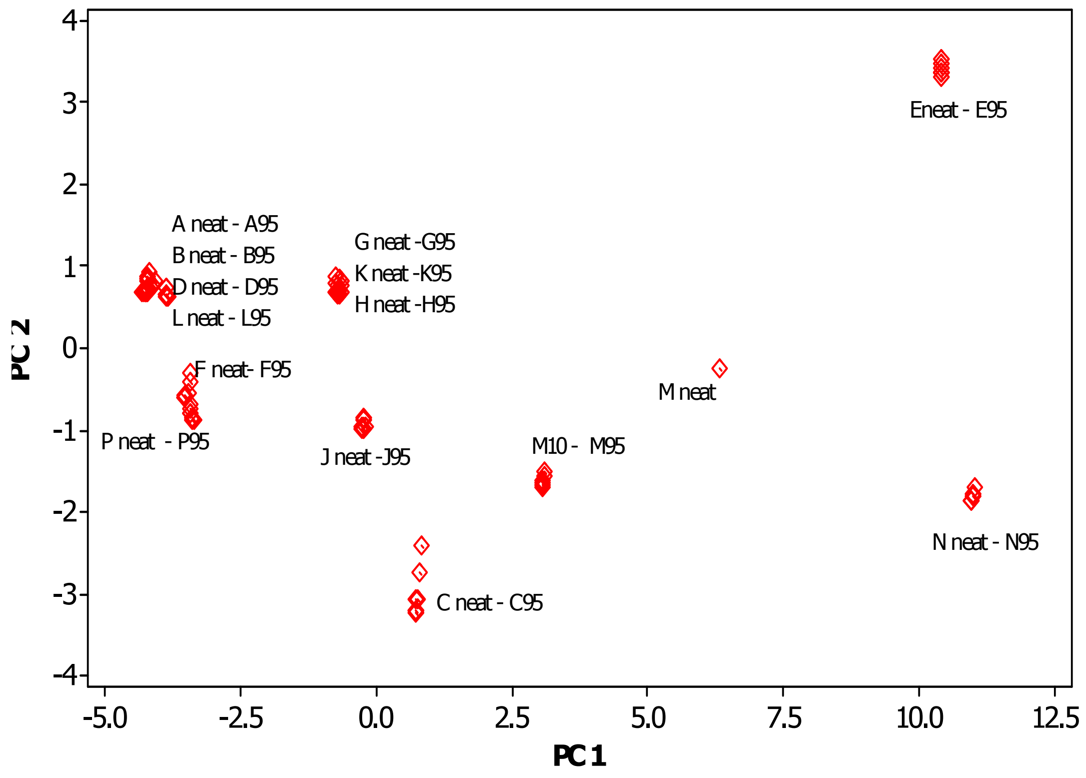


**Figure 4.35 Scores plot of C2-C4 alkylbenzenes region (data matrix 2) of neat (unevaporated) and evaporated constituents from 14 petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation.**

These results are in agreement with the earlier work of Sandercock and Pasquier which suggested similar classification trends for regular and premium petrol grades [51-53]. Some researchers suggest a peak ratio approach which may also be used to differentiate petrol grades [16, 88].

PCA of the indane extracted profiles showed similar but much improved clustering as the overall TIC profiles (data matrix 1). The clustering of two major groups is more prominent where the Tesco, Asda and Morrison regular (M, N and P respectively) samples were grouped on the upper right corner while other samples were grouped in the lower region (figure 4.36). Individualisation of petrol samples based on indanes profiles was not achieved.

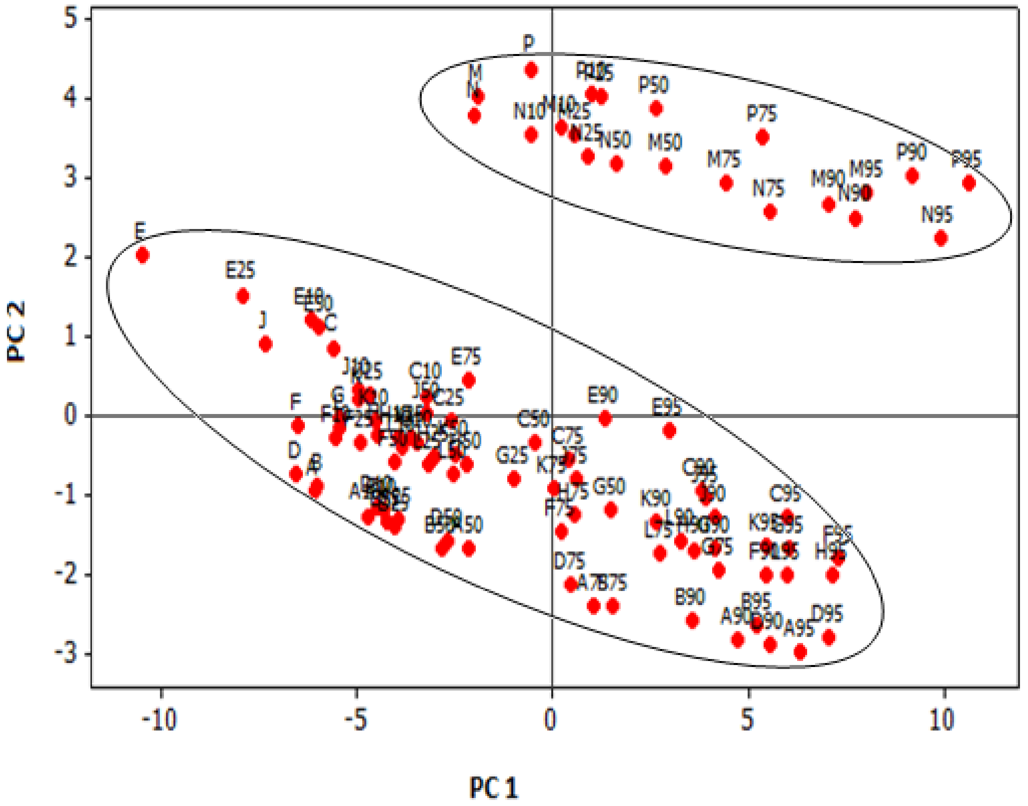


**Figure 4.36 Score plot of indanes profile of 14 neat (unevaporated) and evaporated petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation.**

### *4.8.5.4 HCA Classification for Petrol Samples*

HCA results of data matrix 1 demonstrated similar results to the respective PCA analysis. HCA was performed by Euclidean distance, average linkage and the resulting dendrogram was examined for accurate clustering according to type and brand as shown in figure 4.37.

No substantial clustering on the basis of petrol type or brand was revealed however the HCA dendrogram demonstrated a linkage of the samples according to their degree of evaporation.

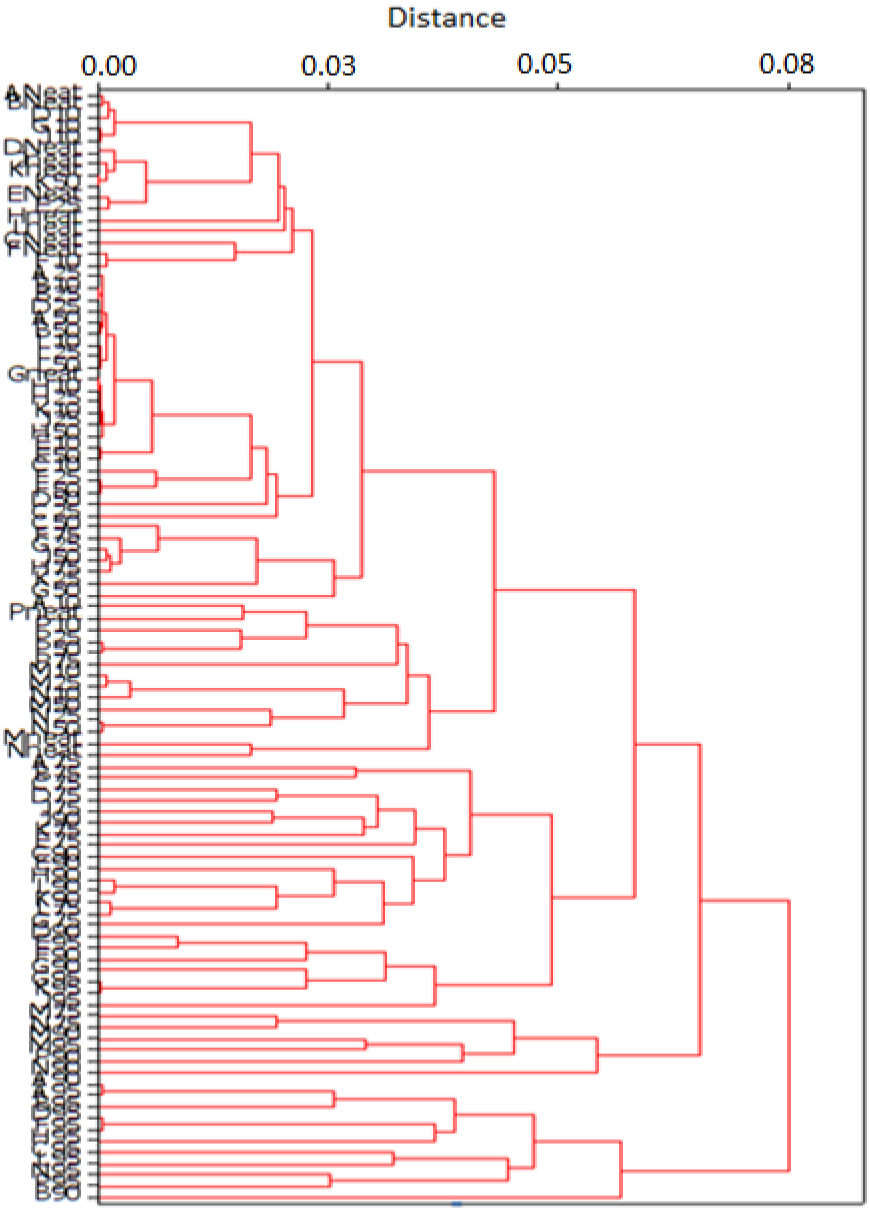


**Figure 4.37 Dendrogram of full TIC chromatogram (data matrix 1) consisting of 14 petrol samples Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BP regular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation.**

HCA was also performed for data matrix 2 by Euclidean distance and average linkage. The resulting dendrogram is presented in figure 4.38. Distinctive clustering of unevaporated to highly evaporated petrol according to brand for some petrol samples is evident. Premium graded petrol from BP, Esso and Sainsbury (A, B and D respectively) were clustered together with Jet regular (L) while BP regular, Esso regular and Shell regular (G, H and K respectively) samples were linked to sample F which was a leaded petrol sample.

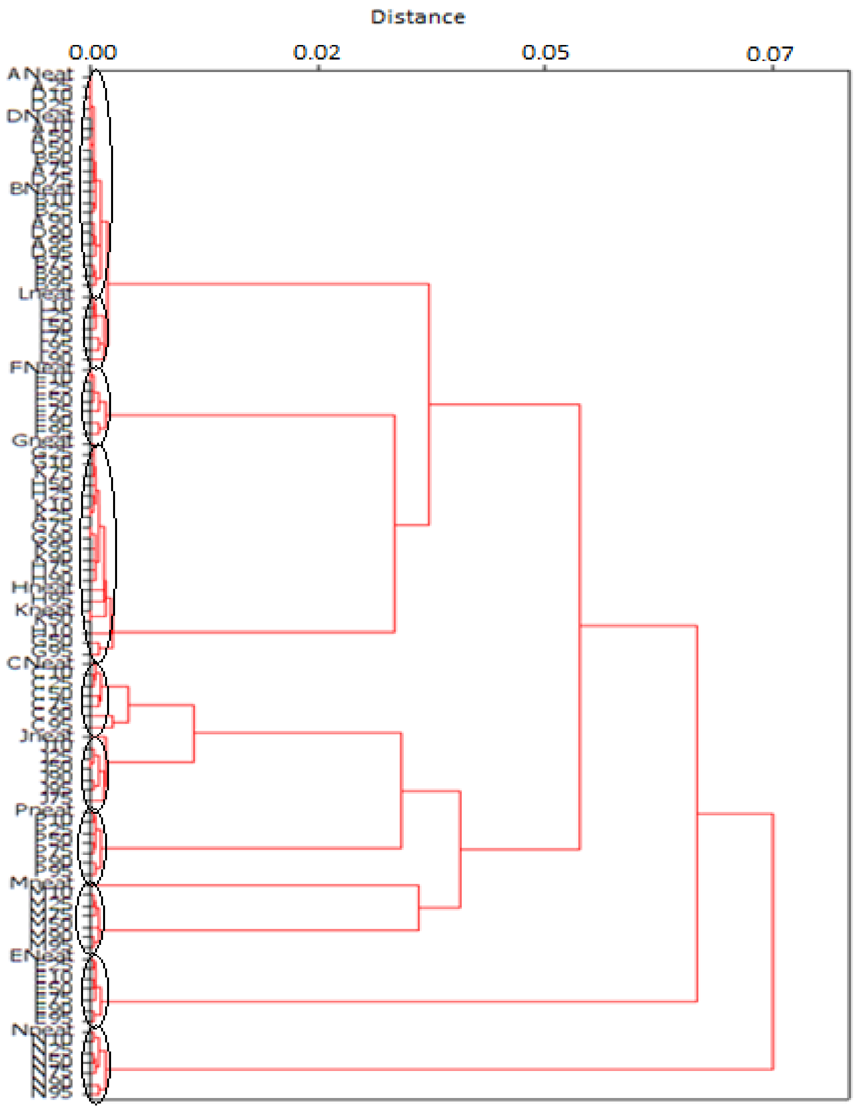


**Figure 4.38 Dendrogram of C2-C4 alkylbenzenes region of neat (unevaporated) and evaporated constituents from 14 petrol samples Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation.**

Results linking premium and regular grades obtained from supermarket fuel stations for example Tesco premium (C) and Sainsbury regular (J), suggest that these samples could have come from the same source. Because information was not available about the distribution lines of these samples within the sampling area, this assumption cannot be verified.

HCA results for data matrix 3, the indane profiles are presented in figure 4.39 but did not reveal any new or more meaningful grouping regarding petrol grades or brand.

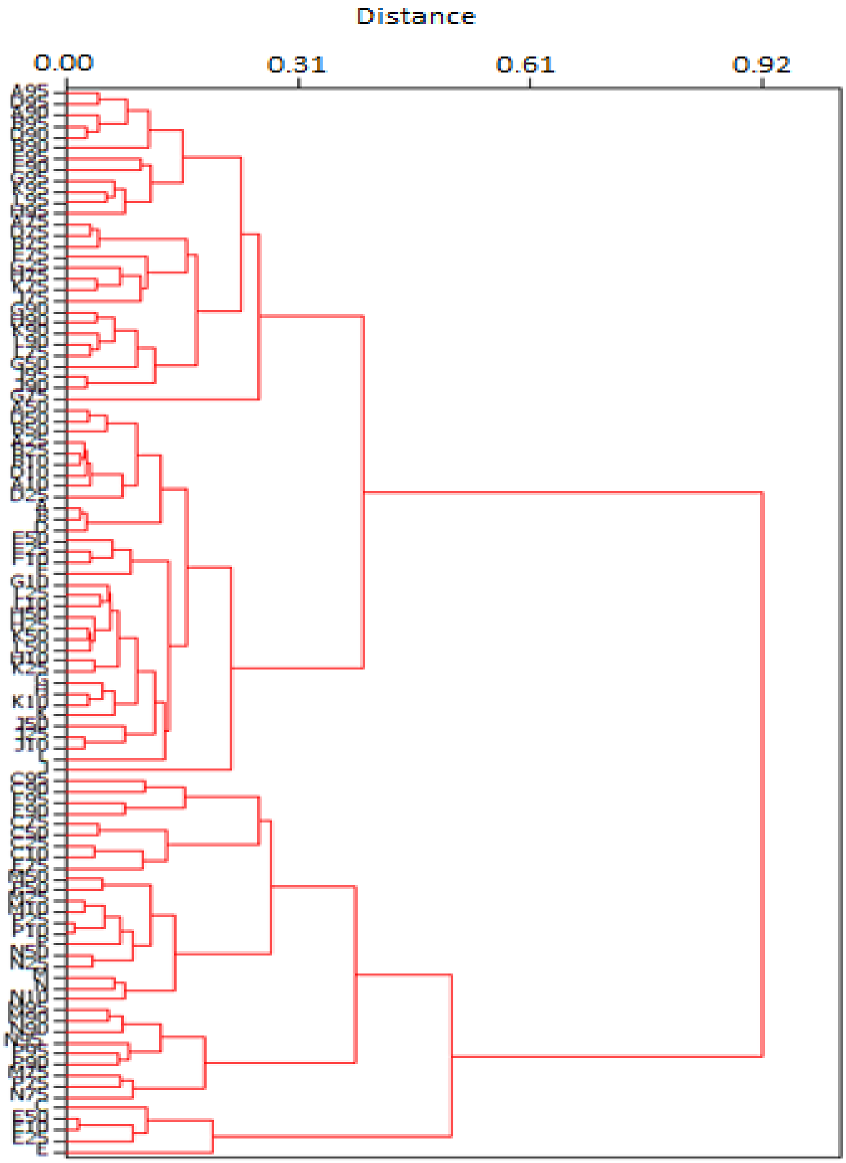


**Figure 4.39 Dendrogram of indane profiles of neat and weathered constituents from 13 unleaded and 1 leaded petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation.**

### *4.8.5.5 SOFM Classification for Petrol Samples*

Similar trends were observed for SOFM analysis as for PCA and HCA when data matrix 1 was examined where most of the highly evaporated samples were placed next to each other in the lower left region for SOFM map shown in figure 4.40.

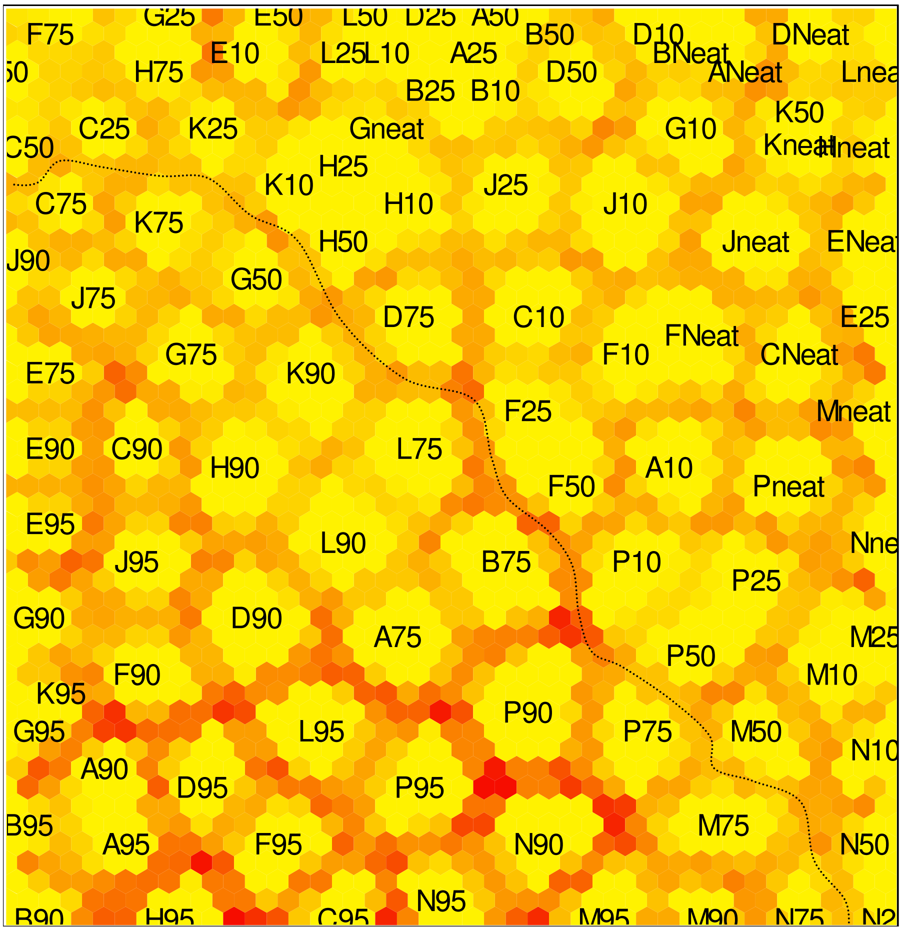


**Figure 4.40 U-matrix of SOFM of the samples using full chromatographic profiles of neat (unevaporated) and evaporated constituents from 14 petrol samples Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation.**

Much better discrimination was obtained when using data matrix 2 (figure 4.41) and differentiation of 7 petrol brands was achieved. These included Tesco super, Shell premium, Four Star leaded, Sainsbury regular, Tesco regular, Asda regular and Morrison regular (C, E, F, J, M, N and P respectively) samples with clear boundaries between the groups. SOFM associated the evaporated samples with their unevaporated counterparts in each case.

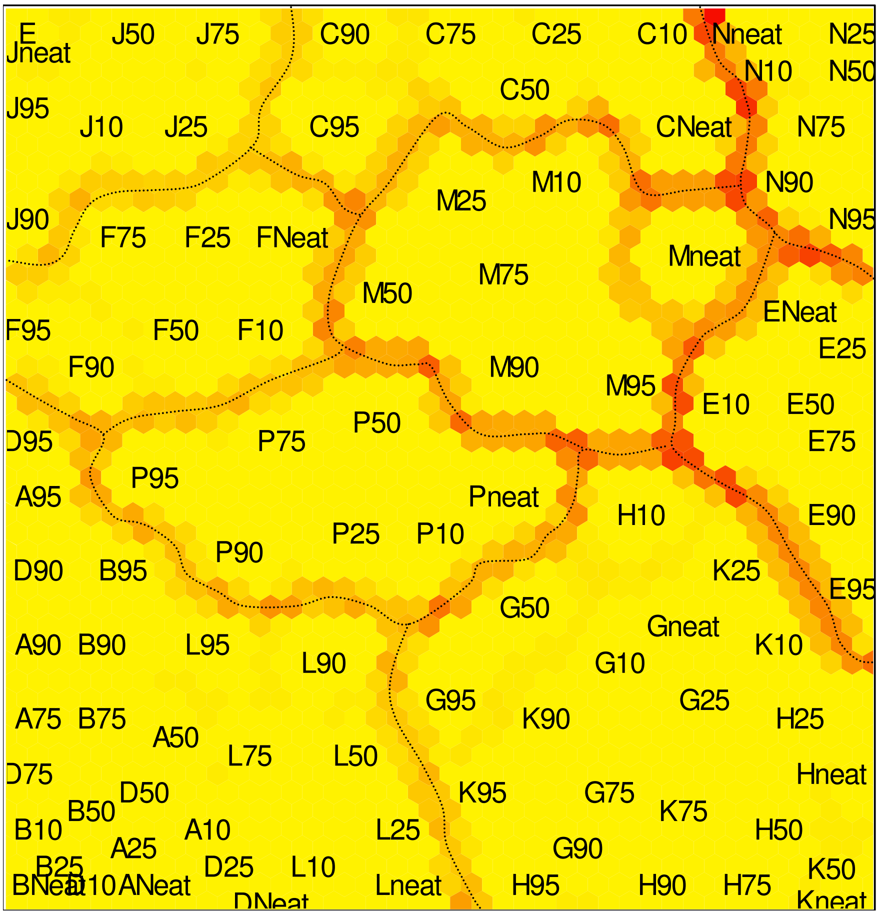


**Figure 4.41 SOFM U-matrix map of C2 to C4 alkylbenzenes profile of neat (unevaporated) and evaporated constituents of 14 petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation. Black lines emphasises sample groupings.**

Similar trends to those observed with PCA and HCA were also observed in the SOFM mapping. Sample BP premium, Esso premium, Sainsbury premium and Jet regular (A, B, D and L respectively) are grouped together while sample BP regular, Esso regular and Shell regular (G, H and K) also formed one group.

The SOFM output map (figure 4.42) for the indane profile classified petrol samples into 3 groups, showing a significant improvement compared to PCA (with only two vague clusters) and HCA. The first group consisted of regular petrol from Tesco, Asda and Morrison (M, N and P respectively), the second grouped samples of Tesco super (C) and Shell premium (E) together and the third group contained all of the other samples. Nonetheless, indane profile also demonstrates that the overall trend of segregation between unevaporated and evaporated sample is still prominent across the map (i.e. samples with similar evaporation level were closely mapped). No definite association of petrol samples with regard to brand was possible with this data set and the indane profile alone is not sufficient for the classification and discrimination of petrol samples.

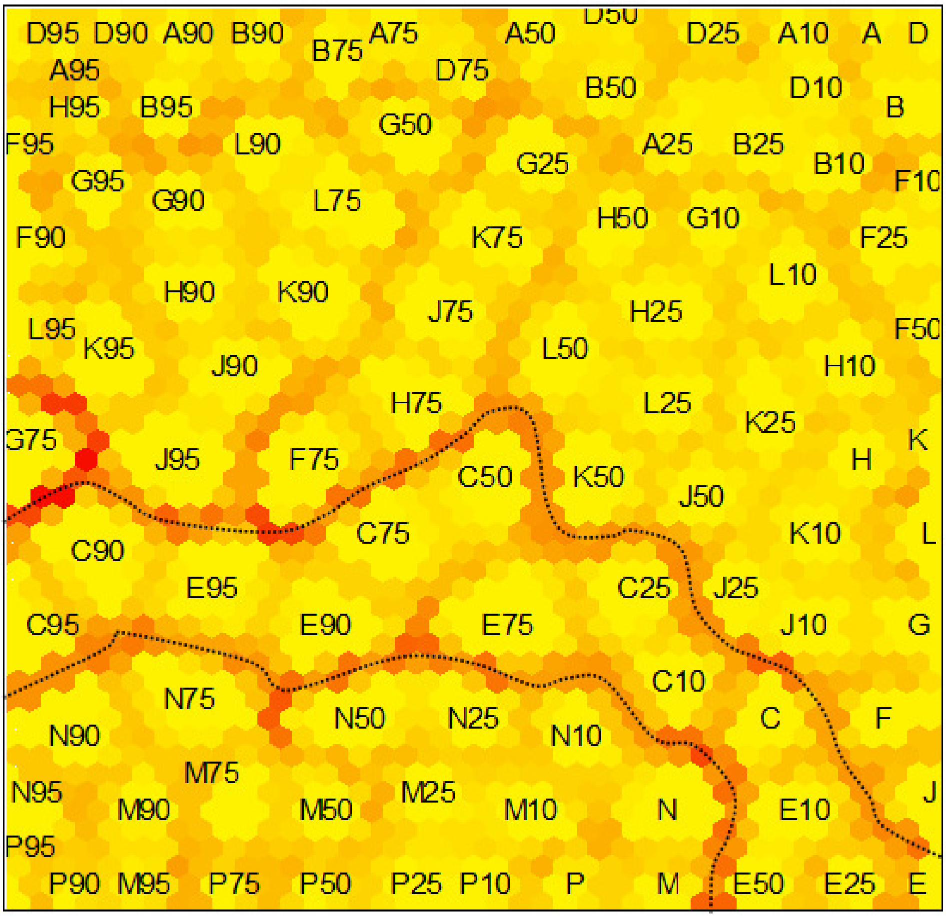


**Figure 4.42 SOFM U-matrix map of indane profiles of neat (unevaporated) and evaporated constituents from 14 petrol samples. Sample codes are; A=BP premium, B=Esso premium, C=Tesco super, D=Sainsbury premium, E=Shell premium, F=Four Star leaded, G=BPregular, H=Esso regular, J=Sainsbury regular, K=Shell regular, L=Jet regular, M=Tesco regular, N=Asda regular and P=Morrison regular. The code numbering designates level of sample evaporation.**

### 4.8.6 Multivariate Analysis of Combined Ignitable Liquid Samples

Aligned chromatograms representing all the sample classes of unevaporated, moderately evaporated and highly evaporated forms is shown in figure 4.43 to figure 4.45 respectively. Initially, the chromatographic patterns are readily distinguished across unevaporated and moderately evaporated samples. In petrol samples especially, further evaporation significantly shifted the abundances of higher hydrocarbon compounds, hence its chromatographic pattern became increasingly similar to MPD chromatographic pattern of the same region (figure 4.45) i.e the white spirit and paintbrush cleaners. The chromatograms for other samples remain distinguished.

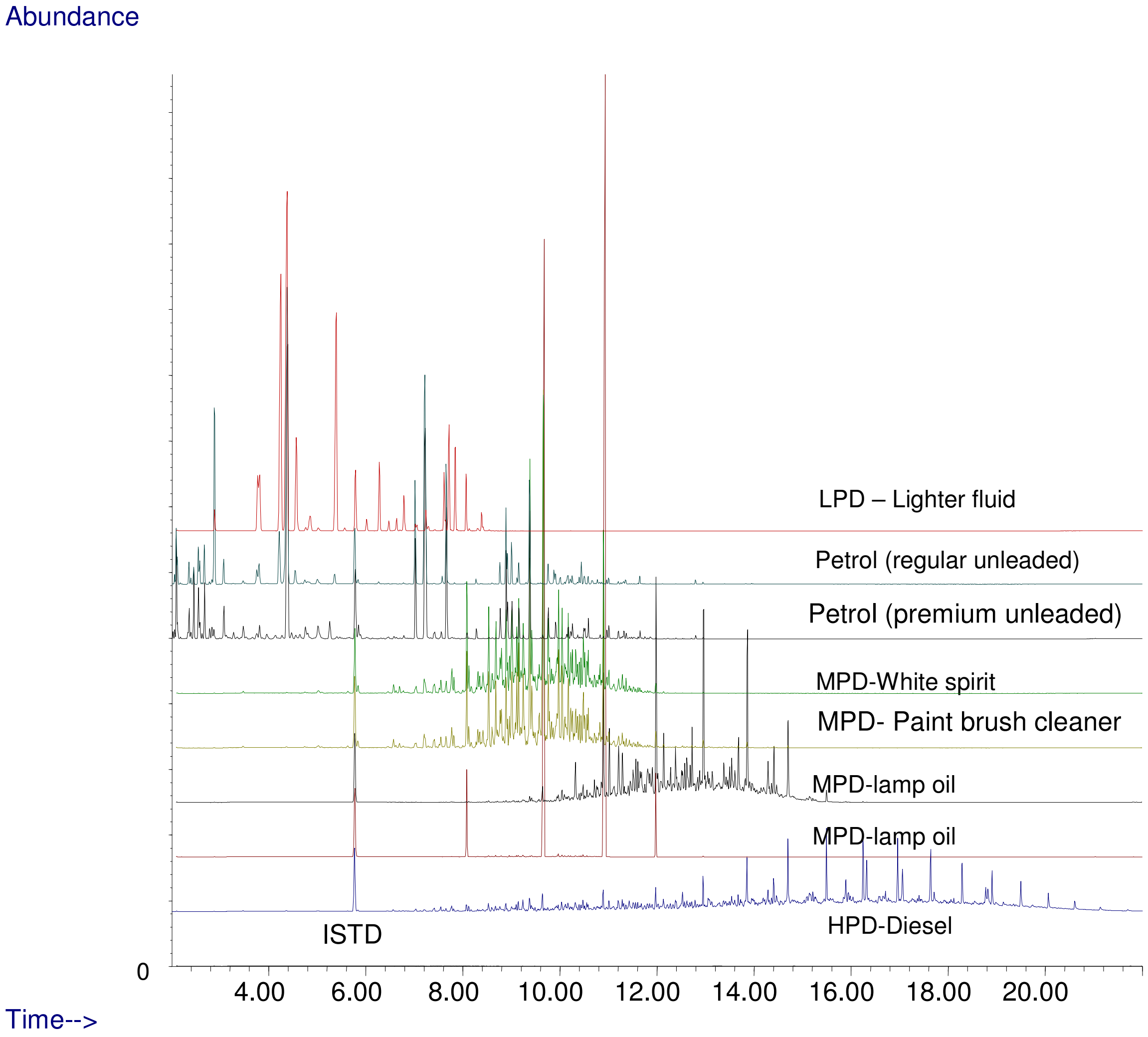


**Figure 4.43 Representative TICs of unevaporated ignitable liquid samples- of the LPD, MPD, HPD and petrol samples.**

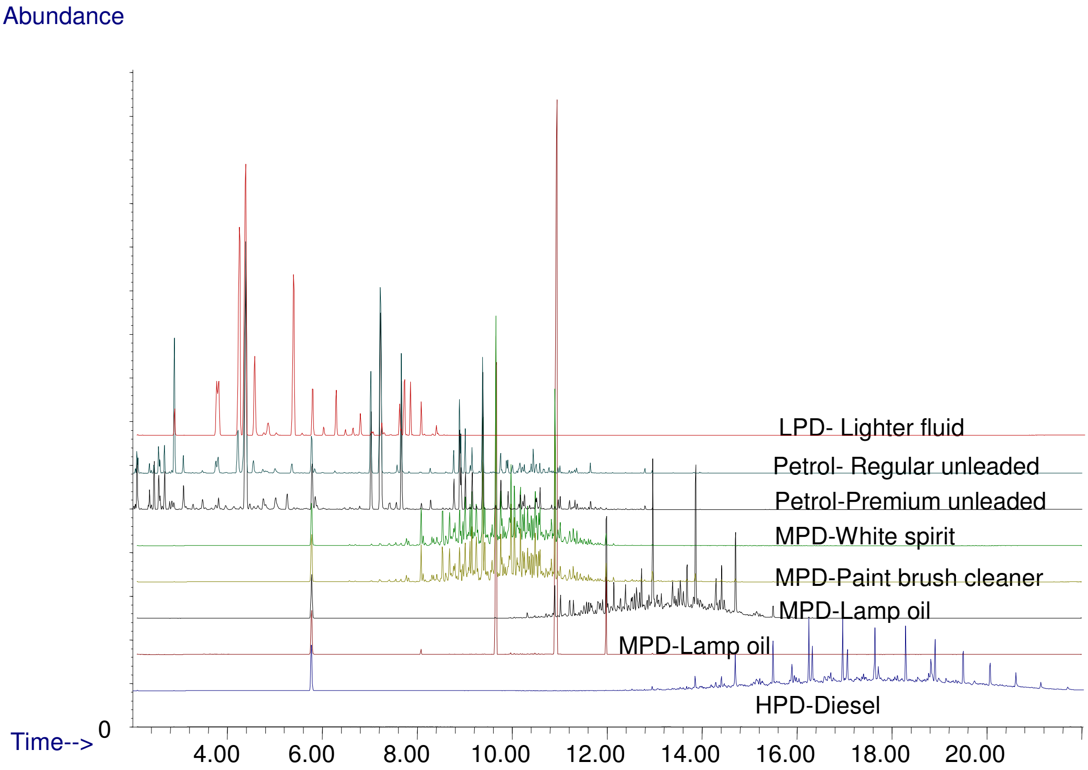


**Figure 4.44 Representative TICs of moderately evaporated (50%) ignitable liquid samples- of the LPD, MPD, HPD and petrol samples.**

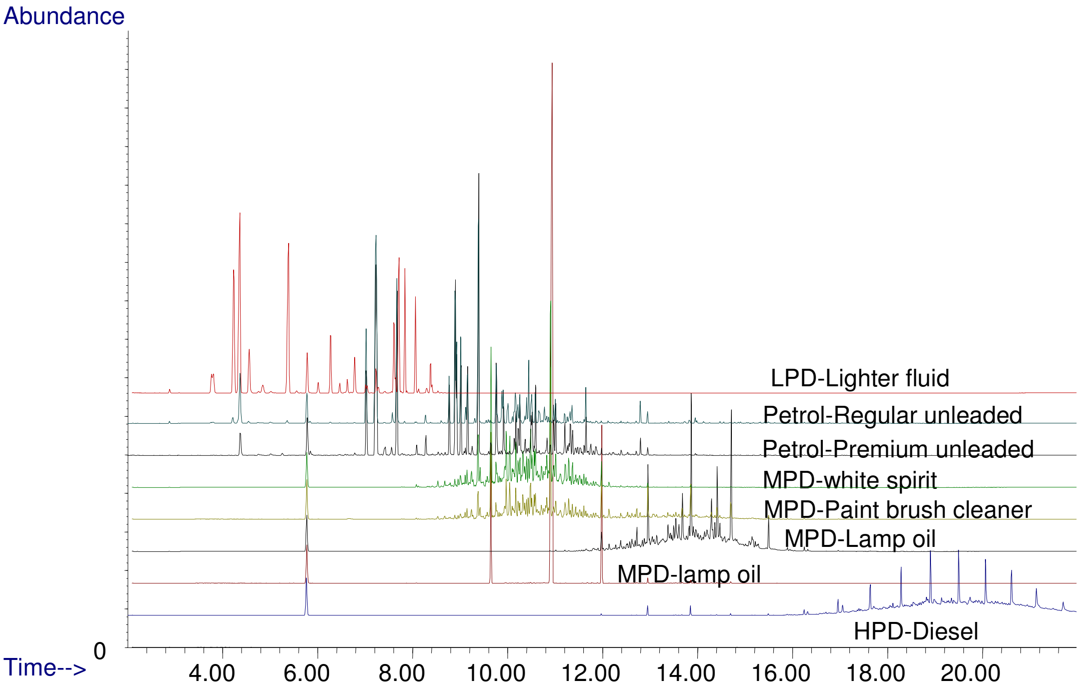


**Figure 4.45 Representative TICs of highly evaporated (95%) ignitable liquid samples of the LPD, MPD, HPD and petrol samples.**

Based on initial results obtained, a combined data matrix was selected from the full chromatogram for LPD samples while partial chromatograms of petrol, diesel and MPD samples were used. Finally, the combined datasets were pre-processed with the sixteenth root power transformation. Although results in section 4.8.2 have demonstrated that fourth root data pre-treatment is sufficient and successfully individualised LPD samples, the corresponding dataset was further transformed to sixteenth root to exercise uniform data pre-treatment technique across all samples within the combined data matrix. The applicability of this strategy to correctly classify or discriminate ignitable liquid samples across wider sample class was evaluated using PCA, HCA and SOFM.

#### *4.8.6.1 PCA Classification*

The PCA score plot accounted for 72.1% of the total variance within the dataset. As shown in figure 4.46, the score plot revealed good clustering of the ignitable liquid samples into their respective classes. A very tight clustering, showing overlapping of the samples of different grade and brands is observed for petrol and diesel groups as such the discrimination of individual samples by brand was not demonstrated. Clustering for LPD and MPD are relatively loose where grouping are based on type and brand are evident for LPD lighter fluids and MPD lamp oil samples. White spirits and paint brush cleaners of MPD samples however are position very closely to each other (convoluted) thus individualisation based on brand is also not possible.

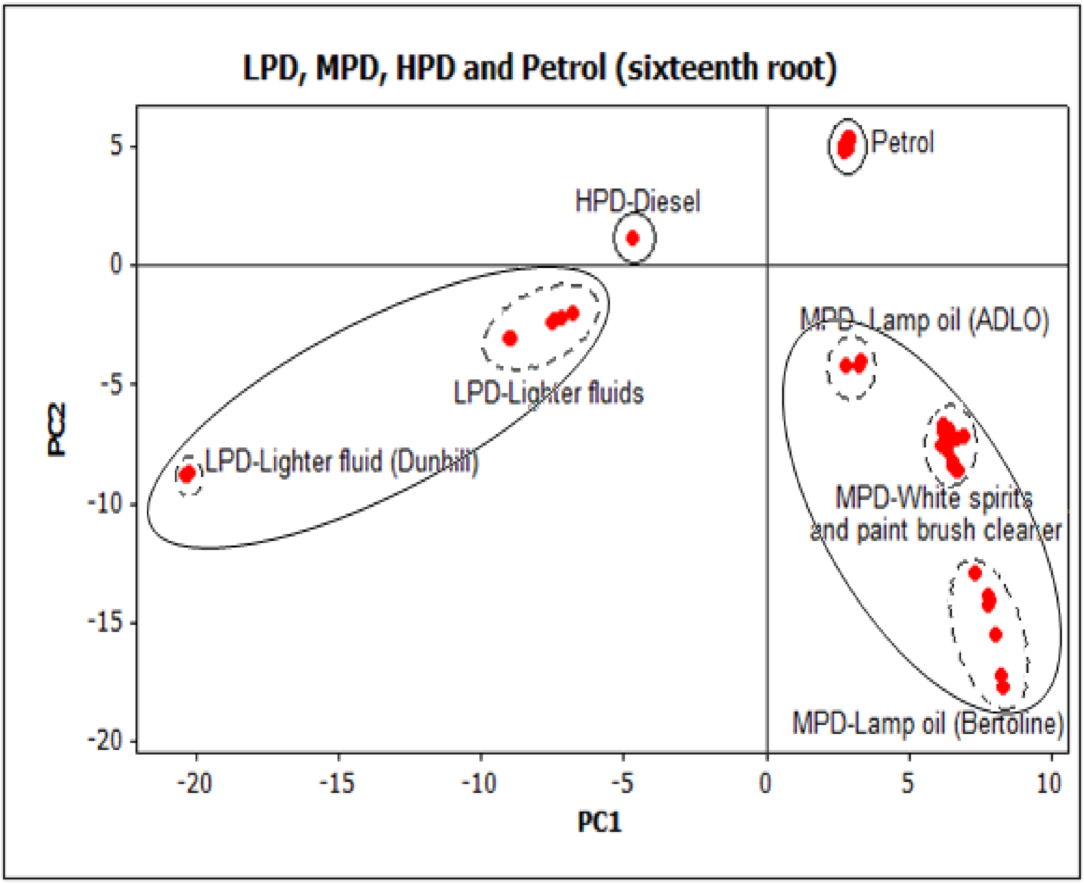


**Figure 4.46 Score plot of PC1 and PC2 for the combined data matrix of petrol and petroleum distillate products.**

### *4.8.6.2 HCA Classification*

For HCA of combined data matrix, the best linkage is revealed using the average linkages strategy. Dendrograms shown in figure 4.47 reveal that apart from ADLO lamp oil, samples within petrol, HPD and MPD are closely linked (based on close distance) and Zippo lighter fuel are distanced from other LPD samples. Apart from these two sample sets, the linkages between evaporated and unevaporated samples from common origin (based on type) were demonstrated in LPD, MPD and petrol samples such as shown previously.  Overall, HCA result reveals better classification as opposed to PCA.

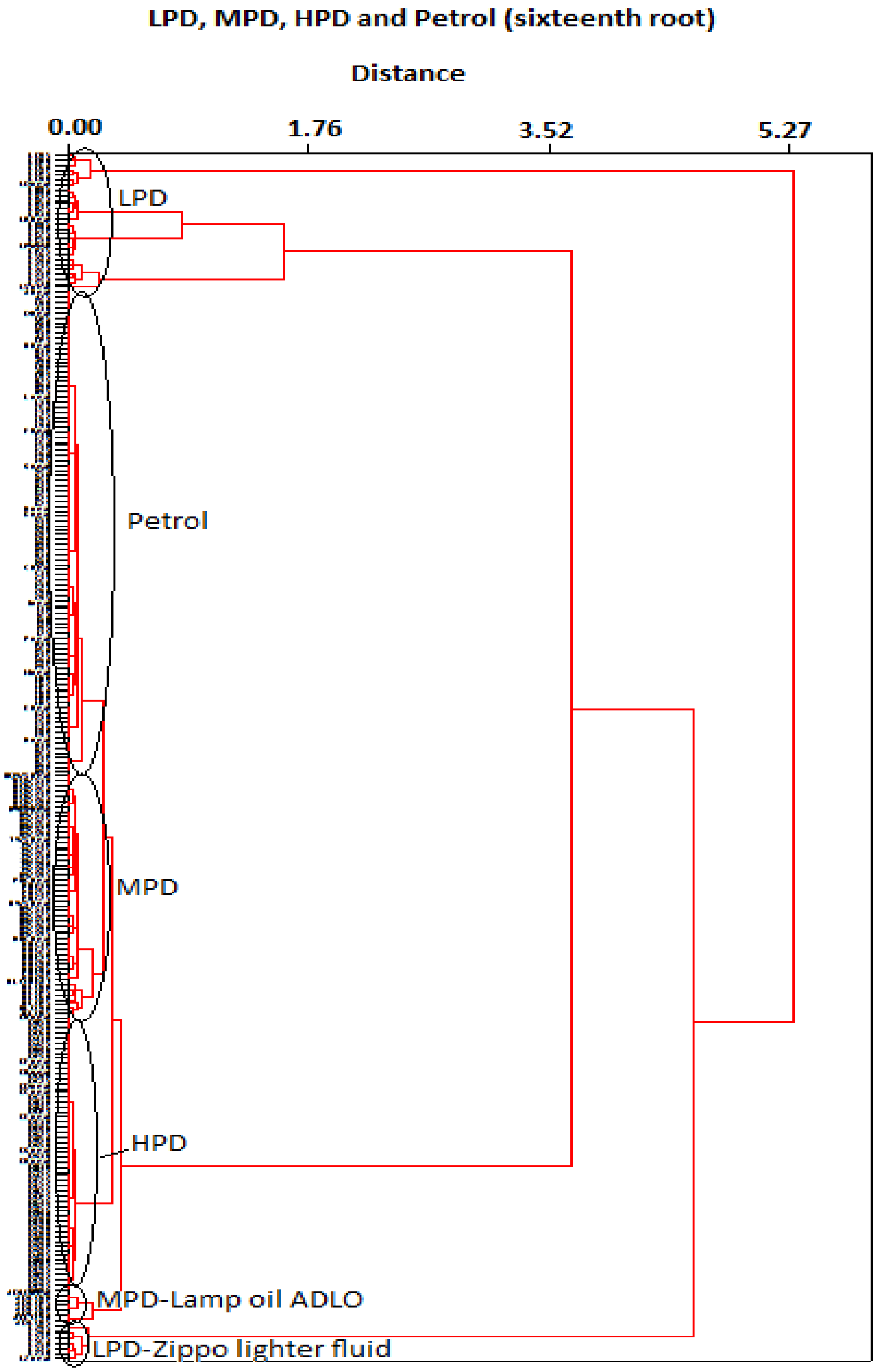


**Figure 4.47 Dendrogram for the combined data matrix of petrol and petroleum distillate products.**

### *4.8.6.3 SOFM Classification*

A very distinctive grouping of the ignitable liquids was evident in the SOFM output map as shown in figure 4.48.

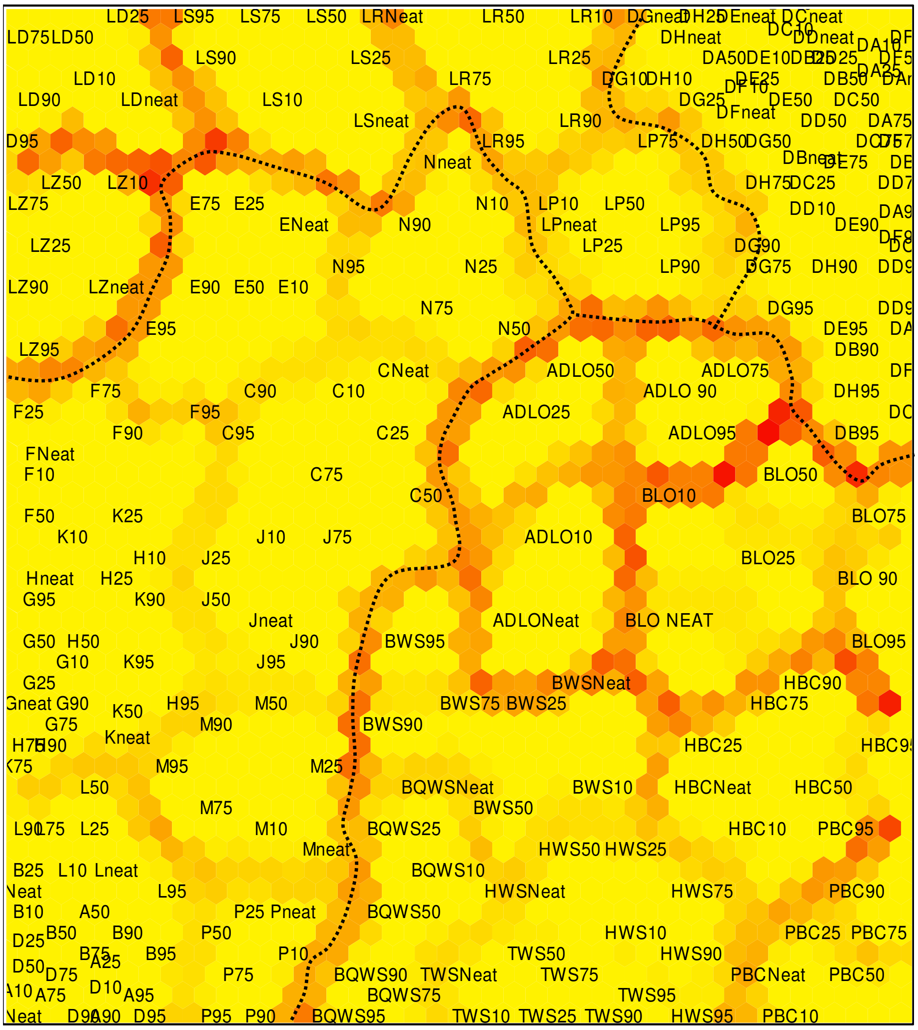


**Figure 4.48The SOFM output map for the combined data matrix of petrol and petroleum distillate products.**

The classifications for LPD and diesel sample are cornered on the upper region of the map while petrol and MPD samples are discriminated on the lower region. In terms of spatial arrangement, SOFM maps is superior to PCA and HCA and reveals clear association of evaporated liquids with the corresponding unevaporated liquid. Except for diesel samples, meaningful association or discrimination within class or subclass based on type and or brand was successfully achieved by this mathematical approach.

## 4.9 Conclusions

This study set out to evaluate the potential for multivariate analysis to provide a more objective method to classify petroleum distillate products. Variable selection and preparation of the data set was crucial to ensure success in the multivariate analysis. Manual peak comparison and examination of mass spectra for peak selection was sufficient for the data analysis undertaken, and although this process is relatively slow it has demonstrated impressive classification results for some of the ignitable liquid groups examined.

Data pre-treatment was essential in order to obtain accurate classifications. These findings also suggest that in general, power transformation deal remarkably well in reducing the impact of larger peaks as well as dealing with missing values in datasets encountered with gradually changing chromatographic patterns as a result of sample evaporation. Selection of characteristic portions of the data is necessary to attempt to relate the evaporated and unevaporated samples together.

Comparison of three multivariate procedures revealed that an artificial neural network using SOFM generally outperforms both PCA and HCA in demonstrating sample linkage. The significant finding to emerge from this study is that SOFM accurately classified fresh and progressively weathered ignitable liquid samples according to type and brand for both the light and medium petroleum distillates as well as some petrol samples based on GC-MS data only even when there was a significant change in the chromatographic profiles. Different sample subclasses could also be successfully indentified and this suggests that this approach may be beneficial for the identification of an unknown liquid sample recovered from a fire scene.

## 4.10 References

1. *ASTM Designation: E 1618 – 06 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry*. 2006, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-11.

2. *ASTM Designation: E 1387 – 01 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography*. 2001, American Society for Testing and Materials International: West Conshohocken, PA. p. 1-10.

3. DeHaan, J.D., *Kirk's fire investigation*. 6 ed. 2007, New York: Brady Press.

4. Almirall, J.R., and Furton, K.G., *Analysis and interpretation of fire scene evidence*. Forensic Science Techniques Series. 2004, Boca Raton: CRC Press. 255.

5. Newman, R., Gilbert, M., and Lothridge, K., *GC-MS Guide to Ignitable Liquids*. 1998, CRC Press: Boca Raton.

6. Newman, R., *Modern laboratory techniques involved in the analysis of fire debris samples*. Fire Investigation, ed. N.N. Daeid. 2004, Boca Raton: CRC Press.

7. Vella, A.J., *Arson investigation using the ion trap detector*. Journal of the Forensic Science Society 1992. **32**(2): p. 131-142.

8. Nowicki, J., *An accelerant classification scheme based on analysis by gas chromatography/Mass Spectrometry (GC-MS)*. Journal of Forensic Sciences, 1990. **35**(5): p. 1064-1086.

9. Nowicki, J., *Analysis of fire debris sample by Gas Chromatography/Mass Spectrometry (GC-MS): Case studies*. Journal of Forensic Sciences, 1991. **36**(5): p. 1536-1550.

10. Lennard, C., Rochaix, V.T., Margot, P., and Huber, K., *A GC-MS database of target compound chromatograms for the identification of arson accelerants*. Science & Justice, 1995. **35**(1): p. 19-30.

11. Keto, R., and Wineman, P.L., *Detection of petroleum-based accelerants in fire debris by target compound gas chromatograph- mass spectrometry*. Analytical Chemistry, 1991. **63**(18): p. 1964-1971.

12. Keto, R.O., *GC/MS data interpretation for petroleum distillate identification in contaminated arson debris*. Journal of Forensic Sciences, 1995. **40**(3): p. 412-423.

13. Stauffer, E., Dolan, J.A., and Newman, R., *Fire Debris Analysis*. 2008, Burlington: Academic Press.

14. Doble, P., Sandercock, M., Pasquier, E.D., Petocz, P., Roux, C., and Dawson, M., *Classification of premium and regular gasoline by gas chromatography/mass spectrometry, principal component analysis and artificial neural networks.* Forensic Science International, 2003. **132**(1): p. 26-39.

15. Cserhati, T., *Multivariate method in Chromatography - A practical guide*. 2009, Chichester: John Wiley and Son.

16. Ichikawa, M., Nonaka, N., Takada, I., and Ishimori, S., *Mass spectrometric analysis for distinction between regular and premium motor gasolines.* Analytical Sciences, 1993. **9**(2): p. 261-267.

17. Tan, B., Hardy, J.K., and Snavely, R.E., *Accelerant classification by gas chromatography/mass spectrometry and multivariate pattern recognition.* Analytica Chimica Acta, 2000. **422**(1): p. 37-46.

18. Bodle, E.S., and Hardy, J.K., *Multivariate pattern recognition of petroleum-based accelerants by solid-phase microextraction gas chromatography with flame ionization detection.* Analytica Chimica Acta, 2007. **589**(2): p. 247-254.

19. Sigman, M.E., and Williams, M.R., *Covariance mapping in the analysis of ignitable liquids by Gas Chromatography/Mass Spectrometry.* Analytical Chemistry, 2006. **78**(5): p. 1713-1718.

20. Sigman, M.E., Williams, M.R., and Ivy, R.G., *Individualization of gasoline samples by covariance mapping and Gas Chromatography/Mass Spectrometry.* Analytical Chemistry, 2007. **79**(9): p. 3462-3468.

21. Petraco, N.D.K., Gil, M., Pizzola, P.A., and Kubic, T.A., *Statistical discrimination of liquid gasoline samples from casework.* Journal of Forensic Sciences, 2008. **53**(5): p. 1092-1101.

22. Hupp, A.M., Marshall, L.J., Campbell, D.I., Smith, R.W., and McGuffin, V.L., *Chemometric analysis of diesel fuel for forensic and environmental applications.* Anal Chim Acta, 2008. **606**(2): p. 159-171.

23. Marshall, L.J., McIlroy, J.W., McGuffin, V.L., and Smith, R.W., *Association and discrimination of diesel fuels using chemometric procedures.* Analytical and Bioanalytical Chemistry, 2009. **394**: p. 2049-2059.

24. Baerncopf, J.M., McGuffin, V.L., and Smith, R.W., *Discrimination of Ignitable liquids from matrix interferences using chemometric procedures*, in *Proceedings of the 61st Annual Scientific Meeting of the American Academy*

*of Forensic Science*. 2009, American Academy of Forensic Sciences: Denver. p. 124-125

25. Monfreda, M., and Gregori, A., *Differentiation of unevaporataed gasoline samples according to their brands, by SPME-GCMS and multivariate statistical analysis.* Journal of Forensic Sciences, 2011. **56**(2): p. 372-380.

26. Intelligent, M.M., *Petrol Forecourt Retailing*. 1996, Mintel International Group Limited: London. p. 76

27. Bridgeman, J.S., *Competition in the supply of petrol in the UK : A report* 1998, Office of Fair Trading: Great Britain.

28. *Petrol in Profile*, in *Shell Education Service*. 1996, Shell U.K. Limited, Caldwell Prince Limited: London.

29. Weyermann, C.l., Marquis, R., Delaporte, C.l., Esseiva, P., Lock, E., Aalberg, L., Jr., J.S.B., Dieckmann, S., Dujourdy, L., and Zrcek, F., *Drug intelligence based on MDMA tablets data I. Organic impurities profiling.* Forensic Science International, 2008. **177**(1): p. 11-16.

30. Esseiva, P., Anglada, F., Dujourdy, L., Taroni, F., Margot, P., Pasquier, E.D., Dawson, M., Roux, C., and Doble, P., *Chemical profiling and classification of illicit heroin by principal component analysis, calculation of inter sample correlation and artificial neural networks* Talanta, 2005. **67**(1): p. 360-367.

31. Muehlethaler, C., Massonnet, G., and Esseiva, P., *The application of chemometrics on Infrared and Raman spectra as a tool for the forensic analysis of paints.* Forensic Science International, 2011. **209**(1-3): p. 173-182.

32. Kher, A., Mulholland, M., Green, E., and Reedy, B., *Forensic classification of ballpoint pen inks using high performance liquid chromatography and infrared spectroscopy with principal components analysis and linear discriminant analysis* Talanta, 2005. **67**(2): p. 360-367.

33. Thanasoulias, N.C., Parisis, N.A., and Evmiridis, N.P., *Multivariate chemometrics for the forensic discrimination of blue ball-point pen inks based on their Vis spectra* Forensic Science International, 2008. **174**(1): p. 16-25.

34. González-Rodríguez, J., Sissons, N., and Robinson, S., *Fire debris analysis by Raman spectroscopy and chemometrics.* Journal of Analytical and Applied Pyrolysis, 2011. **91**(1): p. 210-218.

35. Zupan, J., and Gasteiger, J., *NeuralNetworks in Chemistry and Drug Design*. 1999, Weinheim: Wiley-VCH.

36. Vona, M., *Neural Networks: Classifying Patterns*, in *Investigative Data Mining for Security and Criminal Detection* J. Mena, Editor. 2003, Butterworth / Heinemann: Amsterdam.

37. Hanrahan, G., *Artificial Neural Network in Biological and Environmental Analysis*. 2011, Boca Raton: CRC Press.

38. Marini, F., *Artificial neural networks in foodstuff analyses: Trends and perspectives A review.* Analytica Chimica Acta, 2009. **635**(2): p. 121-131.

39. J.W.Thorpe, and Ismail, D. *Pattern recognition procedures for the classification and prediction of stains originating from wax-based products.* in *California Association of Criminalist, Fall 2006 Seminar*. 2006. Temecul, California.

40. Fei, B.K.L., Eloff, J.H.P., M.S.Oliver, and Venter, H.S., *The use of self-organising maps for anomolous behaviour detection in a digital investigation.* Forensic Science International, 2006. **162**(1-3): p. 33-37.

41. Ismail, D., NicDaeid, N., and Thorpe, J.W. *Clustering of wax-based products: A Self Organising Feature Maps (SOFM) approach.* in *Trinniel Meeting, 5th. European Academy of Forensic Science Institute (ENSFI).* 2009. Glasgow, Scotland.

42. Ismail, D., and NicDaeid, N., *Comparison of smears of wax based products using thin layer chromatography and microspectrophotometric detection.* Journal of Forensic Identification, 2010. **61**(2): p. 136-146.

43. Reed, G., NicDaeid, N., Savage, K., Faulds, K and Ismail, D.,. *The application of Raman spectroscopy to the analysis of blue, red and black gel pen writing inks.* in *63rd Annual Scientific Meeting, American Academy of Forensic Science*. 2011. Chicago, Illanois.

44. Adams, M.J., *Chemometrics In Analytical Spectroscopy*, 1995, Cambridge: The Royal Society of Chemistry.

45. Gardiner, W.P., *Statistical Analysis Methods for Chemists ; A software Based Approach*. 1997, Cambridge: The Royal Society of Chemistry. 360.

46. Bebe, K.R., Pell, R.J., and Seasholtz, M.B., *Chemometric: A Practical Guide*. 1998, New York: John Wiley and Sons, Inc.

47. Brereton, R.G., *Chemometrics for Pattern Recognition.* 2009, West Sussex: John Wiley and Sons.

48. Webb, A., *Statistical Pattern Recognition*. 2nd ed. 2002, West Sussex John Wiley and Sons Ltd.

49. Everitt, B.S., and Dunn, G., *Applied Multivariate Data Analysis*. 2001, London: Arnold

50. Berg, R.A.v., Hoefsloot, H.C., Westerhuis, J.A., Smilde, A.K., and Werf, M.J.v.d., *Centering, scaling, and transformations: improving the biological information content of metabolomics data.* BMC Genomics, 2006. **7**(142): p. 1-15.

51. Sandercock, P.M.L., and Pasquier, E.D., *Chemical fingerprinting of unevaporated automotive gasoline samples.* Forensic Science International, 2003. **134**(1): p. 1-10.

52. Sandercock, P.M.L., and Pasquier, E.D., *Chemical fingerprinting of gasoline 2. Comparison of unevaporated and evaporated automotive gasoline samples.* Forensic Science International, 2004. **140**(1): p. 43-59.

53. Sandercock, P.M.L., and Pasquier, E.D., *Chemical fingerprinting of gasoline Part 3. Comparison of unevaporated automotive gasoline samples from Australia and New Zealand.* Forensic Science International, 2004. **140**(1): p. 71-77.

54. Penn, D.J., Oberzaucher, E., Grammer, K., Fischer, G., Soini, H.A., Wiesler, D., Novotny, M.V., Dixon, S.J., Xu, Y., and Brereton, R.G., *Individual and gender fingerprints in human body odour.* Journal of the Royal Society Interface, 2007. **4**(1): p. 331-340.

55. Buchanan, H.A.S., *An evaluation of isotope ratio mass spectrometry for the profiling of 3,4-Methylenedioxymethamphetamines*, Thesis, *Dept. in Pure and Applied Chemistry*. 2009, University of Strathclyde: Glasgow.

56. Wongravee, K., Heinrich, N., Holmboe, M., Schaefer, M.L., Reed, R.R., Trevejo, J., and Brereton, R.G., *Variable selection using iterative reformulation of training set models for discrimination of samples: Application to Gas Chromatography/Mass Spectrometry of mouse urinary metabolites.* Analytical Chemistry, 2009. **81**(13): p. 5204–5217.

57. Massart, D.L., and Kaufman, L., *The Interpretation of Analytical Chemical Data by the Use of Cluster Analysis.* . 1983, New York: John Wiley & Sons.

58. Hiden, H.G., Willis, M.J., Tham, M.T., and Montague, G.A., *Non-linear principal components analysis using genetic programming.* Computers & Chemical Engineering, 1999. **23**(3): p. 413-425.

59. Jolliffe, I.T., *Principal component analysis*. 1986, New York: Springer-Verlag.

60. Everitt, B.S., *Cluster Analysis*. Third ed. 1993, London: Arnold.

61. Romesburg, H.C., *Cluster analysis for researcher*. 2004, North Carolina: Lulu Press.

62. Einax, J.W., Zwanziger, H.W., and Geib, S., *Chemometrics in Environmental Analysis*. 1997, Weinheim: VCH.

63. Zupan, J., Novi, M., and Ruis~inchez, I., *Kohonen and counterpropagation artificial neural networks in analytical chemistry.* Chemometrics and Intelligent Laboratory Systems, 1997. **38**(1): p. 1-23.

64. Wongravee, K., Lloyd, G.R., Silwood, C.J., Grootveld, M., and Brereton, R.G., *Supervised self organizing maps for classification and determination of potentially discriminatory variables: illustrated by application to nuclear magnetic resonance metabolomic profiling.* Analytical Chemistry, 2010. **82**(2): p. 628-638.

65. *Self Organising Feature Maps (Kohonen Maps); available at* http://www.codeproject.com/KB/recipes/sofm.aspx?msg=2142943 [accessed on 06/06/2011].

66. Kohonen, T., *Self-Organising Maps*. 1995, Heidelberg: Springer-Verlag. 349.

67. Vesanto, J., *SOM−based data visualization methods.* Intelligent Data Analysis, 1999. **3**(2): p. 111−126.

68. Lloyd, G.R., Wongravee, K., Silwood, C.J.L., Grootveld, M., and Brereton, R.G., *Self Organising Maps for variable selection: Application to human saliva analysed by nuclear magnetic resonance spectroscopy to investigate the effect of an oral healthcare product.* Chemometrics and Intelligent Laboratory Systems, 2009. **98**(2): p. 149-161.

69. Smith, R.M., *Arson analysis by mass chromatography.* Analytical Chemistry, 1982. **54**(13): p. 1399A-1409A.

70. Kelly, R.L., and Martz, R.M., *Accelerant Identification in fire debris by Gas Chromatography/Mass Spectrometry techniques.* Journal of Forensic Sciences, 1984. **29**(3): p. 714-722.

71. Wineman, P.L., and Keto, R.O., *Target-compound method for the analysis of accelerant residues in fire debris.* Analytica Chimica Acta, 1994. **288**(1-2): p. 97-110.

72. *HP Manual; Understanding Your ChemStation* 1994, Germany: Hewlett-Packard GmbH.

73. *NIST/EPA/NIH Mass spectral library (NIST 08) v.2.0f*, in *NIST MS Search Software version 2.0f* 1987-2008, The National Institute of Standards and Technology(NIST)© United States of America: Gaithersburg.

74. Brereton, R.G., *Consequences of sample size, variable selection, and model validation and optimisation, for predicting classification ability from analytical data.* Trends in Analytical Chemistry, 2006. **25** (11): p. 1103-1111.

75. Kateman, G., and Smits, J.R.M., *Colored information from a black box?: Validation and evaluation of neural networks.* Analytica Chimica Acta, 1993. **277**(2): p. 179-188.

76. Wang, Z., Stout, S.A., and Fingas, M., *Forensic fingerprinting of biomarkers for oil spill characterisation and source identification*, Environmental Forensics, 2006. **7**(2): p. 105-146.

77. Wang, Z., and Stout, S.A., *Oil Spill Environmental Forensics: Fingerprinting and Source Identification*. 2007, Academic Press: Amsterdam.

78. Wang, Z., and Fingas, M., *Differentiation of the source of spilled oil and monitoring of the oil weathering process using GC-MS.* Journal Chromatography A, 1995. **712**(2): p. 321-343.

79. Baerncopf, J.M., McGuffin, V.L., and Smith, R.W., *Effect of gas chromatography temperature program on the association and discrimination of diesel samples.* Journal of Forensic Sciences, 2010. **55**(1): p. 185-191.

80. Baxendell, P., *The Petroleum Handbook.* Sixth Edition ed. 1983, Amsterdam: Elsevier Science Publisher B.V.

81. *The Petroleum Handbook : Shell* Sixth Edition ed., ed. R.D.-S.G.o. Companies. 1983, Elsevier: Amsterdam.

82. Hirz, R., *Gasoline brand identification and individualization of gasoline lots.* Journal of the Forensic Science Society, 1989. **29**(2): p. 91-101.

83. Wert, H., Brettell, T.A., Desiderio, V.J., and Petraco, N.D.K., *The detection of diamondoid compounds in ignitable liquid residues by gas chromatography/mass spectrometry, Part II*, in *Proceedings of the 61st Annual Scientific Meeting of the American Academy of Forensic Science*. 2009, American Academy of Forensic Sciences: Denver CO. p. 124.

84. Wang, Z., Yang, C., Hollebone, B., and Fingas, M., *Forensic fingerprinting of diamondoids for correlation and differentiation of spilled oil and petroleum products.* Environmental Science Technology, 2006. **40**(18): p. 5636-5646.

85. Wingert, W.S., *Gas Chromatography Mass Spectrometry. analysis of diamondoid hydrocarbons in Smackover petroleums.* Fuel 1992. **71**(1): p. 37-43.

86. *Indane Material Safety Datasheet; available at* *http://msds.chem.ox.ac.uk/IN/indene.html*. [accessed on 12/01/2010]

87. NicDaeid, N., *Fire Investigation*. 2004, Boca Raton: CRC Press.

88. Mann, D.C., *Comparison of automotive gasolines using capillary gas chromatography I: Comparison methodology.* Journal of Forensic Sciences, 1987. **32**(3): p. 606-615.

# CHAPTER 5: ASSESSMENT OF THE ABILITIES OF SOFM TO ASSOCIATE IGNITABLE LIQUIDS BY BRAND IN THE PRESENCE OF INTERFERING PRODUCTS

This chapter explores the interpretation of the chromatographic profiles derived from various common burnt substrates both independently and in the presence of the ignitable liquids under study. A combination of qualitative examination of the total ion chromatographic profiles (TICs), specific component identification using mass spectral profiles and in some cases extracted ion profiles were used. These identified alkanes, cycloalkanes, alkylbenzenes, indanes and naphthalenes which were used to generate the matrices for mathematical analysis using Self Organising Feature Mapping neural networks. The feasibility and superiority of Self Organising Feature Mapping over PCA and HCA to classify samples of common origin has been demonstrated in the previous chapter. As such this chapter focuses on investigating the abilities of SOFM specifically to identify and discriminate the ignitable liquid residues of the materials under test from common interfering products.

## 5.1 Introduction

Fire debris analysis predominantly focuses on the detection and identification of ignitable liquid residues in fire debris, the presence of which may have been indicated by evidence at the scene [1]. This process however can be complicated by the presence of numerous interference-by-products generated as a consequence of the fire. Interference products mainly originate from three common sources; unburned background substrates, pyrolysis products or combustion products. Contaminations from microbial degradation products and fire suppressant activities have also been reported [2-4]. Studies to characterise interfering products have been carried out in an effort to provide a greater elucidation of the effects of these products on fire debris analysis [5-8].

The fire phenomena can be defined "as an exothermic chemical reaction involving the oxidation of substances (a fuel) resulting in the release of energy in the form of heat and light"[9]. The basis of combustion is commonly symbolised by the fire triangle which illustrates the interactivity of heat, oxygen (air), and fuel in the process. In addition, in normal circumstances, prior to the conditions being met to sustain a fire, sufficient energy is required in the environment of the fuel to cause both a phase change to the gaseous state and an ignition of the gaseous fuel/air mixture once within the flammability limits of the fuel.

Combustible materials need to undergo a phase transition from the solid or liquid phase into the gaseous phase in order that flaming combustion (a gas phase phenomenon) can occur [10]. The transition process varies, depending mainly on the type of combustible material and the specific environmental conditions of the fire. Liquid to gaseous phase transition is relatively straight forward involving evaporation and boiling at the surface. Conversion from a solid material to the gaseous phase can occur in a number of different ways illustrated in figure5.1.

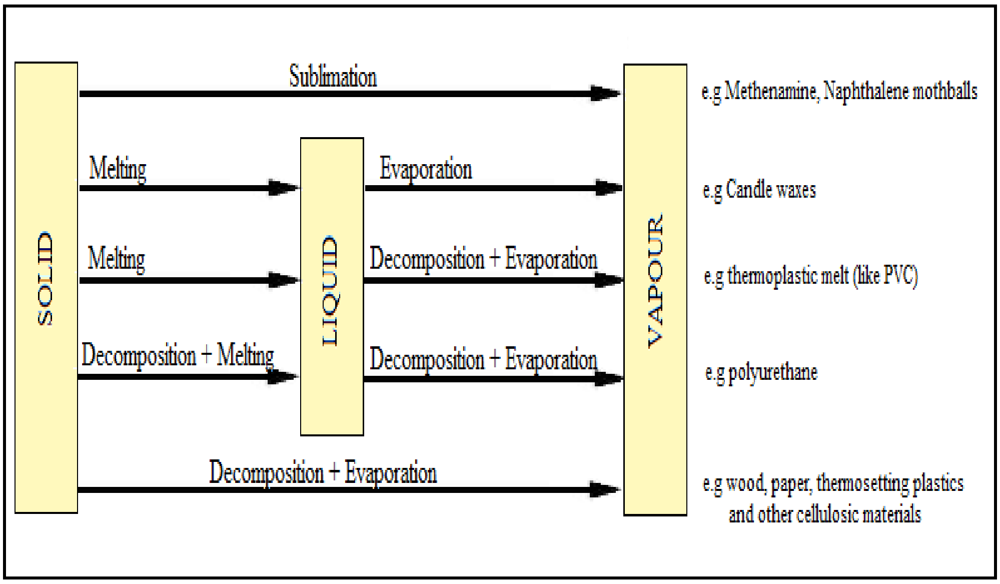


**Figure 5.1 Conversion from solid to vapour phase by different pathways [10, 11].**

When subjected to heat, materials undergo thermal degradation and decomposition. Thermal degradation involves changes in terms of the function and physical appearance of the material whereas thermal decomposition can be described as a process of extensive chemical change caused by heat, where high molecular weight compounds are decomposed to lower molecular weight compounds [12]. The term ‘pyrolysis’ is often used for thermal decomposition. The release of pyrolysis products into air in the vicinity of an ignition source facilitates the flaming combustion process, producing both pyrolysis and combustion products which can interfere with subsequent ignitable liquid identification should such liquids be present.

Solid materials are either natural or synthetic polymeric organic compounds or a mixture of both. Natural polymers include natural rubbers and cellulosic materials such as wood, cotton and wool. Synthetic polymers are generally industrially synthesised from petroleum based feed-stock. Depending on their molecular structure, polymer molecules consist of linear, branched or cross-linking networks of long chain repeating chemical units. Synthetic polymers are divided into two general groups, thermoplastic and thermosetting polymers.

Thermoplastic polymers tend to soften, melt and liquidise when exposed to heat while thermosetting polymers tend to undergo charring when exposed to heat [13]. The fire behaviour of polymeric materials depends partly on the type of material but also on other factors such as additives introduced during manufacturing (fillers, plasticiser or fire retardants), the materials physical form (films, blocks, fibres etc) and other external factors such as temperature, rate of heating and the presence of oxidisers.

### 5.1.1 Pyrolysis

Pyrolysis of natural and synthetic polymeric materials follows several decomposition mechanisms. Thermal decomposition of cellulosic material as a natural polymer can occur via two pathways depending on the temperature. The material will undergo charring if exposed to temperatures below 300°C and undergo tar formation if exposed to temperatures above 300°C as illustrated in figure 5.2 [14, 15]. Charring releases $CO_2$ and $H_2O$ while at the same time leaves a dehydrated carbon backbone, also known as a char. In contrast, tar formation releases flammable gases.

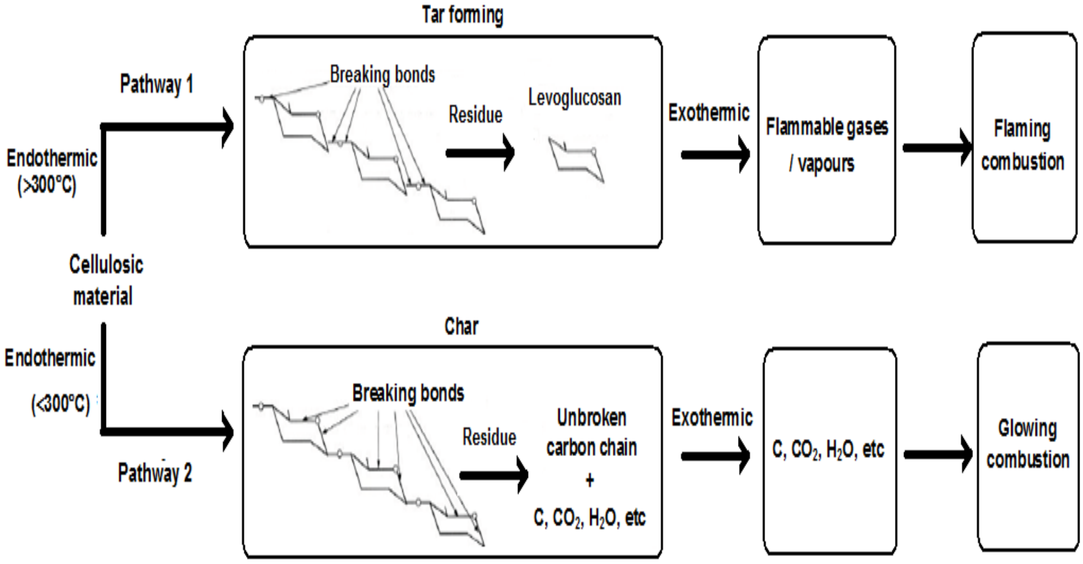


**Figure 5.2 Thermal decomposition pathways of cellulosic materials.**

The most common pyrolysis mechanisms include random scission, side group scission and depolymerisation of hydrocarbon bonds [6, 12, 16]. In reality these mechanisms occur simultaneously and contribute directly to the complexity of pyrolysis products produced. Each of these pyrolysis mechanisms is discussed in brief.

#### *5.1.1.1Random Chain Scission*

The random scission mechanism involves a random breaking of the hydrocarbon chain (between C-C and C-H) producing carbon and hydrogen free radicals that undergo rearrangements as illustrated in figure 5.3. This produces a series of lower molecular weight molecules such as alkanes, alkenes and alkadienes [6]. Polyethylene and polypropylene are among the polymers associated with this type of degradation process.

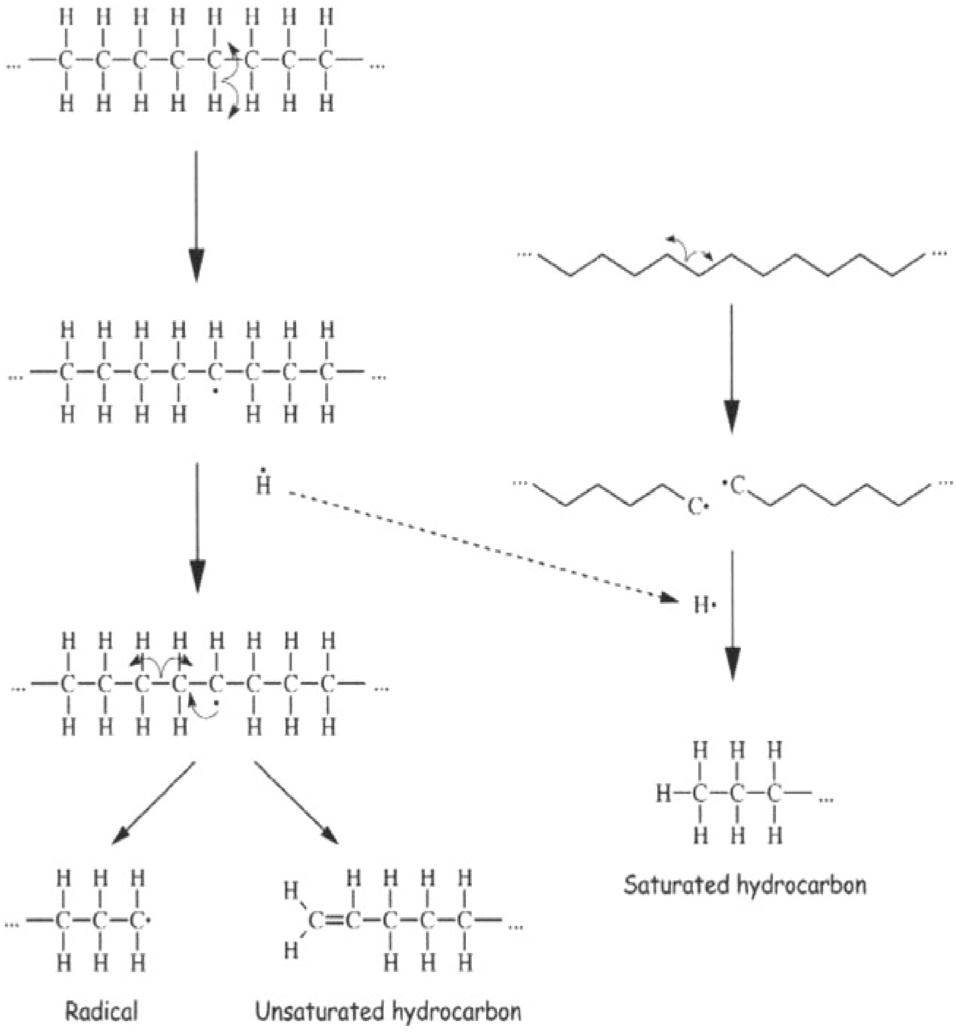


**Figure 5.3 Illustration of random scission mechanism of polyethylene [6].**

### *5.1.1.2 Side Group Scission*

Side group elimination occurs when the group at the end of the hydrocarbon backbone is cleaved, resulting in a polyunsaturated backbone which can then undergo further rearrangement to produce aromatic products such as styrene, toluene, benzene and various naphthalenes [6]. This mechanism is reported as common or polymers such as polyvinyl chloride, polyvinyl alcohol and polyvinyl acetate and is illustrated in figure 5.4 [6, 12].

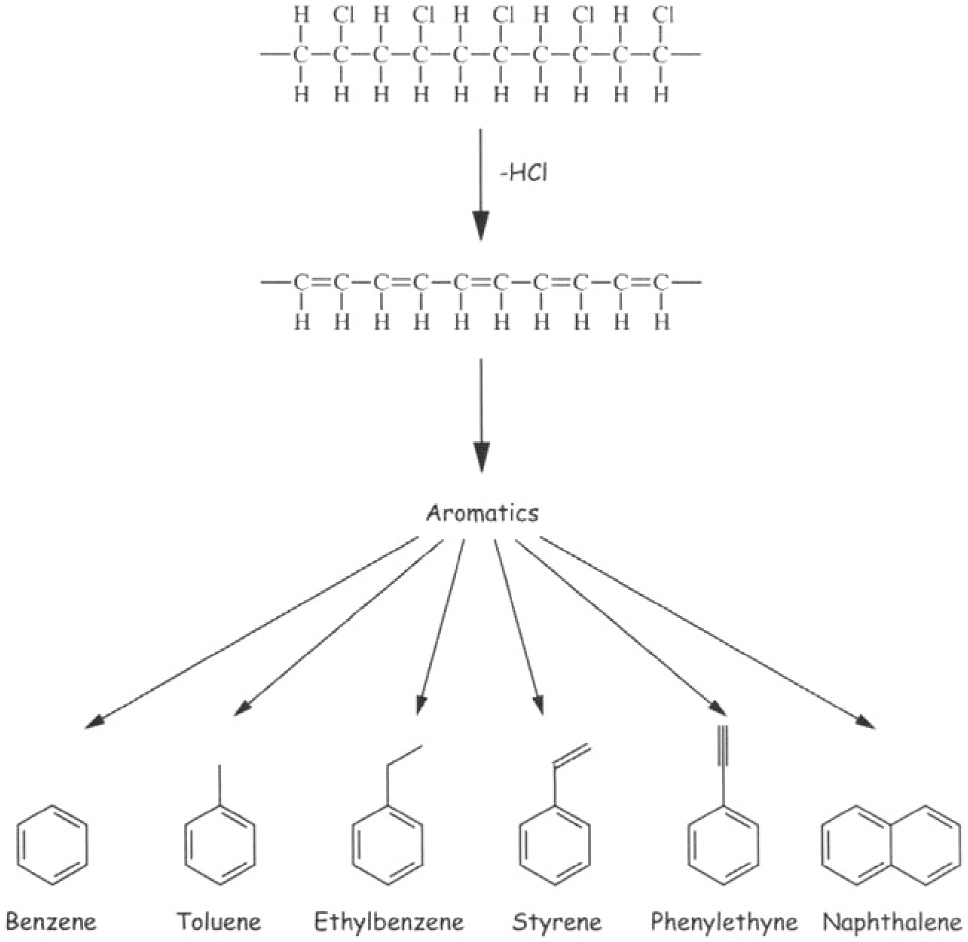


**Figure 5.4 Side group scission of polyvinylchloride [6].**

### *5.1.1.3 Depolymerisation*

Depolymerisation or monomer reversion occurs when the polymer reverts back to its monomeric form as illustrated in figure 5.5. Polymers such as polymethylmethacrylate and poly-α-methylstyrene undergo this type of degradation [6]. Cellulose also undergoes depolymerisation to produce levoglucosan[14].

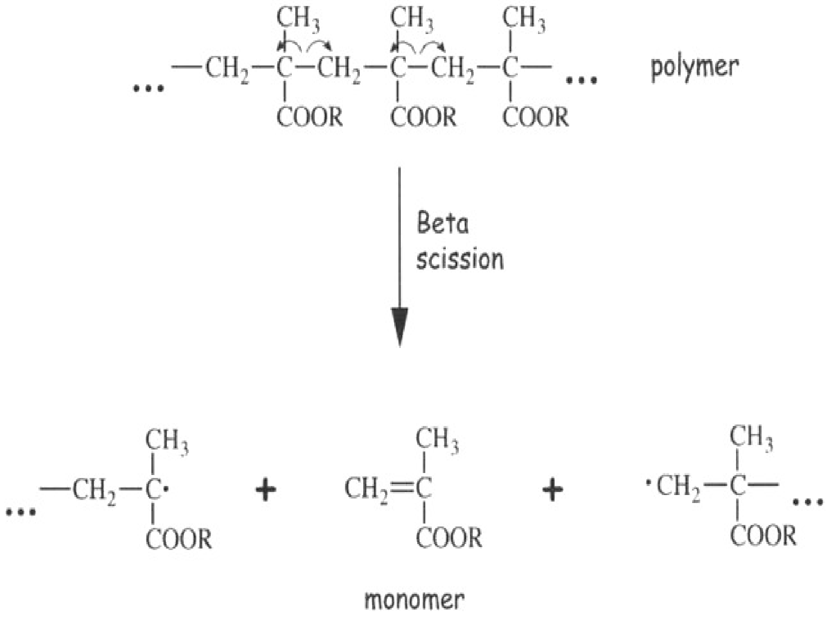


Figure 5.5 Depolymerisation mechanism of polymethylmethacrylate substrate [6].

#### 5.1.1.4 Other Pyrolysis Mechanisms

Chain stripping is a depolymerisation mechanism similar to end chain scission in which atoms or groups are stripped from the main polymer backbone and occurs with materials such as polyvinyl chloride which is illustrated in figure 5.6 [17].

**-CH2-CHCl- → -CH=CH- + HCl**

Figure 5.6 Simplified reaction of chain stripping mechanism [17].

Cross linking has been used in the production of some polymers to improve their structural properties and uses a thermal process to bridge monomers and produce linkages between polymer chains [18]. Cross linking is commonly associated with charring in burnt materials such as polyacrylonitriles, phenolic resins and cellulosic materials [6, 12]. An example of cross linkage in polyacronitriles is provided in figure 5.7.

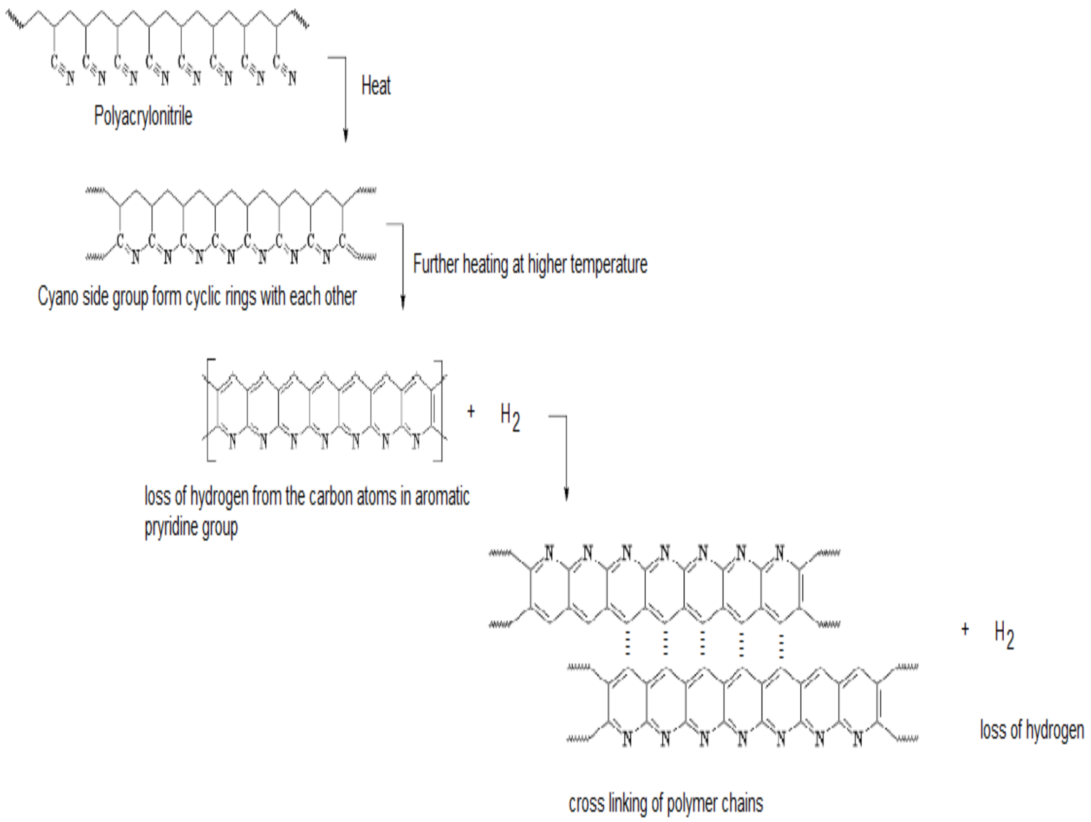


**Figure 5.7 Cross linking mechanism of polyacrylonitrile, adapted from [19].**

### 5.1.2 Combustion Products

Combustion is defined as a complex, dynamic, oxidation reaction generating heat and light [10, 11]. Combustion progresses through the generation of gaseous fuel via a pyrolysis process to the combination of oxygen to form combustion products [17]. As a consequence the occurrence of combustion products and oxygenated by products in fire debris is expected.

Different levels of combustion, complete, partially complete or incomplete combustion occur, depending on the extent of oxygen present. Complete combustion occurs in ideal conditions producing carbon dioxide and water while partially complete and incomplete combustion produces additional carbon monoxide and other products such as soot.

Incomplete combustion occurs in oxygen deficient environments where surface materials undergo combustion in the absence of a flame. This phenomenon is known as glowing or smouldering combustion. Wood charring is a good example of glowing combustion and displays its thermal degradation activity by revealing a visible zonal charring pattern on its residue as illustrated in figure 5.8 [11, 20, 21]. Initiated by direct flame impingement, zone A experiences the highest temperature (> 300°C) where combustion products are released. Heat emitted in this layer causes moisture evaporation in the underneath layer to initiate pyrolysis of the material. Pyrolysis of wood in zone B progresses at temperatures between 200°C to 300°C. Meanwhile, the inner core of wood (zone C) will remain at ambient temperature for a considerable time.

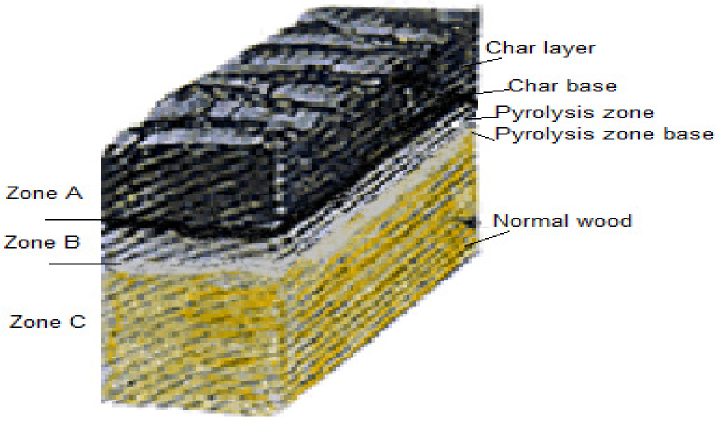


**Figure 5.8 Char layers of wood structure, adapted from Buchanan[20].**

The various combustion processes often occur concurrently, thus producing mixtures of carbon dioxide, carbon, carbon monoxide, water vapour, nitrogen, nitrogen oxide along with other toxic gases, oxygenates by-products and soot. Hence, the by-products released from combustion of particular substrate are uncertain and can vary tremendously.

### 5.1.3 Background Substrates

Interference from substrate material is a major hindrance in ignitable liquid residue analysis as many items, natural or synthetic, are used ubiquitously and have been shown to produce volatile compounds when exposed to fire [22-29]. Volatiles from unburnt substrates (pre-fire) are categorised as background products. These are hydrocarbon volatiles which may originate from the actual compounds present in the substrates themselves, solvents that are used during the manufacturing process or deposition of contaminants or residues on the substrates [5, 25, 30, 31].

The effects of interference products from burnt substrates (wood, textiles and paper) was first suggested in 1968 [32] and the misidentification of ignitable liquids in fire debris analysis as a result of interference products which may be present has been reported in the literature [22, 24, 31, 33]. Research conducted by Tranthim-fryer and DeHaan also reported positive indications by hydrocarbon detecting canines to pyrolysis products from burnt carpet and underlay [1]. Interference patterns from uncontaminated petroleum based products rather than ignitable liquids were also reported by other researchers, emphasising the importance of the necessity of analysis of control samples and the importance of having an understanding of the chromatographic profiles associated with background matrices [30, 31, 34].

The building and construction sector in the UK utilises in the region of 800,000 tonnes of plastics annually with polyvinylchloride (PVC) being the most common type of plastic material use in the industry[35]. Other common materials include polyurethane, polyethylene and polystryrene. Such materials are known to produce volatile compounds which are comparable to the boiling range and chromatographic patterns of commonly encountered ignitable liquids when analysed with GC-FID or GC-MS. Smith suggested GC-MS as a more appropriate tool in distinguishing between both sets of products [33]. The application of GC-MS methods for distinguishing pyrolysates from fire debris samples in case samples was also discussed by Nowicky [36].

Identification of combustion products from carpet materials was first reported by Howard and Mckague in 1984 [26] and later comprehensively studied by DeHaan and Bonarious using GC-FID, pyrolysis GC and GC-MS [37]. According to this work, carpet pyrolysis products appear in most of the medium distillate peak range. However, the authors claim discrimination is possible by examining distinctive irregularities in the chromatographic peak pattern distribution, the presence of large unresolved groups and obvious single peaks such as styrene indicating possible by products from pyrolysis activity.

Berstch concentrated on extracted pyrolysis products from carpet and carpet padding [28]. Volatile compounds were extracted using activated charcoal strips and a passive headspace technique and analysed using GC-MS [28]. Results demonstrated that burnt carpet contained small amounts of alkylbenzenes and naphthalenes which are also some of the diagnostic compounds for petrol. Berstch proposed using extracted ion chromatograms and isomer ratios to distinguish the alkylbenzenes and naphthalenes derived from the substrate pyrolysis product rather than an ignitable liquid. Other researchers used a similar approach to discriminate pyrolysis products from highly contaminated samples [1, 38, 39].

Several studies have been reported focusing on comparison amongst types of interference sources in order to systematically distinguish the interference products, aiming to minimise confusion in chromatographic interpretation when they are present [5, 7, 37]. Amirall *et al*, attempted to characterise and identify background, pyrolysis and combustion products of interfering products from controlled burns of common household materials [8]. Passive headspace techniques, GC-MS and pyrolysis GC were employed. The findings, presented in table 5.1, are in agreement with other studies and indicated that the materials tested produced some by products commonly identified as targeted compounds in ignitable liquid samples including some alkanes, branched alkanes and aromatic hydrocarbons. Previous research also suggests that the most common types of materials submitted for fire debris analysis include various types of floor coverings such as carpets, various types of timber and different common plastic materials [40, 41]. As such, an understanding of the chromatographic profiles of these materials is important.

**Table 5.1 Identified compounds encountered from the controlled burning experiment of 35 samples [8].**

| Frequency of occurrence in % | Compound |
|---|---|
| 97.1 | Toluene |
| 82.4 | Styrene |
| 73.5 | Naphthalene |
| 64.7 | Benzaldehyde |
| 64.7 | Ethylbenzene |
| 55.9 | Indene |
| 55.9 | Phenylethyne |
| 35.3 | m,p-Xylenes |
| 29.4 | 1-Methylnaphthalene |
| 29.4 | 2-Methylnaphthalene |
| 26.5 | Acetophenone |
| 26.5 | Furaldehyde |
| 26.5 | 5-Methyl-2-furancarboxaldehyde |
| 26.5 | Tetradecane |
| 23.5 | α-Methylstyrene |
| 23.5 | 2-Ethyl-1-hexanol |
| 23.5 | Biphenyl |
| 23.5 | Tridecane |
| 20.6 | Dodecane |
| 20.6 | Pentadecane |
| 20.6 | Undecane |
| 17.6 | o-Xylene |
| 14.7 | 2,3-Dihydro-1,1,3-trimethyl-3-phenyl-1H-indene |

The different sources of interference products are summarised in figure 5.9 below.

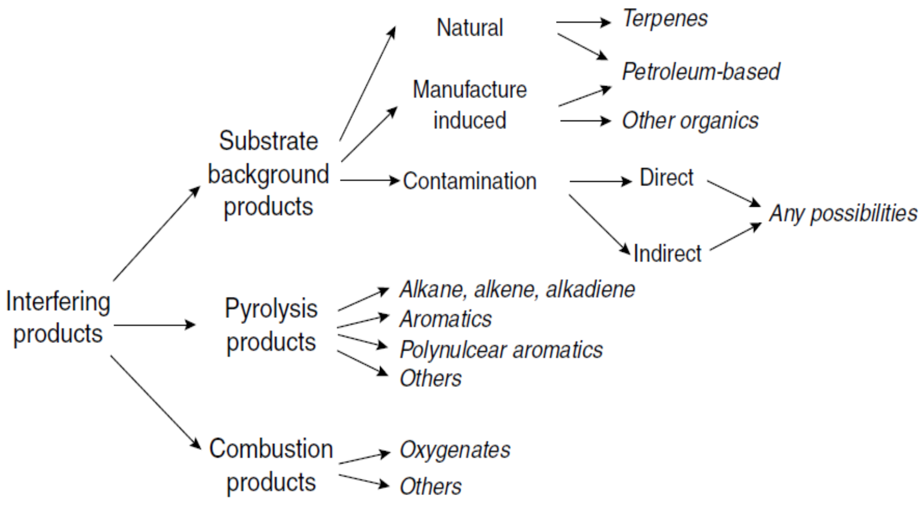


**Figure 5.9 Summarisation of sources of interference products in fire debris [9].**

## 5.2 Experimental Methods

### 5.2.1 Preparation of Interference Products.

Eleven substrates (listed in table 5.2) were prepared according to the methods outlined in chapter 3. The substrates were chosen to reflect common materials encountered in fire debris as reported in previous literature. Each substrate was spiked with 15µL of ignitable liquid and burnt as described in section 3.4.2. The spiked samples were produced for each ignitable liquid substrate combination. Only one test sample was obtained for each combination as the objective of the study was to generate a range of ignitable liquid products in the presence of pyrolysis products rather than demonstrate reproducibility of the sample / by product matrix. Volatiles from the burnt substrates were extracted using the passive headspace technique mentioned previously in section 3.4.4.

**Table 5.2 Eleven materials chosen for ignitable liquid - substrate study.**

| **Substrate** | **Code** |
|---|---|
| 100% Polypropylene carpet with rubber backing | S1 |
| 100% Polypropylene carpet with woven jute backing | S2 |
| Vinyl sheet | S3 |
| Vinyl tile | S4 |
| CD casing | S5 |
| Polyurethane foam | S6 |
| Carrier bag (Polyethylene bag) | S7 |
| Red Pine | S8 |
| Medium Density Fibreboard (MDF) | S9 |
| Plywood | S10 |
| Newspaper | S11 |

The temperature during sample preparation was recorded to ensure that thermal decomposition was occurring. Extracts were analysed using the GC-MS method previously outlined in section 2.2.1 and total ion chromatographic profiles were compared to unevaporated and sequentially evaporated profiles of the various ignitable liquids under study. The chromatograms were compared using the superimposition techniques available on the Chemstation software (E.02.00.493).

### 5.2.2 Prediction by SOFM Model

Compounds having similar retention time were manually aligned to the target chromatograms from the reference ignitable liquid chromatograms. Peaks which were known to be from the interference products were not considered. Missing compounds were replaced by zero values. Prior to SOFM analysis, similar data processing steps outlined for the ignitable liquid reference samples were carried out (section 4.3.2). Peak abundance was normalised against the internal standard, power transformed to the 16th root and row scaled before being subjected to the SOFM procedure. SOFM artificial neural network analysis was performed using Viscovery®SOMine (version 5.0.2, Viscovery Software GmbH).

## 5.3 Results and Discussions

### 5.3.1 Pyrolysis and Combustion Products from Common Substrates.

The total ion chromatograms from burnt substrates and examination of the corresponding extracted ion profiles (appendix H) are presented in figures 5.9 to 5.19. The prominent peaks were identified tentatively (with percentage match probability), by referring to the NIST mass spectral database (version 2.0f). Identification of some peaks however, could not be established and were labelled as unknown. The identification table for each substrate is presented below each chromatogram. Compounds commonly associated with the specific ignitable liquid analysed are highlighted in bold. In all chromatograms, the internal standard peak, tetrachloroethylene appears at approximately 5.77 minutes.

#### *5.3.1.1 Flooring Materials*

The flooring materials analysed consisted of a number of polypropylene carpet materials, vinyl tiles and vinyl sheet floor coverings. The chromatographic patterns from burnt polypropylene carpet presented quite a complex profile of volatiles. Both polypropylene carpets and vinyl sheets demonstrated chromatographic profiles with a Gaussian like distribution pattern of compounds, usually associated with the chromatographic signature of medium and heavy petroleum distillate products. In addition, volatiles from these substrates occupy the same volatility range of petroleum distillates products and thus may interfere with petroleum distillate volatiles if examination is based on the chromatographic pattern only.

### *Polyproplyene carpets*

Two polypropylene carpet samples were analysed, one with rubber backing and one which was jute backed. The extracted ion chromatograms of polypropylene carpets indicated the presence of alkane, alkenes, cycloalkanes, alkylbenzenes and low abundance of naphthalenes. Further identification of the compounds present in the polypropylene carpet tested (figure 5.10 and figure 5.11) was in agreement with previous work where 2,4 dimethyl heptene and other alkane isomers were reported together with the presence of styrenes, toluenes and benzene in samples of carpet with rubber backing [1, 26]. In the preparation of samples under the test conditions some combustion products were also identified, namely 4-methyl-2-heptanone and 4,6-dimethyl-2-heptanone indicative of thermal oxidation [42]. Due to experimental limitations, it was difficult to conclusively distinguish between pyrolysis product and combustion products however, potential pyrolysis products and combustion products are highlighted in light and darker shade respectively, in the following tables.

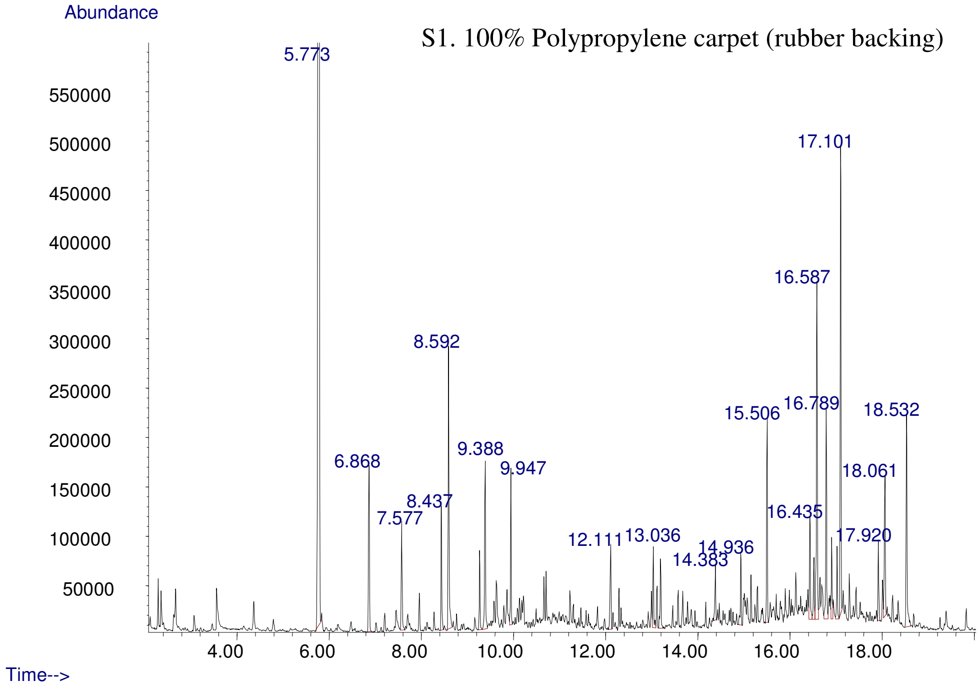


**Figure 5.10 Chromatogram of sample S1. 100% Polypropylene carpet with rubber backing.**

**Table 5.3 Peak identification of volatile compounds extracted from burnt polypropylene carpet (rubber backing).**

| RT | Compound | Match probability |
|---|---|---|
| 3.568 | Methyl isobutyl ketone | 62.2 |
| 4.367 | **Toluene** | 32.7 |
| 4.792 | 4-Methylheptane | 65.1 |
| 6.868 | 2,4-Dimethyl-1-heptene | 55.2 |
| 7.577 | Styrene | 36.6 |
| 8.437 | 4-Methyl-2-heptanone | 83.7 |
| 8.592 | Benzaldehyde | 67.0 |
| 9.268 | 4,6-Dimethyl-2-heptanone | 87.2 |
| 9.388 | 2,6-Dimethyl-1,6-octadiene | 7.84 |
| 9.947 | Limonene | 19.3 |
| 11.645 | **Naphthalene** | 46.2 |
| 12.111 | Cyclopentylbenzene | 23.6 |
| 13.036 | unknown | |
| 13.195 | 2-Isopropyl-5-methyl-1-heptanol | 7.17 |
| 14.383 | Dodecenyl succinic anhydride | 9.92 |
| 14.936 | 2-Hexyl-1-decanol | 5.69 |
| 15.506 | unknown | |
| 16.435 | unknown | |
| 16.520 | 11,13-Dimethyl-12-tetradecen-1-ol acetate | 23.7 |
| 16.587 | unknown | |
| 16.789 | Nonadecanol | 3.21 |
| 16.908 | 3,7,11-Trimethyl-1-dodecanol | 4.90 |
| 17.023 | (4-Octyldodecyl)cyclopentane | 4.47 |
| 17.101 | unknown | |
| 17.920 | unknown | |
| 18.061 | unknown | |
| 18.532 | unknown | |

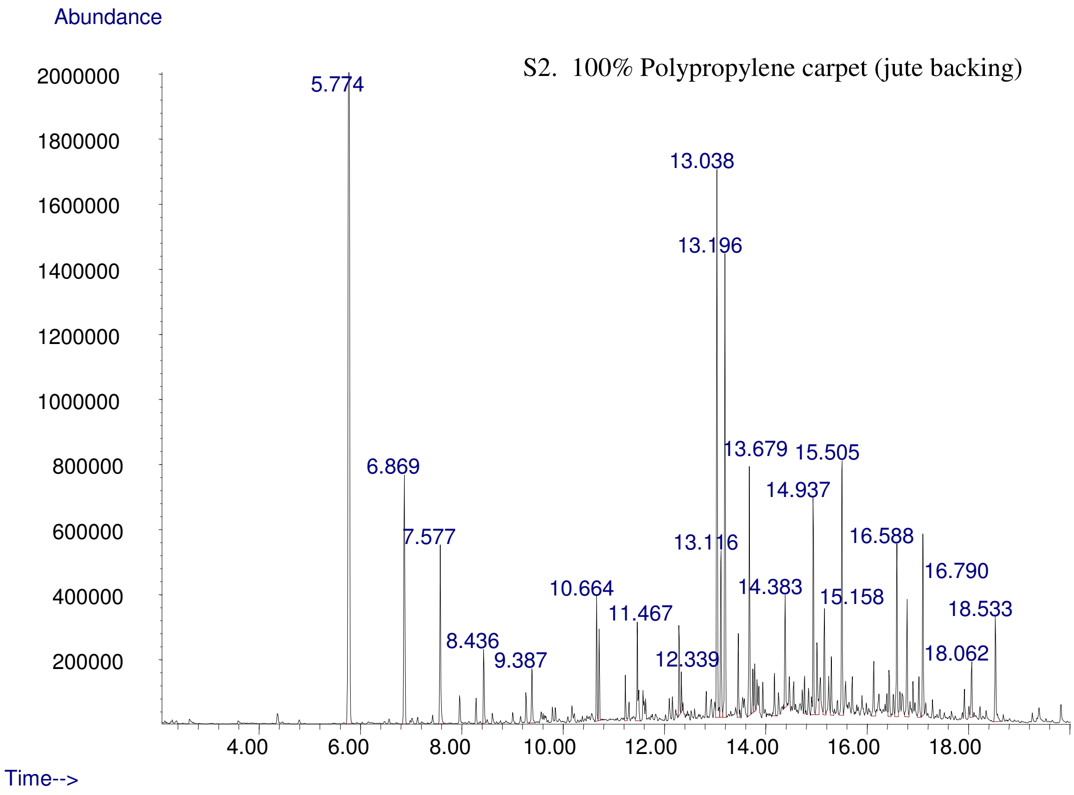


**Figure 5.11 Chromatogram of sample S2 100% polypropylene carpet with jute backing.**

**Table 5.4 Peak identification of volatile compounds extracted from burnt polypropylene carpet (jute backing).**

| RT | Compound | Match probability |
|---|---|---|
| 4.352 | **Toluene** | 43.2 |
| 6.587 | 2,4-Dimethyl-1-heptene | 58.0 |
| 7.581 | Styrene | 38.9 |
| 7.961 | 1,2,3,4,5-pentamethyl cyclopentane, | 10.8 |
| 8.285 | unknown | |
| 8.436 | 4-Methyl-2-heptanone | 84.8 |
| 9.269 | 4,6-Dimethyl-2-heptanone | 71.8 |
| 9.387 | 4,6-Dimethyl-5-hepten-2-one | 37.6 |
| 10.664 | 2-Isopropyl-5-methyl-1-heptanol | 3.67 |
| 10.713 | 1,1-Dimethyldecyl hydrosulfide | 6.68 |
| 11.231 | 3,7,11-Trimethyl-1-dodecanol | 4.89 |
| 11.302 | unknown | 3.82 |
| 11.467 | (2,4,6-Trimethylcyclohexyl) methanol | 15.9 |
| 11.579 | 2,10-dimethyl-9-Undecenol | 9.22 |
| 11.645 | **Naphthalene** | 52.3 |
| 12.097 | 6,10,14-Trimethyl-2-pentadecanone | 10.6 |
| 12.161 | 2-Hexyl-1-decanol | 4.47 |
| 12.291 | 4,4,8-Trimethyl-non-7-en-2-one | 48.2 |
| 12.339 | unknown | 38.2 |
| 13.038 | 2-Isopropyl-5-methyl-1-heptanol | 5.75 |
| 13.116 | unknown | |
| 13.196 | unknown | |
| 13.458 | 2-Hexyl-1-decanol | 3.62 |

***Table 5.4 continued***

| | | |
|---|---|---|
| 13.679 | 13,13-Dimethyltetradecen-1-ol acetate | 6.00 |
| 14.383 | Dodecenyl succinic anhydride | 10.6 |
| 14.937 | 3,7,11,15-Tetramethylhexadecanol | 6.32 |
| 15.013 | unknown | |
| 15.158 | unknown | |
| 15.296 | unknown | |
| 15.505 | 11,13-Dimethyl-12-tetradecen-1-ol acetate | 10.6 |
| 16.131 | unknown | 7.99 |
| 16.435 | unknown | |
| 16.588 | 1-Octacosanol | 2.91 |
| 16.790 | Nonadecyl pentafluoropropionate | 4.37 |
| 17.102 | unknown | 7.63 |
| 17.921 | unknown | |
| 18.062 | unknown | 11.3 |
| 18.533 | unknown | |
| 19.826 | unknown | 13.3 |

### *Vinyl Sheeting and Vinyl Tiles*

Vinyl tiles with adhesive backing and vinyl sheeting made from PVC material were examined. The chromatograms and data are presented in figure 5.11 and figure 5.12. The total ion chromatogram of the vinyl sheeting contains a range of medium petroleum distillates while the vinyl tiles (containing adhesive) contain a range of volatile components within the heavy petroleum distillate range. Previous work reported that samples containing adhesives have indicated the presence of compounds such as xylenes, cumenes, dihydroindenes, naphthalenes and methyl-naphthalenes [34]. Some of these compounds were identified in the samples of vinyl analysed in this study. When the extracted ion profiles were examined the alkane, cycloalkane and alkylbenzene profiles were prominent for both samples however the naphthalene and indane profiles showed relatively weaker signals for the vinyl sheet sample than the vinyl tile sample.

When polyvinylchloride, the main component in vinyl sheeting and vinyl tile, is exposed to intense heat or fire, its degradation involves the release of hydrogen chloride, forming conjugated double bonded structures. Further rearrangements, produce a significant level of aromatic hydrocarbon compounds [6, 10, 37]. Identification of chlorine containing compounds was reported by Hugget and Levin [43]. The results presented in figure 5.12 and 5.13 identified various compounds including benzene, toluene, styrene, naphthalene and some chlorine-containing compounds such as chlorobutane, chlorooctane, chloromethylheptane and dodecylchloride which concur with the previous literature.

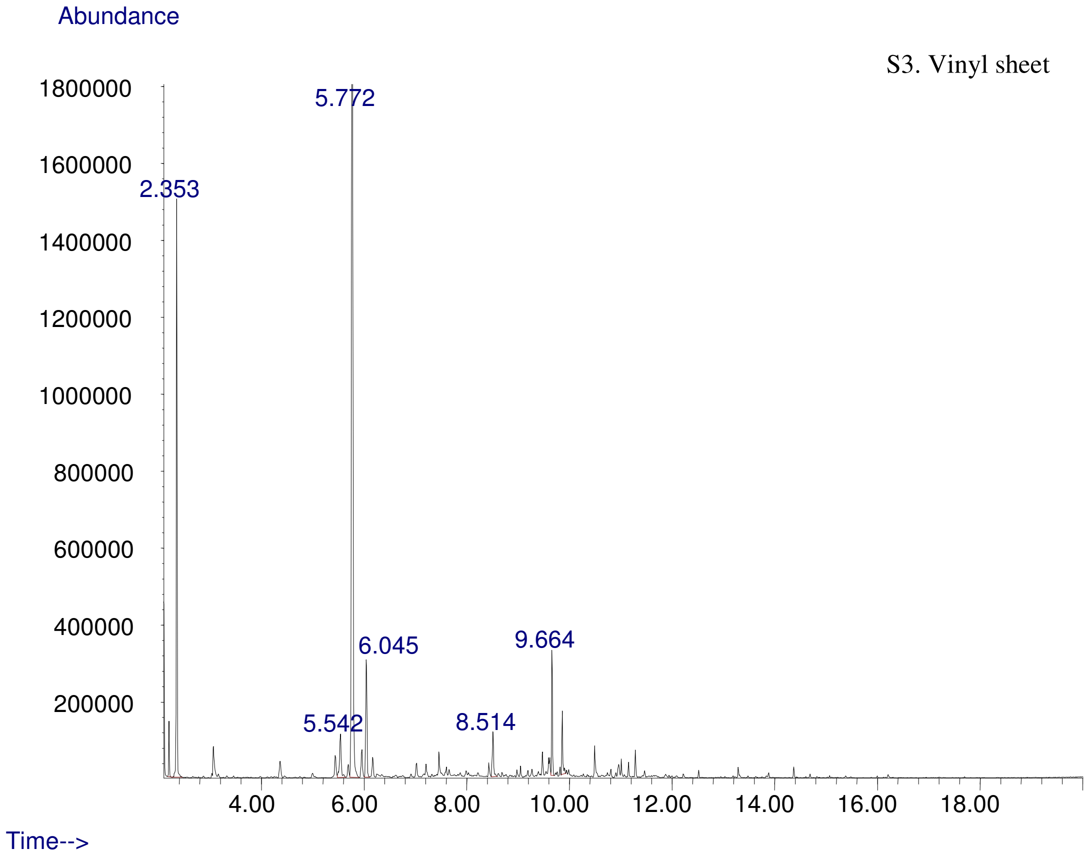


**Figure 5.12Chromatogram of sample S3 Vinyl sheet.**

**Table 5.5 Peak identification of volatile compounds extracted from burnt vinyl sheet.**

| **Rt** | **Compound** | **Match probability %** |
|---|---|---|
| 2.201 | 1-Chlorobutane | 85.8 |
| 2.353 | Benzene | 75.6 |
| 3.068 | Methyl methacrylate | 68.2 |
| 4.365 | **Toluene** | 23.2 |
| 5.542 | 2-Ethylhexene | 67.0 |
| 6.045 | 3-Methyl-2-heptene | 18.6 |
| 6.172 | Octacene | 17.4 |
| 7.460 | 3-Heptanone | 38.4 |
| 7.579 | Styrene | 38.9 |
| 8.514 | Isobutyl methacrylate | 55.6 |
| 9.468 | Chlorooctane | 10.6 |
| 9.664 | Chloromethyl heptane | 67.3 |
| 9.859 | Ethylhexanol | 58.6 |
| 10.49 | unknown | |
| 11.287 | Ethylhexyl acetate | 63.1 |

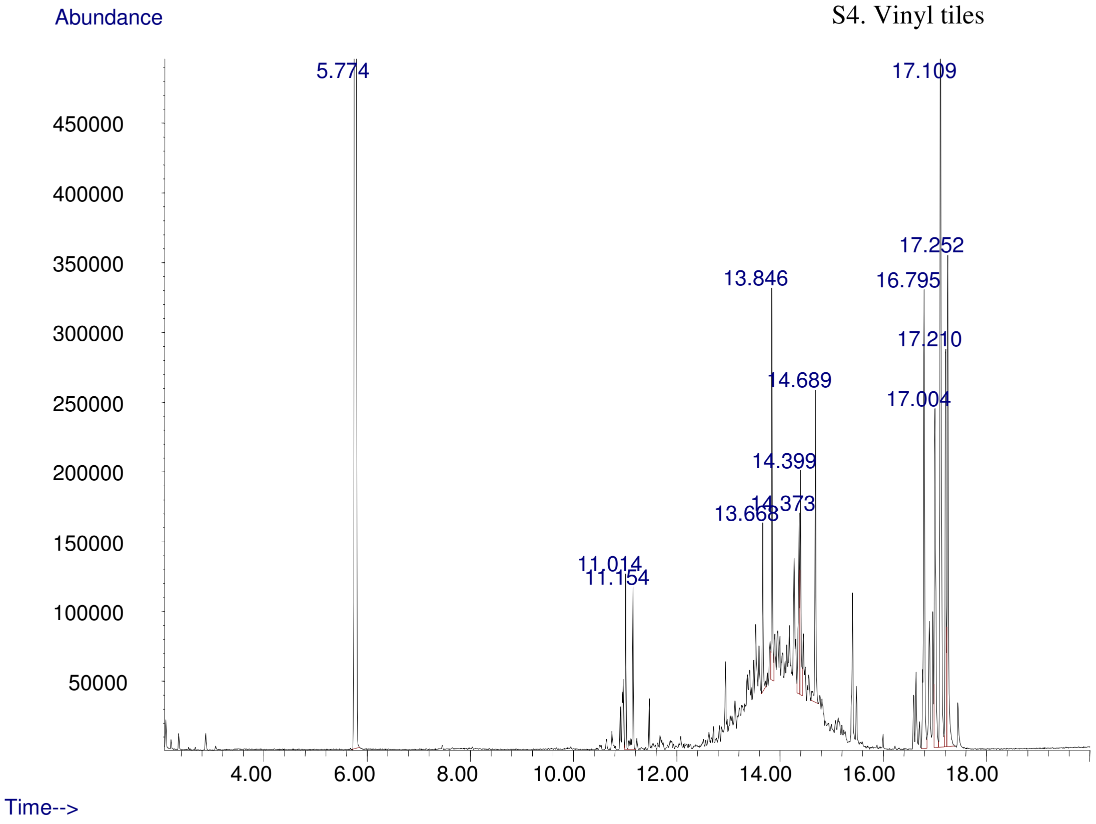


**Figure 5.13 Chromatogram of sample S4 vinyl tiles.**

**Table 5.6 Peak identification of volatile compounds extracted from burnt vinyl tiles.**

| **RT** | **Compound** | **Match probability** |
|---|---|---|
| 2.353 | Benzene | 75.6 |
| 7.579 | Styrene | 38.9 |
| 11.014 | unknown | |
| 11.154 | Dodecyl chloride | 15.7 |
| 11.702 | **Naphthalene** | 43.5 |
| 12.949 | 2-Hexyl-1-octanol | 8.60 |
| 13.531 | 2,6,10-trimethyl dodecane (branched alkane) | 15.1 |
| 13.668 | 2,6,10-Trimethyltetradecane | 21.5 |
| 13.846 | **Tetradecane** | 12.2 |
| 14.278 | Unknown | |
| 14.373 | Chlorotetradecane | 21.0 |
| 14.399 | 2,6,10-Trimethyltetradecane | 17.4 |
| 14.689 | **Pentadecane** | 16.2 |
| 15.408 | unknown | |
| 16.795 | Isopentyl benzoate | 14.1 |
| 16.897 | 2-Octyl benzoate | 18.4 |
| 17.004 | Benzoic acid, tridecyl ester | 17.8 |
| 17.109 | Benzoic acid, tetradecyl ester | 21.4 |
| 17.210 | Diisobutyl phthalate | 15.5 |
| 17.252 | Benzoic acid pentadecyl ester | 19.8 |

### *5.3.1.2 Polymeric House Hold Materials*

*Polystyrene Compact Disk (CD) Casings*

The total ion chromatogram of general purpose polystyrene polymer (GPPS) used to make compact disk cases [44] is presented in figure 5.14. When the extracted ion profiles were examined, ion profiles for cycloalkanes/alkenes, alkylbenzenes and naphthalenes were prominent, in contrast to alkanes which were present at low relative abundance. As described in the literature, polystyrene undergoes depolymerisation and side group scission, producing mostly aromatic products and mainly, the styrene monomer [6, 45, 46]. Gurman *et al*. compiled an extensive list of volatile products generated from the thermal decomposition of polystyrene (under various conditions) and some were identified in this study [46]. Pyrolysis products identified included toluene, benzene, ethylbenzene, α-methylstyrene and 1,3 diphenylpropane. The only combustion product identified was benzaldehyde.

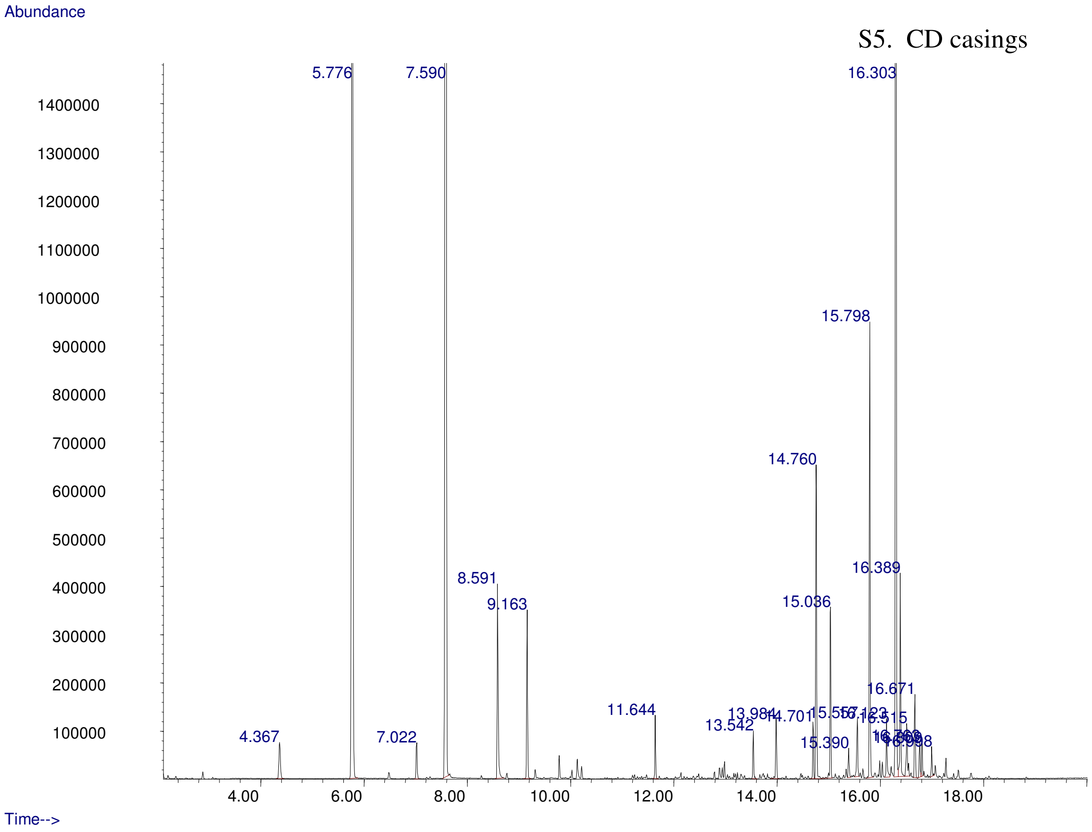


**Figure 5.14 Chromatogram of sample S5 polystyrene CD casing.**

**Table 5.7 Peak identification of volatile compounds extracted from polystyrene CD casing.**

| RT | Compound | Match probability |
|---|---|---|
| 4.367 | **Toluene** | 33.9 |
| 7.022 | **Ethylbenzene** | 62.1 |
| 7.590 | Styrene | 49.2 |
| 8.591 | Benzaldehyde | 70.2 |
| 9.613 | α-Methylstyrene | 34.6 |
| 11.644 | **Naphthalene** | 41.6 |
| 13.542 | Biphenyl | 52.2 |
| 13.984 | Diphenylmethane | 50.1 |
| 14.701 | 1,2-Diphenylethylene | 17.9 |
| 14.760 | Bibenzyl | 93.4 |
| 15.036 | α-Methyldibenzyl | 79.3 |
| 15.386 | 1,2-Diphenylcyclopropane | 20.3 |
| 15.552 | Benzene, 1,1’-(1-butene-1,4-diyl)bis | 37.8 |
| 15.798 | 1,3-Diphenylpropane | 96.1 |
| 16.123 | (2-Phenyl-4-pentenyl)benzene | 90.3 |
| 16.303 | 1,2,3,4-Tetrahydro-2-phenylnaphthalene | 24.1 |
| 16.389 | 1-Phenyl-2-(2-vinylphenyl)ethanone | 27.9 |
| 16.515 | (2-Phenylcyclobutyl)benzene | 62.4 |
| 16.671 | 1,2,3,4-Tetrahydro-1-phenylnaphthalene | 84.9 |
| 16.763 | unknown | |
| 16.809 | unknown | |
| 16.998 | 4-Phenyl-3-butenylbenzene | 82.5 |

### *Polyurethane Foam*

Flexible Polyurethane foam (PU) is a substance that has common applications in upholstery, furniture and mattresses and is routinely used in both domestic and commercial properties. Observation has shown that polyurethane produces yellow thick smoke and readily catches fire [47]. Thermal decomposition of flexible PU foam is known to produce isocyanate, polyol (alcohol containing multiple hydroxyl groups) and volatile polyureas [42]. Wooley and Ferrel identified 23 compounds including benzene, toluene, indene and naphthalene from PU smoke [42], however none of these specific compounds were identified in the samples prepared for this study which are presented in figure 5.15.

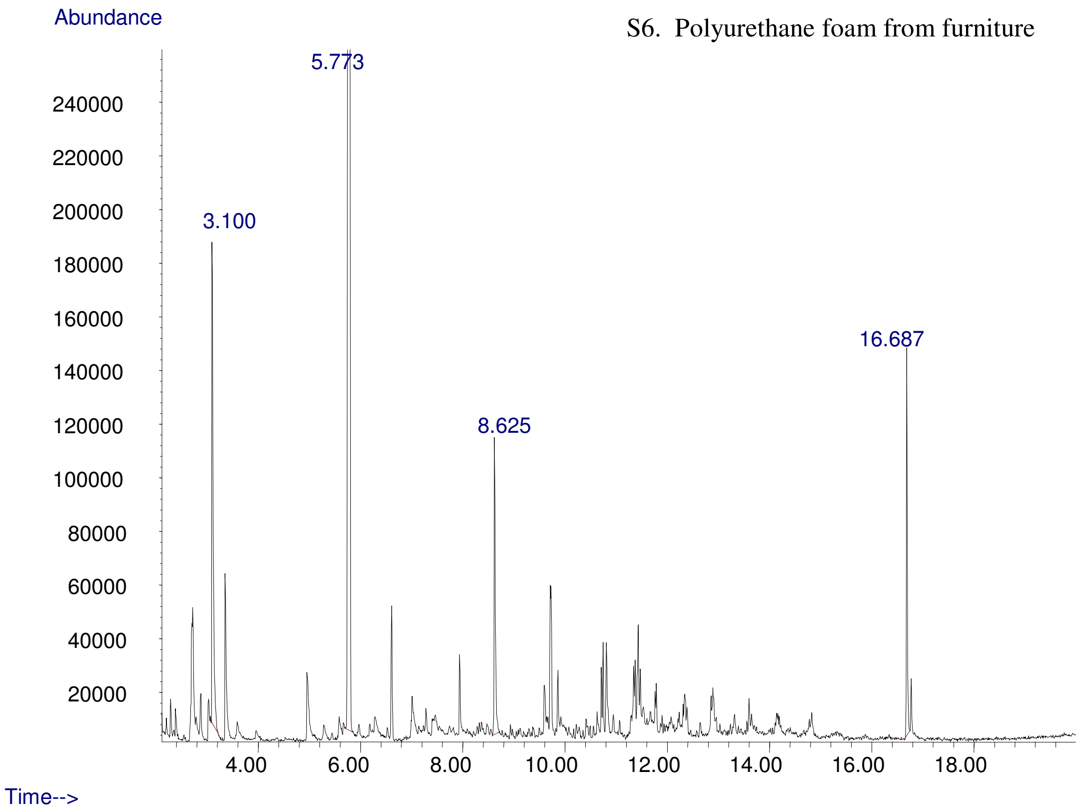


**Figure 5.15 Chromatogram of sample S6 polyurethane foam.**

**Table 5.8 Peak identification of volatile compounds extracted from burnt polyurethane foam from furniture.**

| **Rt** | **Compound** | **Match probability %** |
|---|---|---|
| 2.710 | 1-Chloro-2-propanol | 91.8 |
| 3.126 | Propyl acetate | 93.7 |
| 3.358 | 2,2,4-trimethyl-1,3-Dioxolane, | 89.3 |
| 4.957 | 2-Ethyl-4-methyl-1,3-dioxolane | 89.1 |
| 6.605 | Hexamethylcyclotrisiloxane | 93.0 |
| 7.937 | unknown | |
| 8.625 | Propylene acetate | 10.7 |
| 9.720 | Octamethyltetrasiloxane | 73.0 |
| 10.758 | unknown | |
| 10.808 | 3-(3-Isopropoxypropoxy)-1-propanol | 50.2 |
| 11.374 | unknown | |
| 16.693 | Tris(1-chloro-2-propyl)phosphate | 60.1 |

### *Carrier bag (polyethylene)*

A pattern resembling that of heavy petroleum distillates containing a homologous series of diene, alkane and alkene from burnt plastic carrier bags of polyethylene material as shown in figure 5.16. Examination of the extracted ion chromatogram reveals a low relative abundance of alkylbenzene and naphthalene profile in comparison to that of diesel. In addition, the absence of pristine and phytane can easily differentiate polyethylene from diesel samples.

Pyrolysis of polyethylene, mostly by random scission degradation produces a wide range of alkane and alkene products within the C2 to C23 hydrocarbon range [12, 48]. Hodgkin and co-workers also detected acetone, acetaldehyde, acetic acid and small amount of acrolein as polyethylene oxidative product, however, none of these are detected in this case.

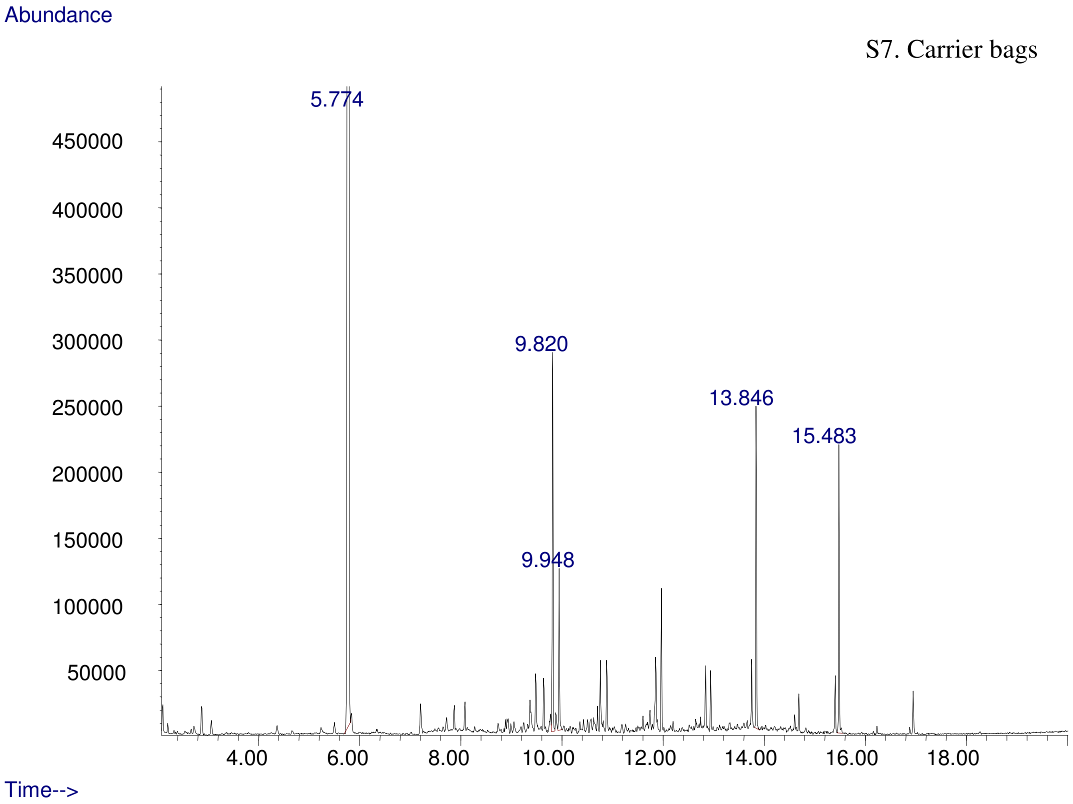


**Figure 5.16 Chromatogram of sample S7 carrier bags.**

**Table 5.9 Peak identification of volatile compounds extracted from carrier bags.**

| RT | Compound | Match probability |
|---|---|---|
| 4.368 | **Toluene** | 44.2 |
| 7.207 | **o-Xylene** | 33.6 |
| 7.872 | Nonene | 28.5 |
| 8.081 | **Nonane** | 27.9 |
| 9.472 | Decene | 6.48 |
| 9.645 | **Decane** | 19.3 |
| 9.820 | Isopropyltoluene | 22.0 |
| 9.948 | Limonene | 36.8 |

***Table 5.9 continued***

| | | |
|---|---|---|
| 10.761 | Undecene | 7.40 |
| 10.886 | **Undecane** | 15.8 |
| 11.644 | **Naphthalene** | 45.6 |
| 11.857 | Dodecene | 5.26 |
| 11.971 | **Dodecane** | 33.1 |
| 12.482 | Tridecene | 6.24 |
| 12.941 | **Tridecane** | 23.1 |
| 13.757 | Tetradecene | 4.98 |
| 13.849 | Teradecane | 35.9 |
| 14.598 | Pentadecene | 4.58 |
| 14.689 | Pentadecane | 48.9 |
| 15.405 | Hexadecene | 3.95 |
| 15.483 | **Hexadecane** | 33.1 |
| 16.945 | **Nonadecane** | 14.1 |

### 5.3.1.3 Wood

The pyrolysis and combustion of the three major components in wood i.e hemicelluloses, cellulose and lignin, produces compounds which include water vapour, methane, methanol, acrolein and limonene (pine) [9, 11]. The presence of levoglucosan, acetic acid, furans, 2-furaldehyde, 2,3-butanedione, phenol, cresol, and xylenols are also reported [14, 21]. The chromatographic profiles of pine wood and some wood product samples are presented in figures 5.17 to 5.19. Limonene, furaldehydes, furans and phenolic compounds were identified. Apart from the presence of toluene, the results indicated that burnt pine wood, MDF and plywood substrates generated volatile compounds that did not resemble ignitable liquid patterns and as such could easily be distinguished.

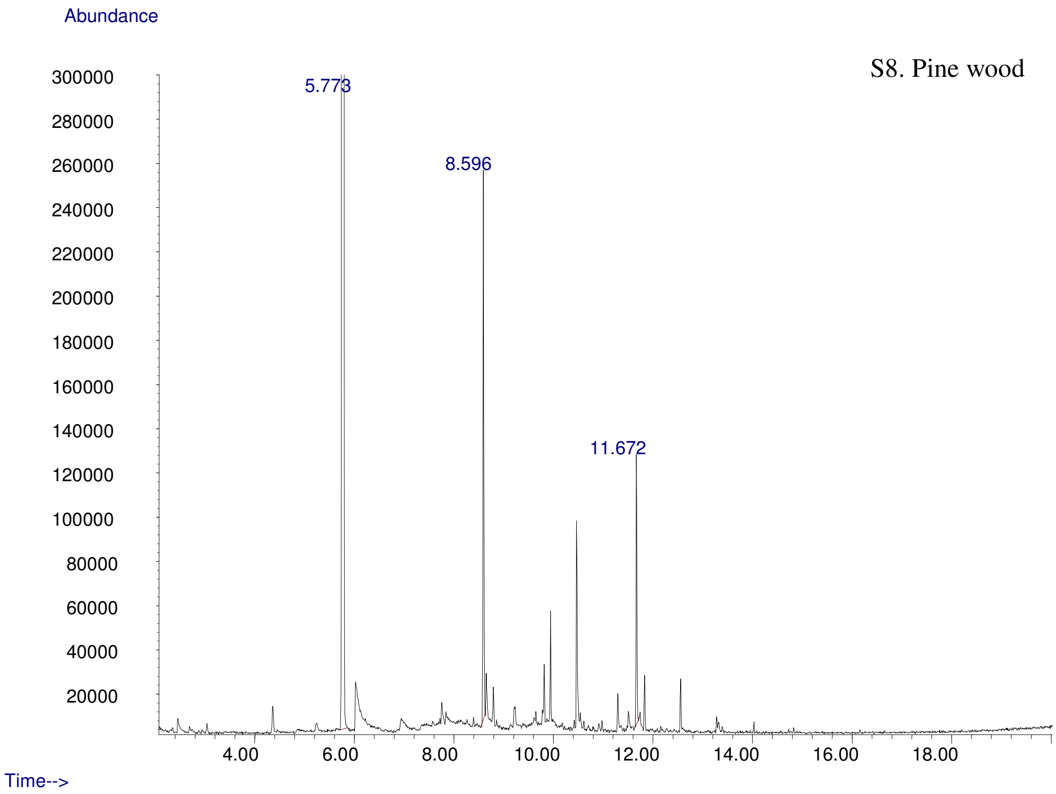


**Figure 5.17 Chromatogram of sample S8 pine wood.**

**Table 5.10 Peak identification of volatile compounds extracted from burnt pine wood.**

| RT | Compound | Match probability |
|---|---|---|
| 4.359 | Toluene | 45.3 |
| 6.080 | Furaldehyde | 65.2 |
| 8.596 | Dimethylsiloxane cyclic trimer | 20.1 |
| 9.817 | m-Isopropyltoluene | 13.3 |
| 9.942 | Terpene d-limonene | 20.9 |
| 10.458 | 2-methoxyphenol | 62.1 |
| 11.674 | 2-methoxy-4-methylphenol | 47.3 |
| 11.832 | Unknown | |
| 12.556 | 4-ethyl-2-methoxyphenol | 61.7 |

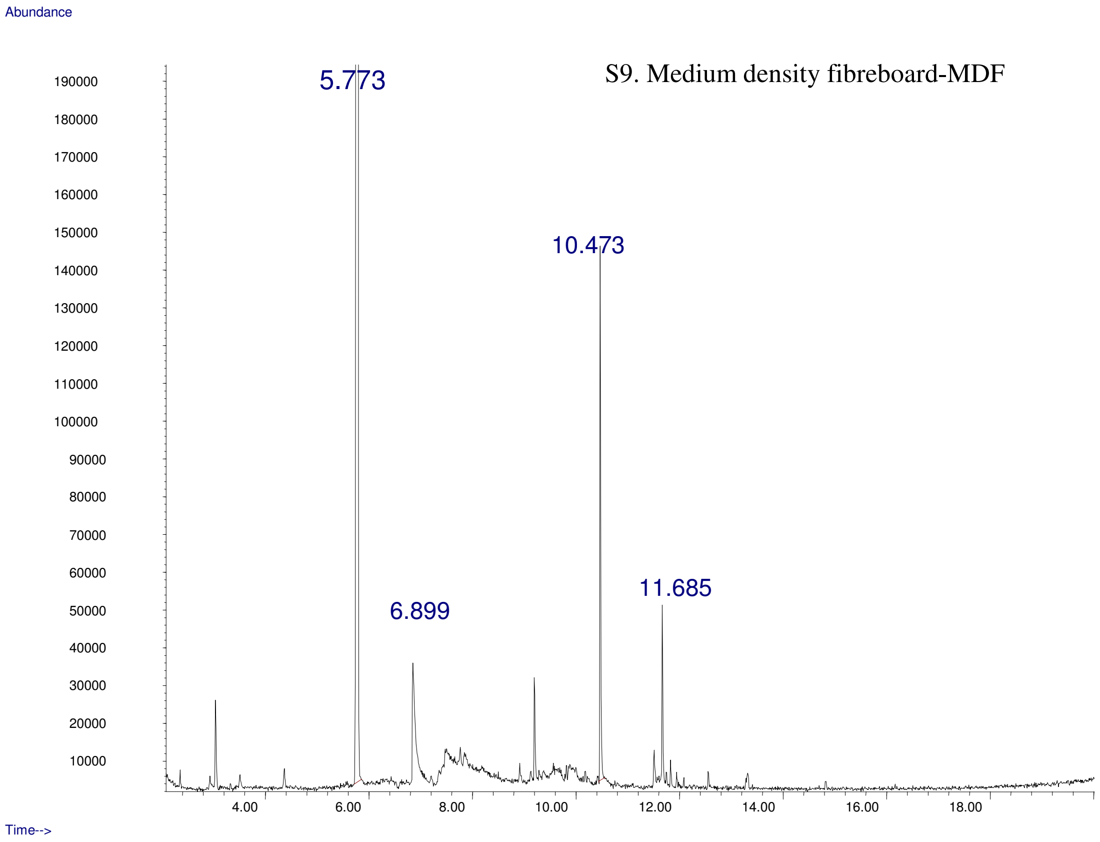


**Figure 5.18 Chromatogram of sample S9 Medium density fibreboard (MDF).**

**Table 5.11 Peak identification of volatile compounds extracted from burnt medium density fibre board.**

| RT | Compound | Match probability |
|---|---|---|
| 3.028 | 2,5-Dimethylfuran | 79.9 |
| 4.352 | Toluene | 43.4 |
| 6.899 | 2-Furanmethanol | 62.9 |
| 9.204 | 2-Furanmethanol acetate | 80.8 |
| 10.473 | 2-methoxyphenol | 74.2 |
| 11.685 | unknown | |

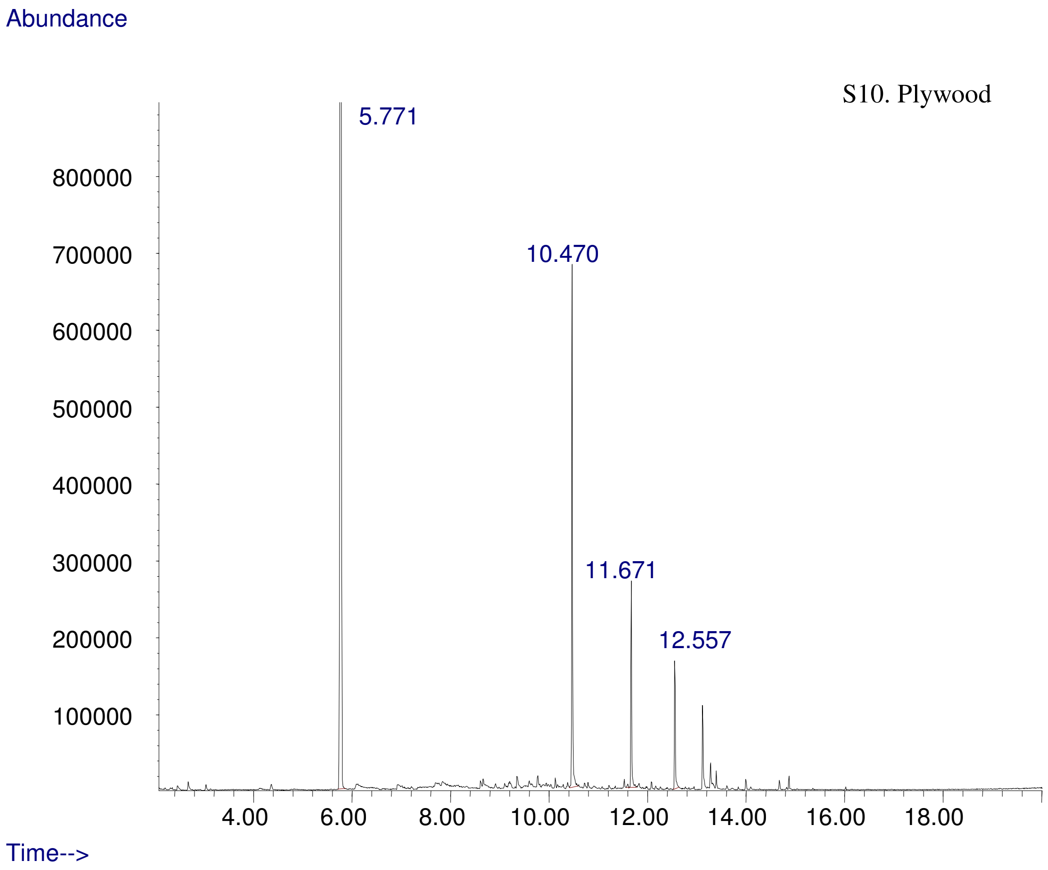


**Figure 5.19 Chromatogram of sample S10 plywood.**

**Table 5.12 Peak identification of volatile compounds extracted from burnt plywood.**

| RT | Compound | Match probability |
|---|---|---|
| 2.679 | 2,3-Pentanedione | 68.6 |
| 3.037 | 2,5-Dimethylfuran | 59.4 |
| 4.360 | Toluene | 46.5 |
| 10.470 | 3,5,5-Trimethyl-2-cyclopentenone | 46.5 |
| 11.671 | 2-methoxy-4-methyl- phenol | 19.1 |
| 12.557 | 4-ethyl-2-methoxy- phenol | 81.5 |
| 13.122 | 2,6-Dimethoxyphenol | 84.4 |

### 5.3.1.4 Newspaper

Previous work has suggested that burnt newspaper could produce a chromatographic result typical of a heavy petroleum distillate pattern, containing alkane peaks between C13 and C17 [34]. Such profiles were not obvious in the results derived from this work however a zoomed section of total ion chromatograph, presented in figure 5.20 did indicate a small abundance of interfering volatile product but these were not identifiable.

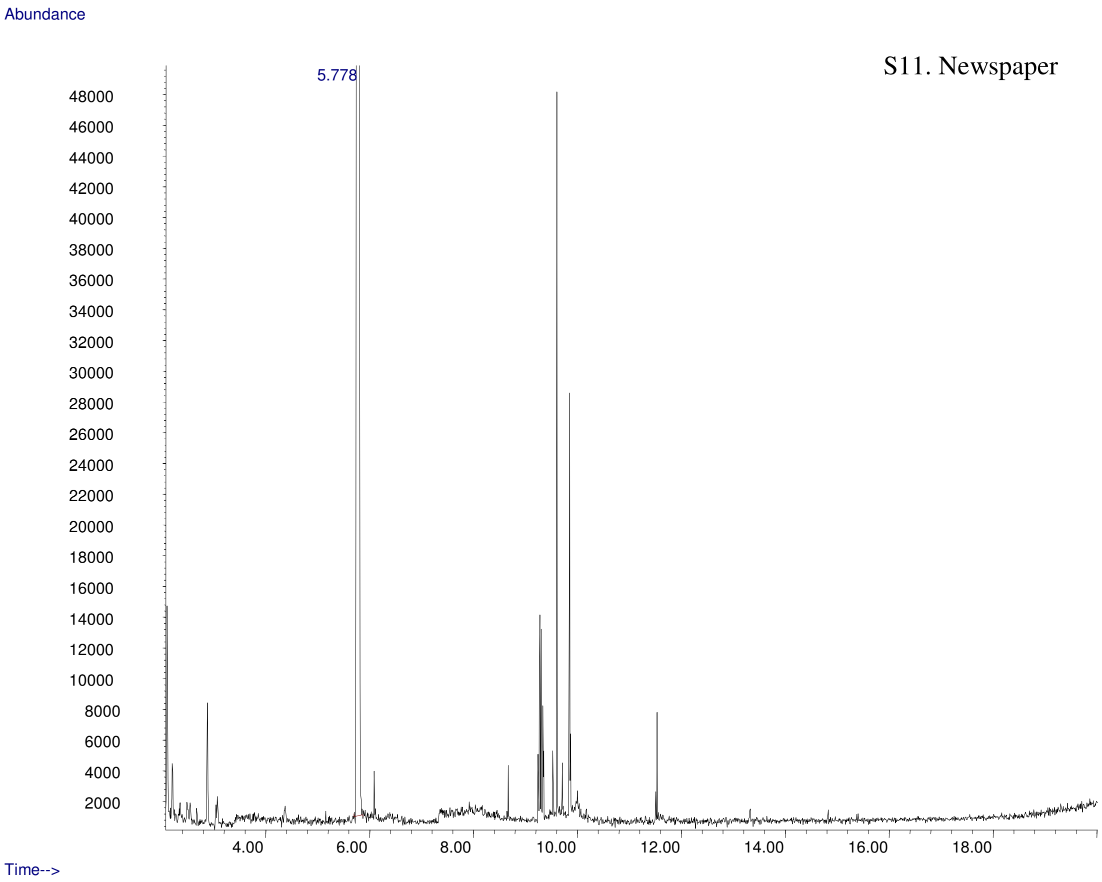


**Figure 5.20 Chromatogram of sample S11 burnt newspaper.**

### 5.3.2 General Conclusions in Relation to Substrate Interfering Products

Volatiles from burnt substrates produce significant chromatographic patterns that could readily hamper the identification of ignitable liquids potentially present in debris samples. Identification of component peaks has indicated the presence of volatile compounds produced by the substrates which are also characteristic of ignitable liquids. In particular the frequent occurrence of toluene, benzene, naphthalene, styrene and methylstyrenes has been identified. As such the presence alone of these compounds should be interpreted carefully as they do not necessarily indicate the presence of an ignitable liquid. In certain cases, the use of extracted ion profiles to identify a collection of volatile components indicative of a particular hydrocarbon group is crucial. The relative abundance of the compounds within the profiles for selected ions once known, can be compared to those of known ignitable liquids profiles.

### 5.3.3 Burning of Selected Substrate Materials in the Presence of Ignitable Liquids

The temperatures recorded during the preparation of substrate and ignitable liquid samples are presented in table 5.13. Even though, burning was carried out under controlled laboratory conditions, the temperature during sample preparation was seen to fluctuate considerably within the range of 100°C to 350°C and occasionally as high as 400°C. These temperatures may not reflect those experienced with a typical fire, but are adequate to produce the intended residue samples for this study [10, 49].

All samples that were prepared did not produce interfering products or ignitable liquid profiles and as such, only those which did were taken forward for the data analysis phase. Interfering product sample recovery was random and unpredictable when burnt in the presence of the ignitable liquids. In most cases, the ignitable liquid residues were retained in samples where the substrate was carpet, vinyl sheet and polyethylene plastic bags. The wood substrates failed to produce any ignitable liquid residues. These observations are in agreement with the work by Borusiewicz *et al.* which examined various factors contributing to ignitable liquid residue recovery [50]. Borusiewicz concluded that the type and the absorbent nature of the burnt substrate directly influenced the ability of the substrates to retain ignitable liquids.

**Table 5.13: Maximum temperature recorded during the burnings for simulated fire debris samples. Highlighted are the samples which produced chromatographic patterns which contained interfering products (in total 128 ) and were tested for prediction using the SOFM model.**

| | S1 PP Carpet/ rubber | S2 PP Carpet woven | S3 Lino sheet | S4 Lino tile | S5 CD casing | S6 PU foam | S7 Carrier bag | S8 Red Pine | S9 MDF | S10 Plywood | S11 Newspaper |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LPD | | | | | | | | | | | |
| Ronsonol | 298 | 261 | 392 | 247 | 292 | 360 | 240 | 269 | 346 | 231 | 160 |
| Swan | 322 | 277 | 254 | 212 | 353 | 225 | 324 | 261 | 217 | 196 | 232 |
| Dunhill | 206 | 233 | 202 | 204 | 190 | 330 | 194 | 207 | 188 | 176 | 252 |
| Perma | 229 | 191 | 189 | 161 | 386 | 309 | 282 | 428 | 309 | 465 | 242 |
| Zippo | 241 | 149 | 165 | 151 | 311 | 202 | 214 | 173 | 264 | 135 | 210 |
| MPD | | | | | | | | | | | |
| BQWS | 131 | 156 | 152 | 166 | 182 | 162 | 162 | 215 | 193 | 200 | 293 |
| BERTOLINE WS | 215 | 176 | 184 | 190 | 207 | 204 | 168 | 188 | 187 | 189 | 293 |
| HOMEBASE WS | 173 | 197 | 187 | 175 | 163 | 324 | 171 | 168 | 203 | 163 | 324 |
| TESCO WS | 131 | 209 | 248 | 184 | 171 | 167 | 331 | 137 | 128 | 191 | 285 |
| HBC | 164 | 209 | 224 | 190 | 188 | 266 | 191 | 180 | 181 | 168 | 266 |
| PBC | 219 | 221 | 221 | 229 | 223 | 228 | 196 | 263 | 213 | 181 | 175 |
| ADLO | 198 | 214 | 196 | 210 | 215 | 214 | 136 | 171 | 188 | 119 | 247 |
| BLO | 164 | 173 | 191 | 194 | 177 | 136 | 172 | 191 | 175 | 123 | 132 |
| HPD | | | | | | | | | | | |
| DA | 227 | 238 | 200 | 125 | 310 | 136 | 127 | - | - | - | 138 |
| DB | 200 | 233 | 253 | 221 | 249 | 267 | 204 | 237 | 249 | 176 | 266 |
| DC | 168 | 194 | 182 | 214 | 177 | 165 | 129 | - | - | - | 165 |
| DD | 190 | 161 | 198 | 132 | 286 | 163 | 120 | - | - | - | 221 |
| DE | 127 | 114 | 185 | 177 | 192 | 232 | 167 | - | - | - | 191 |
| DF | 206 | 201 | 210 | 188 | 110 | 125 | 250 | - | - | - | 211 |
| DG | 171 | 191 | 175 | 185 | 198 | 179 | 136 | - | - | - | 332 |
| DH | 241 | 255 | 298 | 244 | 179 | 271 | 177 | - | - | - | 366 |

***Table 5.13 continued***

| Petrol | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Petrol A | 155 | 134 | 150 | 152 | 124 | 170 | 140 | 140 | 169 | 192 | 172 |
| Petrol B | 159 | 189 | 117 | 132 | 190 | 194 | 180 | 135 | 186 | 165 | 193 |
| Petrol C | 111 | 196 | 107 | 193 | 186 | 190 | 260 | 193 | 203 | 185 | 285 |
| Petrol D | 103 | 118 | 131 | 110 | 111 | 132 | 193 | 124 | 105 | 206 | 132 |
| Petrol E | 175 | 187 | 175 | 189 | 176 | 231 | 106 | 182 | 177 | 101 | 202 |
| Petrol F | 283 | 224 | 210 | 121 | 327 | 481 | 380 | 176 | 257 | 261 | 255 |
| Petrol G | 306 | 321 | 307 | 298 | 209 | 398 | 403 | 227 | 181 | 213 | 416 |
| Petrol H | 291 | 275 | 277 | 240 | 508 | 197 | 228 | 195 | 139 | 147 | 273 |
| Petrol J | 189 | 192 | 169 | 165 | 205 | 198 | 229 | 146 | 227 | 223 | 178 |
| Petrol K | 187 | 170 | 109 | 165 | 170 | 162 | 195 | 156 | 135 | 287 | 230 |
| Petrol L | 166 | 165 | 186 | 124 | 460 | 260 | 209 | 312 | 144 | 141 | 160 |
| Petrol M | 135 | 160 | 104 | 181 | 174 | 182 | 191 | 108 | 197 | 114 | 161 |
| Petrol N | 177 | 168 | 180 | 148 | 370 | 122 | 145 | 250 | 192 | 180 | 223 |
| Petrol P | 182 | 178 | 198 | 219 | 321 | 221 | 125 | 181 | 146 | 109 | 269 |

Key: Sampling code for ignitable liquid samples
BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO= After Dark lamp oil.
DA=diesel Asda, DB=diesel Esso, DC=diesel Jet, DD=diesel Sainsbury, DE=diesel Shell, DF=diesel Morrison, DG=diesel BP andDH= diesel Tesco
For petrol samples, the code represent A=BP premium grade, B=Esso premium grade, C=Tesco super grade, D=Sainsbury premium grade, E=Shell premium grade, F=leaded 4 Star, G=BP regular grade, H=Esso regular grade, J=Sainsbury regular grade, K=Shell regular grade, L=Jet regular grade, M=Tesco premium grade, N=Asda regular grade and P=Morrison regular grade

### 5.3.4 Classification of Ignitable Liquid Residues using SOFM Model

The chromatographic data of ignitable liquid residues from 128 burnt substrates were compared to the ignitable liquid reference collection using a direct superimposition technique. Data processing for the normalised chromatographic data of ignitable liquid residues samples were performed using power transformed (sixteenth root) and row scaled such as described in chapter 4 (section 4.7.2). The ability of the SOFM approach to discriminate ignitable liquid residues based on class characteristics was tested by incorporating these 128 samples into the existing ignitable liquid combined data matrices. Consequently, data matrices of 372 samples with 151 variables were established and then subjected to SOFM analysis. Figure 5.21 reveal the output map from the corresponding data matrix.

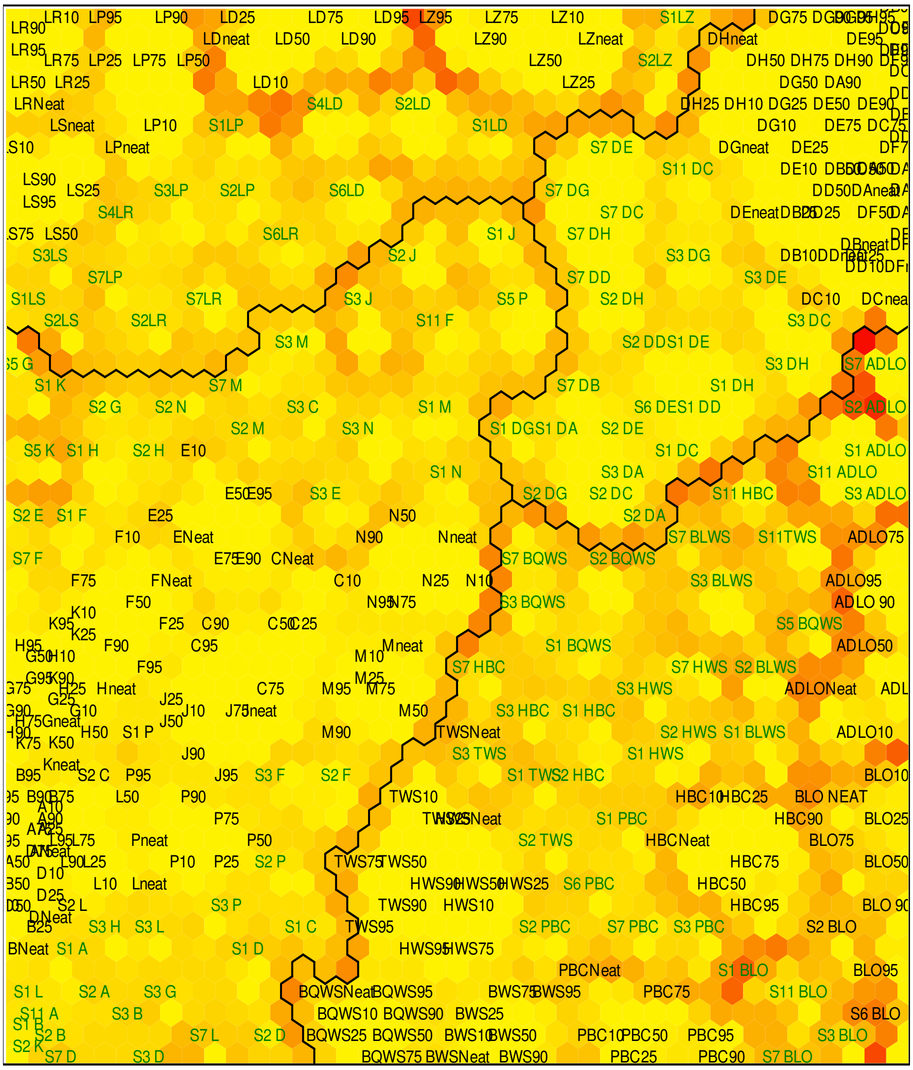


**Figure 5.21 SOFM output maps showing the classification of ignitable liquid residues based on the class characteristic. Key code for LPD are LP=Perma, LS=Swan, LR=Ronsonol, LZ=Zippo and LD=Dunhill. Other samples are labelled as in table 5.13.**

Reference ignitable liquids and substrate with residue samples are labelled in black font and green font respectively. The output map revealed four distinct clusters on the basis of class characteristics. The clusters are emphasised with the black segmentation lines to highlight these groupings. All the LPD and HPD samples were located on the upper left and right region respectively while petrol and MPD groups dominate the central and lower region of the map. Most importantly, SOFM mapping correctly assign all ignitable liquid residue samples derived from the variety of substrates to their respective ignitable liquid class group. .This demonstrates the abilities of this mathematical approach to link ignitable liquid residues in fire debris to a specific class of ignitable liquid.

Further investigation was performed at a subclass level to determine the applicability of SOFM to associate ignitable liquid residues, with the presence of interfering products back to its original brand of product.

### 5.3.5 Chromatographic Observation and SOFM Predictions for Light Petroleum Distillates Residues

Direct superimposition was used to compare the lighter fluid chromatographic profiles with those of the substrates and representative examples of the superimposed chromatograms of some lighter fluids and the substrates are presented in figure 5.22 – figure 5.24. In general the total ion chromatographic pattern from lighter fluid residues could be easily recognised and distinguished from those of the substrates. Because of the low boiling points of the components within the lighter fluid samples they elute relatively early in the chromatogram and as such do not interact with those of the interfering products. In the substrate spiked samples, the lighter fluid residues were detected in lower abundance compared to the reference unevaporated lighter fluid. This is understandable given the aggressive evaporation and the manner in which the residue compounds were retrieved. Consequently, not all of the burnt samples presented enough detail within the total ion chromatograms to facilitate further data analysis. In total, 17 lighter fluid and substrate residue samples were tested using the SOFM model in an attempt to re-associate the fighter fluid samples with their original brands.

A.

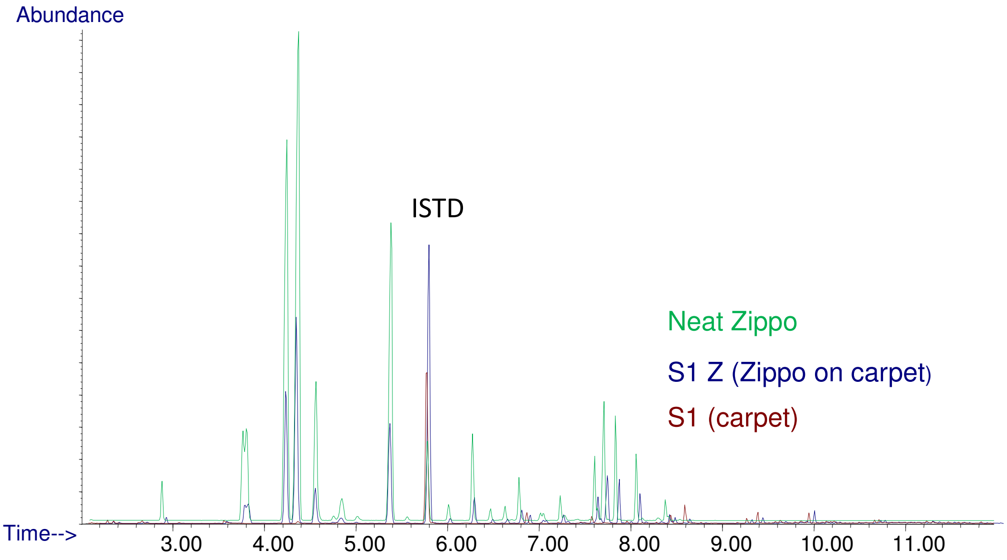


**Figure 5.22 TICs of LPD residues in comparison to neat IL and IP profiles of Zippo lighter fluid on polypropylene carpet with rubber backing( code =S1Z).**

B.

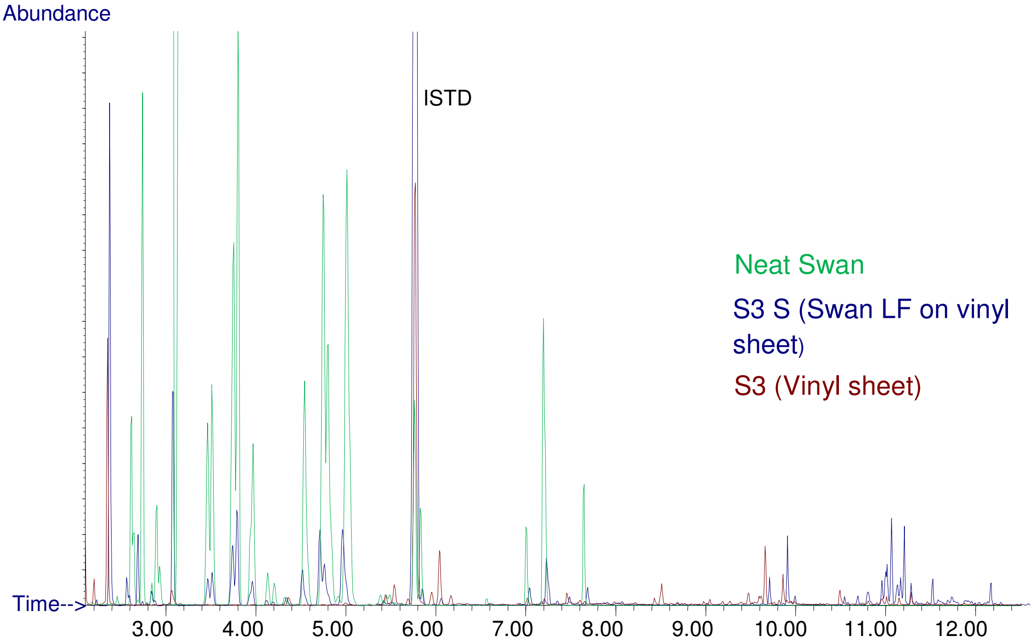


**Figure 5.23 TICs of LPD residues in comparison to neat ignitable liquid and interference product profiles of Swan lighter fluid on vinyl sheeting( code = S3S).**

C.

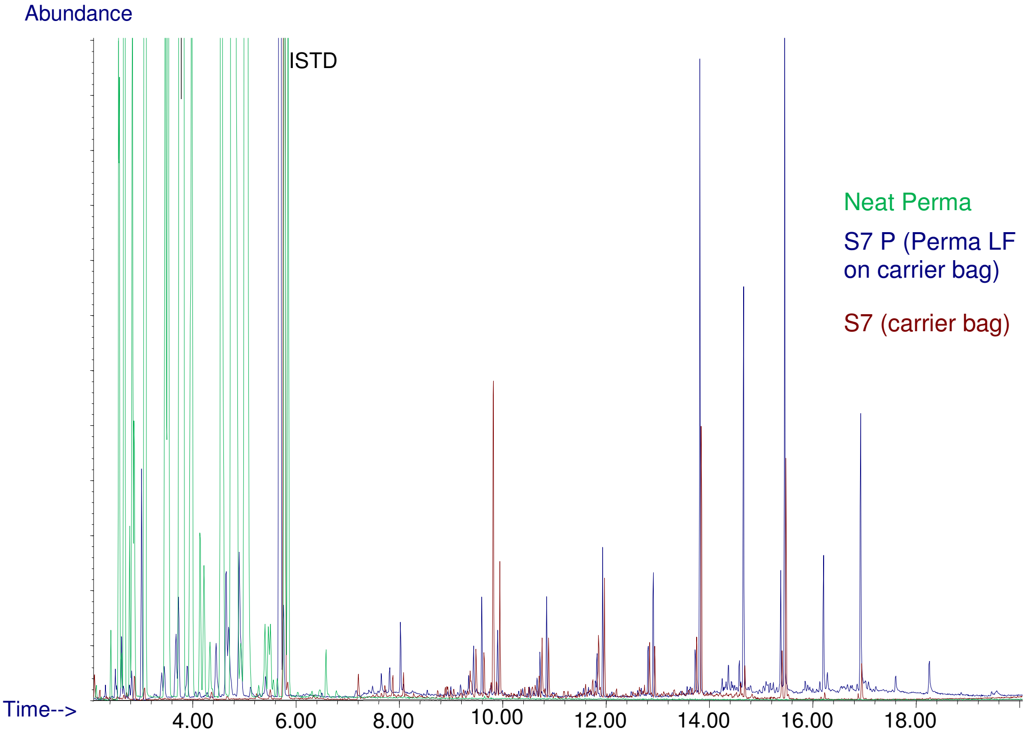


**Figure 5.24 TICs of LPD residues in comparison to neat IL and IP profiles of Perma lighter fluid on carrier bag( code = S7 P).**

The results obtained from the SOFM model are presented in figure 5.25. Because prior knowledge of these samples was available, autoprediction (based on Euclidean distance) was applied in a manner similar to that used in other studies [51-54]. The boundary lines have been outlined to emphasise the groupings between the samples. The residue samples were compared with the chromatographic results of the unevaporated and evaporated liquid lighter fluid samples.

The results indicate that the chromatographic profiles of the burnt substrates in combination with Zippo, Perma and Ronsonol lighter fluids were closely positioned to their unevaporated brands, suggesting a close association of these residues to the original source. Residues from Swan and Dunhill lighter fluid burnt with the substrates did not portray any association to their original unevaporated samples.

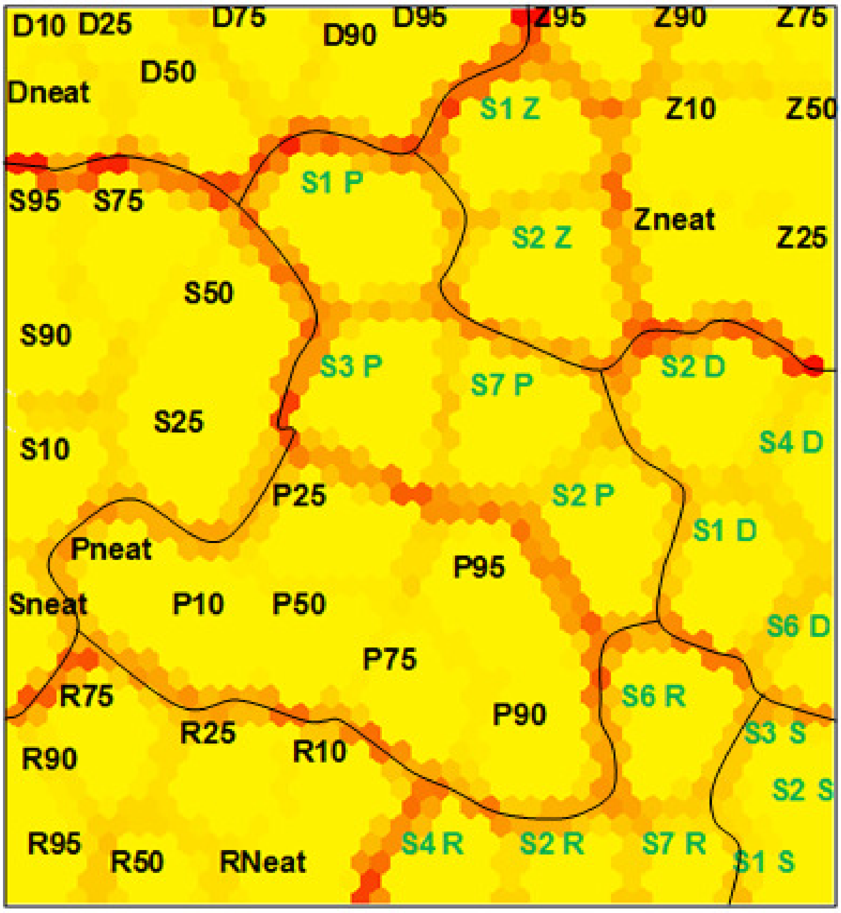


**Figure 5.25 The output map of residues (in green) and reference liquid (in black) LPD. (For residue sample, code S numerical represent the substrate followed by the ignitable liquid code which are R=Ronsonol, Z=Zippo, S=Swan, P=Perma and D=Dunhill).**

Limitations exist in the model because of the distortion in chromatographic pattern which will occur as the samples evaporate and the consequent loss of some major compounds. This introduces more zero values into the data matrix. Another critical factor is the difference in the abundance of the chromatographic peaks when comparing the unevaporated and evaporated ignitable liquid samples with those obtained when the ignitable liquids were burnt in the presence of the substrates and the residues extracted using passive headspace analysis.

This problem was acknowledged by Marshall *et al.* when they tried to relate diesel residues to their original source [55]. The authors suggested that multiplication of the signal obtained from the sample residue to make it comparable to that of the reference ignitable liquid may be a viable option that can be considered for future work.

Other related studies reported the use of the same method when preparing both reference collection samples and residue samples, for example using SPME extraction or passive headspace ACS extraction [56, 57]. This practise is, however, uncommon in fire debris analysis as most reference databases are build from direct liquid analysis of ignitable liquids and as such this approach was followed in the present study to evaluate the abilities of the mathematical methods to resolve sample association issues.

Despite these limitations, the SOFM model has demonstrated a potential approach which could lead to the discrimination of residual lighter fuel samples by brand.

### 5.3.6 Chromatographic Observation and SOFM Predictions for Medium Petroleum Distillate Residues

In general, compared to lighter fluid and substrate residues, the medium petroleum distillate and substrate residues revealed a general increase in the absorbance of the compounds recovered. Further chromatographic observations indicated that, although most of the interfering product compounds had a similar retention time range as the medium petroleum distillate samples, examination of the ignitable liquid and substrate residue chromatograms did not show a drastic chromatographic distortion of medium petroleum distillate pattern and as such were easily discriminated from the interfering product patterns. Examples of superimposed chromatograms obtained from burnt carpet, vinyl sheet and plastic materials on their own with the relevant unevaporated medium petroleum distillate are shown in figure 5.26 to figure 5.29. In total, 38 medium petroleum distillate residue samples provided data sufficient for SOFM analysis.

A.

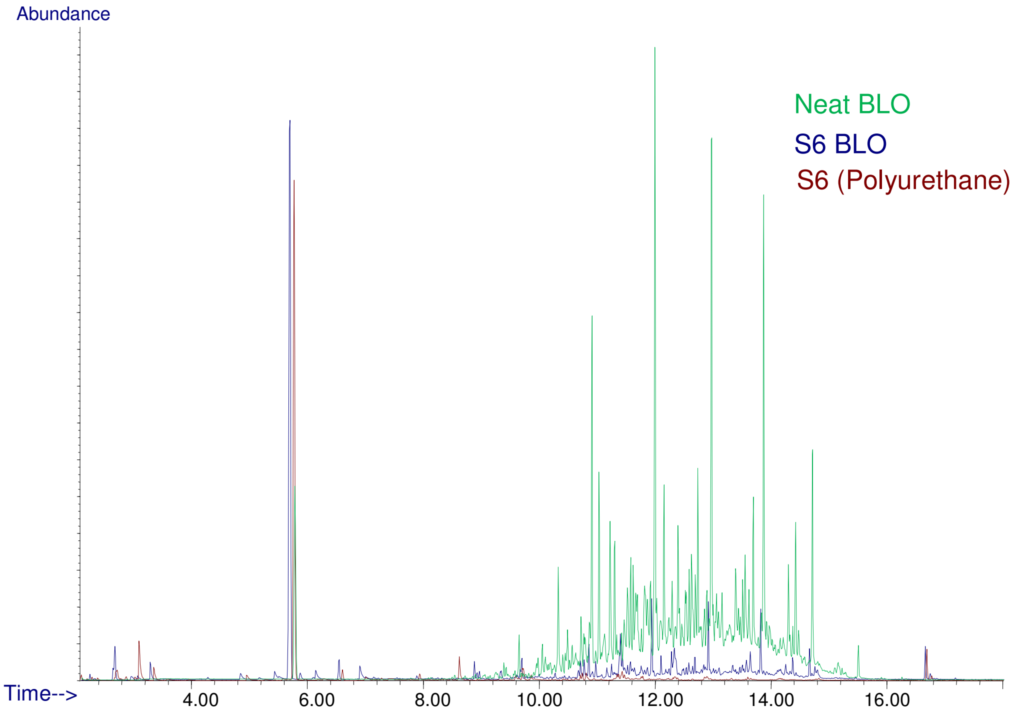


**Figure 5.26 TICs of MPD residues in comparison to neat ignitable liquid and interfering product profiles of Bertoline lamp oil on polyurethane foam (code=S6BLO).**

B.

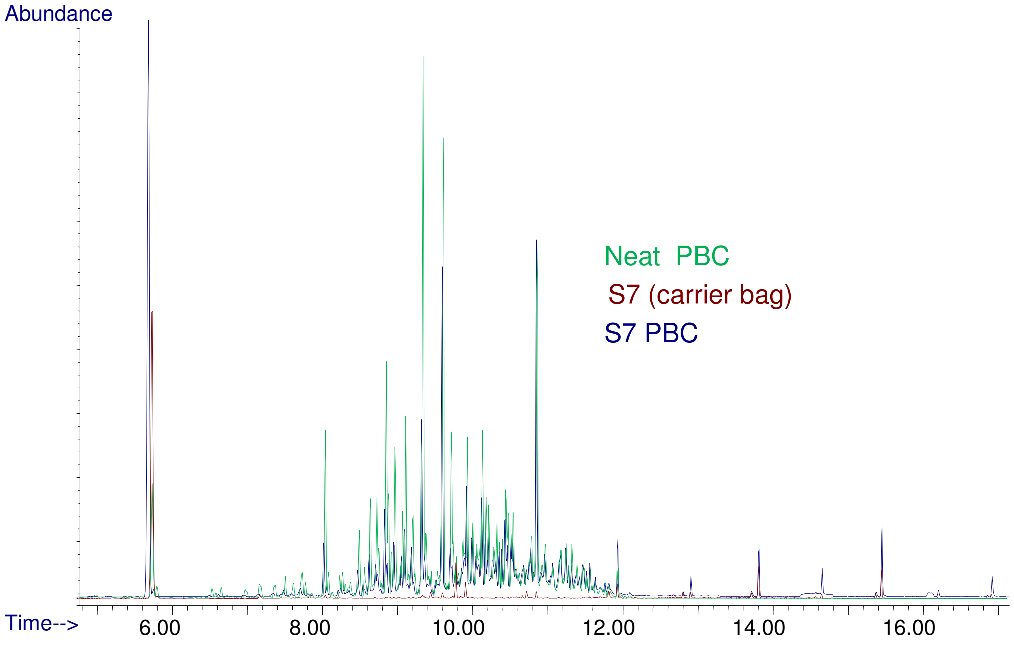


**Figure 5.27 TICs of MPD residues in comparison to neat ignitable liquid and interfering product profiles of Polycell brush cleaner on polyurethane foam (code= S7PBC).**

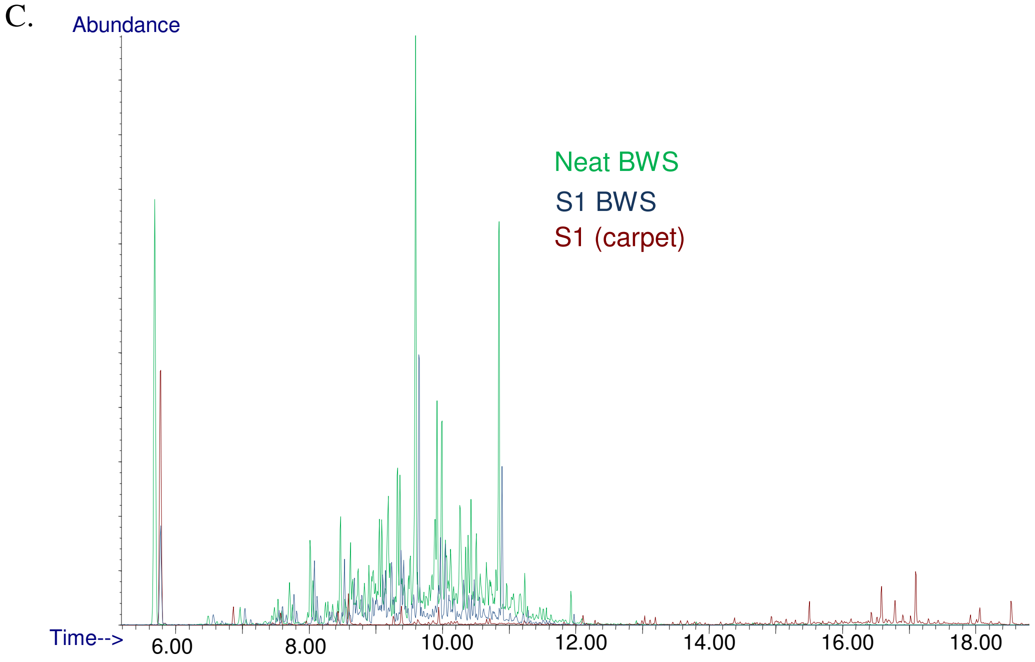


**Figure 5.28 TICs of MPD residues in comparison to neat ignitable liquid and interfering product profiles of Bertoline white spirit on polypropylene carpet (code= S1BWS).**

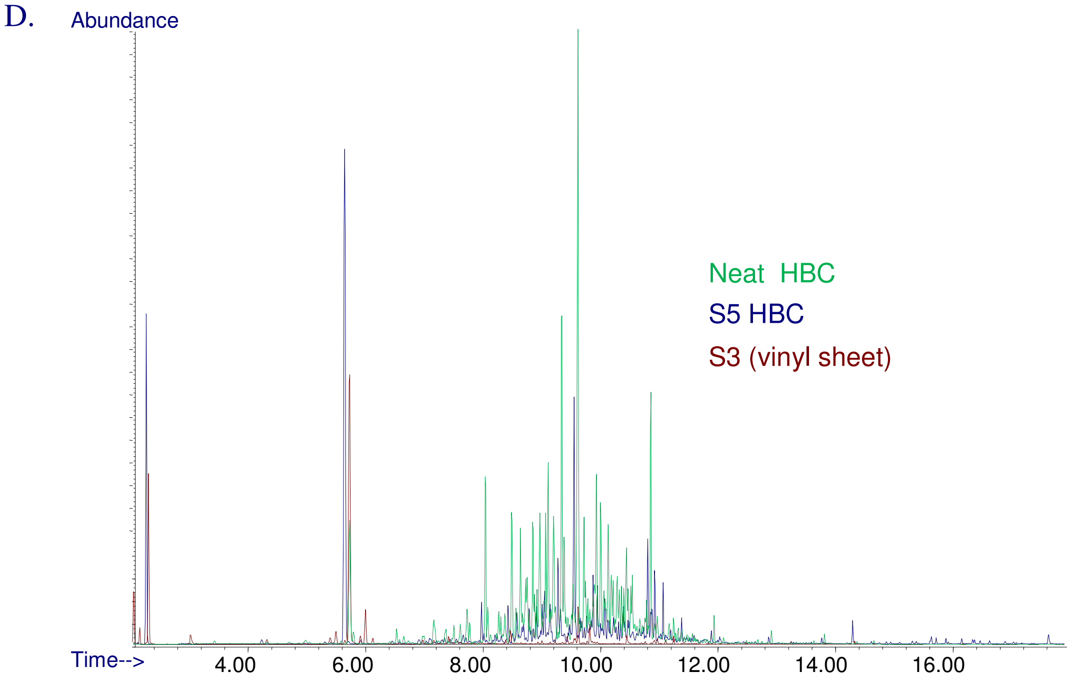


**Figure 5.29 TICs of MPD residues in comparison to neat ignitable liquid and interfering product profiles of Homebase brush cleaner on vinyl sheet (code= S3HBC).**

The output map for the SOFM analysis is presented in figure 5.30.

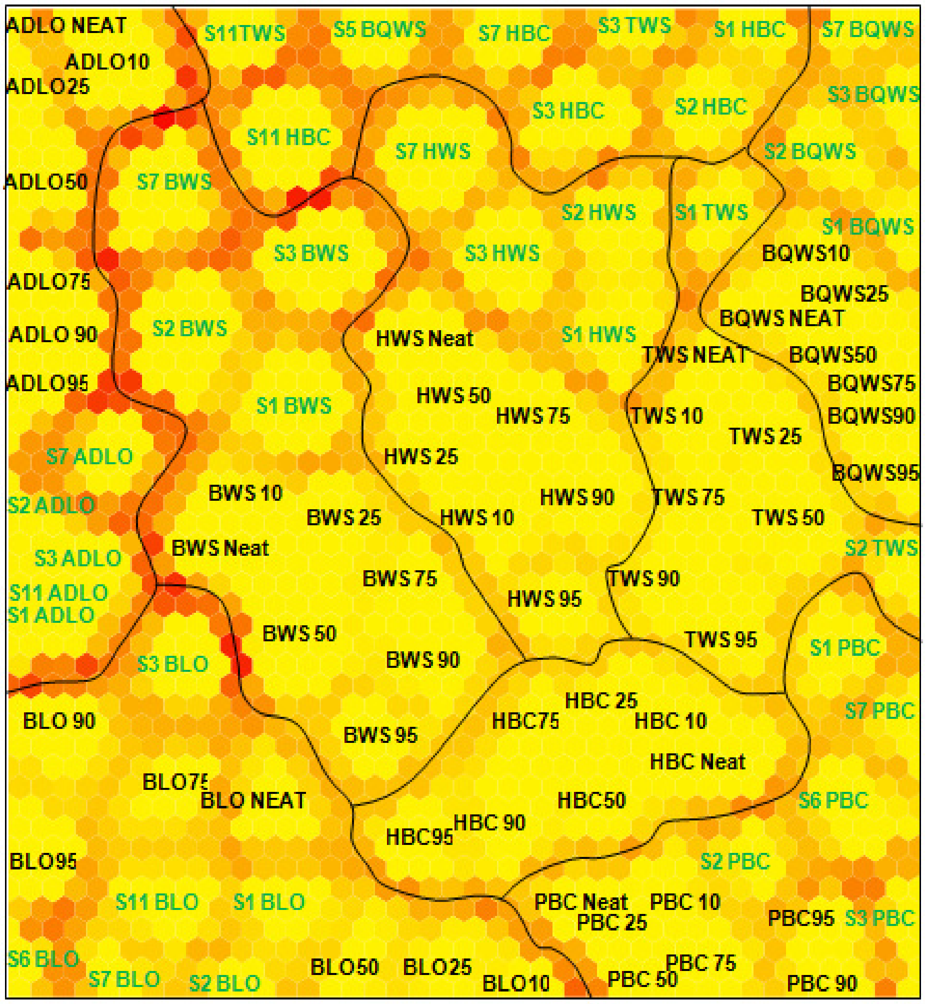


**Figure 5.30 The output map of residues (in green) and reference liquid (in black) MPD. (For residue sample, code Snumerical represent the substrate followed by the ignitable liquid code, BWS= Bertoline white spirit, HWS=Homebase white spirit, BQWS= B&Q white spirit, TWS=Tesco white spirit, PBC=Polycell brush cleaner, HBC=Homebase brush cleaner, BLO=Bertoline lamp oil and ADLO= After Dark lamp oil).**

Full discrimination of the lamp oils samples (ADLO and BLO) from the other medium petroleum distillate samples are clearly presented on the output map, with the former appearing to the left. Based on brand, both of these lamp oil brands and residue samples were successfully discriminated into their respective groups. Similarly, all residues from the Polycell brush cleaner (PBC), Bertoline white spirit (BWS) and Homebase white spirit (HWS) were correctly classified into their respective groups.

However, some mis-association occurred within a number of the white spirit samples, notably Tesco white spirit (TWS) in the presence of burnt vinyl flooring and newspaper and B&Q white spirit (BQWS) residue in the presence of burnt polyurethane foam. None of the Homebase brush cleaner (HBC) residue samples were successfully linked to the unevaporated or sequentially evaporated liquid samples, and were instead positioned amongst the white spirit group. It was evident that HBC residues cannot be differentiated from the white spirit residues post-fire.

### 5.3.7 Chromatographic Observation and SOFM Predictions for Heavy Petroleum Distillates Residues

In total, twenty five chromatographic profiles were obtained from the burnt substrate and diesel samples. It would be expected that, as the diesel was subjected to higher temperatures the chromatograms would skew towards the higher molecular weight and less volatile end of the chromatographic profile. However this was not observed when diesel was burnt in combination with the various substrates examined. Similar trends regrardless of the substrates were observed across all samples. A number of examples of the chromatograms obtained from the extracted substrate and diesel samples are presented in figure 5.31 and indicate the presence of hydrocarbon compounds from n-pentadecane (C15) to octadecane (C18) which is not entirely consistent with weathered diesel patterns recorded earlier (figure 4.22).

Some authors suggest that the skewing of chromatograms of heavy petroleum distillates towards the lighter more volatile end as an “overloading” effect of the adsorption medium [58, 59]. Alternatively, the incubation time or incubation temperature (80°C) used during the adsorption phase of the activated charcoal strip may not sufficiently volatilise higher boiling point carbon compounds and as such these may be decreased or absent in the resultant chromatogram. However, the extraction of a standard accelerant mixture of 50%evaporated petrol and 50% diesel (1:1 ratio) using the same extraction method did not exhibit these effects. The difference observed between the diesel samples as liquid samples and those produced in the presence of the substrates (where the ‘heavier end’ of the diesel would be expected but is missing), may be due to the interaction between the substrate and liquid either prior to, or during the burning process. It was noted though that pristine and phytane were present in each sample.

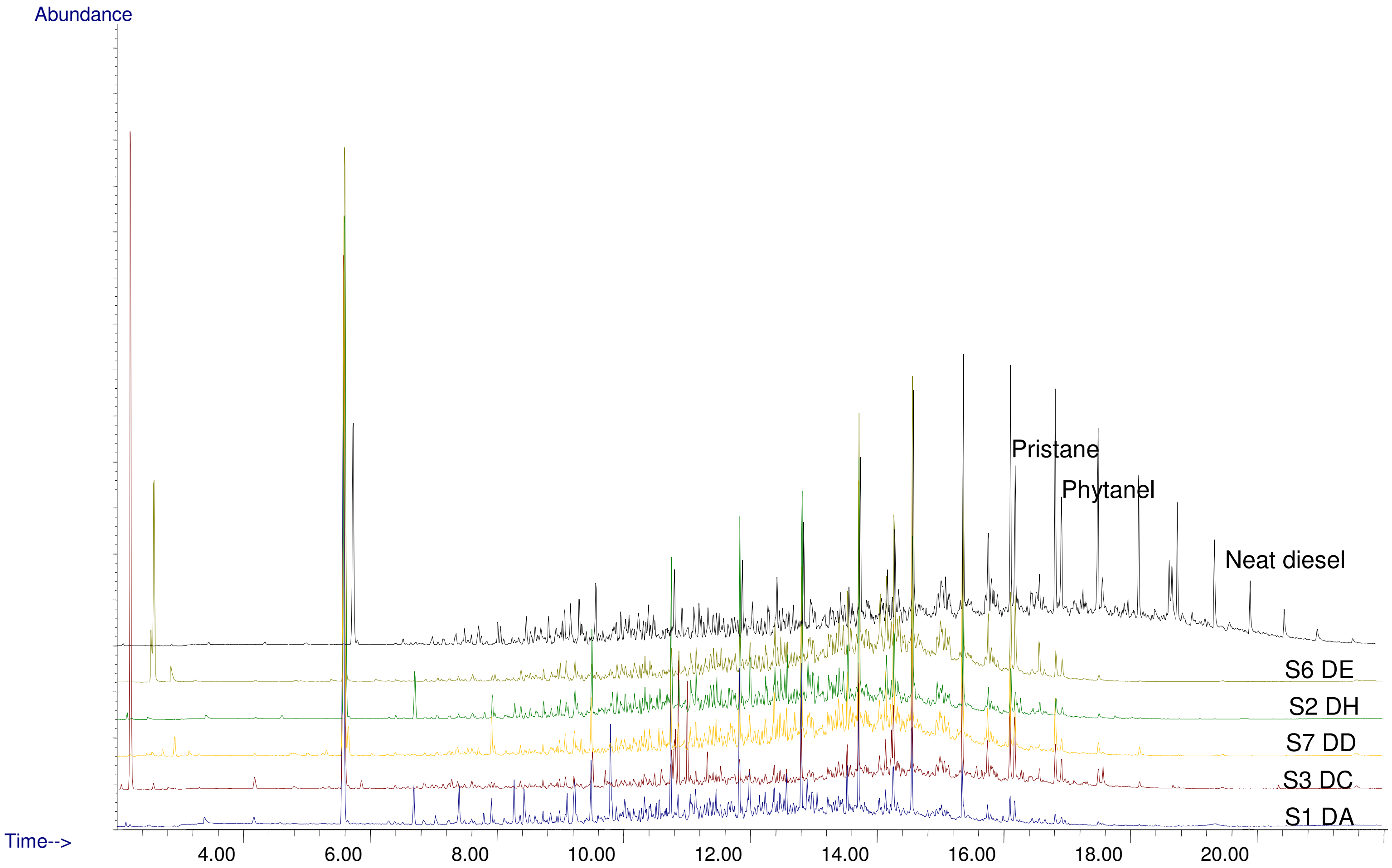


**Figure 5.31 .Representative TICs of diesel residues from substrate samples extracted using ACS –passive headspace method The samples are Asda diesel burnt on polypropylene carpet (S1DA), Jet diesel burnt on vinyl sheet (S3DC), Sainsbury diesel burnt on polyurethane foam (S7DD), Tesco diesel burnt on polypropylene jute backing (S2DH)and Shell diesel burnt on CD casing (S6DE).**

It has been demonstrated that liquid diesel samples can be generally classified into two groups as indicated by the results in chapter 4 where diesel obtained from the retail outlets ASDA, Sainsbury and Morrison were grouped with Esso and Jet, (samples DA, DB, DC, DD and DF) while diesel from Shell, BP and Tesco (samples DE,DG and DH) were also grouped together. When the substrate and diesel residue samples are added to the original data set, these groupings remained, with the exception of 90% weathered Shell diesel which was classified into the alternative group. The SOFM output map is presented in figure 5.32,

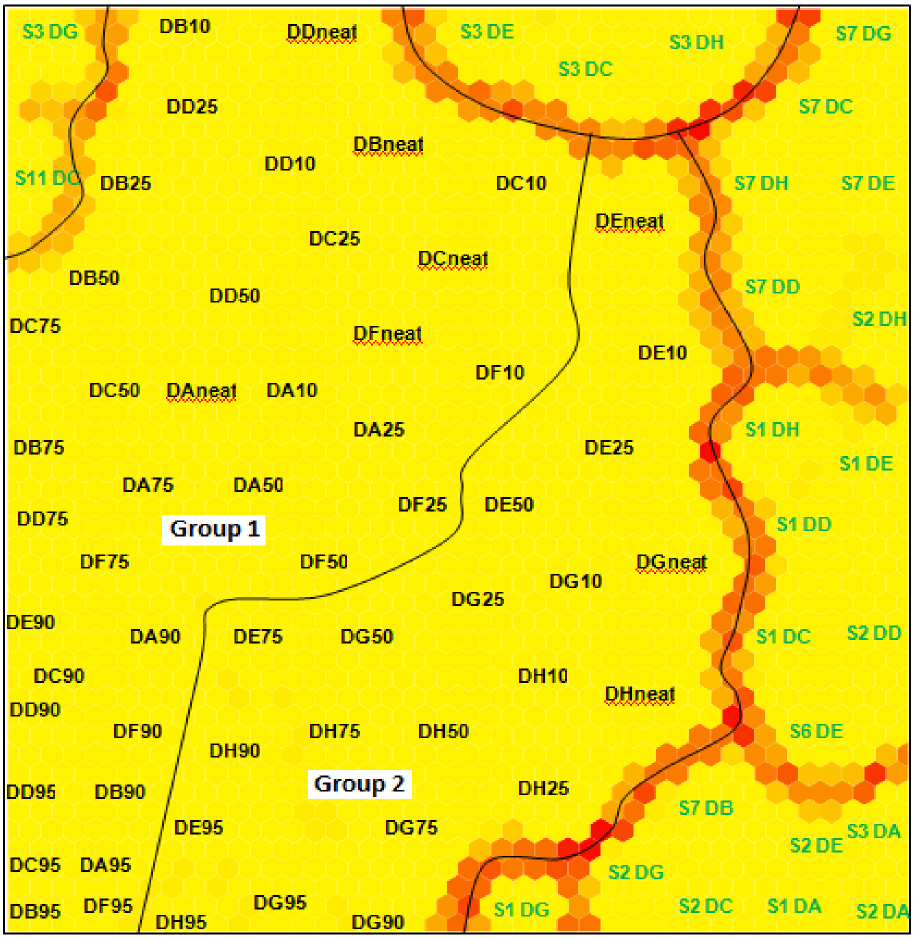


**Figure 5.32 The output map of diesel residues (in green) and diesel reference liquid (in black). For residue sample, code S numeric represent the substrate followed by the diesel brand code.**

### 5.3.8 Chromatographic Observation and SOFM Predictions for Petrol Residues

The chromatographic profiles of some petrol residues are presented in figures 5.33 to figure 5.36. These illustrate to various degrees the pattern distortion when petrol is exposed to heat in the presence of the various substrates.

In some cases, distortions of the toluene peak and peaks corresponding to other compounds were evident, however the C2 alkylbenzene to C4 akylbenzene, a characteristic region for petrol, can still be useful for the identification of petrol in the sample in all cases.

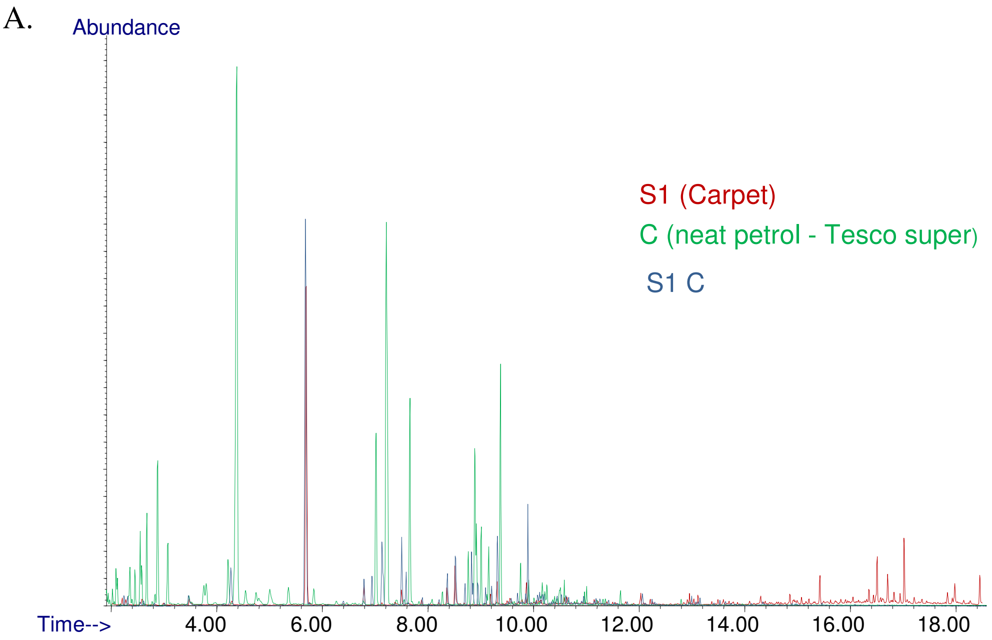


**Figure 5.33 TIC of petrol residue (Tesco super petrol on polypropylene carpet, S1 C), in comparison to neat petrol and interference product reference sample.**

B.

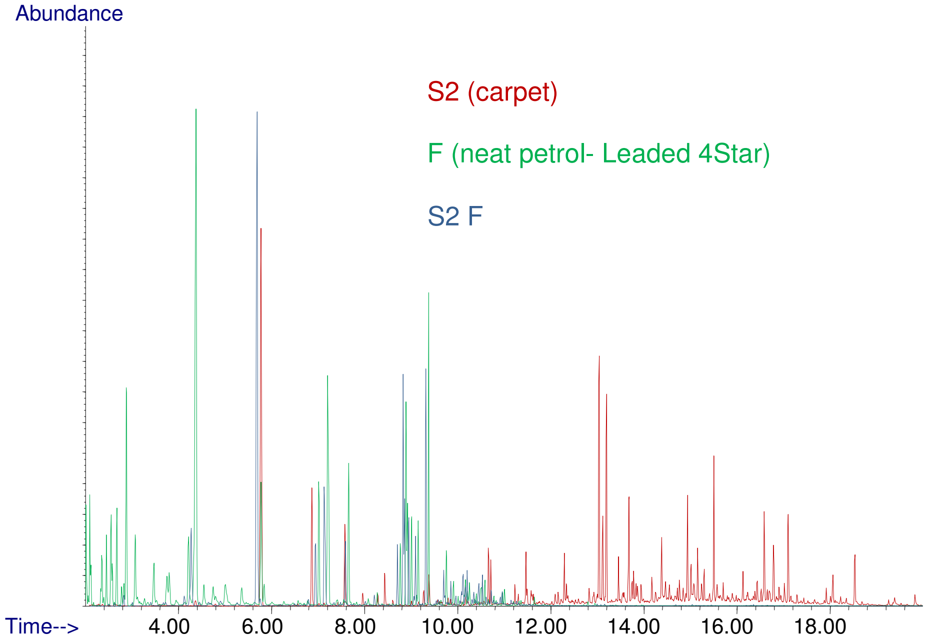


**Figure 5.34 TIC of petrol residue (Leaded 4 Star petrol on polypropylene carpet with jute backing, S2F), in comparison to neat petrol and interference product reference sample.**

C.

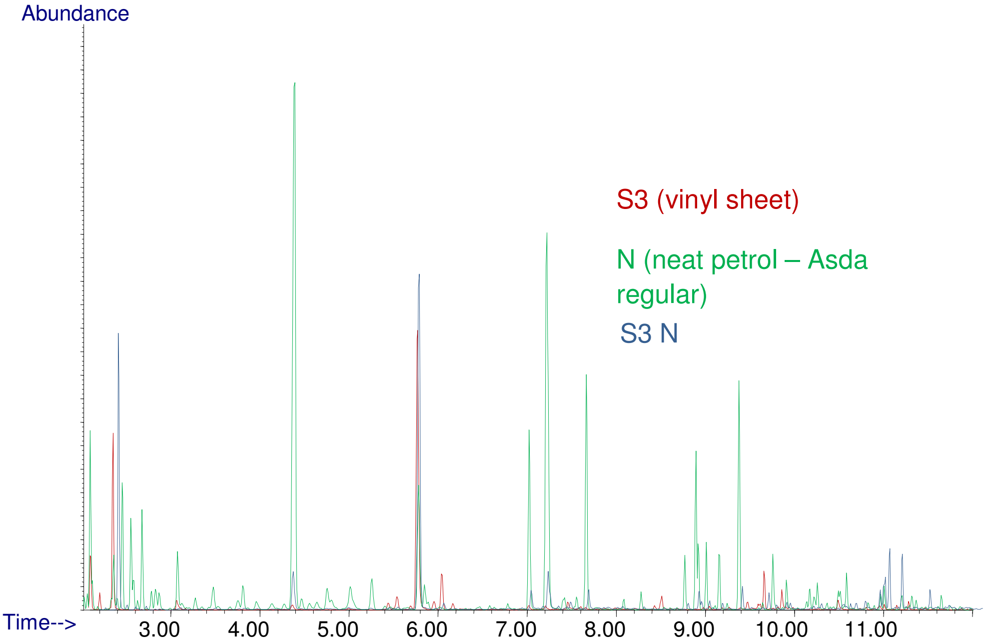


**Figure 5.35 TIC of petrol residue (Asda regular grade petrol on vinyl sheet, S3N), in comparison to neat petrol and interference product reference sample.**

D.

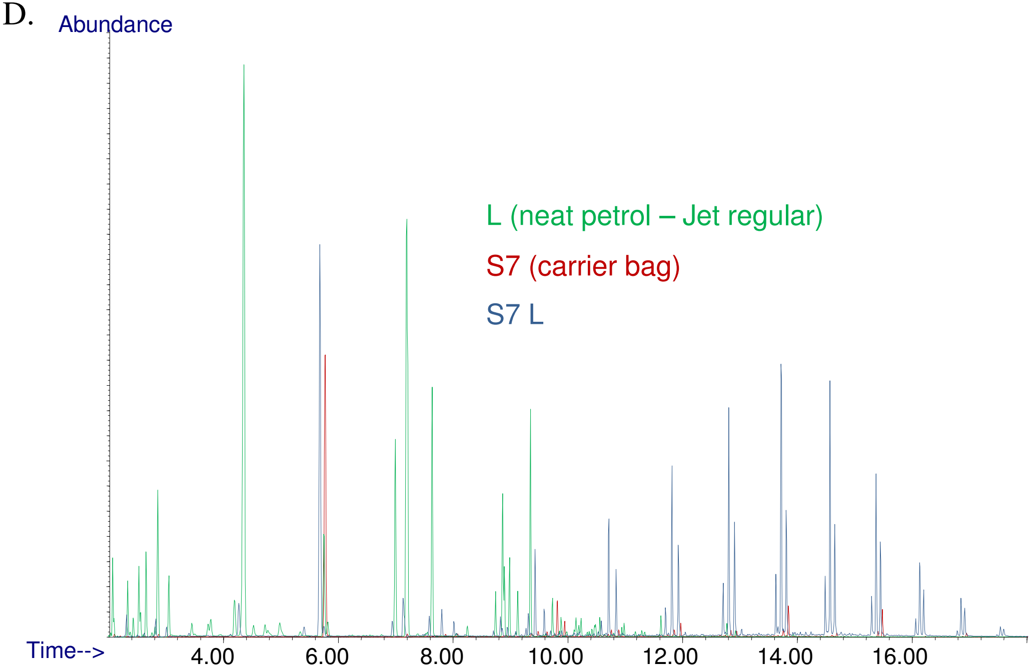


**Figure 5.36 TIC of petrol residue (Jet regular grade petrol on carrier bag, S7L), in comparison to neat petrol and interference product reference sample.**

The SOFM output map for the combined unevaporated, evaporated and substrate with petrol residual samples is presented in figure 5.37. Even with the inclusion of the substrate with petrol residue data, the output map still revealed the 9 groupings of unevaporated and evaporated samples presented previously (chapter 4 in section 4.8.5.5).

Two distinctive divisions can be seen from the output map where the substrate with petrol residue samples are mapped on the right hand side while unevaporated and evaporated liquid samples are mapped on the left. With prior knowledge, some of the neighbouring nodes (substrate with petrol residue samples) can be assigned.

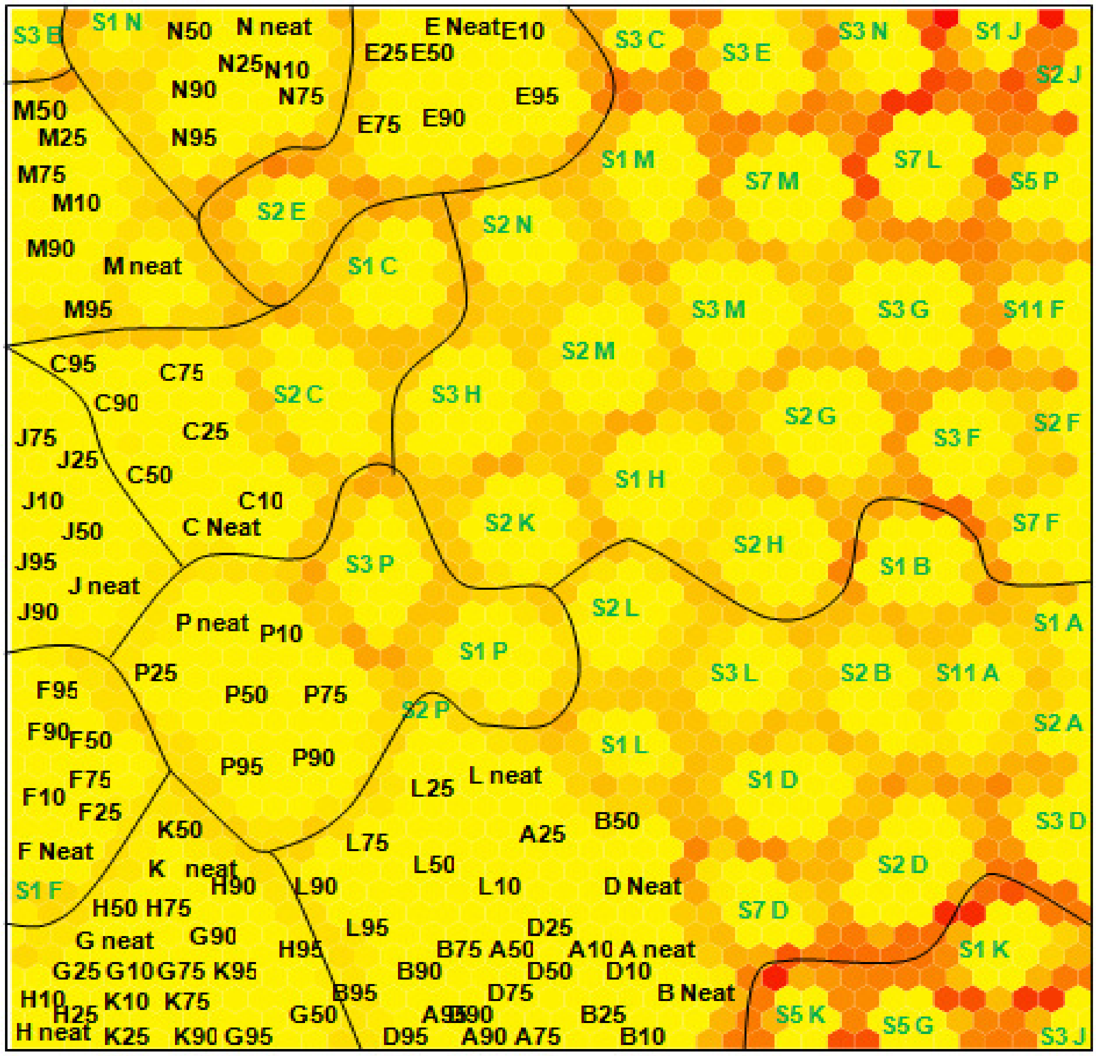


**Figure 5.37 The output map of petrol residues (in green) and neat reference liquid (in black). For residue sample, code S numeric represent the substrate followed by the petrol brand code.**

Of the 47 substrate and petrol residues samples, 20 were correctly associated to their respective petrol group, suggesting a close association between them. However, more than half of the petrol residues could not be associated to any of the previously established groups, thus no meaningful classification in term of petrol grades or brands could be suggested.

## 5.4 Conclusions

This work described in this chapter aimed to investigate the discriminating abilities of SOFM neural networks in the analysis of ignitable liquid residue samples which were extracted from various burnt substrates and as such also contained interfering chromatographic products from those substrates. Chromatographic patterns of ignitable liquids which are subject to heating undergo compositional changes. In the presence of substrate materials co-elution of several compounds from the burned substrates with compounds from the ignitable liquid can occur and consequently alters the chromatographic pattern compared to its original unevaporated pattern. The use of data derived from two different sample preparation methods (liquid and evaporated liquid samples and passive headspace ACS extracted samples) is commonly accepted practice in fire debris analysis and as such was considered for the purposes of this work.

The application of SOFM has successfully classified all ignitable liquid residues by class. Clear distinctions between LPD, MPD, HPD and petrol in the presence of matrix interference products were convincingly achieved. Thus SOFM was able to identify the class of ignitable liquid present in spiked substrate samples irrespective of the background substrate pyrolysis or combustion products which may be present. This result has great potential in providing an objective means of identifying the class of ignitable liquid present in fire debris samples, a process currently carried out subjectively in most forensic laboratories.

SOFM was less successful in linking ignitable liquids recovered from spiked pyrolysed substrate samples to their specific brands. Better results were achieved for lighter fluid and MPD samples than diesel or petrol samples. This mimics the results obtained when using the mathematical technique on the unevaporated and evaporated liquid samples only.

In some cases the differences in the chromatographic response of the compound peaks observed within the total ion chromatograms between the liquid samples and the extracted samples may have been a major hindrance in establishing linkages between degraded ignitable liquids in the extracted samples and their original unevaporated/evaporated liquid samples. This may partly explain the poor classification in the case of lighter fluids and MPD's given these ignitable liquids were linked by brand when the liquid samples were chromatographed and the results mathematically investigated.

Despite these limitations, the results obtained are encouraging and suggest that a more rigorous study focusing on an SOFM classification for all classes of ignitable liquids presented would be warranted. The potential of using the SOFM model for associating the original source of the residual samples is obvious and with further investigation and understanding, SOFM has a potential application in forensic fire debris analyses which could reduce the subjectivity associated with visual comparisons of the chromatograms obtained.

## 5.5 References

1. Tranthim-Fryer, D.J., and DeHaan, J.D., *Canine accelerant detectors and problems with carpet pyrolysis products.* Science & Justice, 1997. **37**(1): p. 39-46.

2. McGee, E., and Lang, T.L., *A study of the effects of a micelle encapsulator fire suppression agent on dynamic headspace analysis of fire debris samples.* Journal of Forensic Sciences, 2002. **47**(2): p. 267-274.

3. Turner, D.A., and Goodpaster, J.V., *The Effect of Microbial Degradation on the Chromatographic Profiles of Tiki Torch Fuel, Lamp Oil, and Turpentine.* Journal of Forensic Sciences, 2011. **56**(4): p. 984-987.

4. Kirkbride, K.P., Yap, S.M., Andrews, S., Pigou, P.E., Klass, G., Dinan, A.C., and Peddie, F.L., *Microbial Degradation of Petroleum Hydrocarbons: Implications for Arson Residue Analysis.* Journal of Forensic Sciences, 1992. **37**(6): p. 1585-1599.

5. Stauffer, E., *Identification and characterization of interfering products in fire debris analysis*, Thesis in Chemistry Department. 2001, Florida International University: Florida. p. 268.

6. Stauffer, E., *Concept of pyrolysis for fire debris analysts.* Science & Justice 2003. **43**(1): p. 29 - 40.

7. Fernandes, M.S., Lau, C.M., and Wong, W.C., *The effect of volatile residues in burnt household items on the detection of fire accelerants.* Science & Justice 2002. **42**(1): p. 7 - 15.

8. Almirall, J.R., and Furton, K.G., *Characterization of background and pyrolysis products that may interfere with the forensic analysis of fire debris.* Journal Analytical and Applied Pyrolysis, 2004. **71**(1): p. 51-67.

9. NicDaeid, N., *Fire Investigation*. 2004, Boca Raton: CRC Press.

10. Drysdale, D., *An introduction to fire dynamics*. 1998, Chicester: John Wiley and Sons Ltd.

11. DeHaan, J.D., *Kirk's Fire Investigation*. 6 ed. 2007, New York: Brady Press.

12. Beyler, C.L., and Hirschler, M.M., *Thermal decomposition of polymer*, in *The SFPE Handbook*, P.J. DiNenno, Editor. 2002, National Fire Protection Agency: Quincy. p. 1-111.

13. Harper, C.A., *Modern plastic handbook*. 2000, New York: McGraw Hill.

14. Nimlos, M.R., and Evans, R.J., *Levoglucosan pyrolysis.* Fuel Chemistry, 2002. **47**(1): p. 393-394.

15. NicDaeid, N., *Fire Investigation: Concepts and Chemistry*. 2011, University of Strathclyde: Glasgow.

16. Moldoveanu, S.C., *Analytical Pyrolysis of Synthetic Organic Polymers*. Techniques and Instrumentation in Analytical Chemistry. Vol. 25. 2005, Amsterdam: Elsevier.

17. Hirschler, M.M., *Flammability and fire performance*, in *PVC Handbook*, C.E. Wilkes, Summers, J.W., and Daniels, C.A., Editors. 2005, Carl Hanser Verlarg: Munich p. 420-423.

18. Rawlins, J.W., and Whittermore, J., *In Commodity Plastics*, in *Polymer Grafting and Crosslinking*, J.W.R.a.P.R. Amit Batthacharya, Editor. 2009, John Wiley and Sons: New Jersey.

19. *Materials Chemistry; available at* [*http://web.mit.edu/3.082/www/team2_f01/chemistry.html*](http://web.mit.edu/3.082/www/team2_f01/chemistry.html) [accessed on 24/12/2011].

20. Buchanan, A.H., *Structural design for fire safety*. 2002, Chicester: Lohn Wiley and Sons Ltd.

21. Browne, F.L., *Theories of the combustion of wood and its control*. 1963, Report 2136: United States Forest Products Laboratory. 69.

22. Stone, I.C., and J.N. Lamonte, *False positive in analysis of fire debris.* The Fire and Arson Investigator, 1984. **34**(3): p. 36-40.

23. Higgins, M., *Turpentine, accelerant or natural???* The Fire and Arson Investigator, 1987. **38**(2): p. 10.

24. Lentini, J.J., *Scientific protocols for fire investigation.* Protocols in Forensic Science. 2006, Boca Raton: Taylor & Francis Gp, CRC Press.

25. Lentini, J.J., *Persistence of floor coating solvents.* Journal of Forensic Sciences, 2001. **46**(6): p. 1470-1473.

26. Howard, J., and McKague, A.B., *A fire investigation involving combustion of carpet material.* Journal of Forensic Sciences, 1984. **29**(3): p. 919-922.

27. Jackowski, J.P., *The incidence of ignitable liquid residues in fire debris as determined by a sensitive and comprehensive analytical scheme.* Journal of Forensic Sciences, 1997. **42**(5): p. 828-832.

28. Bertsch, W., *Volatiles from carpet: A source of frequent misinterpretation in arson analysis.* Journal of Chromatography A, 1994. **674**(1-2): p. 329-333.

29. Clodfelter, R.W., and Hueske, E.E., *A comparison of decomposition products from selected materials with common arson accelerants.* Journal of Forensic Science, 1977. **22**(1): p. 116-118.

30. Lentini, J.J., *Differentiation of asphalt and smoke condensates from liquid petroleum distillates using GC/MS.* Journal of Forensic Sciences, 1998. **43**(1): p. 97-113.

31. Cavanagh, K., Pasquier, E.D., and Lennard, C., *Background interference from car carpets - the evidential value of petrol residues in cases of suspected vehicle arson.* Forensic Science International, 2002. **125**(1): p. 22-36.

32. Ettling, B.V., and Adams, M.F., *The study of accelerant residues in fire remains.* Journal of Forensic Sciences, 1968. **13**(1): p. 76-89.

33. Smith, R.M., *Arson analysis by mass chromatography.* Analytical Chemistry, 1982. **54**(13): p. 1399A-1409A.

34. Lentini, J.J., Dolan, J.A., and Cherry, C., *The petroleum-laced background.* Journal of Forensic Sciences, 2000. **45**(5): p. 986-989.

35. *Plastics in the UK economy - a guide to polymer use and the oppurtunities for recycling; available at http://www.plasticsintheuk.org.uk.* [accessed on 15/05/2011].

36. Nowicki, J., *Analysis of fire debris sample by Gas Chromatography/Mass Spectrometry (GC-MS): Case studies.* Journal of Forensic Sciences, 1991. **36**(5): p. 1536-1550.

37. Dehaan, J.D., and Bonarius, K., *Pyrolysis products of structure fires.* Journal of the Forensic Science Society, 1988. **28**(5-6): p. 299-309.

38. Keto, R.O., *GC/MS data interpretation for petroleum distillate identification in contaminated arson debris.* Journal of Forensic Sciences, 1995. **40**(3): p. 412-423.

39. Gilbert, M.W., *The use of individual extracted ion profiles versus summed extracted ion profiles in fire debris analysis.* Journal of Forensic Sciences, 1998. **43**(4): p. 871-876.

40. Bertsch, W., and Zhang, Q.W., *Sample preparation for the chemical analysis of debris in suspect arson cases.* Analytica Chimica Acta, 1990. **236**: p. 183-195.

41. Bwalya, A.C., *An extended survey of combustible contents in canadian residential living rooms*. 2004, Institute for Research in Construction, National Research Council Canada. p. 25.

42. W.D.Wooley, and P.J.Fardell, *Basic aspects of combustion technology.* Fire Safety Journal, 1982. **5**(2): p. 29-48.

43. Hugget, C., and Levin, B.C., *Toxicity of the pyrolysis and combustion products of poly(vinyl chlorides): A literature assessment.* Fire and Materials, 1987. **11**(3): p. 131-142.

44. *General purpose polystyrene (GPPS); available at http://www.bpf.co.uk/plastipedia/polymers/GPPS.aspx*. [accessed on 14/05/2011].

45. Faravelli, T., Pinciroli, M., Pisano, F., Bozzano, G., Dente, M., and E.Ranzi, *Thermal degradation of polystyrene.* Journal of Analytical and Applied Pyrolysis, 2001. **60**(1): p. 103-121.

46. Gurman, J.L., Baier, L., and Levin, B.C., *Polystyrene: A review of the literature on the products of thermal composition and toxicity.* Fire and Materials, 1987. **11**(2): p. 109-130.

47. W.D.Woolley, and Raftery, M.M., *Smoke and toxicity hazards of plastics in fires.* Journal of Hazardous Materials, 1975. **1**(1): p. 215-222.

48. Hodgkin, J.H., Galbraith, M.N., and Chonga, Y.K., *Combustion Products from Burning Polyethylene.* Journal of Macromolecular Science: Part A - Chemistry, 1982. **17**(1): p. 35-44.

49. Putorti, A.D., and J.McElroy, *Report of Test: Full scale for house fire experiment for InterFire VR*. 1998, Building and Fire Research Laboratory, National Institute of Standards and Technology, U.S Department of Commerce: Gaithersburg.

50. Borusiewicz, R., Zie-Palus, J., and Zadora, G., *The influence of the type of accelerant, type of burned material, time of burning and availability of air on the possibility of detection of accelerants traces.* Forensic Science International, 2006. **160**(2-3): p. 115-126.

51. Brereton, R.G., *Chemometrics for Pattern Recognition*. 2009, West Sussex: John Wiley and Sons.

52. M.Fonseca, A., Biscaya, J.L., Aires-de-Sousa, J., and Lobo, A.M., *Geographical classification of crude oils by Kohonen self-organising maps.* Analytica Chimica Acta, 2006. **556**(1): p. 374-382.

53. J.W.Thorpe, and Ismail, D. *Pattern recognition procedures for the classification and prediction of stains originating from wax-based products*. in *California Association of Criminalist, Fall 2006 Seminar*. 2006. Temecul, California.

54. Ismail, D., *The application of pattern recognition techniques to data derived from the chemical analysis of common wax based products and ignitable liquids*, in *Pure and Applied Chemistry*. 2010, University of Strathclyde: Glasgow. p. 302.

55. Marshall, L.J., McIlroy, J.W., McGuffin, V.L., and Smith, R.W., *Association and discrimination of diesel fuels using chemometric procedures.* Analytical and Bioanalytical Chemistry, 2009. **394**: p. 2049-2059.

56. Monfreda, M., and Gregori, A., *Differentiation of unevaporataed gasoline samples according to their brands, by SPME-GCMS and multivariate statistical analysis.* Journal of Forensic Sciences, 2011. **56**(2): p. 372-380.

57. Baerncopf, J.M., McGuffin, V.L., and Smith, R.W., *Association of ignitable liquid residues to neat ignitable liquids in the presence of matrix interferences using chemometric procedures.* Journal of Forensic Sciences, 2011. **56**(1): p. 70-81.

58. Stauffer, E., Dolan, J.A., and Newman, R., *Fire Debris Analysis*. 2008, Burlington: Academic Press.

59. Newman, R.T., Dietz, W.R., and Lothridge, K., *The use of activated charcoal strips for fire debris extractions by passive diffusion. Part 1: The effects of time,temperature, strip size, and sample concentration.* Journal of Forensic Sciences, 1996. **41**(3): p. 361-370.

# CHAPTER 6: GENERAL CONCLUSIONS AND FUTURE WORK

## 6.1 Summary of Conclusions

GC-MS has been widely applied to the classification and identification (to sub-class level) of ignitable liquid and ignitable liquid residue samples. The interpretation of GC-MS results in the identification and characterisation of ignitable liquids currently occurs (operationally) via a mixture of visual observation, manual comparison and personal interpretation of the questioned chromatographic profiles to those derived from ignitable liquid reference collections. Such methods can be highly subjective and, as a consequence, problematic. Further difficulties can be introduced when pyrolysis and combustion products are present in the sample and can complicate pattern interpretation leading to ignitable liquid misclassification, false positive or negative results or no determination [1].

This work was undertaken in order to develop a means of objectively classifying common ignitable liquids such as petrol and petroleum distillates products. The work is based on the application of mathematical procedures using multidimensional chromatographic data. The hypothesis was that multivariate pattern recognition techniques would facilitate the comparison process particularly when there was a large number of samples and variables, and as a consequence could produce an objective determination of what is essentially a subjective pattern matching activity.

In order to reflect the common practice and procedures in laboratory fire debris analysis, this study initially developed two sets of reference collections. Firstly, an ignitable liquid reference collection, focusing on petrol and petroleum distillate products. This included a series of sequentially evaporated samples of a wide range of different brands of the various ignitable liquids under study. Secondly, a reference of common substrates was prepared by pyrolysing and burning a series of commonly encountered household materials and extracting the combustion and pyrolysis products from these substrates.

Finally a series of test samples were prepared to combine the unevaporated ignitable liquids in the study with the substrate materials to simulate fire debris samples.

In dealing with mathematical analysis of chromatographic profiles derived from petroleum distillate samples, each class (petrol, light petroleum distillates, medium petroleum distillates and heavy petroleum distillates) represented their own challenges, predominantly due to the range of carbon compounds within their composition. Narrow boiling point materials such as light petroleum distillates ($C_4$-$C_8$) did not show much of pattern shift on evaporation, while the petrol class ($C_4$-$C_{12}$), medium petroleum distillates ($C_8$-$C_{13}$) and heavy petroleum distillates represented by diesel ($C_8$-$C_{20}$) exhibited a more pronounced pattern shift on evaporation. To capture these compositional and pattern changes and ensure that they were reflected in the resultant data matrix used for the mathematical analysis, data selection and data pre-treatment methods were considered and examined within each ignitable liquid grouping. The success of the multivariate analysis methods do not only rely on the mathematical algorithm alone but appeared also to be directly influenced by two crucial factors; the data selection and data pre-processing methods. Data selection became essential as the presence of zero points (which represented the absence of a particular variable in a sample) could skew the data matrix, biasing the model. Hence, partial chromatograms, focusing on the region that represented the most characteristic feature for a particular sample were used.

Power root transformation and scaling were used to address differences in the magnitude of the data providing a robust dataset representing the overall changes between unevaporated and sequentially evaporated ignitable liquid chromatographic profiles. In general, the sixteenth root power transformation was found to be the most successful in providing meaningful sample classifications. This finding demonstrates the effectiveness of a data pre-treatment strategy for gradually changing chromatographic profiles as it captures the overall changes in chromatographic pattern and can have general applicability in ignitable liquid sample studies.

With pattern recognition techniques, similar or non similar patterns within multidimensional datasets, are translated into more meaningful diagrams, revealing the relationship between the samples in a two dimensional format facilitating a better understanding. Two unsupervised pattern recognition schemes were utilised in this work as they naturally cluster and link groups of similar attributes (or variables) without the need for prior training of the mathematical algorithms. Using data obtained from the ignitable liquid reference collection, classification using conventional unsupervised multivariate pattern recognition methods specifically Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were performed and compared. This study also introduced the use of an unsupervised artificial neural network technique using Self Organising Feature Mapping (SOFM) to the interpretation of ignitable liquid samples and residues.

PCA computes latent variables to generate new coordinates which in turn are projected into two dimensional space (plot) showing the clustering, if present, for samples. Ideally, principal component (PC) scores should represent 80% variation of the dataset to be accounted for. In circumstances where the first two PCs do not satisfy this requirement, examinations of additional plots can be helpful. Variables which are responsible for the clustering can be identified through their loading values. HCA provides the analyst with various linkages strategies that can be explored systematically. Each strategy produces a different clustering outcome, thus providing the analyst with strategy options that best represent a particular dataset. Despite flexibilities offered in both techniques, the problem of overcrowding of the visualisation space occurs with large datasets. The SOFM map provides a much clearer visualisation of the sample linkages and as such can reveal or demonstrate close connections or neighbourhoods of samples which are similar to each other on a planar map. Component maps which underpin the final SOFM output map can facilitate the investigation of the effects of each variable on the sample linkage.

### *Discrimination between Ignitable Liquid Classes*

The use of mathematical analysis for the classification or discrimination of the ignitable liquid samples based on class characteristics was successful using all methods under study. In general the techniques examined facilitated the clustering of evaporated samples correctly within their correct ignitable liquid classes despite significant compositional and pattern change through evaporation. This is the lowest level of discrimination expected, where the multivariate analysis can link evaporated samples to the correct class rather than the correct brand within a given class.

### *Discrimination Based on Sample Types and or Brand*

Classification at subclass level (based on types and or brand) by PCA analysis demonstrated poor discrimination of the light petroleum distillate samples (lighter fluid samples) and the medium petroleum distillate samples and some misclassification occurred. Poor discrimination of petrol and diesel samples was achieved. HCA analysis successfully grouped most of the evaporated and unevaporated samples of the light petroleum distillates (lighter fluid samples) and the medium petroleum distillates by brand. HCA was partially successful in resolving petrol samples by brand, however failed to group diesel samples by brand. SOFM surpassed PCA and HCA and correctly clustered the sequentially evaporated and unevaporated samples of all light and medium petroleum distillates and 57% of petrol samples under test, but again failed to group the diesel samples. Classification of evaporated and unevaporated diesel samples proved to be the most challenging and, regardless of the multivariate methods applied, none successfully resolved these samples by brand.

### *Classification of Ignitable Liquid Residues in Substrate Samples using SOFM Analysis*

As the most effective of the multivariate techniques in this study, SOFM was further investigated for the classification of ignitable liquids in the presence of interfering products from substrate pyrolysis and combustion. It is difficult to regulate the recovery of interfering products as the combustion process is complicated and unique even if burning was carried out under the same circumstances. Therefore, qualitative (rather than quantitative) reproducibility of chromatographic patterns are often considered enough for comparison purposes.

In all cases, the ignitable liquid samples were correctly classified into their respective classes regardless of the substrate. This is a significant and important result as it demonstrates that the development of the SOFM model can objectively discriminate between the various ignitable liquids under study and group them correctly together with their evaporated products even in the presence of interfering products. This is normally carried out subjectively by the analyst. Furthermore, SOFM also demonstrated promise in linking evaporated and unevaporated samples together by brand in some cases even in the presence of interfering products.

## 6.2 Recommendations for Further Work

Because data analysis was undertaken manually, the process of aligning and deciphering the chromatographic data was labour intensive and time consuming. However, successful classification, association and discrimination using chemometric and neural network procedures were obtained. To facilitate and speed-up the process, automated peak aligning using specialised software for chromatographic data would be a viable option[2, 3].

Further refinements of the data selection strategies particularly with petrol and diesel samples would be advantageous. SOFM could be further refined through exploration of the data selection to improve the validation success for petrol and diesel in particular and explore whether this would improve upon the linkages achieved. It would also be useful to explore other data selection strategies such as the use of extracted ion chromatograms and extracted ion profiles of aliphatic, aromatic, alkylbenzenes or combinations of these for use with the mathematical methods. Another potential data selection method is the peak area ratios of specific components or chromatographic regions.

For ignitable liquid residue analysis, various other means of extraction can be employed and introduced into the reference data matrix to compare their effectiveness when subjected to the mathematical procedures. It would be more valuable if the underlying issue of signal strength is dealt with as the work detailed here clearly demonstrated the need for signal multiplication to overcome the issue of low abundance in the TICs of residual samples.

It would also be beneficial to explore the appropriateness of the direct comparison of chromatographic profiles derived from liquid samples with those derived from extracted samples. This is the practice currently used by operational forensic science laboratories.

The SOFM neural network in particular, has demonstrated substantial associative abilities among petroleum distillates samples at class and sub class (brand) level and in residual traces. Further work could be extended to other classes of ignitable liquids such as isoparaffinic, aromatic, and naphthenic products.

## 6.3 References

1. Hendrikse, J., *ENFSI collaborative testing programme for ignitable liquid analysis: A review.* Forensic Science International, 2007. **167**(2-3): p. 213-219.

2. Johnson, K.J., Wright, B. W., Jarman, K. H. and Synovec, R.E., *High-speed peak matching algorithm for retention time alignment of gas chromatographic data for chemometric analysis.* Journal of Chromatography A, 2003. **996**(1-2): p. 141-155.

3. Nederkassel, A.M., Daszykowski, M., Eilers, P.H.C., and Heyden, Y.V., *A comparison of three algorithms for chromatograms alignment.* Journal of Chromatography A, 2006. **1118**(2): p. 199-210.

# APPENDICES

# Appendix A: Statistical Calculation to Determine Instrumental Limit of Detection (LOD)

The limit of detection was calculated using the method as outlined in Miller and Miller [1]. The peak areas of the target compounds from the ignitable liquid standard solutions are presented in table A.1. Because no results were obtained from 0.001% vol/vol standard solution, calculation was performed assuming that the analyte abundance is zero at zero concentration. The calculation for the toluene standard (highlighted) is shown in this appendix as an illustration of the method.

**Table A.1 Peak areas (y, $10^7$) from ignitable liquid standard compounds.**

| **Compounds** | **x, concentration %v/v ($10^{-3}$)** | | | | |
|---|---|---|---|---|---|
| | **0.0000** | **5.0000** | **10.0000** | **25.0000** | **50.0000** |
| Toluene | 0.0000 | 2.2942 | 4.4795 | 9.9679 | 18.3023 |
| p-Xylene | 0.0000 | 2.5116 | 4.9385 | 10.7228 | 19.8359 |
| m-Ethyltoluene | 0.0000 | 2.7625 | 5.4357 | 11.6231 | 20.8203 |
| o-Ethyltoluene | 0.0000 | 2.8904 | 4.6528 | 11.8551 | 21.4548 |
| 1,2,4-Trimethylbenzene | 0.0000 | 2.8286 | 5.5664 | 12.0343 | 21.6851 |
| C8 | 0.0000 | 1.3858 | 2.6946 | 6.0282 | 11.1734 |
| C10 | 0.0000 | 1.6089 | 3.1687 | 6.8104 | 12.4502 |
| C12 | 0.0000 | 1.8606 | 3.6994 | 7.9251 | 14.3503 |
| C14 | 0.0000 | 2.1775 | 4.2299 | 8.9418 | 16.0841 |
| C16 | 0.0000 | 3.0740 | 4.5059 | 9.2379 | 17.5896 |
| C18 | 0.0000 | 2.5070 | 5.0052 | 10.0051 | 18.7005 |
| C20 | 0.0000 | 2.5903 | 5.3357 | 11.4371 | 19.9888 |

**Step 1:** Determination of linear regression

$$Y = a + bX \qquad \textbf{.......................Equation 1}$$

Whereby, $X$ = the explanatory variable

$Y$ = the dependent variable.

$b$ = the slope of the line

$a$ = the intercept (the value of $y$ when $x$ = 0)

**Step 2:** Determination of correlation coefficient, $R^2$ using

$$r = \frac{\sum_i\{(x_i - \bar{x})(y_i - \bar{y})\}}{\left\{[\sum_i(x_i - \bar{x})^2][\sum_i(y_i - \bar{y})^2]\right\}^{\frac{1}{2}}} \qquad \textbf{..................... Equation 2}$$

Calculation for eq.1 and eq 2 were performed using Excel® 2007 (version 12.0.6654.5003). For simplicity, further calculations were carried out in a tabulated format as shown below:

**Table A.2 Calculated data for toluene standard.**

| | x | $x^2$ | x-x $_{ave}$ | (x-x $_{ave}$)$^2$ | y | y^ | [y-y^] | [y-y^]$^2$ |
|---|---|---|---|---|---|---|---|---|
| | 0 | 0.000 | -18.0 | 324.00 | 0.0000 | 0.4953 | -0.4953 | 0.2458 |
| | 5 | 25.000 | -13.0 | 169.00 | 2.2942 | 2.3048 | -0.0105 | 0.0001 |
| | 10 | 100.000 | -8.0 | 64.00 | 4.4795 | 4.1138 | 0.3657 | 0.1337 |
| | 25 | 625.000 | 7.0 | 49.00 | 9.9679 | 9.5408 | 0.4271 | 0.1824 |
| | 50 | 2500.000 | 32.0 | 1024.00 | 18.3023 | 18.5858 | -0.2834 | 0.0803 |
| **Sum** | **90.00** | **3250.000** | | **1630.00** | | | | **0.6424** |
| **Ave** | **18.00** | **650.000** | | | | | | |

y^ is $y_{intercept}$ where y^=0.3618 (0) + 0.4958 =0.4958

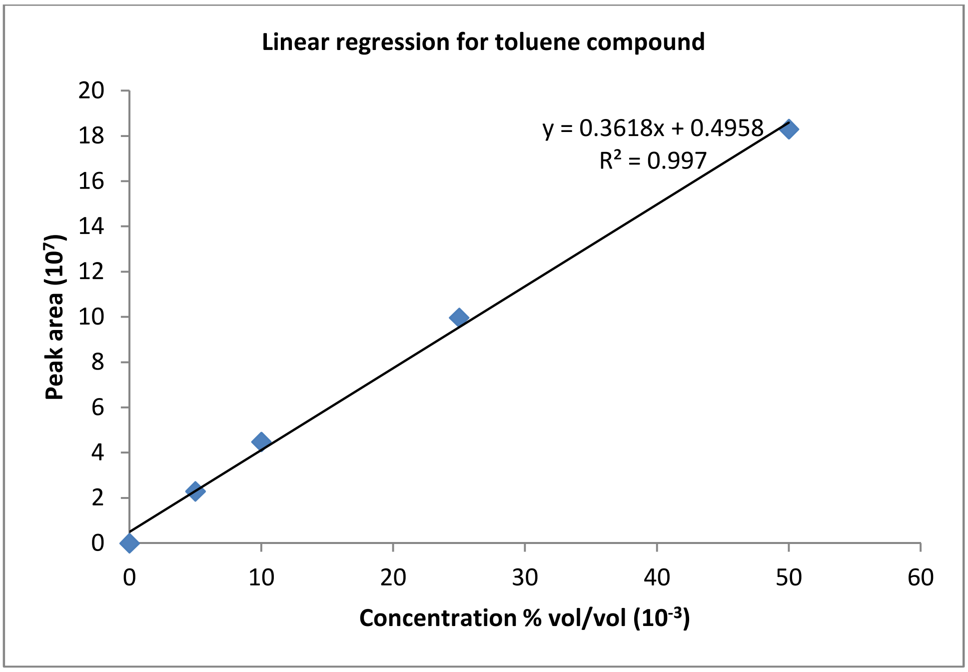


**Figure A.1 Calibration curve for Toluene.**

**Step 3:** Calculate the estimate of random errors in the y-direction, $S_{y/x}$ by

$$s_{y/x} = \sqrt{\frac{\sum_i (y_i - \bar{y}_i)^2}{n-2}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{Equation 3}$$

$$\mathbf{S_{y/x}} = \sqrt{\frac{\mathbf{0.6424}}{\mathbf{3}}} \; \mathbf{=0.46275567}$$

n= 5, therefore n-2=3, and for t-distribution at 95% confidence limit is 3.18,

**Step 4:** Calculate $s_b$, the standard deviation and confidence limits of the slope by

$$s_b = \frac{s_{y/x}}{\sqrt{\sum_i (x_i - \bar{x}_i)^2}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{Equation 4}$$

$$\mathbf{S_b} = \frac{0.4627567}{\sqrt{(1630)}} = \frac{0.421186}{40.3732} \; \mathbf{= 0.011462}$$

The t-value for (n-3) = 5,

degrees of freedom and the 95% confidence limit is 3.18 and the 95% confidence limit for b is therefore;

b = 0.3618 ± (3.18x0.011462) = **0.3618 ± 0.03644916**

**Step 5:** Calculate $\mathbf{s_a}$, the standard deviation and confidence limits of the intercept for regression line for this data by

Standard deviation of intercept:

$$s_a = s_{y/x}\sqrt{\frac{\sum_i x_i^2}{n\sum_i (x_i - \bar{x})^2}} \quad \textbf{.................................. Equation 5}$$

$$\mathbf{s_a} = 0.4627567\sqrt{\frac{3250}{5(1630)}} \ \mathbf{= 0.2922238}$$

The 95% confidence limit for a is;

a = 0.4958 ± (3.18x0.2922238) = **0.4958 ± 0.9292716**

**Step 6:** Calculate the limit of detection by

$$Limit\ of\ detection = \ y_B + 3s_B \textbf{......................Equation 6}$$

Where, $y_B$ is the value of a and $s_B$ is the value of Sy/x

The value of y at the detection limit is = 0.4958+3(0.4627) = **1.8840701**

By substituting y in the linear regression equation in order to yield x, the concentration at the limit of detection

y=0.4958+ 0.3618x

1.8840701 = 0.4958+0.3618x

x = **3.83712**

therefore the toluene concentration yield at the limit of detection is $3.8371\text{x}10^{-3}$ %vol/vol.

**Reference:**

1. Miller, J.C. and Miller, J.N., *Statistics for Analytical Chemistry*. 3rd Edition, 1993, London: Ellis Harwood.

2. Stone D. C., and Ellis J., 2006, Dept of Chemistry, University of Toronto, http://www.chem.utoronto.ca/coursenotes/analsci/StatsTutorial/LimDetect.html, accessed on 02/12/2011

# Appendix B: Overlay of Total Ion Chromatograms (TICs) of Unevaporated and Evaporated Light Petroleum Distillates Samples.

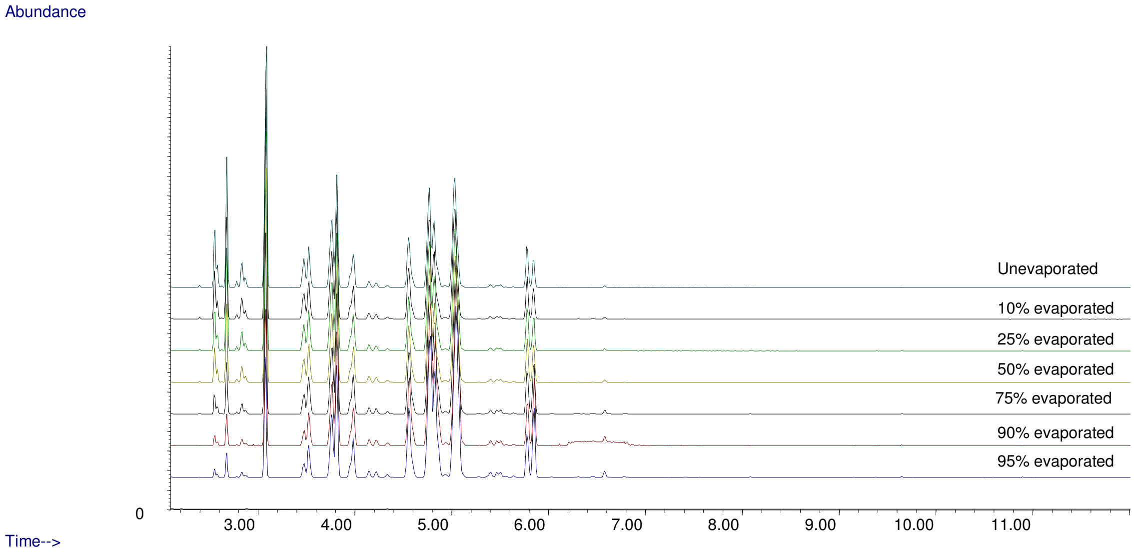


Figure B.1 TICs of unevaporated to highly evaporated Perma lighter fuel.

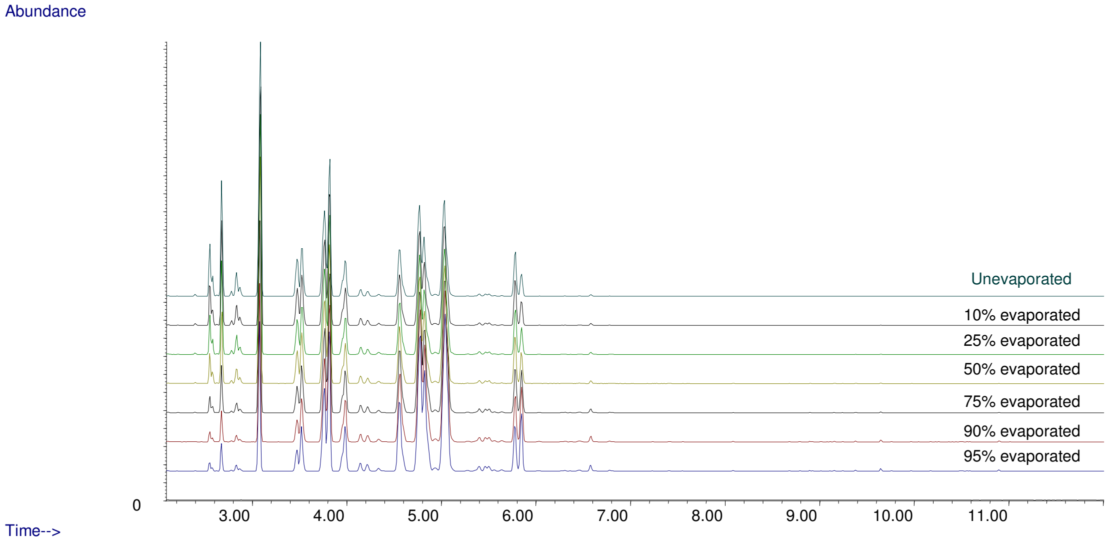


Figure B.2 TICs of unevaporated to highly evaporated Ronsonol lighter fuel.

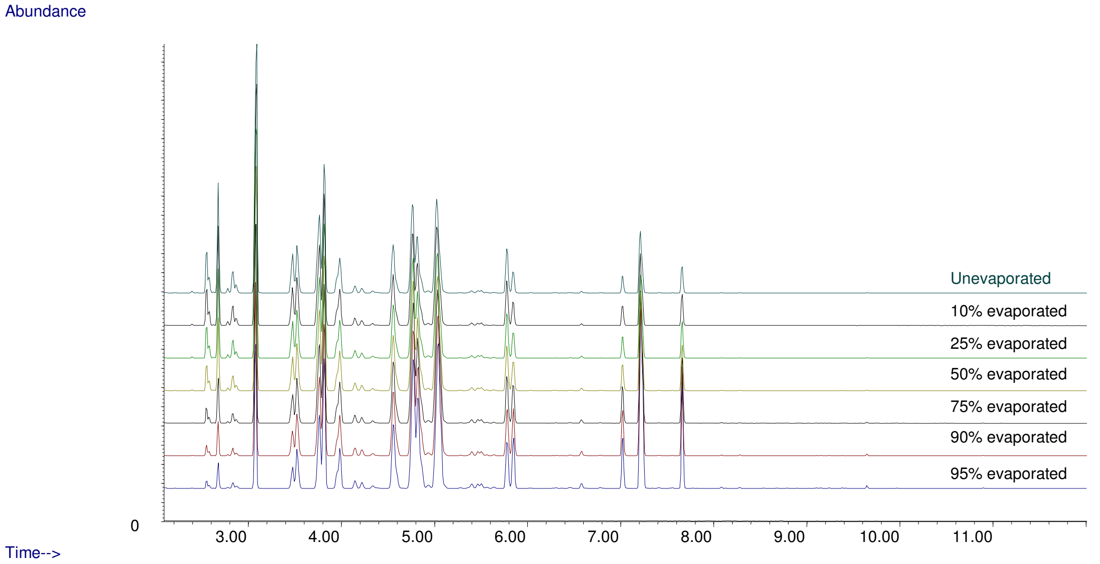


Figure B.3 TICs of unevaporated to highly evaporated Swan lighter fuel.

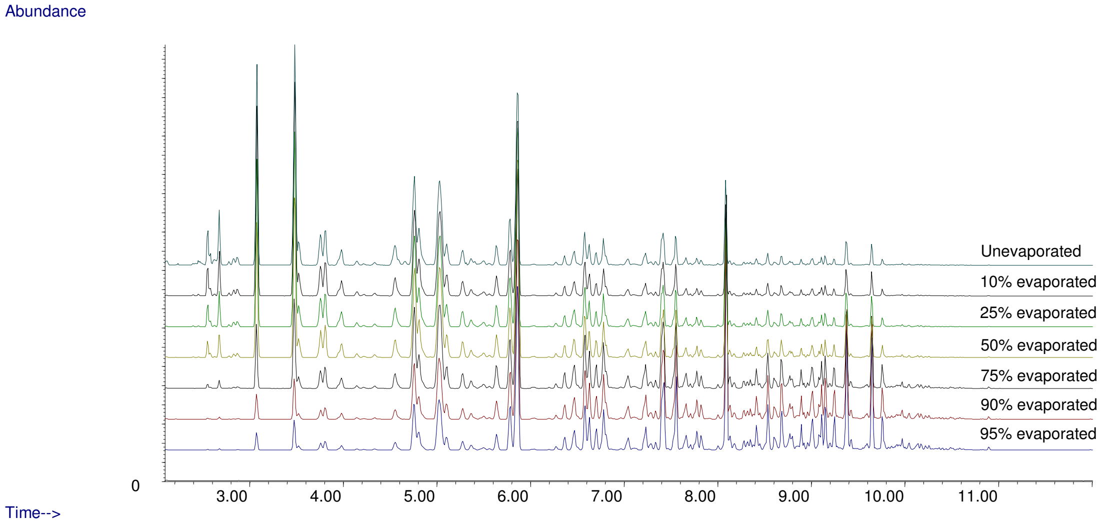


Figure B.4 TICs of unevaporated to highly evaporated Dunhill lighter fuel.

# Appendix C: Overlay of Total Ion Chromatograms (TICs) of Unevaporated and Evaporated Medium Petroleum Distillate Samples.

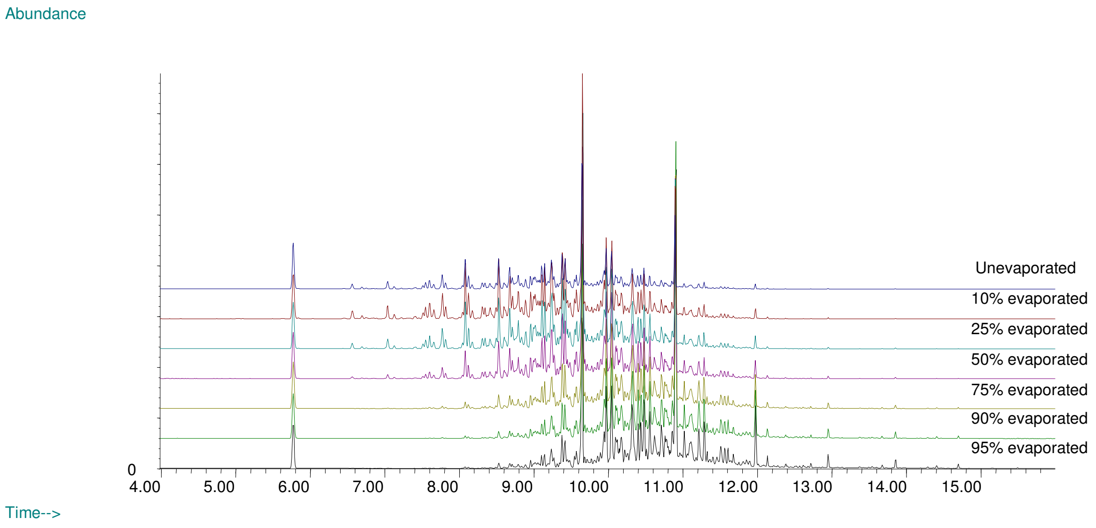


Figure C.1 TICs of unevaporated to highly evaporated Bertoline white spirit.

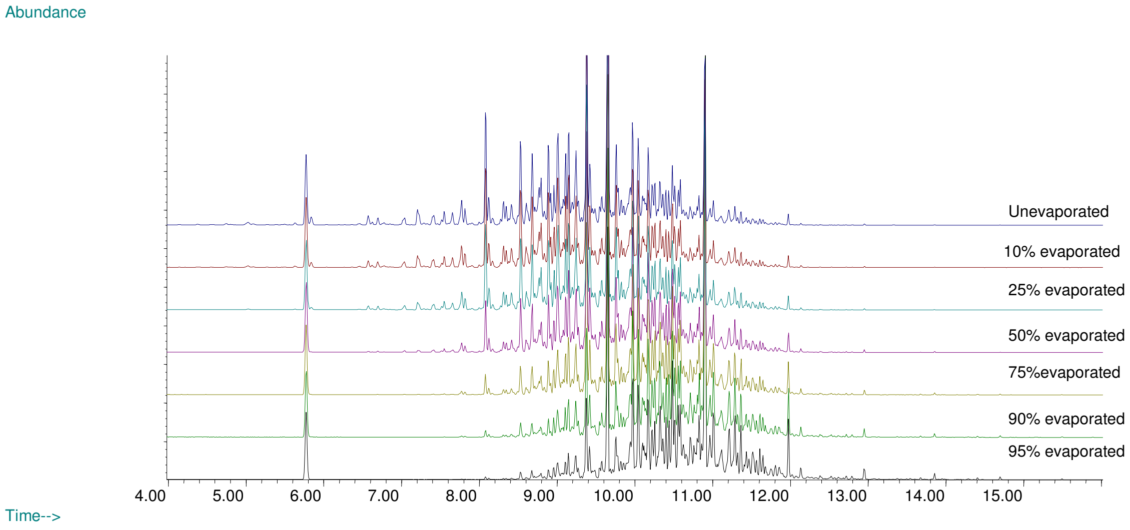


Figure C.2 TICs of unevaporated to highly evaporated B&Q white spirit.

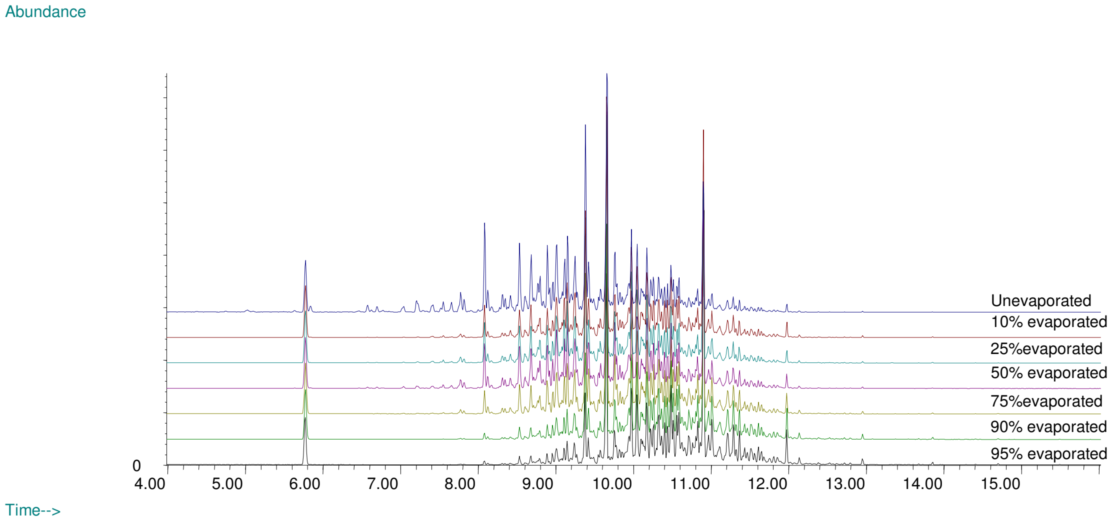


Figure C.3 TICs of unevaporated to highly evaporated Homebase white spirit.

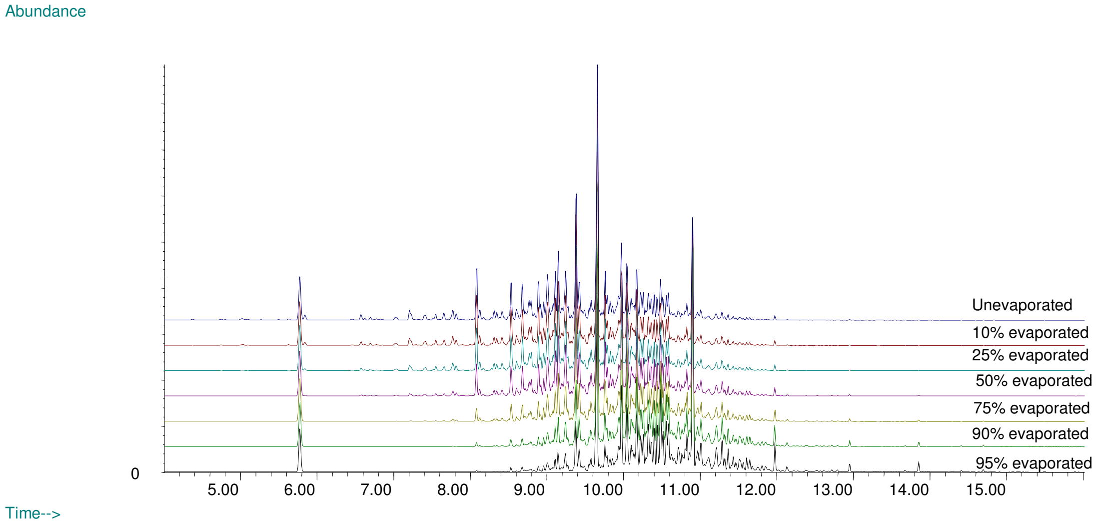


Figure C.4 TICs of unevaporated to highly evaporated Tesco white spirit.

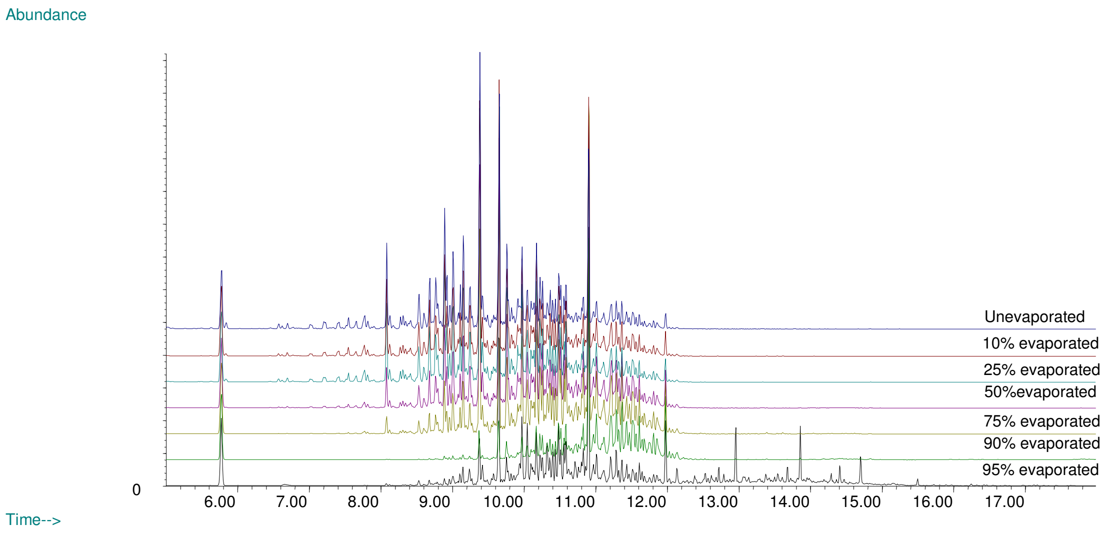


Figure C.5 TICs of unevaporated to highly evaporated Polycell brush cleaner.

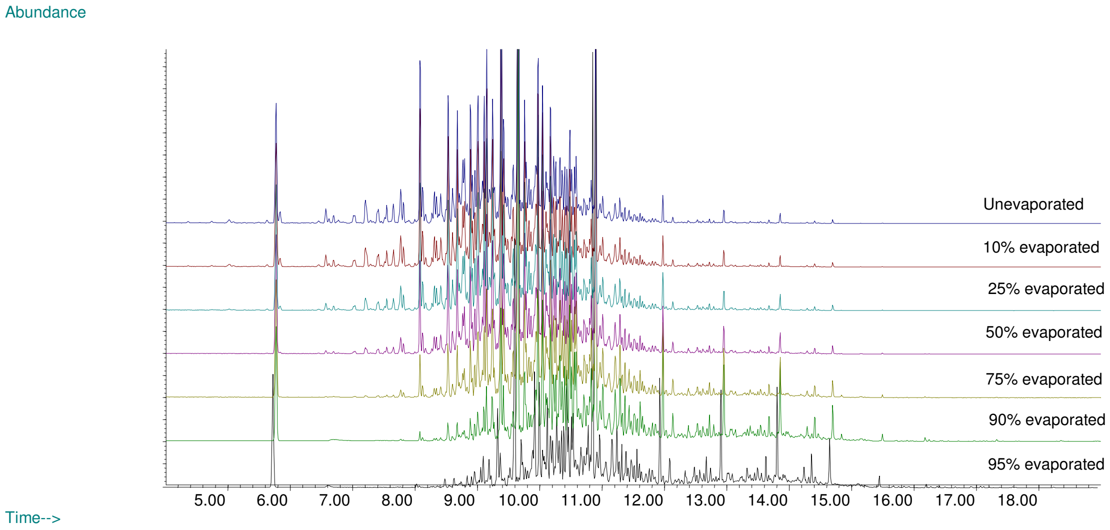


Figure C.6 TICs of unevaporated to highly evaporated Homebase brush cleaner.

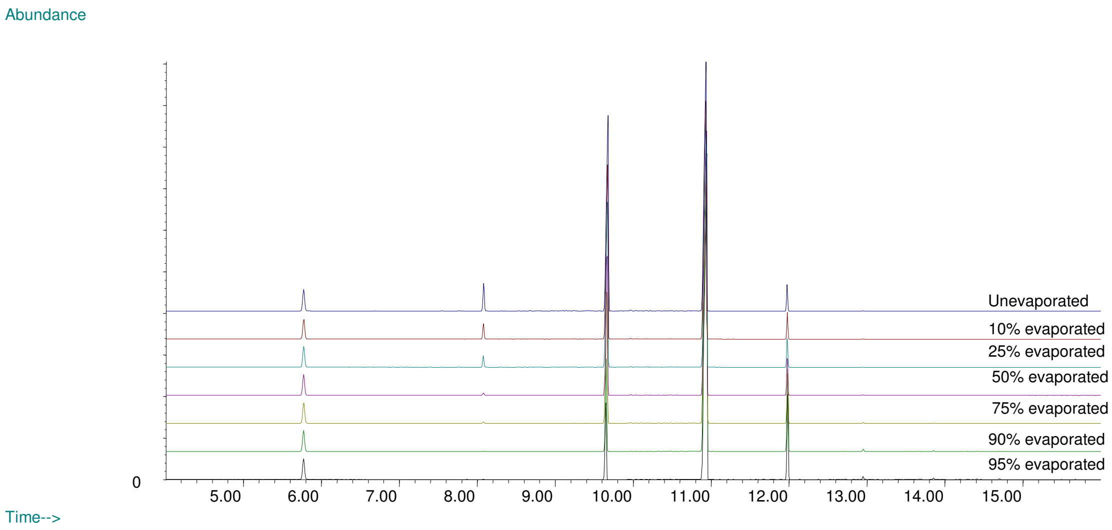


**Figure C.7 TICs of unevaporated to highly evaporated** After dark lamp oil

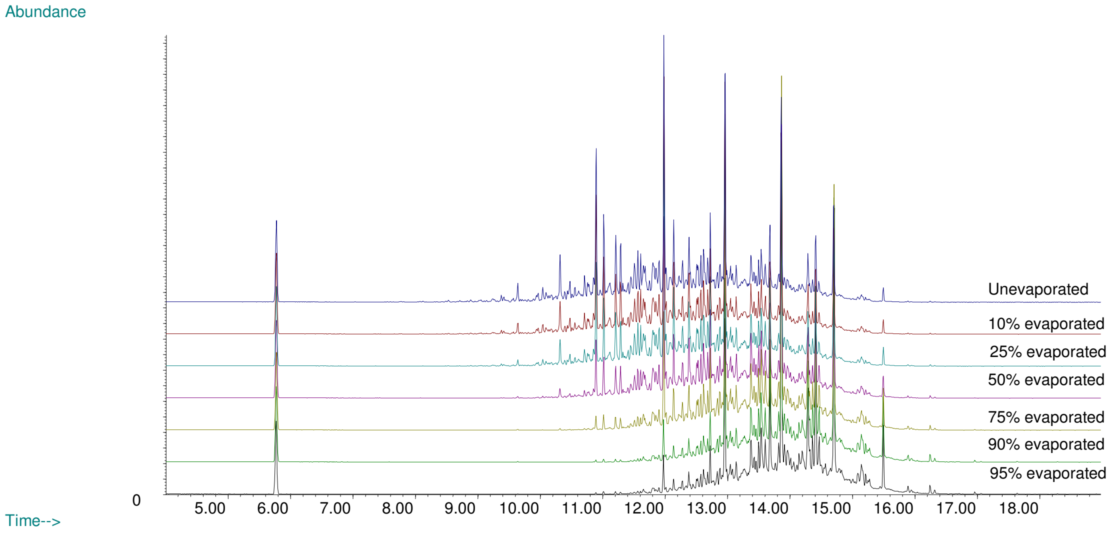


**Figure C.8 TICs of unevaporated to highly evaporated Bertoline lamp oil.**

# Appendix D: Overlay of Total Ion Chromatograms (TICs) of Unevaporated and Evaporated High Petroleum Distillate Samples.

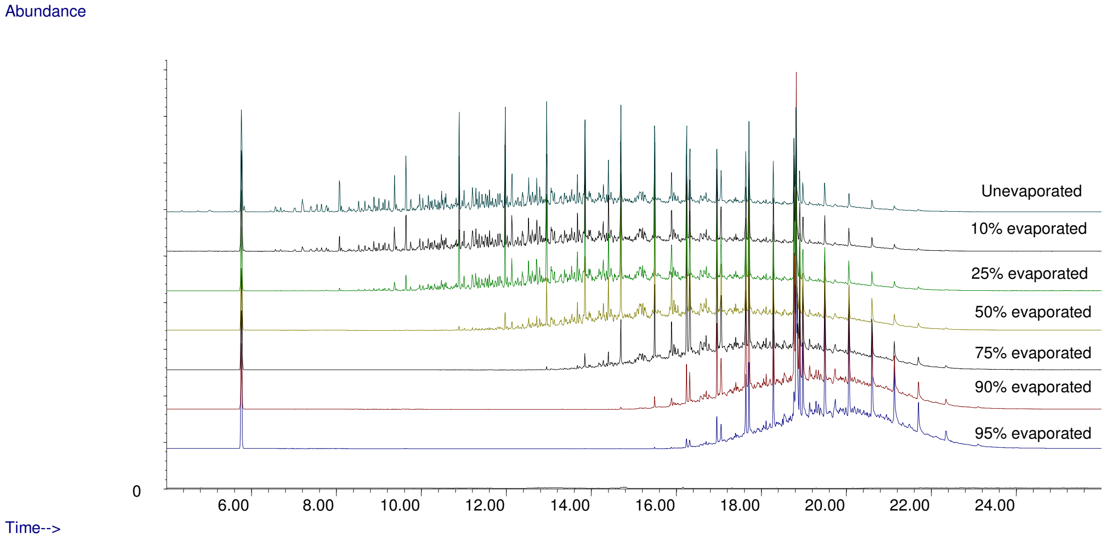


**Figure D.1 TICs of unevaporated to highly evaporated Asda diesel.**

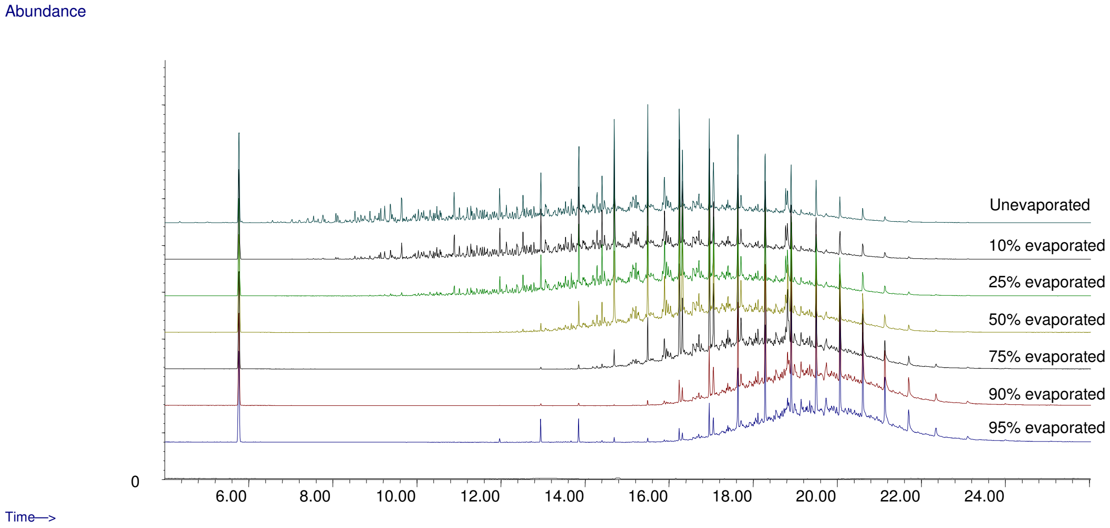


**Figure D.2 TICs of unevaporated to highly evaporated BP diesel.**

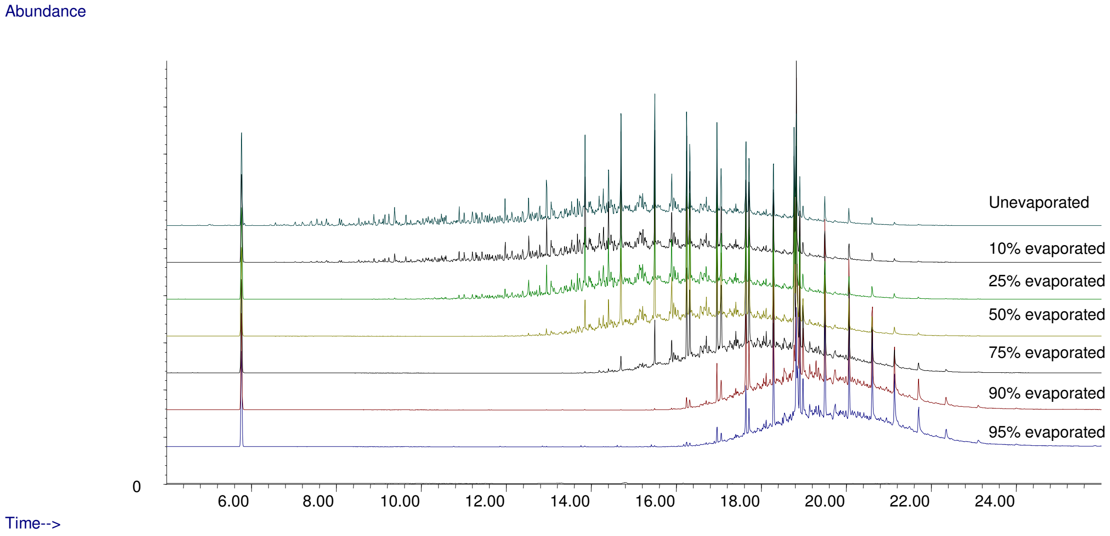


Figure D.3 TICs of unevaporated to highly evaporated Esso diesel.

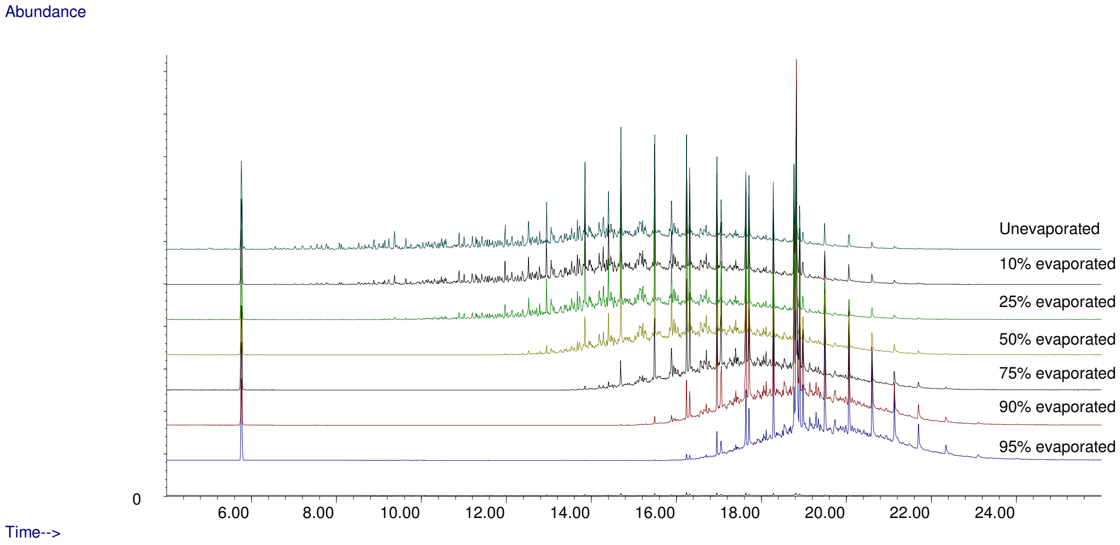


Figure D.4 TICs of unevaporated to highly evaporated Jet diesel.

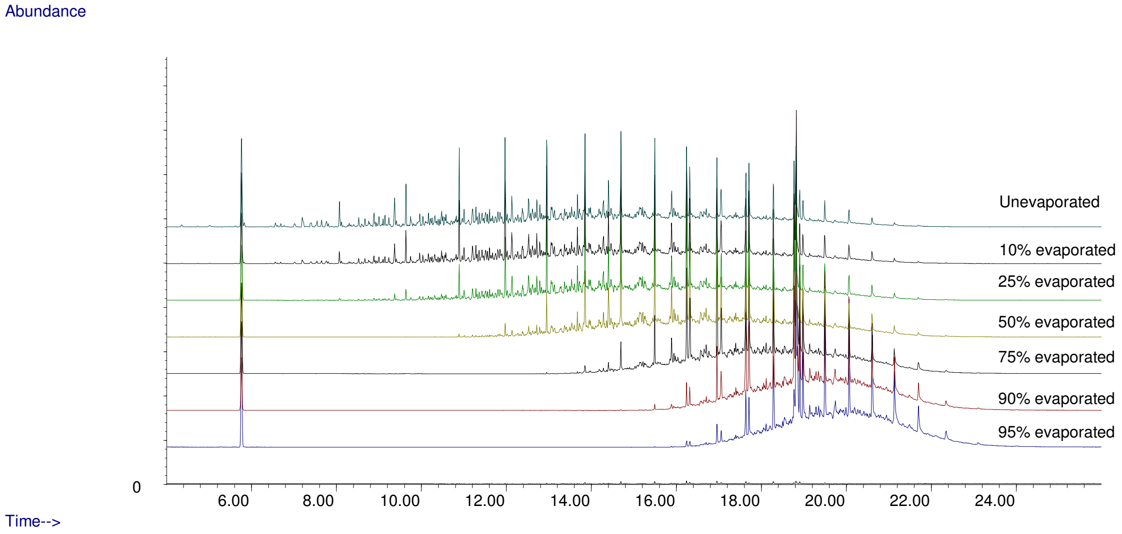


Figure D.5 TICs of unevaporated to highly evaporated Morrison diesel.

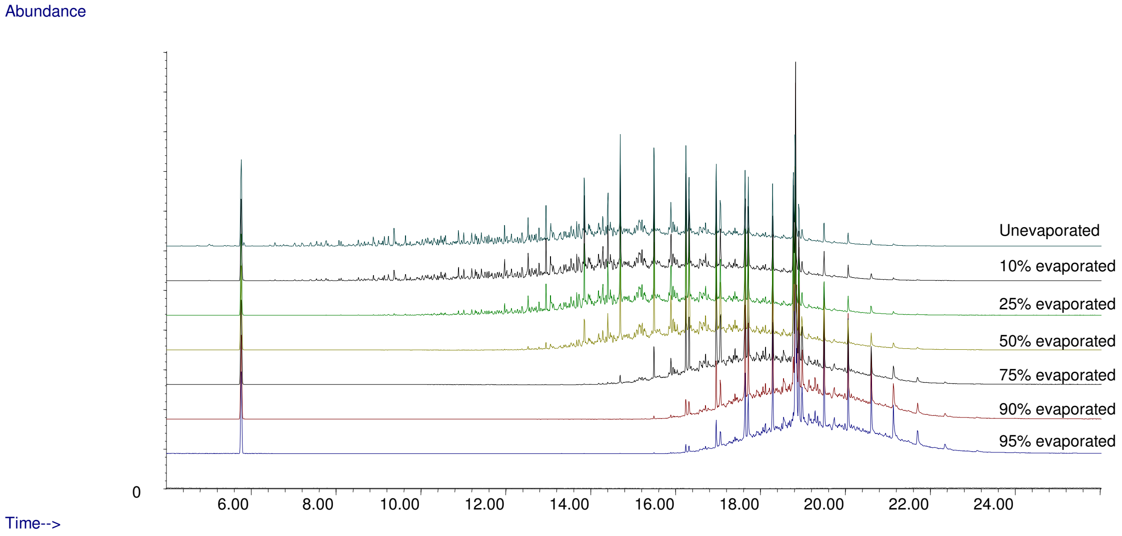


Figure D.6 TICs of unevaporated to highly evaporated Sainsbury diesel.

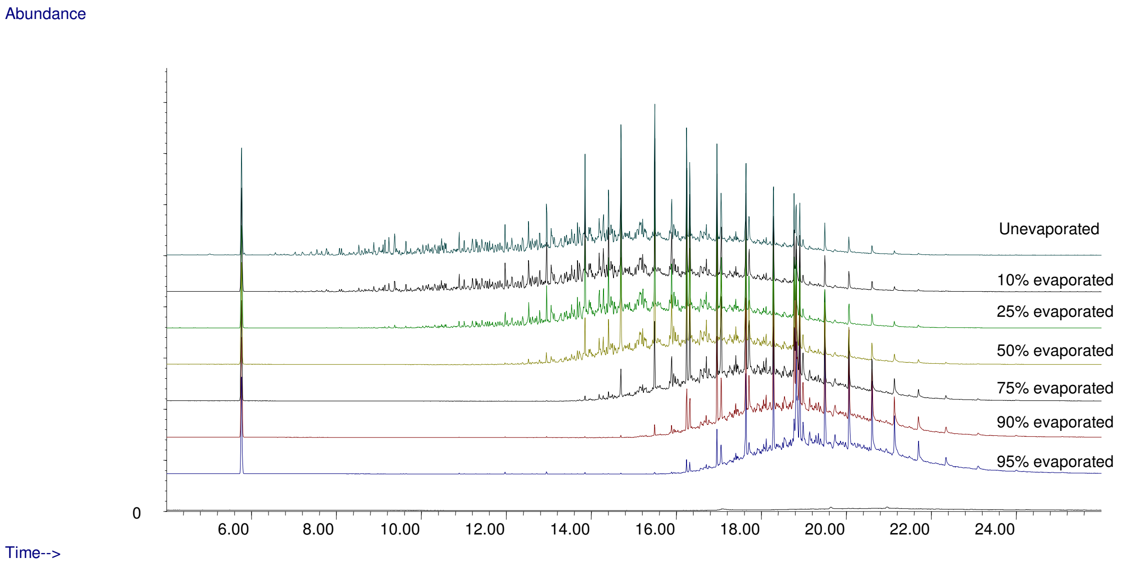


**Figure D.7 TICs of unevaporated to highly evaporated Shell diesel.**

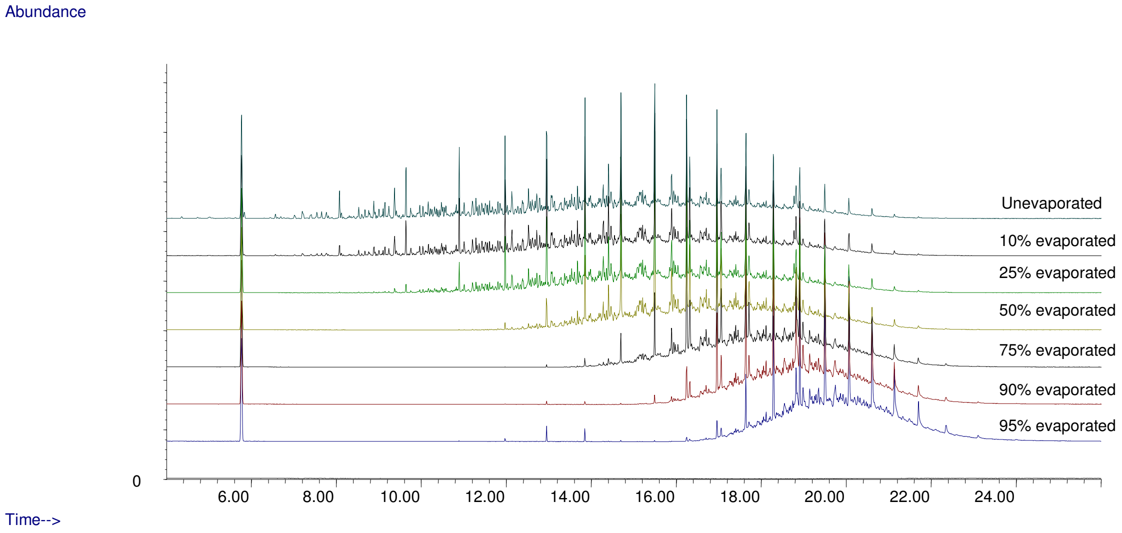


**Figure D.8 TICs of unevaporated to highly evaporated Tesco diesel.**

# Appendix E: Overlay of Total Ion Chromatograms (TICs) of Unevaporated and Evaporated Petrol Samples.

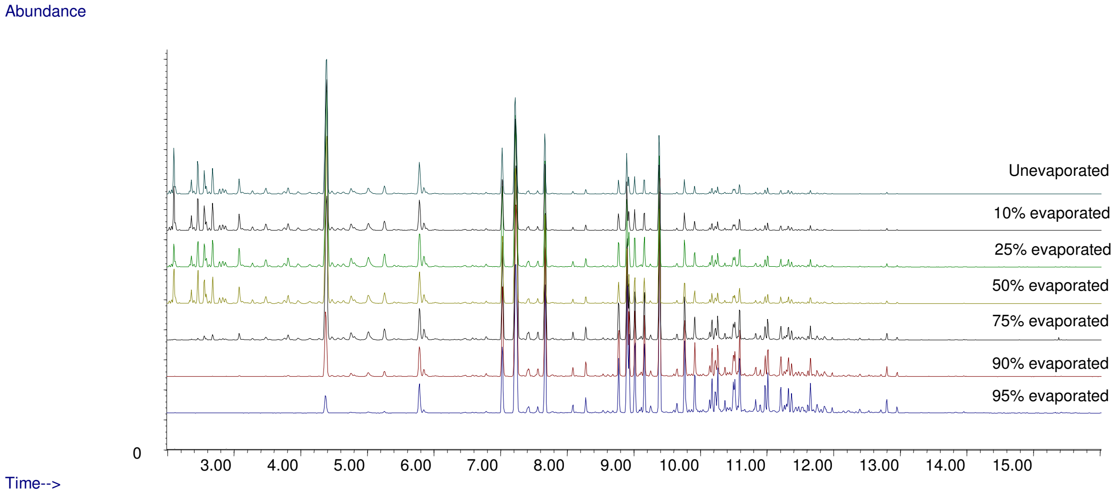


Figure E.1 TICs of unevaporated to highly evaporated regular petrol (Asda).

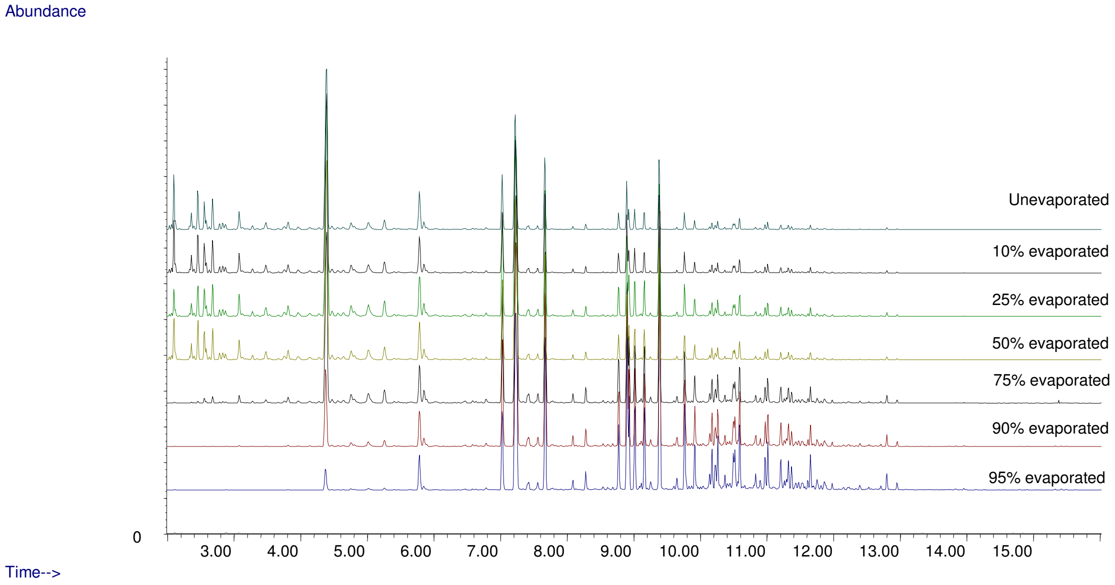


Figure E.2 TICs of unevaporated to highly evaporated regular petrol (Esso).

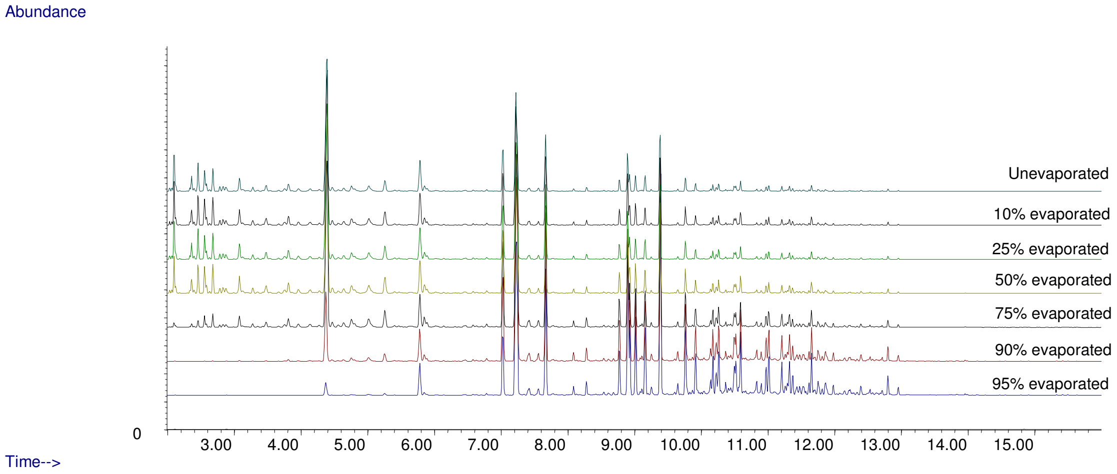


Figure E.3 TICs of unevaporated to highly evaporated regular petrol (Morrison).

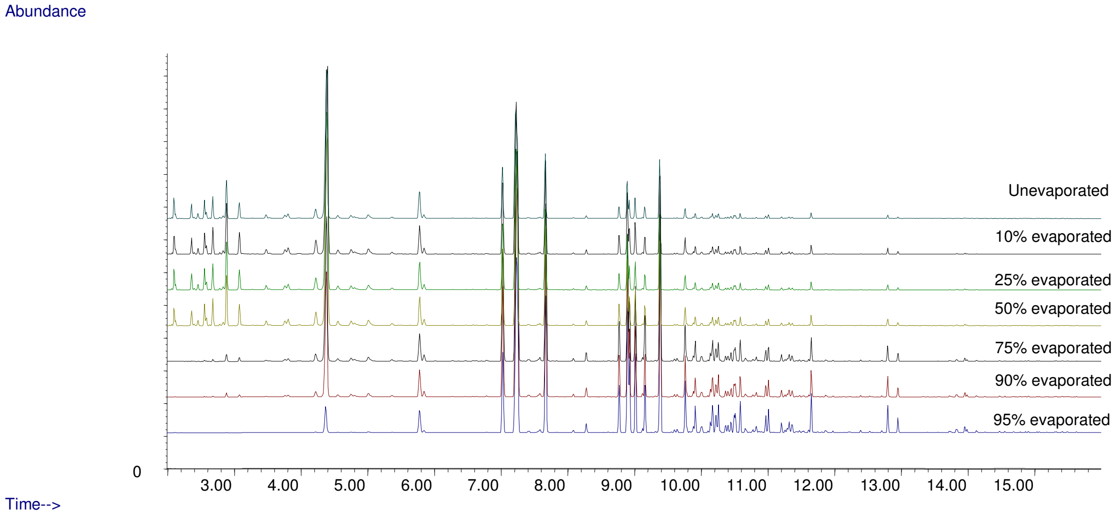


Figure E.4 TICs of unevaporated to highly evaporated regular petrol (Jet).

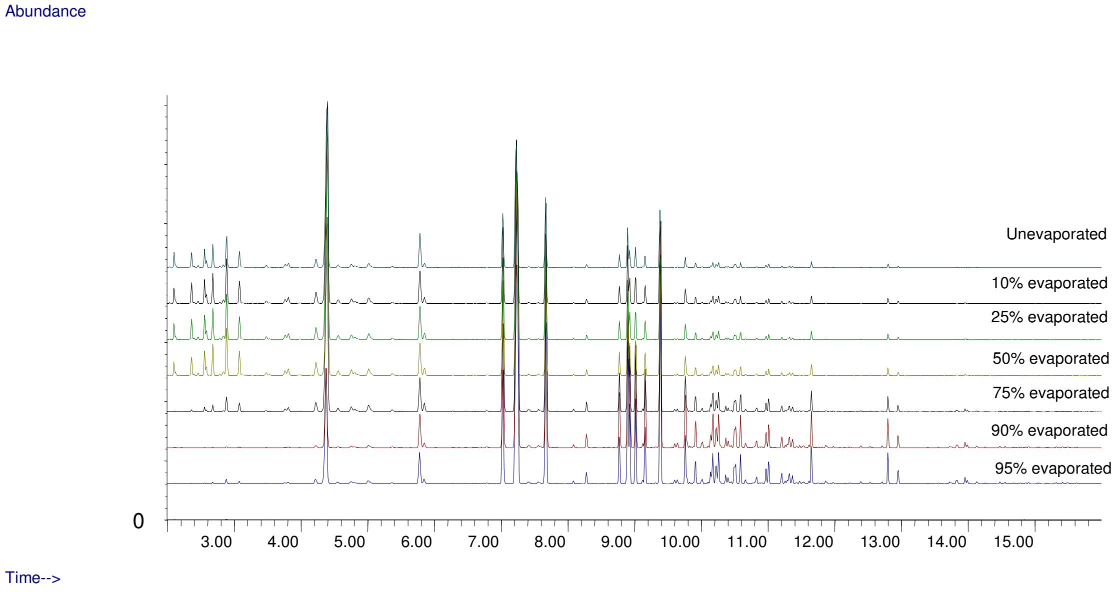


Figure E.5 TICs of unevaporated to highly evaporated regular petrol (Sainsbury).

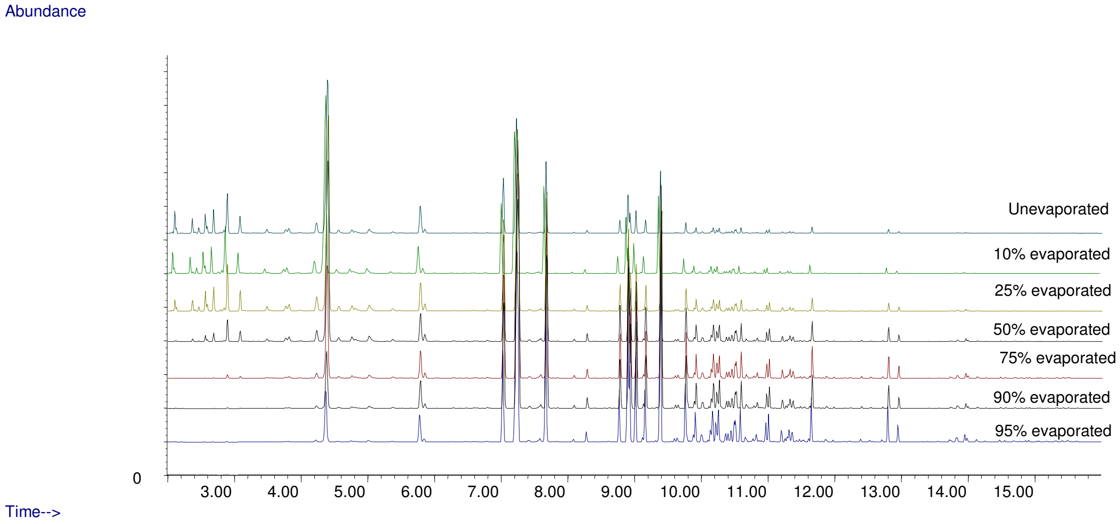


Figure E.6 TICs of unevaporated to highly evaporated regular petrol (BP)

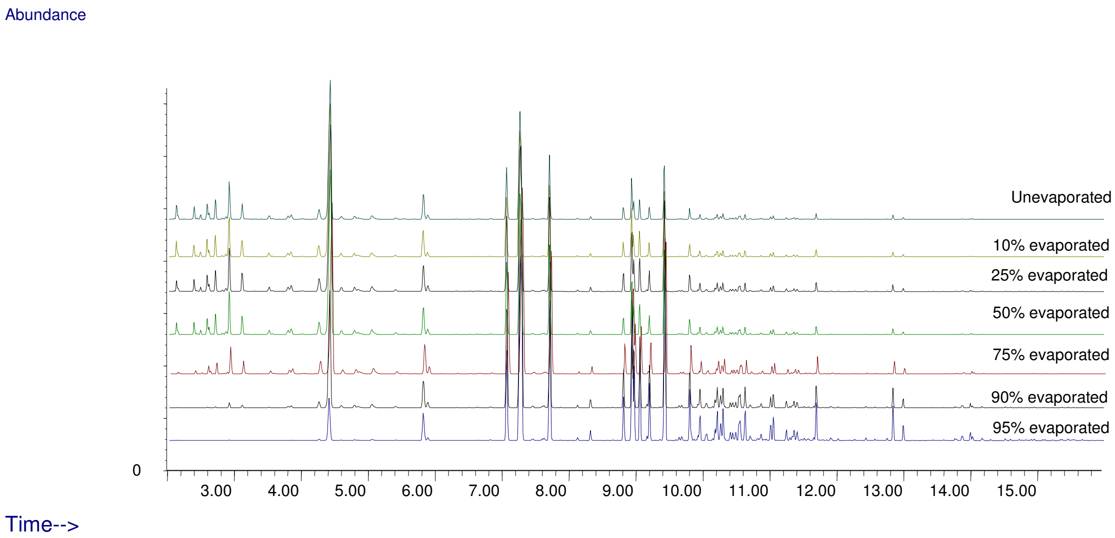


Figure E.7 TICs of unevaporated to highly evaporated regular petrol (Shell).

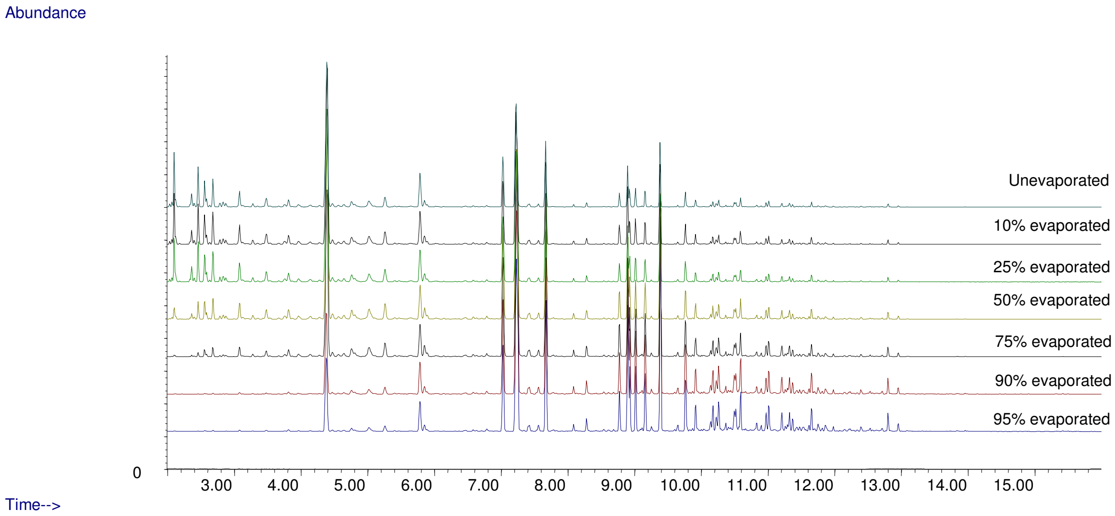


Figure E.8 TICs of unevaporated to highly evaporated regular petrol (Tesco).

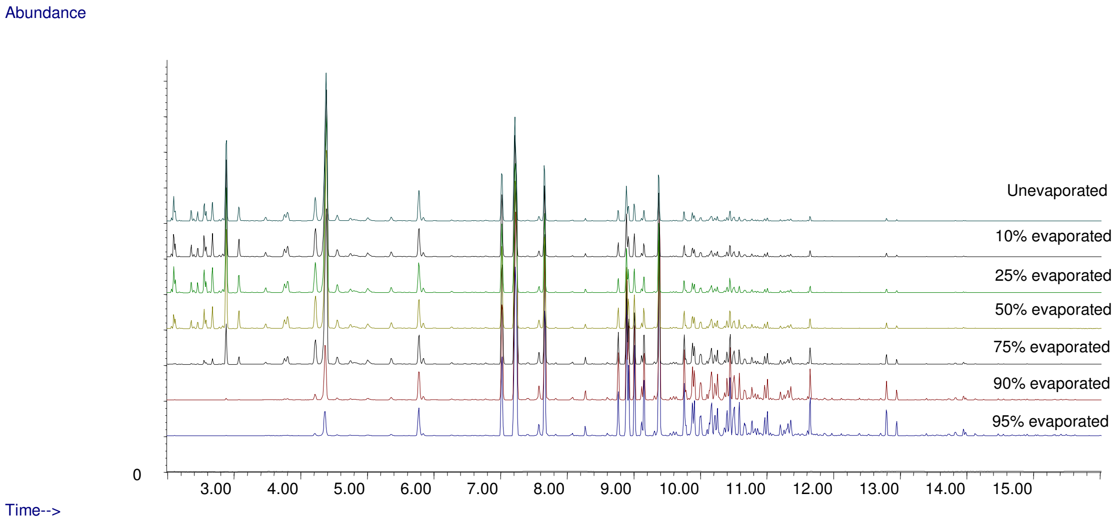


**Figure E.9 TICs of unevaporated to highly evaporated premium petrol (BP).**

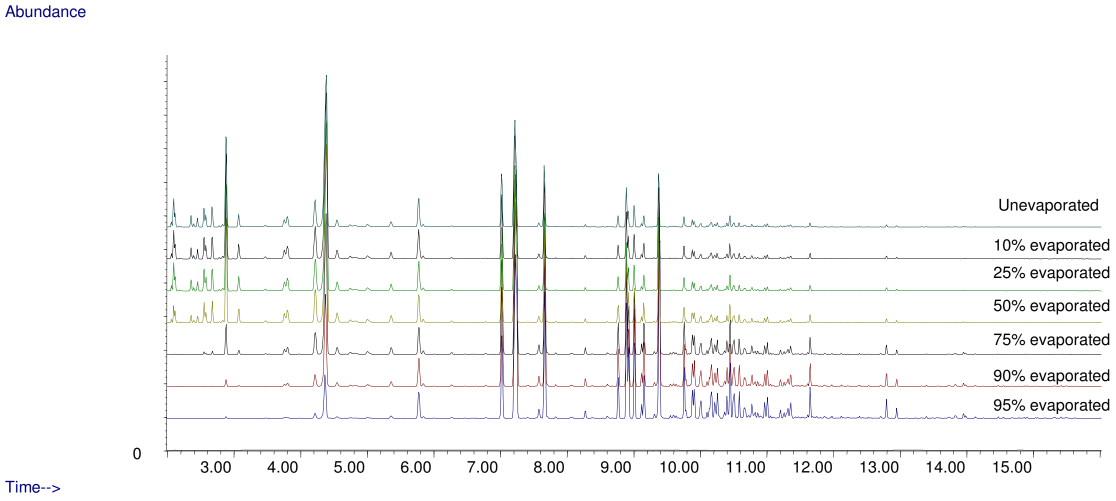


**Figure E.10 TICs of unevaporated to highly evaporated premium petrol (|Esso).**

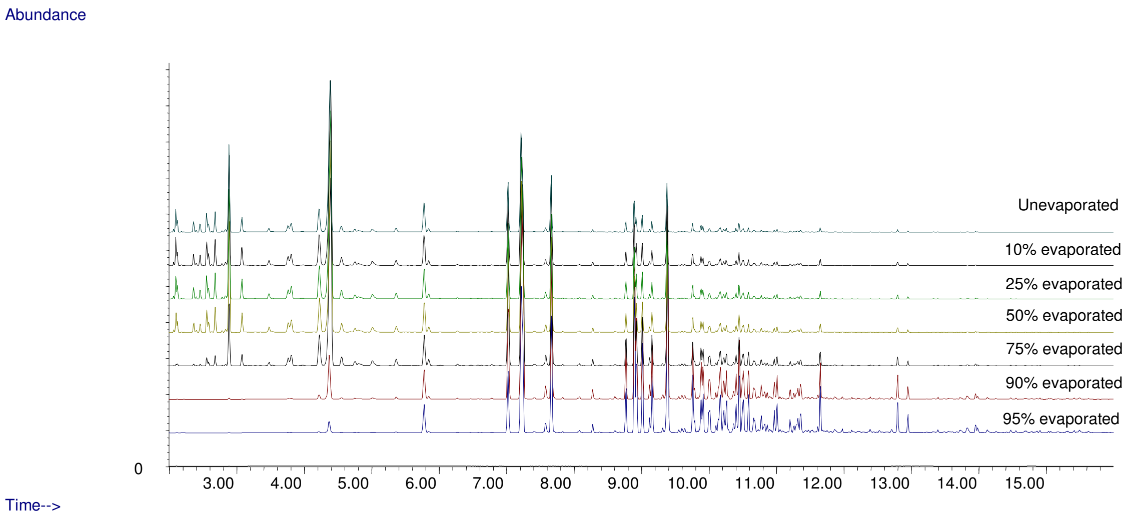


Figure E.11 TICs of unevaporated to highly evaporated premium petrol (Sainsbury).

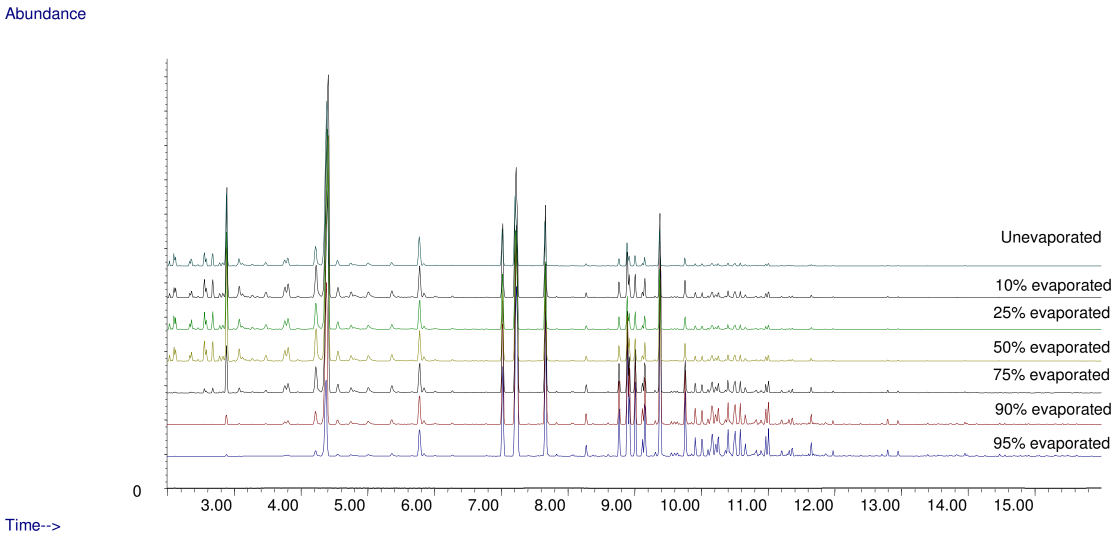


Figure E.12 TICs of unevaporated to highly evaporated premium petrol (Shell).

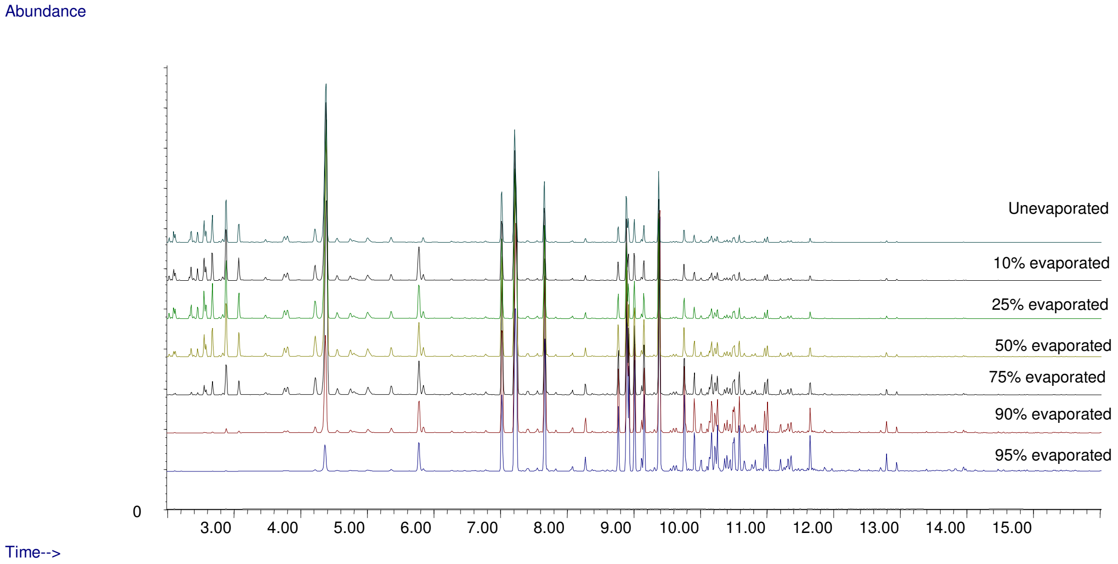


**Figure E.13 TICs of unevaporated to highly evaporated super petrol (Tesco).**

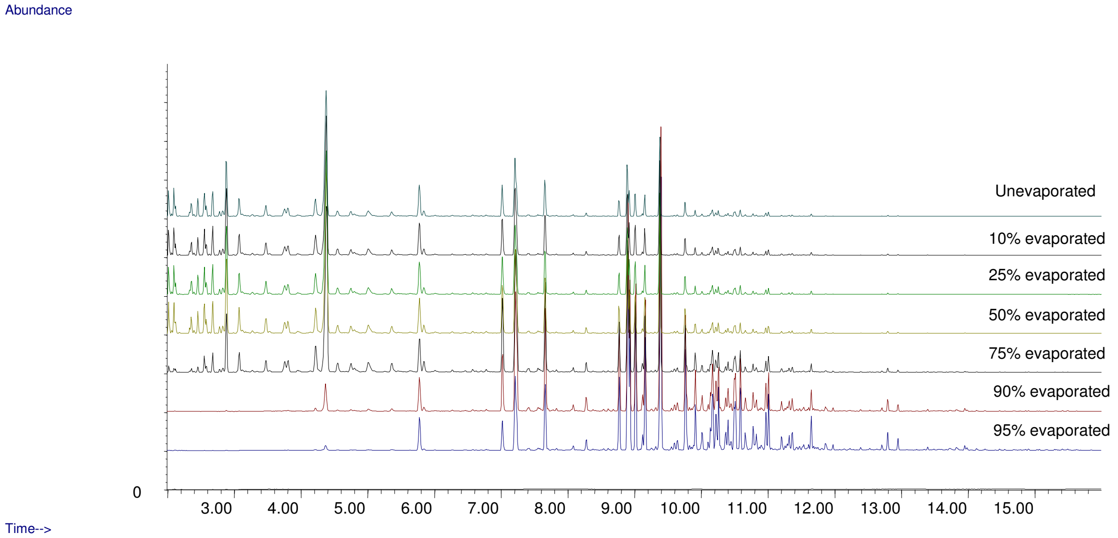


**Figure E.14 TICs of unevaporated to highly evaporated leaded petrol (Four Star).**

## Appendix F: Total Ion Chromatograms (TICs) of Interfering Products from Burnt Substrates

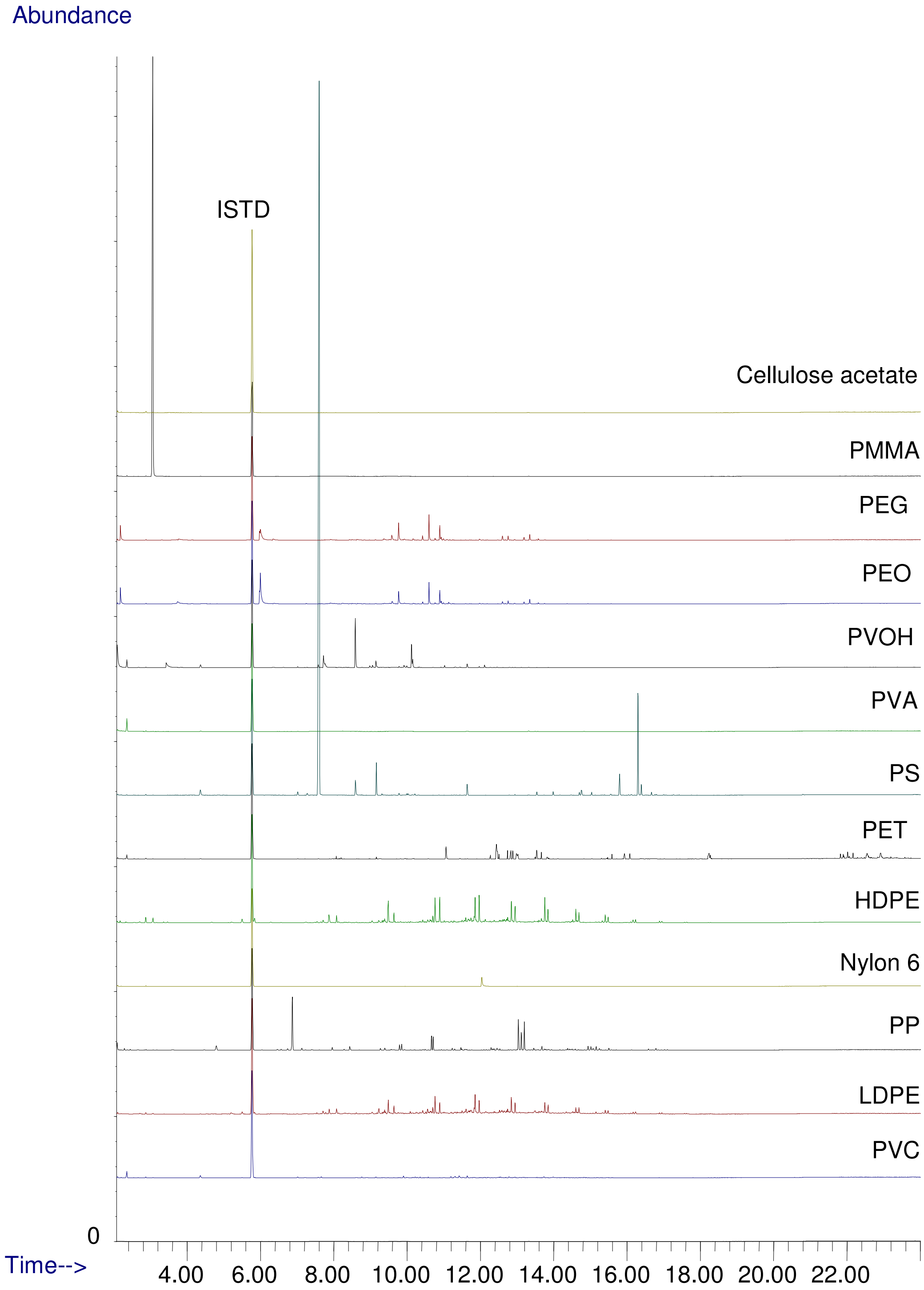


**Figure F.1 Zoomed TIC patterns showing interfering products from burnt polymeric materials**

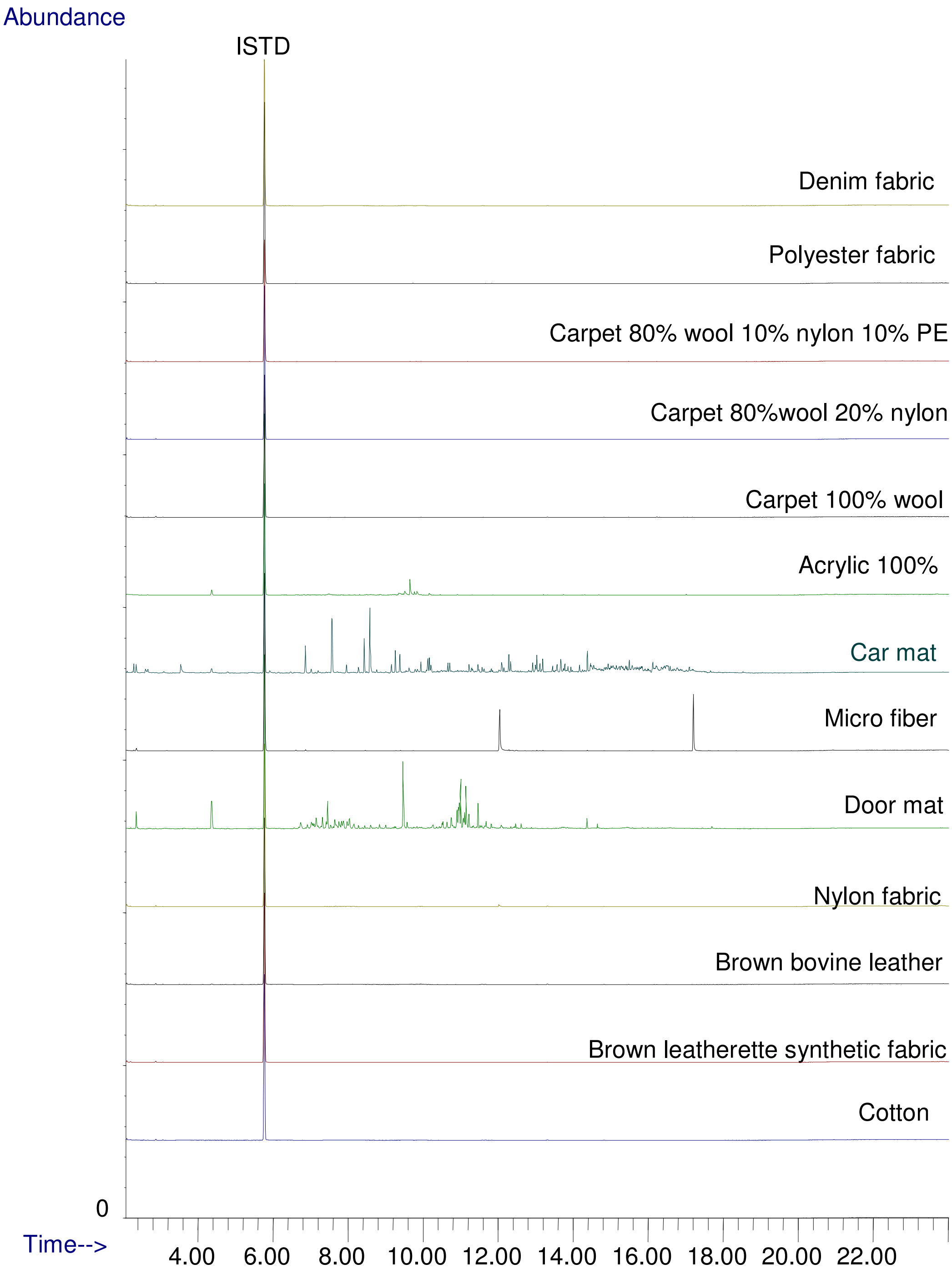


**Figure F.2 Zoomed TIC patterns showing interfering products from burnt household materials**

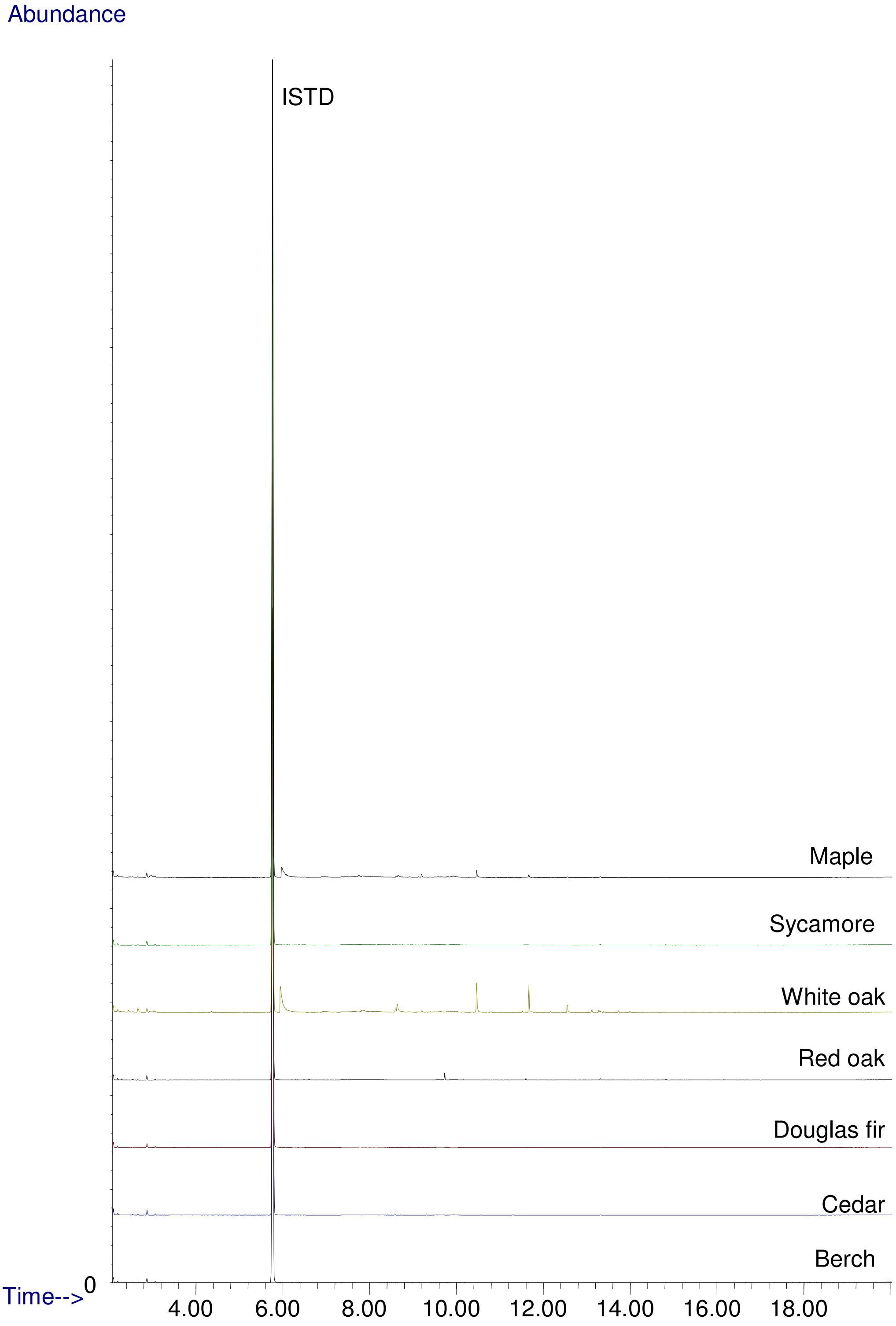
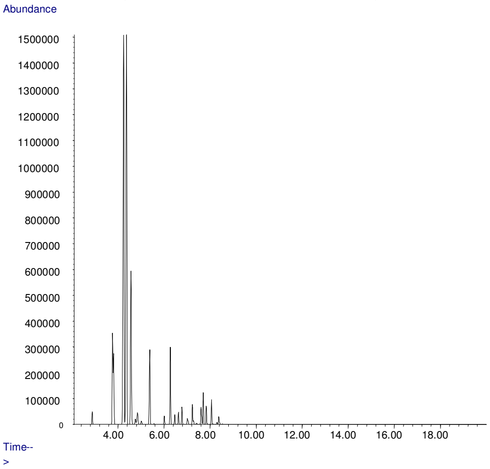


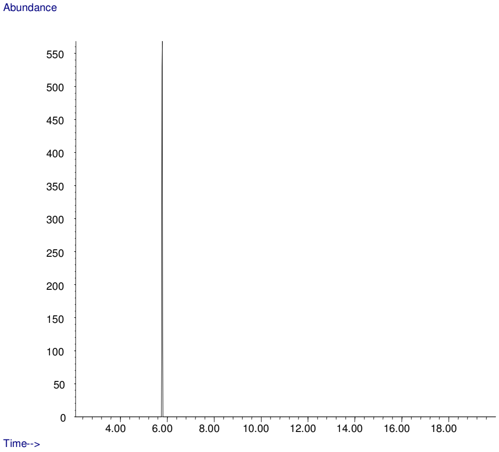
**Figure F.3 Zoomed TIC patterns showing interfering products from burnt wood samples**

# Appendix G: Extracted Ion Profiles of Unevaporated Ignitable Liquids.

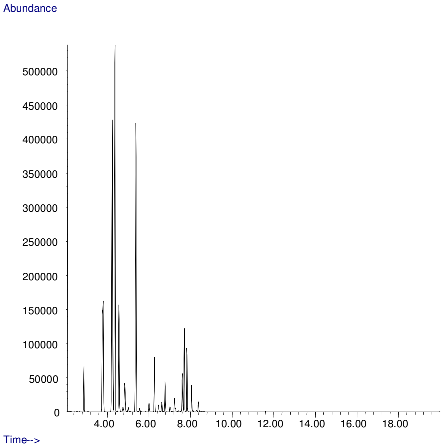
Alkanes (m/z 43,57,71,85,99)



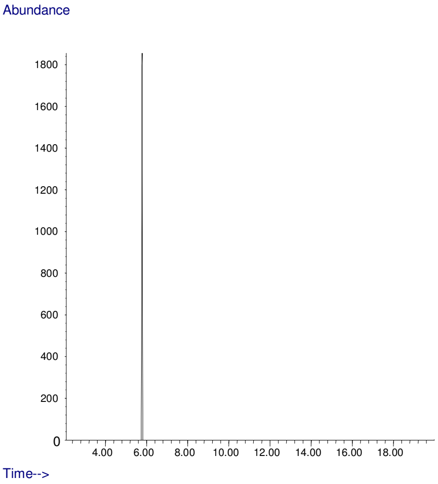
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

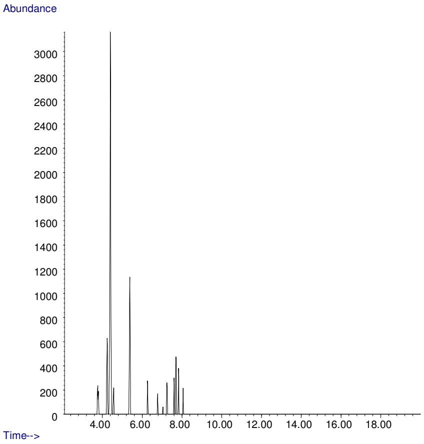
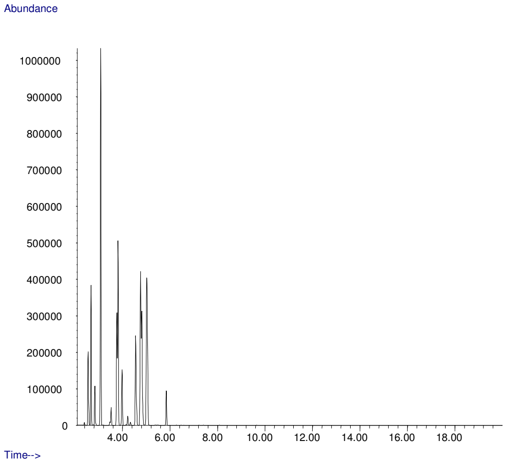
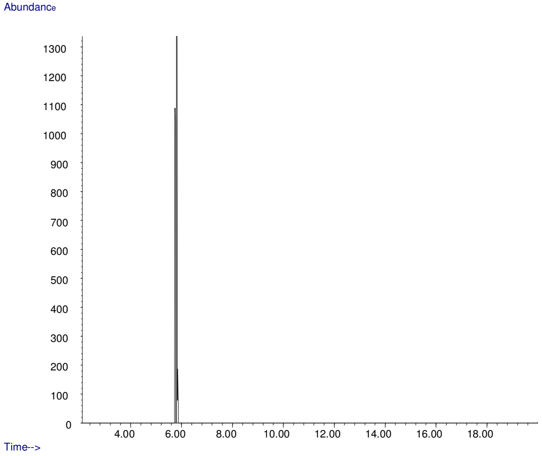


**Figure G.1 EIPs of light petroleum distillate product (Zippo lighter fuel).**

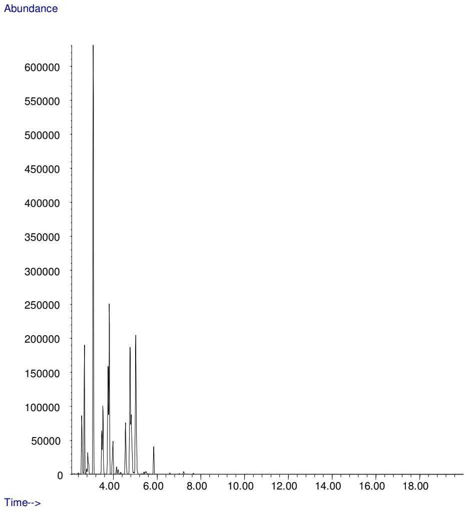
Alkanes (m/z 43,57,71,85,99)



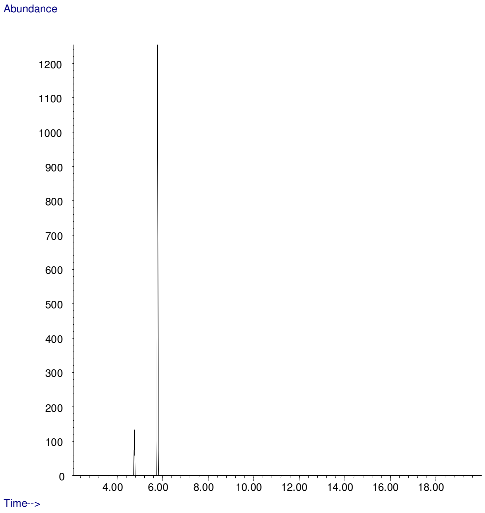
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

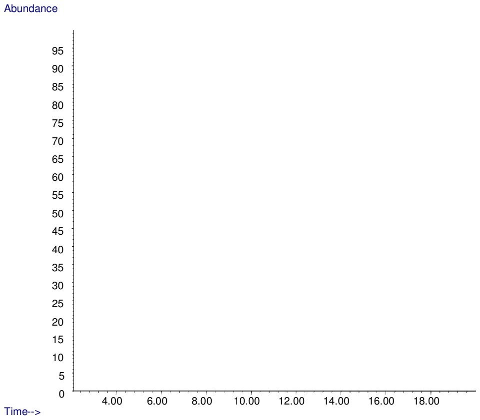
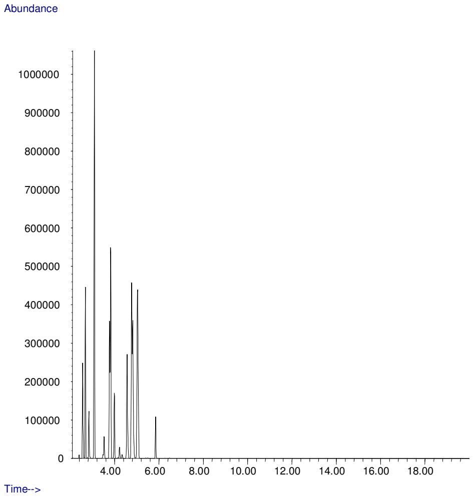
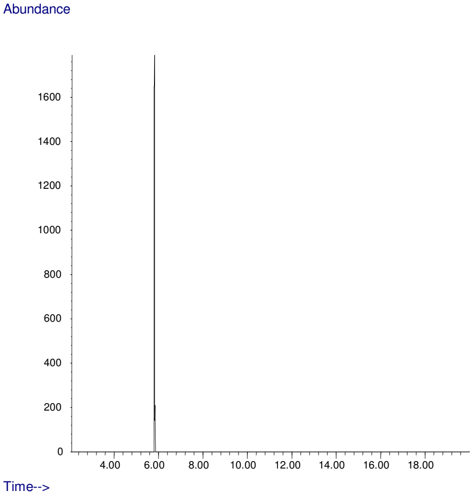


**Figure G.2 EIPs of light petroleum distillate product (Swan lighter fluid).**

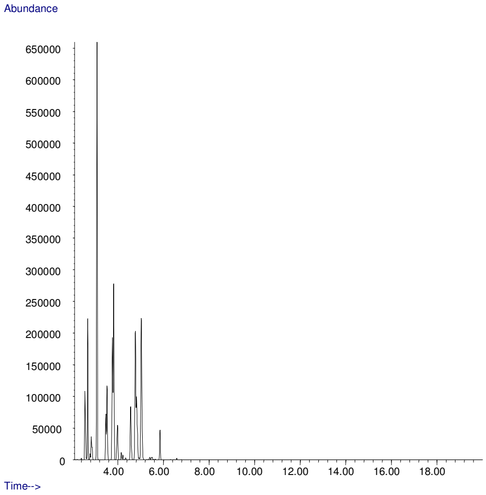
Alkanes (m/z 43,57,71,85,99)



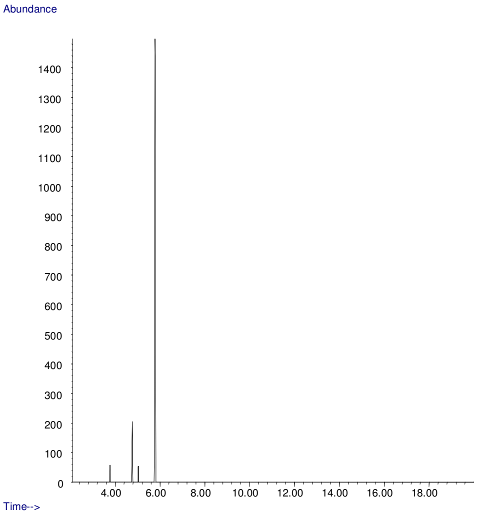
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

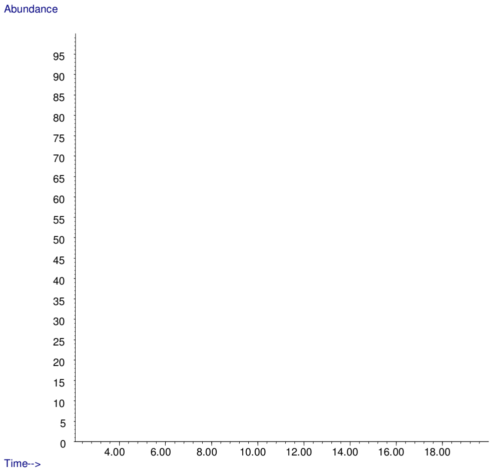
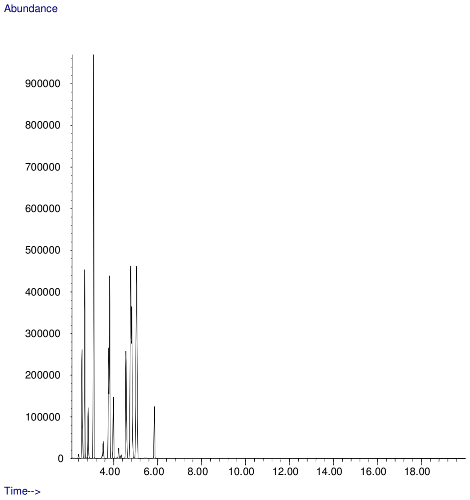
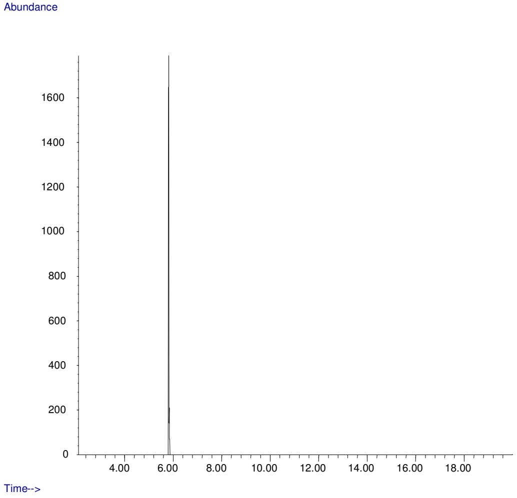


**Figure G.3 EIPs of light petroleum distillate product (Ronsonol lighter fuel).**

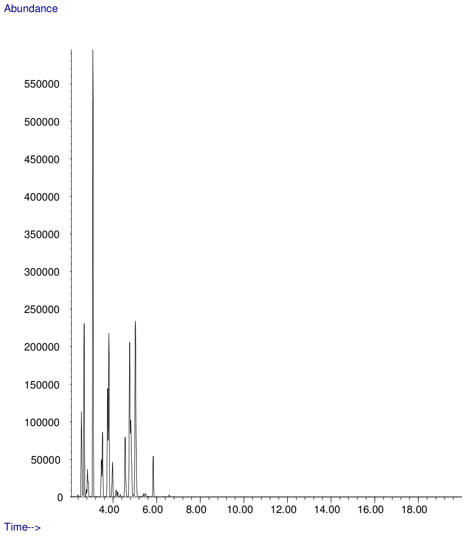
Alkanes (m/z 43,57,71,85,99)



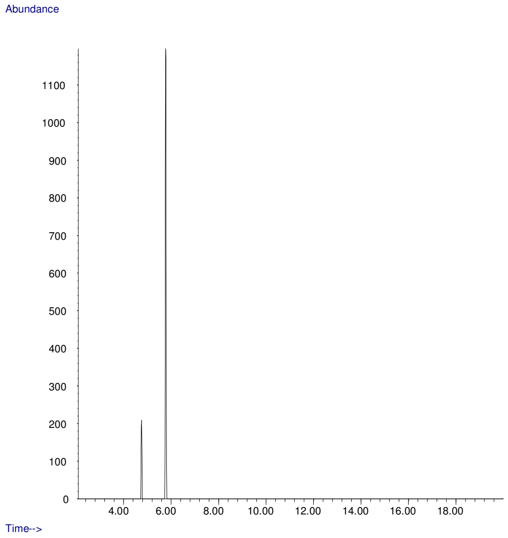
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

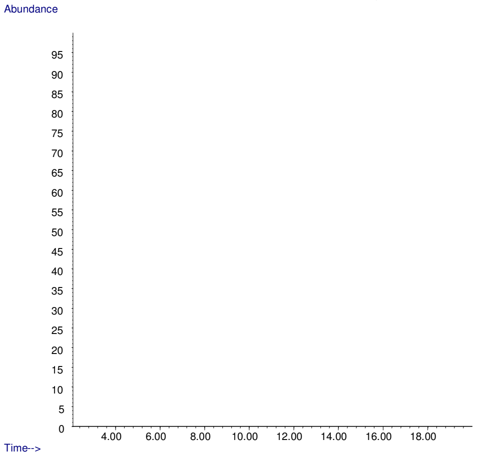
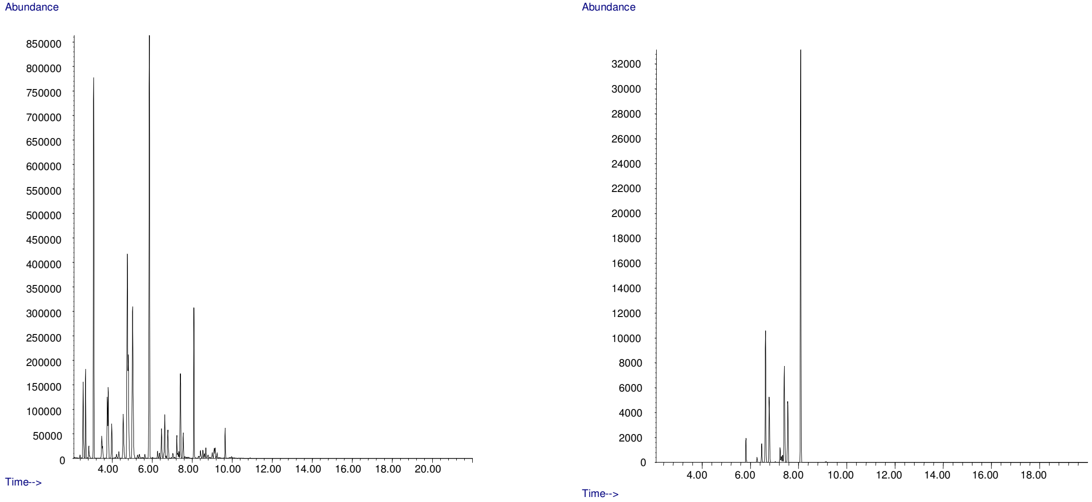
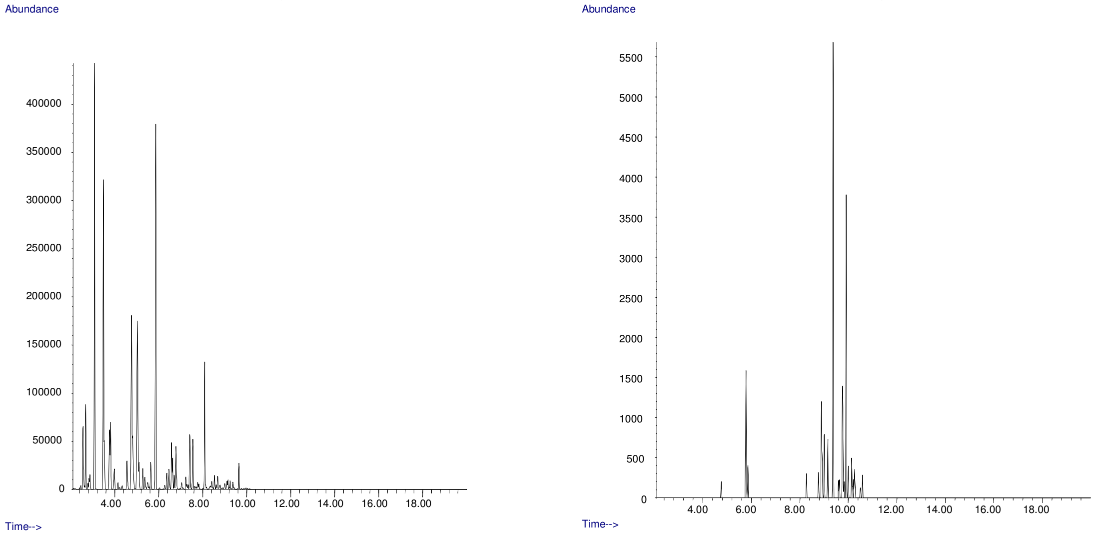


**Figure G.4 EIPs of light petroleum distillate product (Swan lighter fuel).**



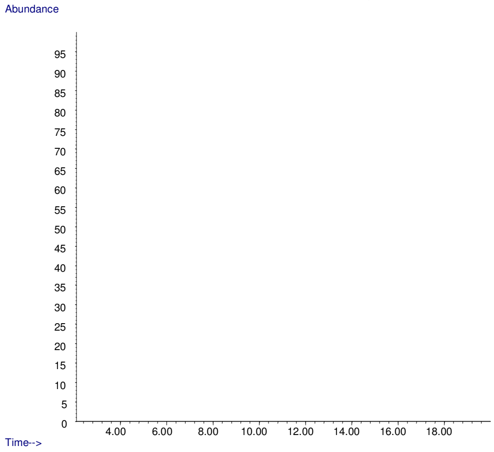
Alkanes (m/z 43,57,71,85,99)

Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)

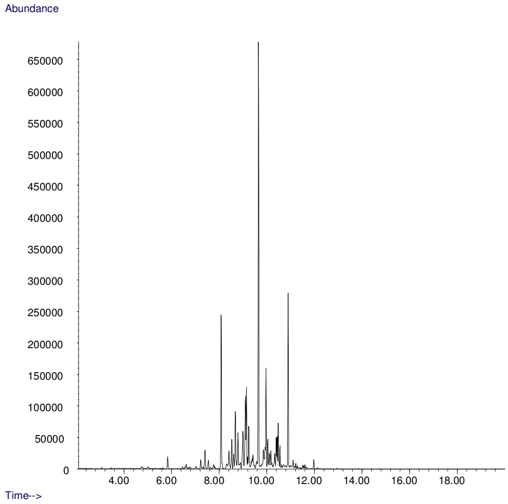
Indanes
(m/z 117, 118, 131,132)



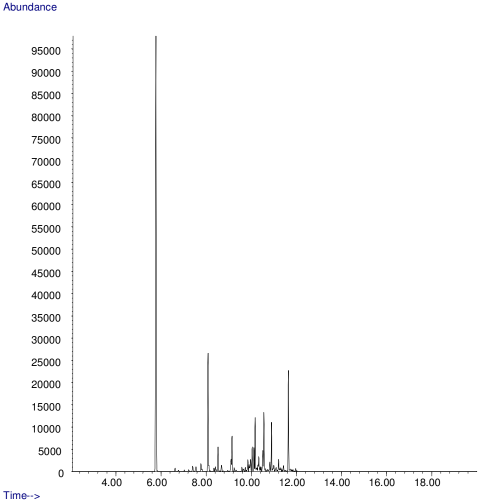
Alkylbenzenes
(m/z 91,92,105,106,119,120)

**Figure G.5 EIPs of light petroleum distillate product (Dunhill lighter fuel).**

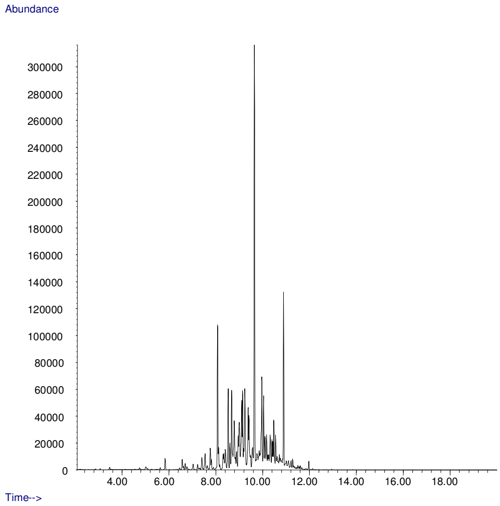
Alkanes(m/z 43,57,71,85,99)



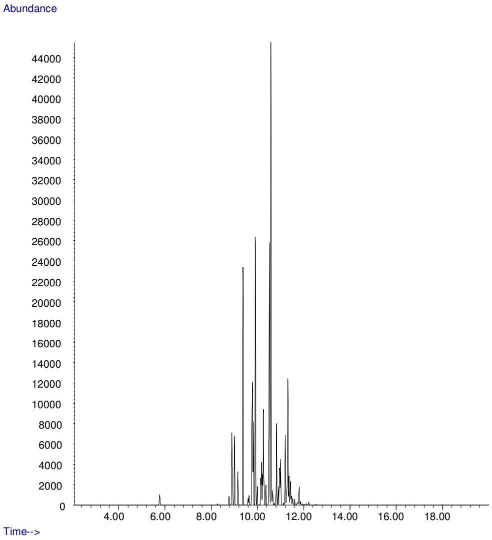
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

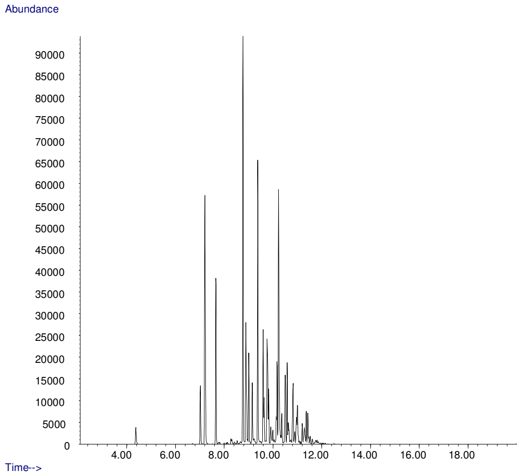
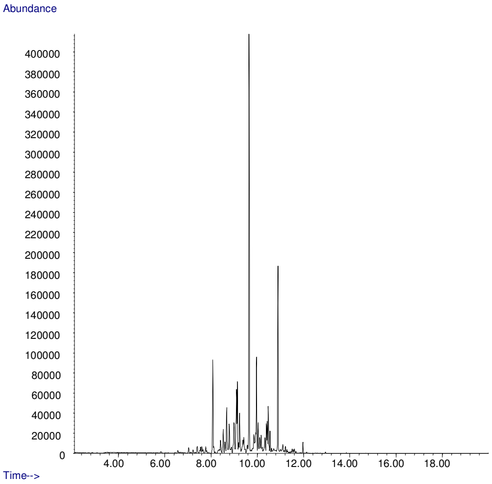
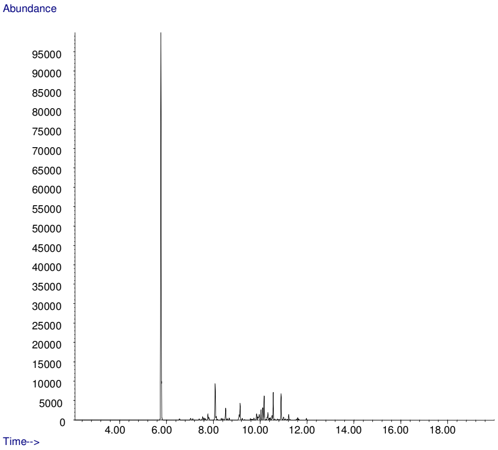


**Figure G.6 EIPs of medium petroleum distillate product (B&Q white spirit).**

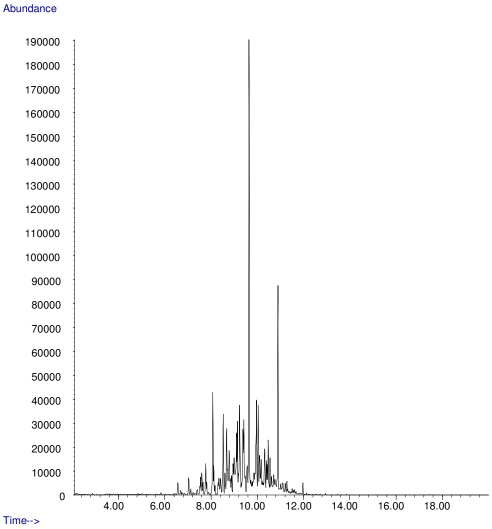
Alkanes (m/z 43,57,71,85,99)



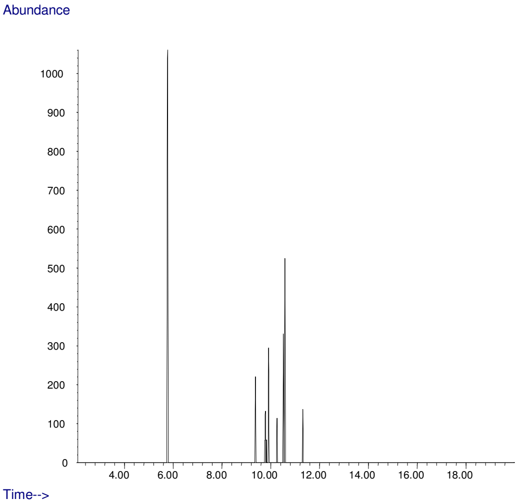
Naphthalenes
(m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes
(m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

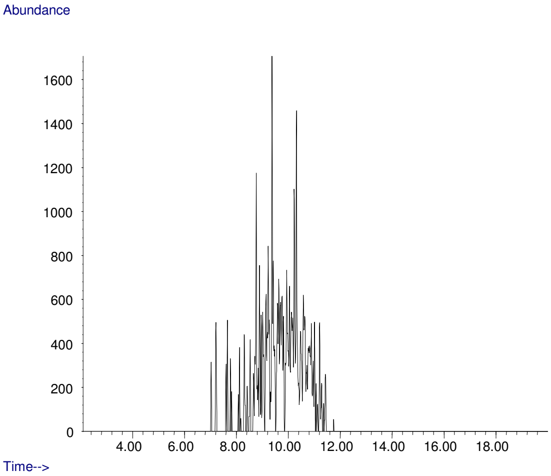
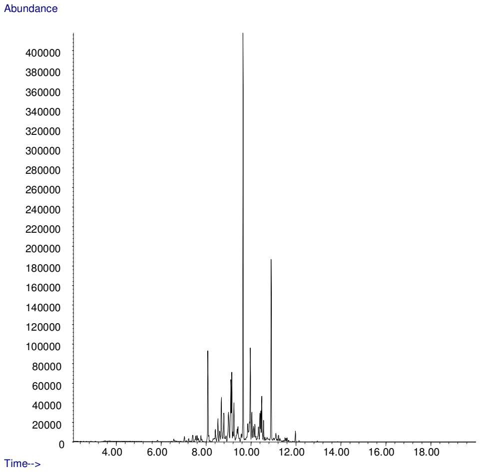
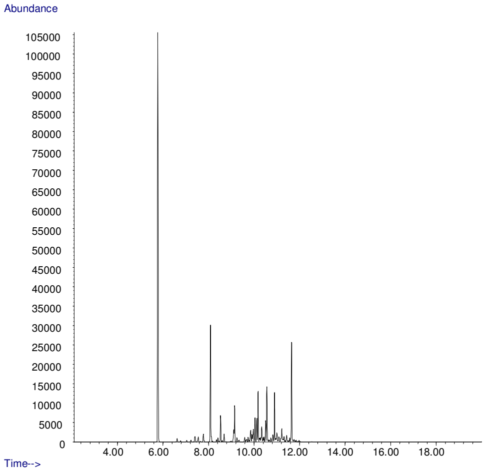


**Figure G.7 EIPs of medium petroleum distillate product (Bertoline white spirit).**

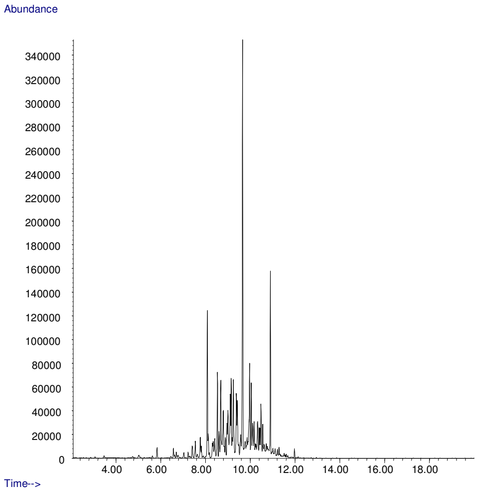
Alkanes (m/z 43,57,71,85,99)



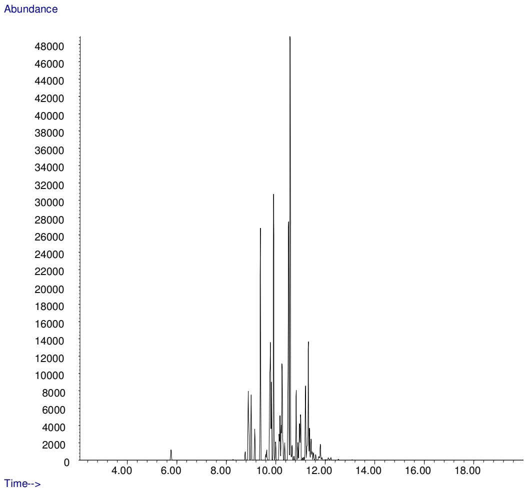
Naphthalenes
(m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes
(m/z 117, 118, 131,132)



Alkylbenzene (m/z 91,92,105,106,119,120)

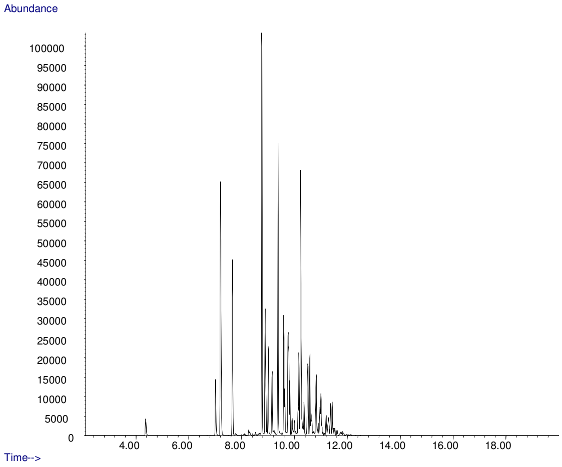
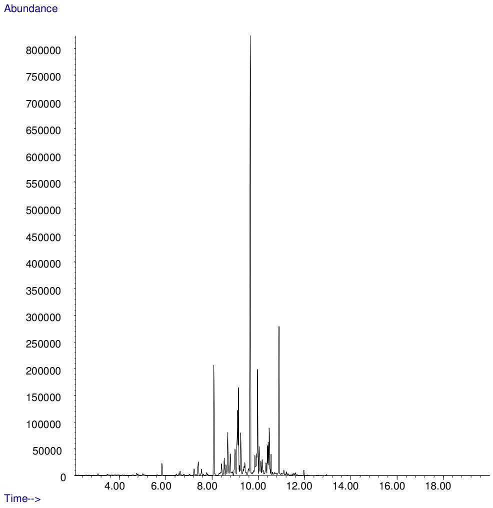
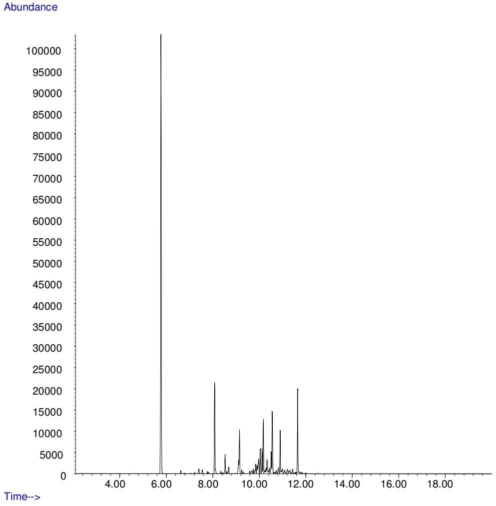


**Figure G.8 EIPs of medium petroleum distillate product (Homebase white spirit).**

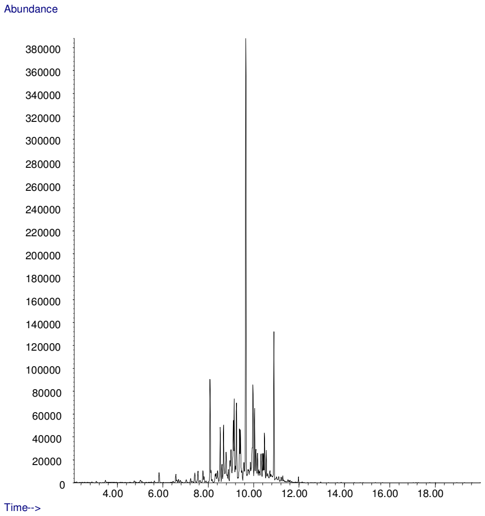
Alkanes (m/z 43,57,71,85,99)



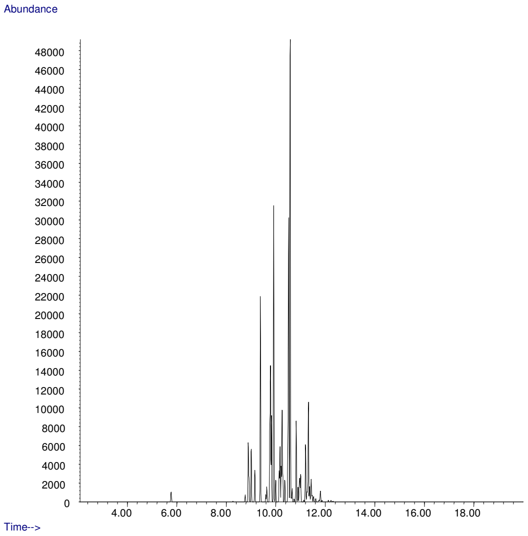
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes(m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzene (m/z 91,92,105,106,119,120)

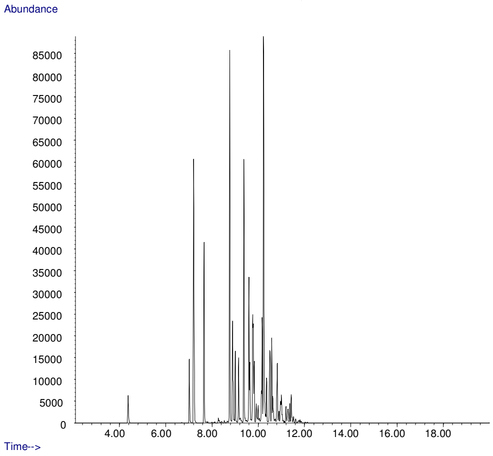
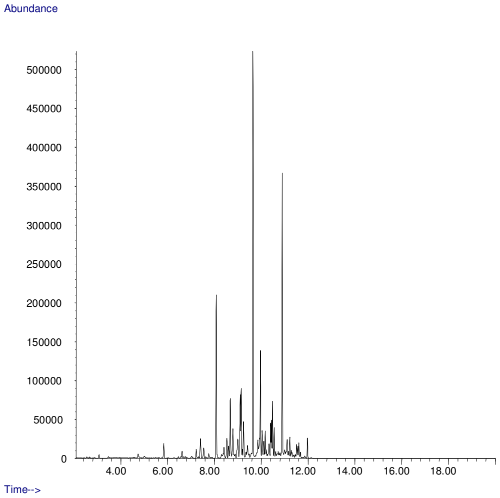
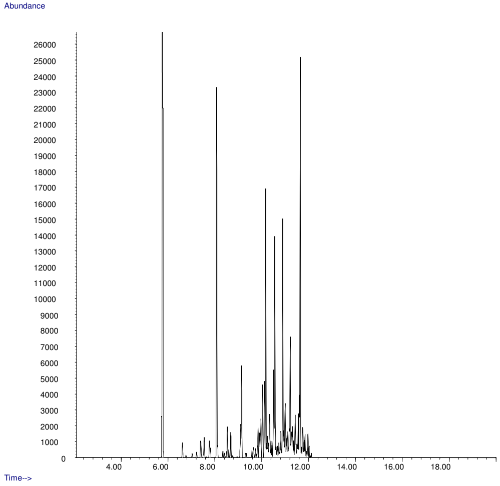


**Figure G.9 EIPs of medium petroleum distillate product (Tesco white spirit).**

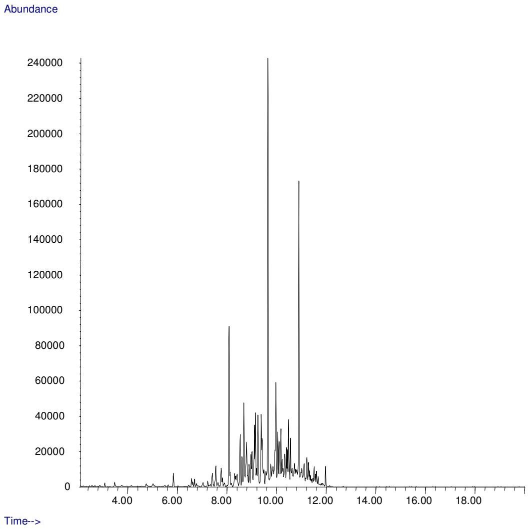
Alkanes (m/z 43,57,71,85,99)



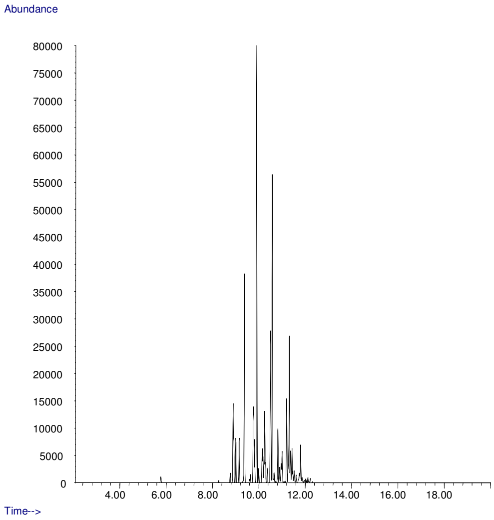
Naphthalenes(m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

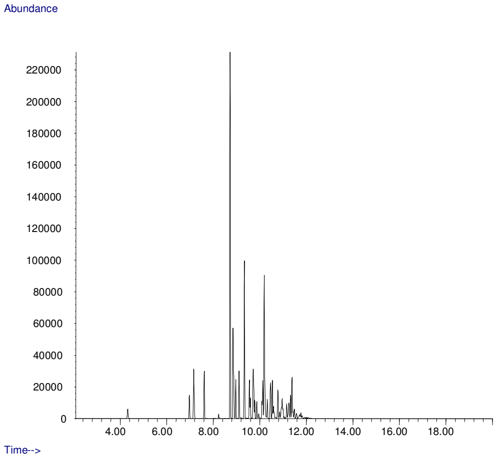
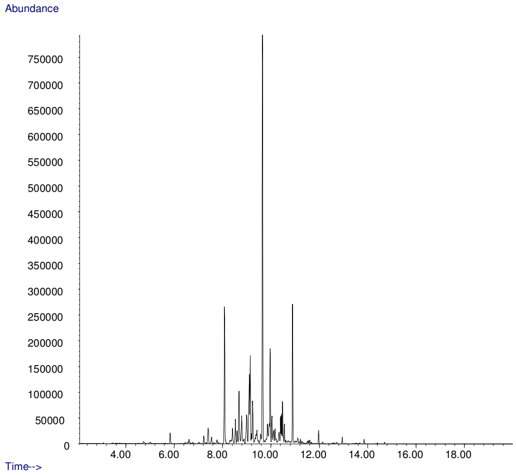
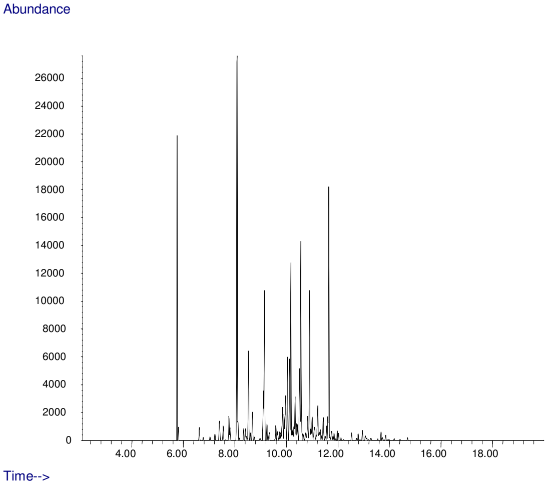


**Figure G.10 EIPs of medium petroleum distillate product (Polycell brush cleaner).**

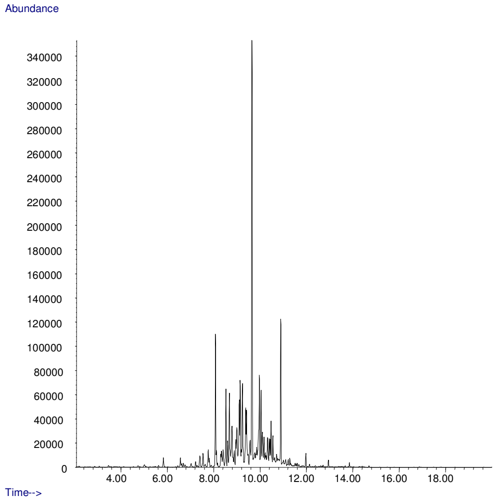
Alkanes (m/z 43,57,71,85,99)



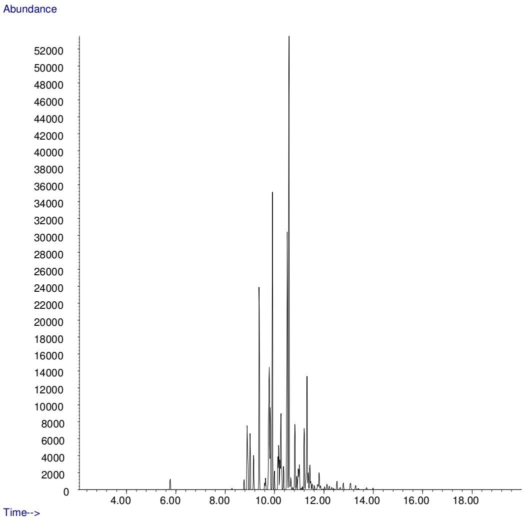
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

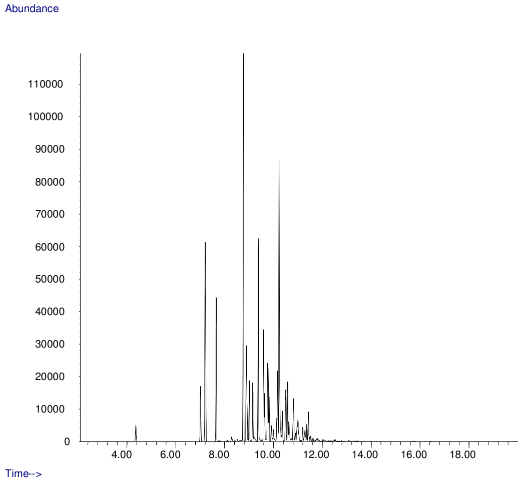
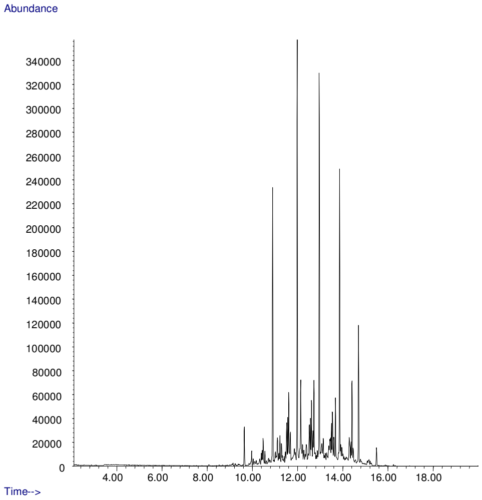
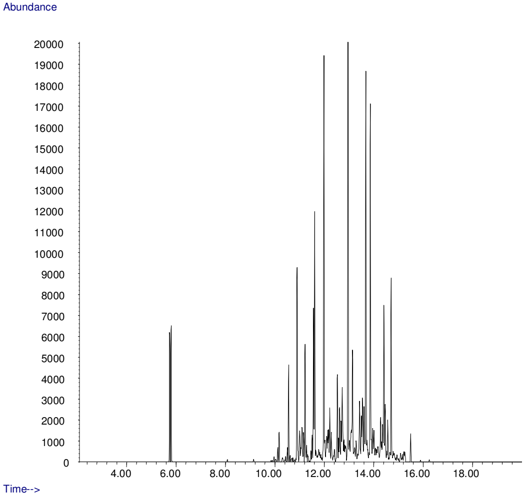


**Figure G.11 EIPs of medium petroleum distillate product (Homebase brush cleaner).**

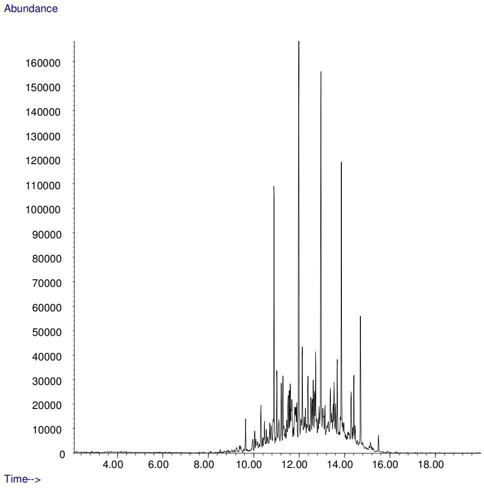
Alkanes (m/z 43,57,71,85,99)



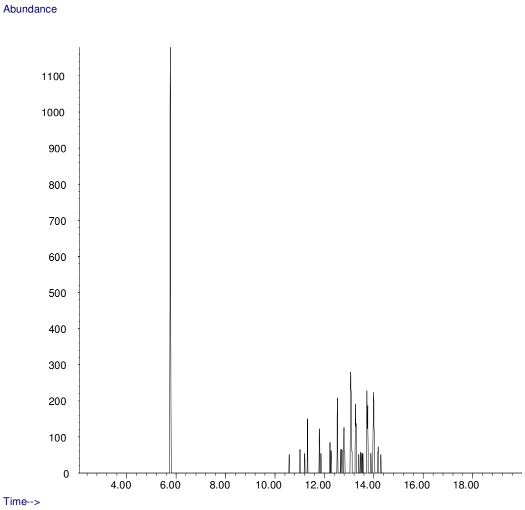
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

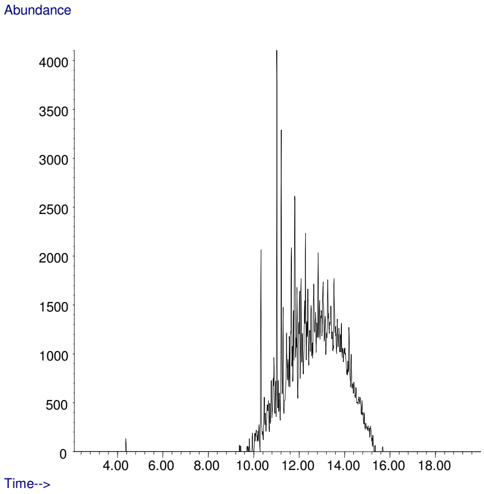
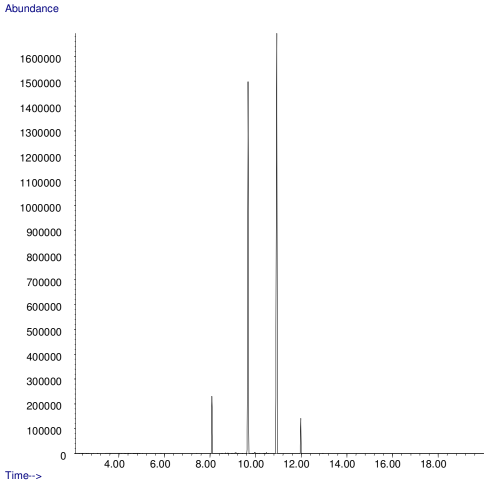
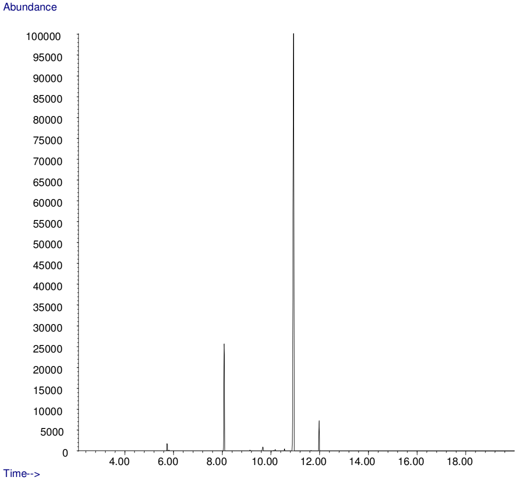


**Figure G.12 EIPs of medium petroleum distillate product (Bertoline lamp oil).**

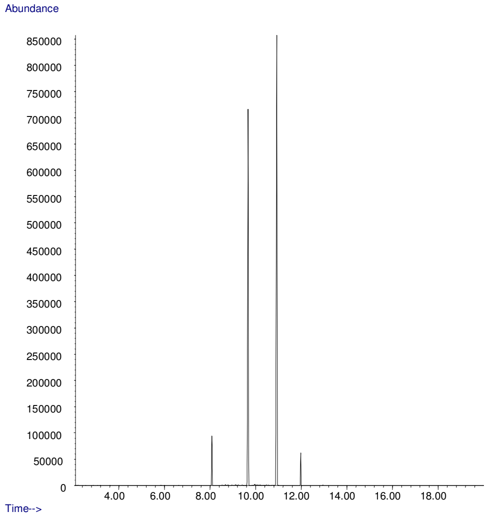
Alkanes (m/z 43,57,71,85,99)



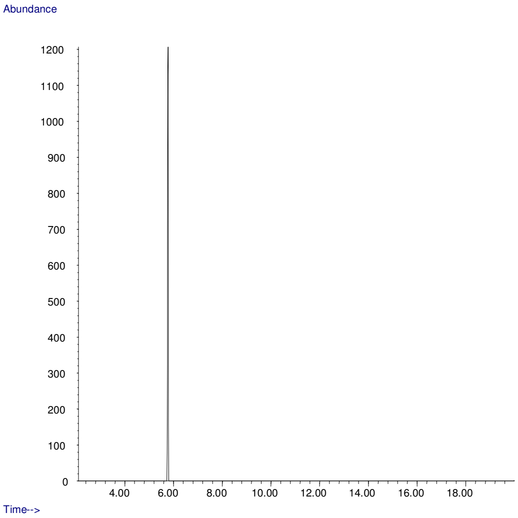
Naphthalenes(m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

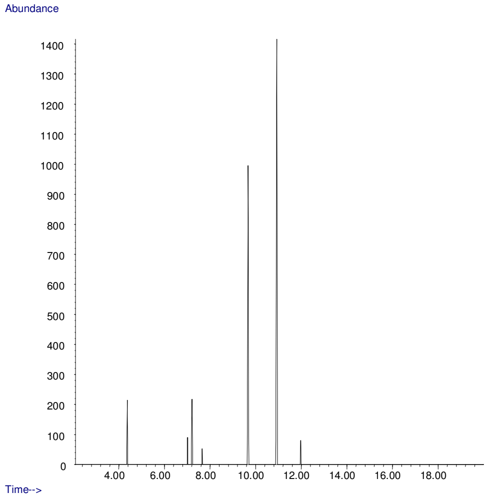
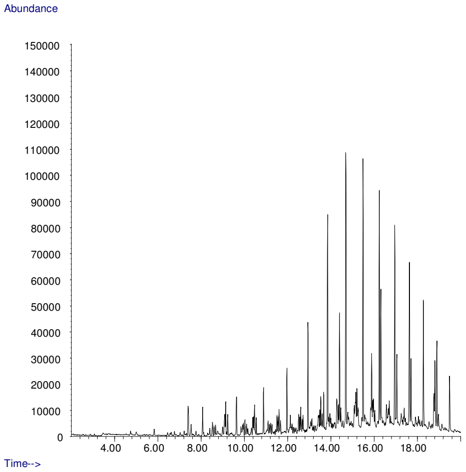
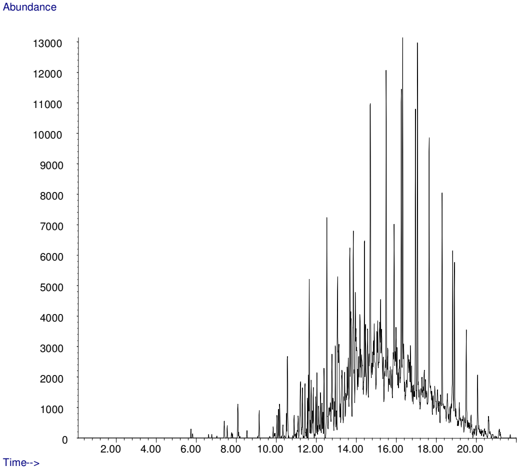


**Figure G.13 EIPs of medium petroleum distillate product (After dark lamp oil).**

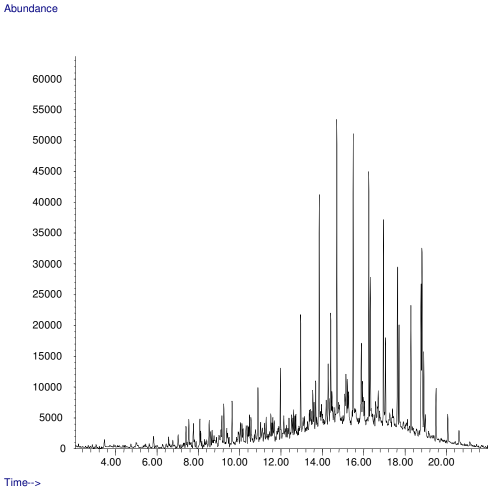
Alkanes (m/z 43,57,71,85,99)



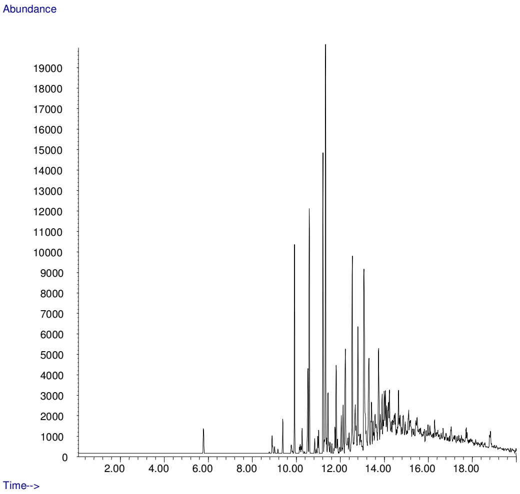
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

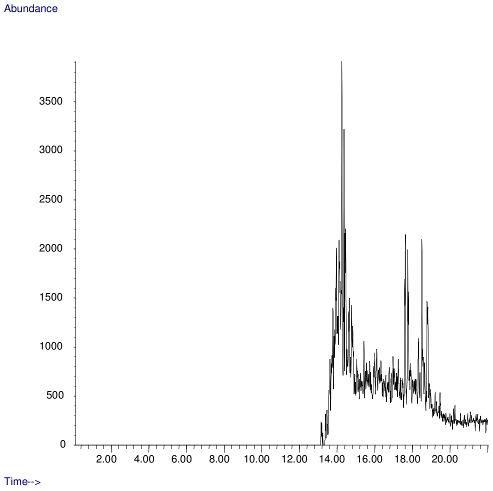
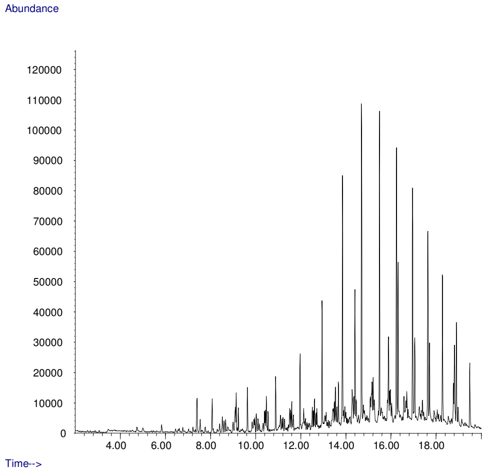
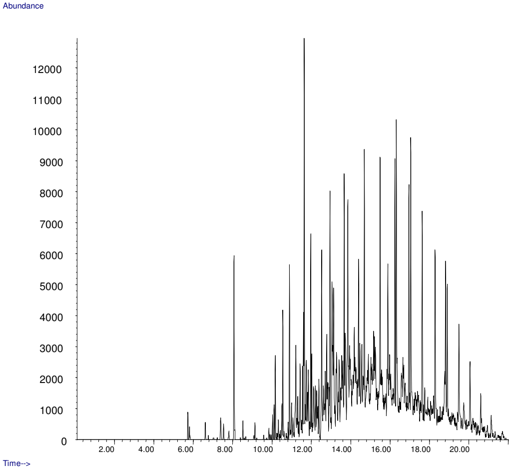


**Figure G.14 EIPs of heavy petroleum distillate product (Esso diesel).**

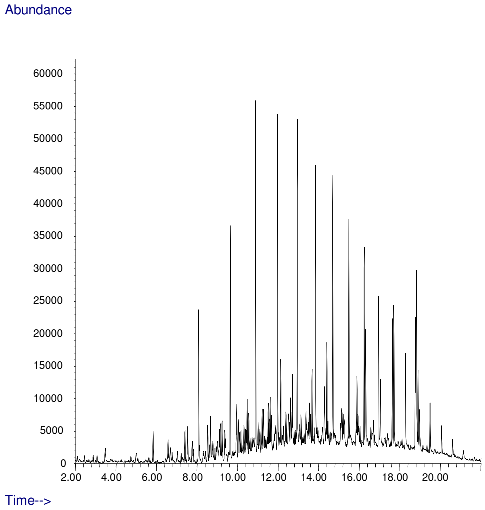
Alkanes (m/z 43,57,71,85,99)



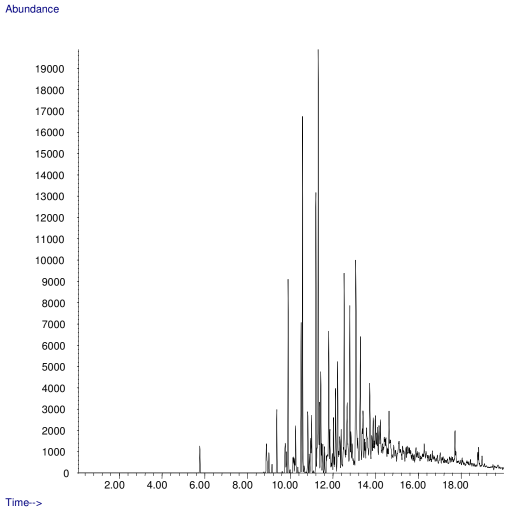
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

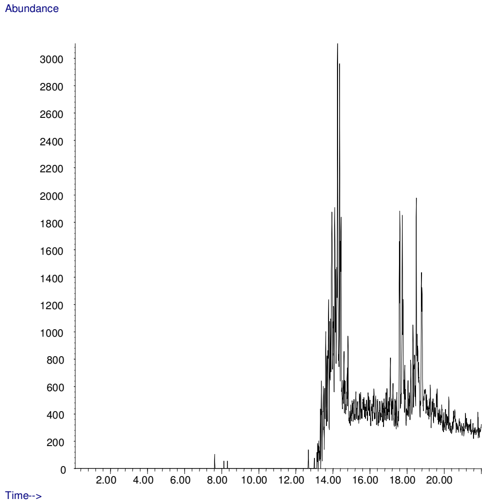
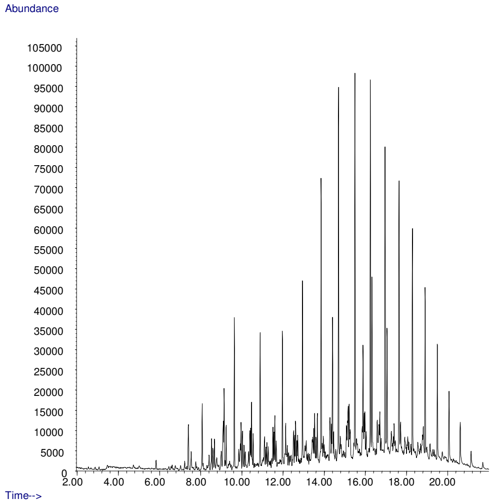
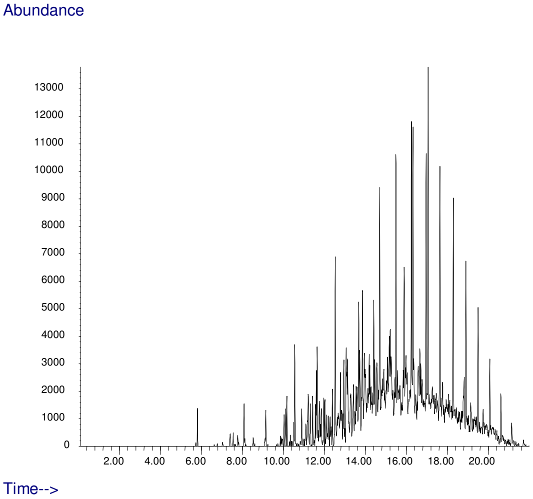


**Figure G.15 EIPs of heavy petroleum distillate product (Asda diesel).**

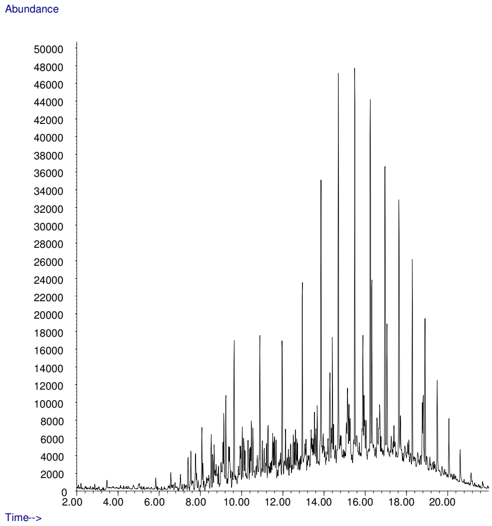
Alkanes (m/z 43,57,71,85,99)



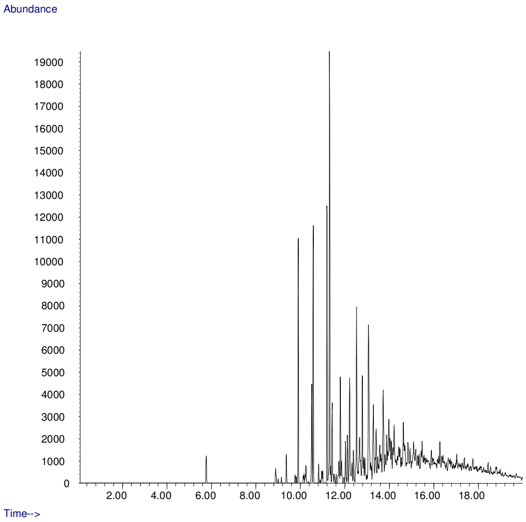
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

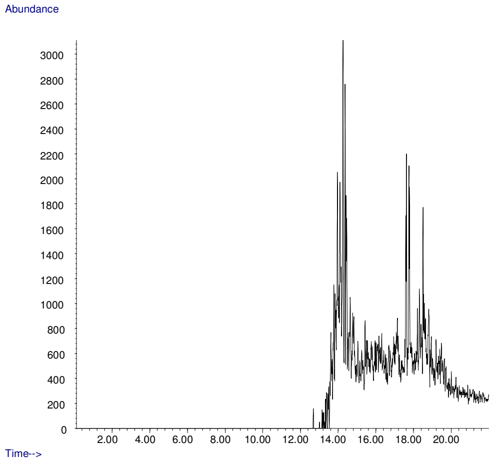
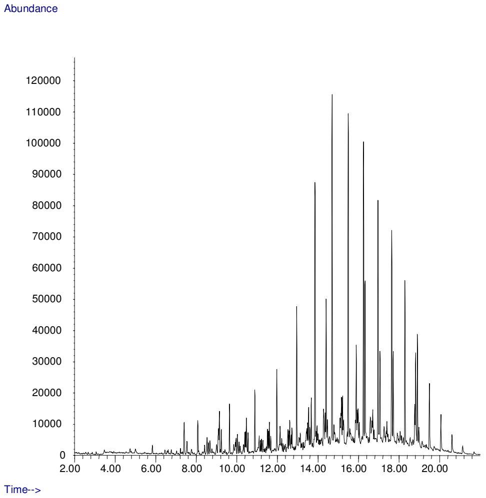
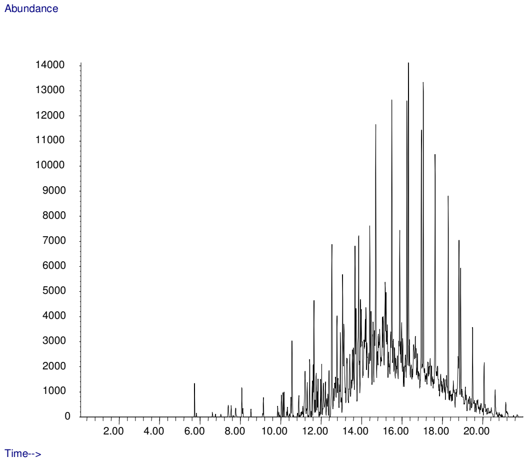


**Figure G.16 EIPs of heavy petroleum distillate product (BP diesel).**

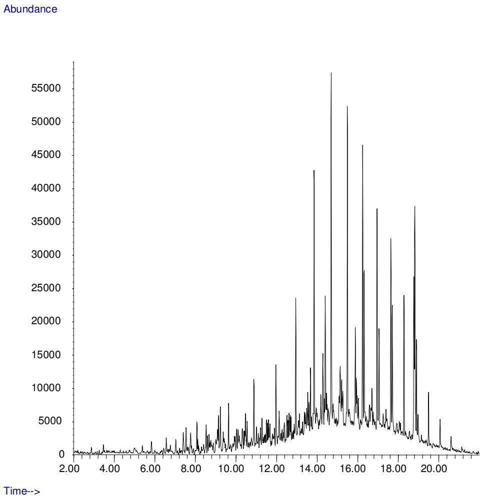
Alkanes (m/z 43,57,71,85,99)



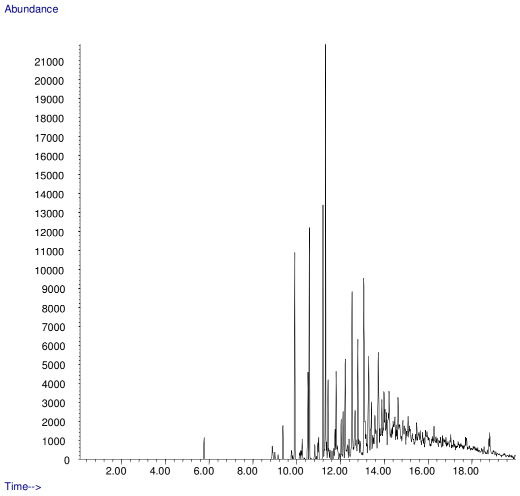
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

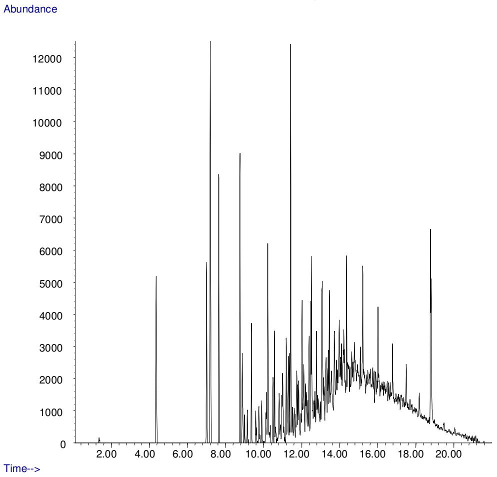
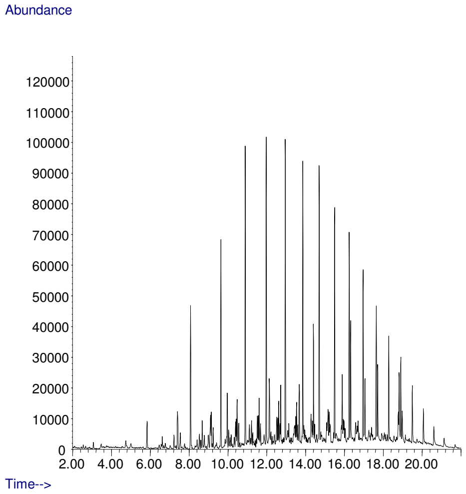
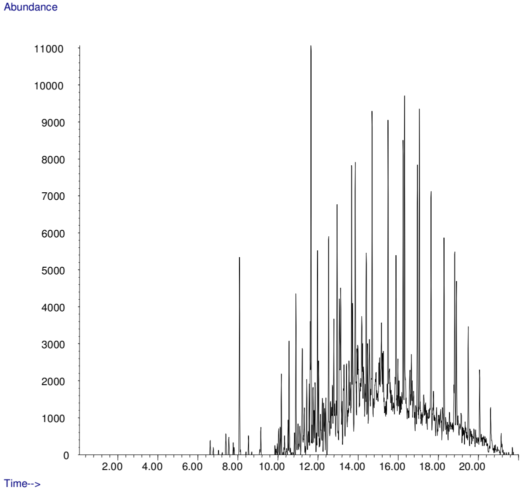


**Figure G.17 EIPs of heavy petroleum distillate product (Jet diesel).**

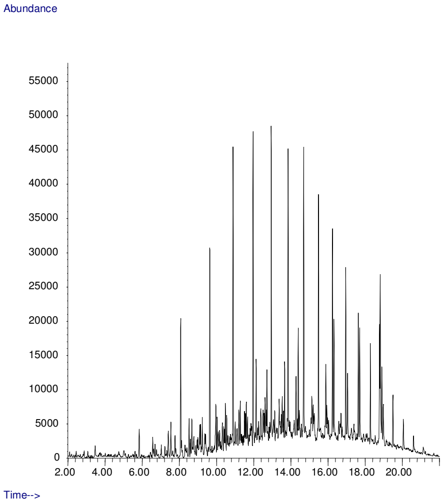
Alkanes (m/z 43,57,71,85,99)



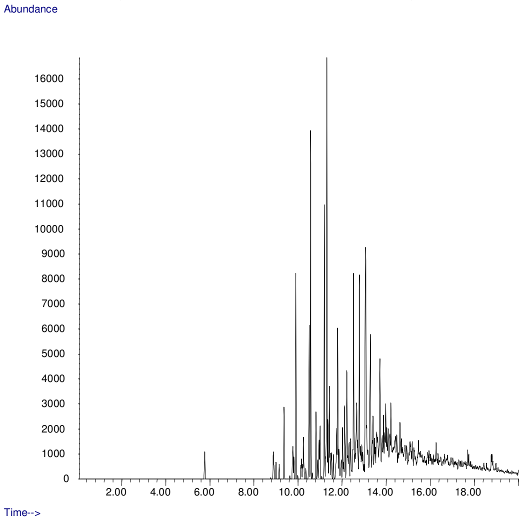
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

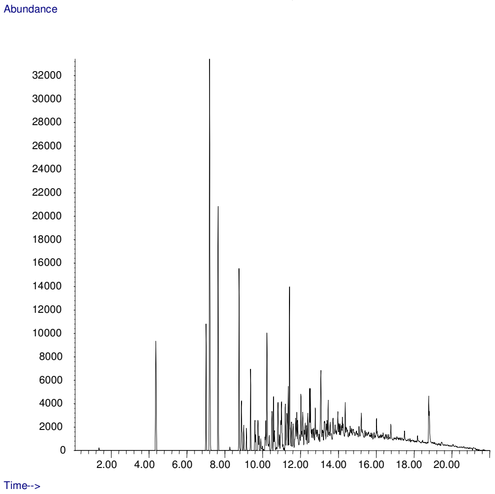
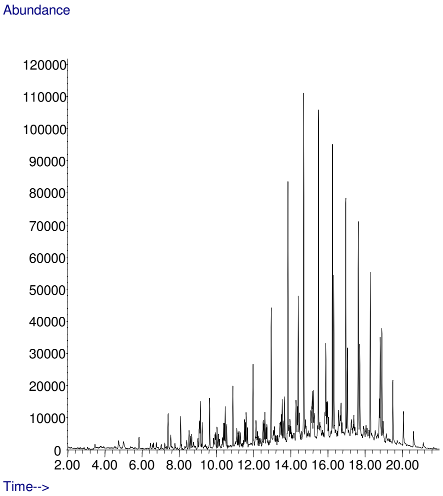
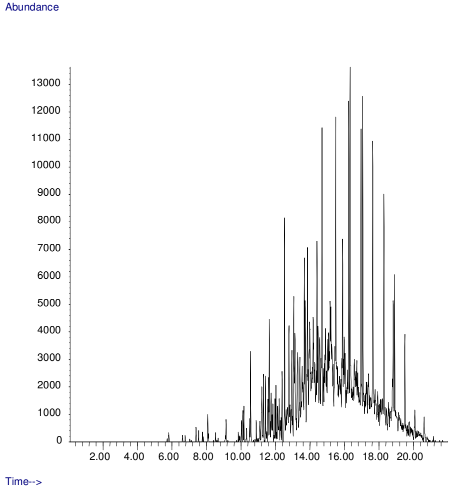


**Figure G.18 EIPs of heavy petroleum distillate product (Morrison diesel).**

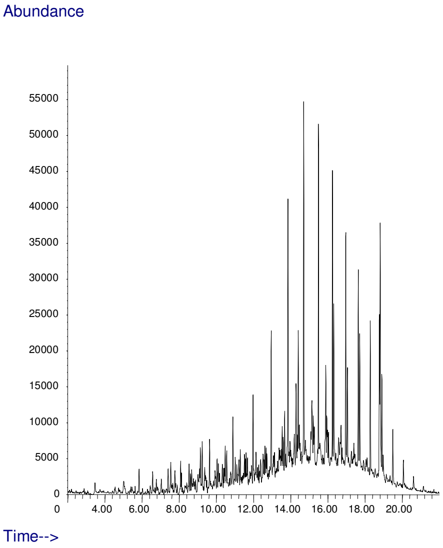
Alkanes (m/z 43,57,71,85,99)



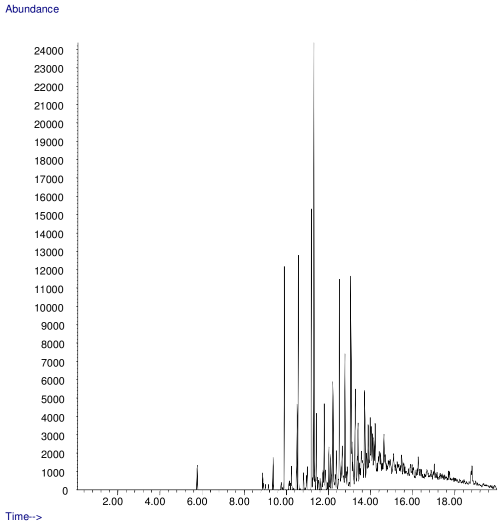
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

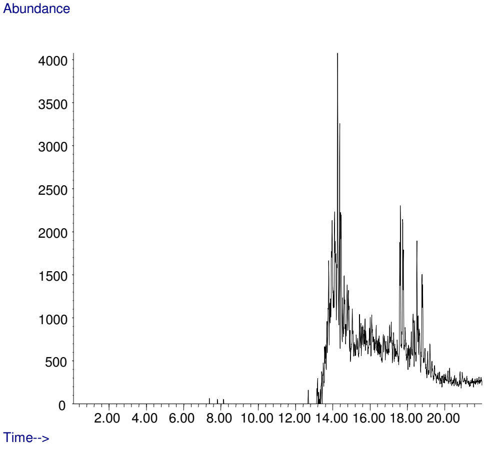
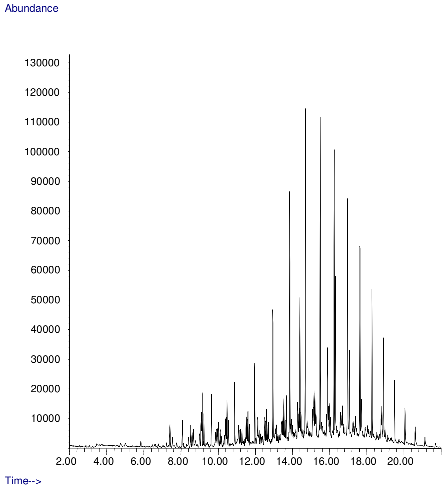
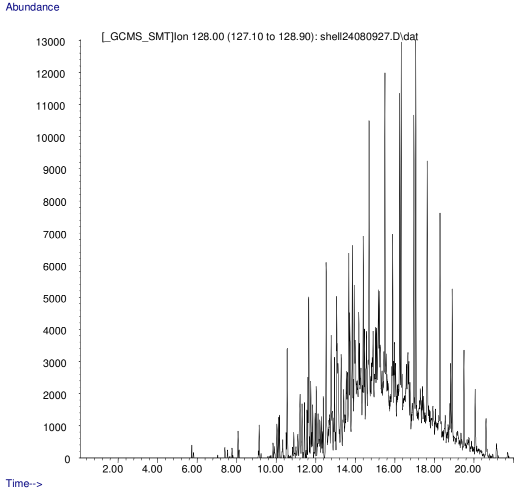


**Figure G.19 EIPs of heavy petroleum distillate product (Sainsbury diesel).**

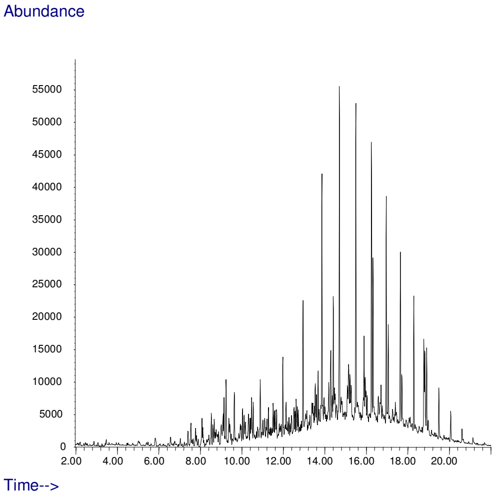
Alkanes (m/z 43,57,71,85,99)



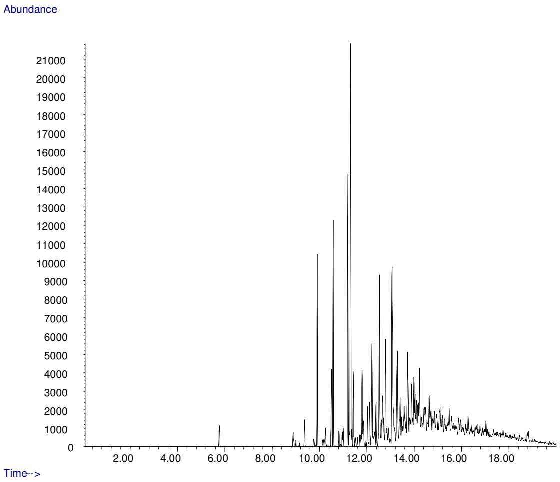
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

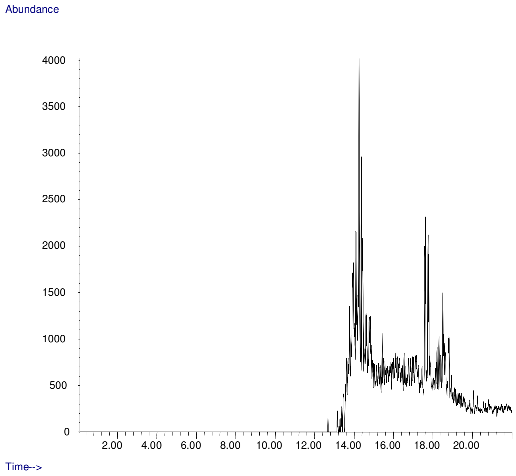
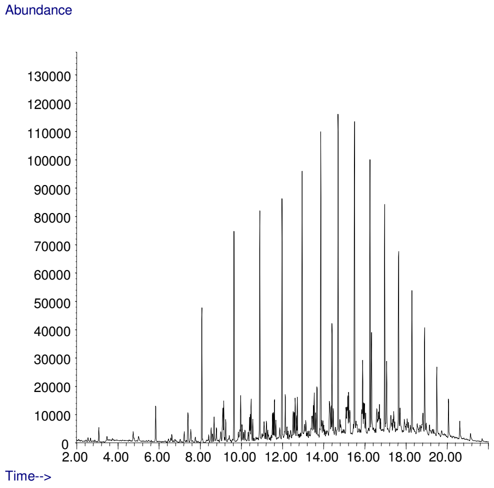
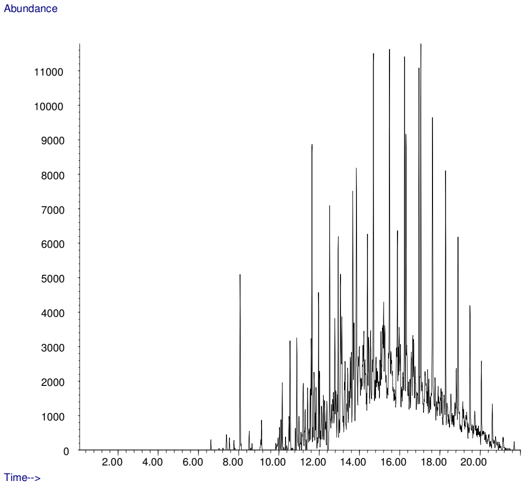


**Figure G.20 EIPs of heavy petroleum distillate product (Shell diesel).**

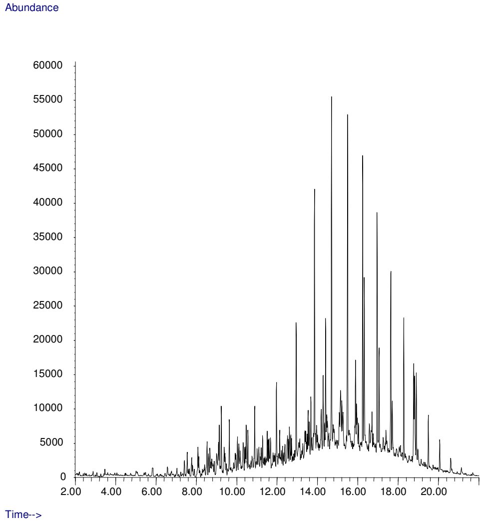
Alkanes (m/z 43,57,71,85,99)



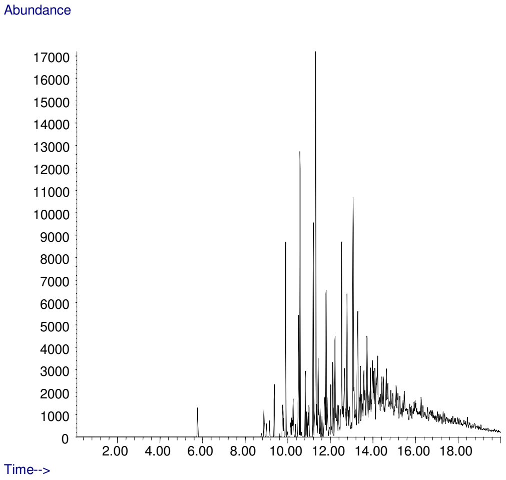
Naphthalenes
(m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

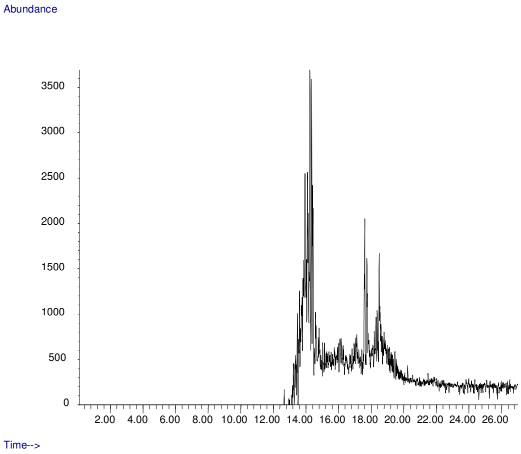
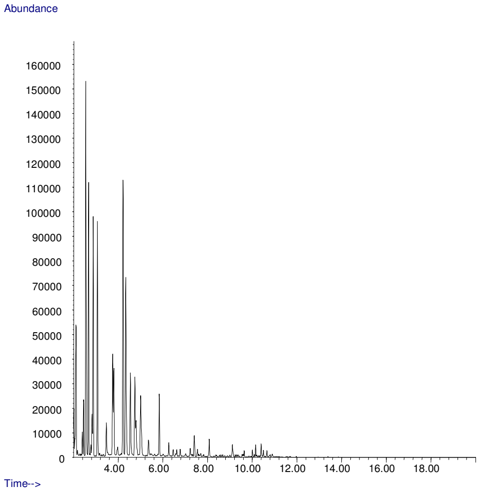
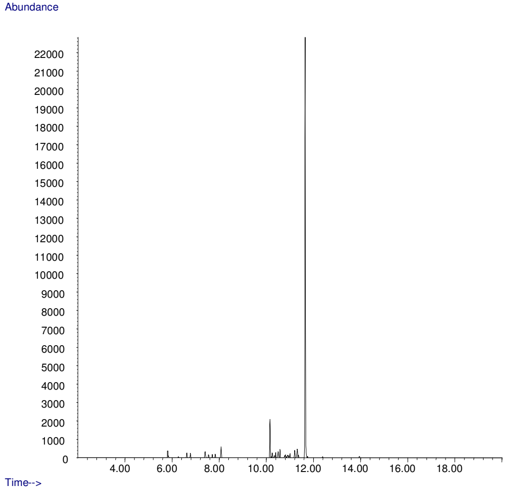


**Figure G.21 EIPs of heavy petroleum distillate product (Tesco diesel).**

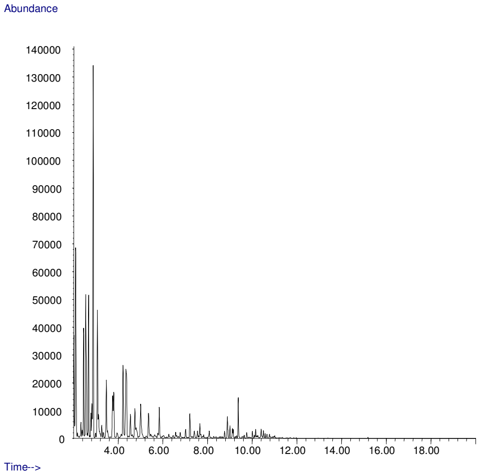
Alkanes (m/z 43,57,71,85,99)



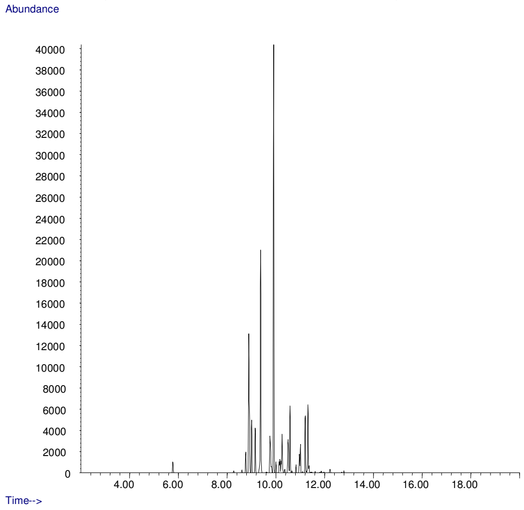
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

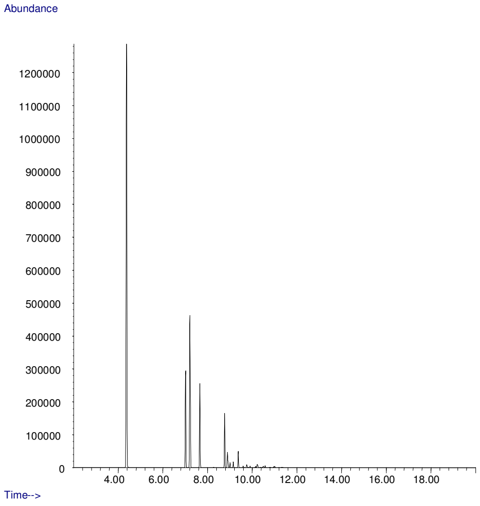
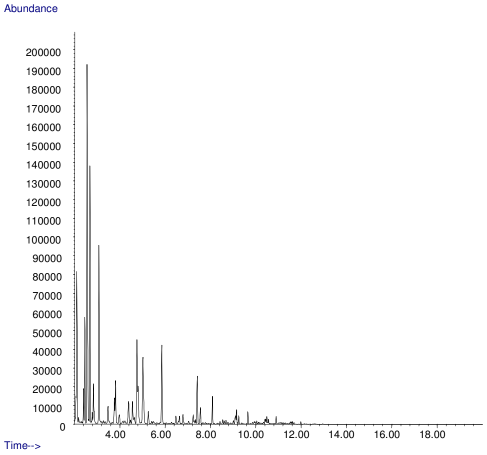
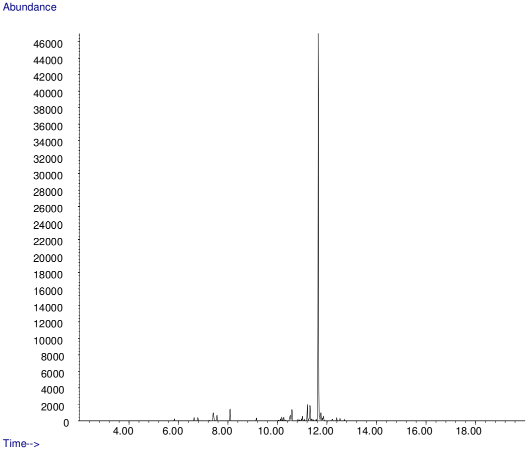


**Figure G.22 EIPs of regular leaded petrol (Four Star).**

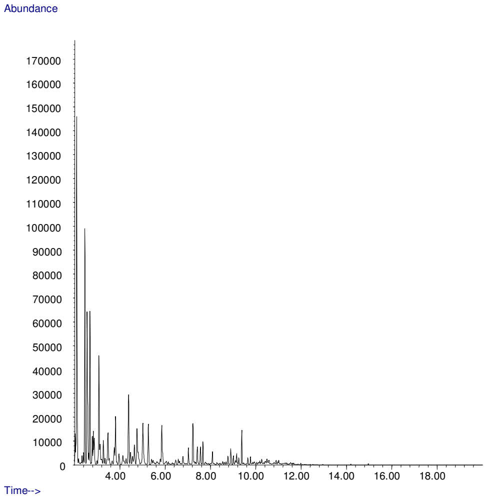
Alkanes (m/z 43,57,71,85,99)



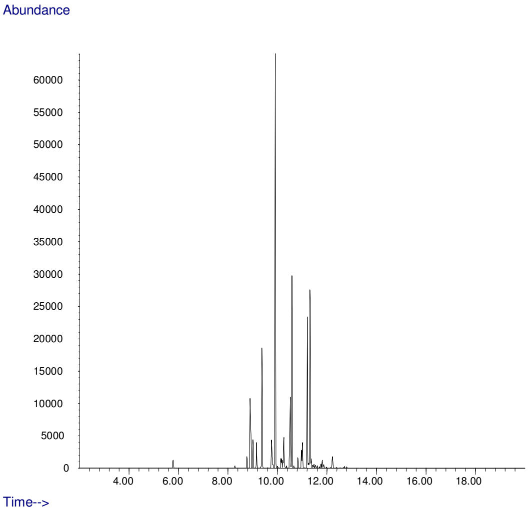
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

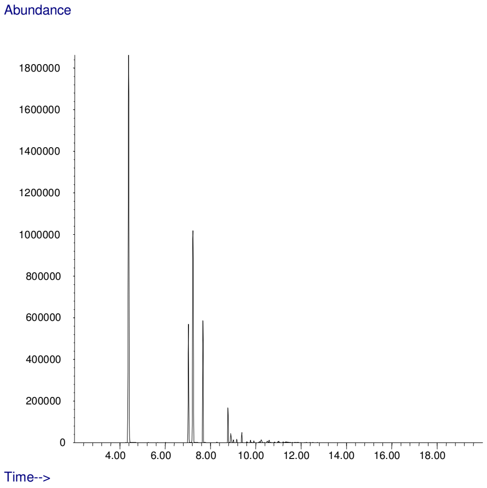
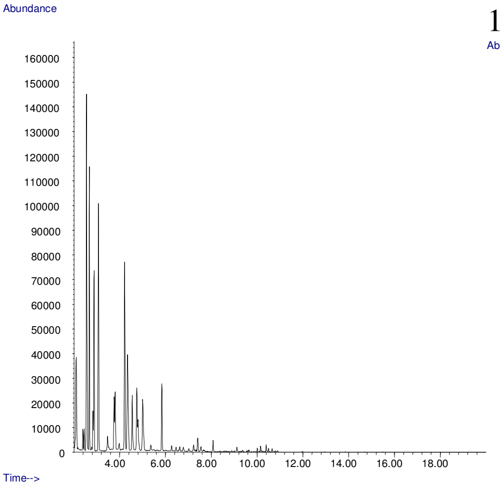
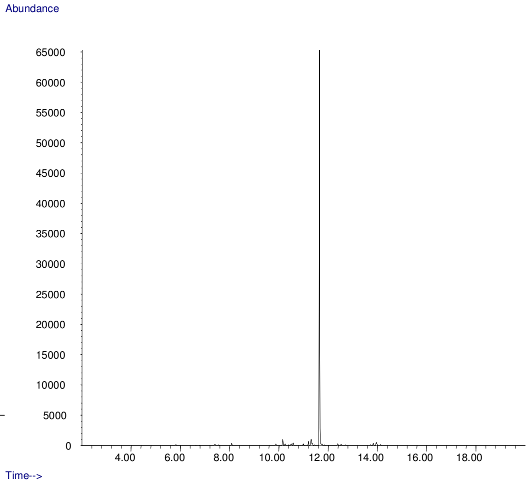


**Figure G.23 EIPs of regular leaded petrol (Asda).**

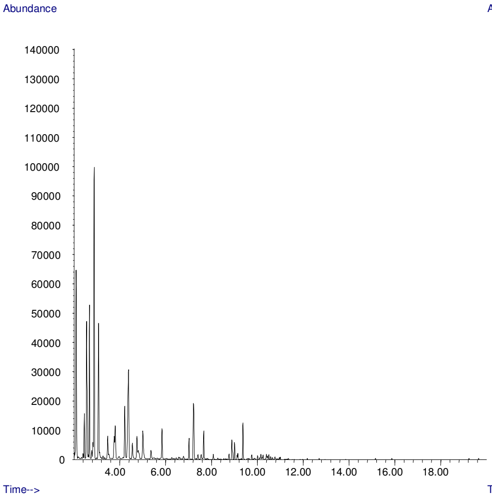
Alkanes (m/z 43,57,71,85,99)



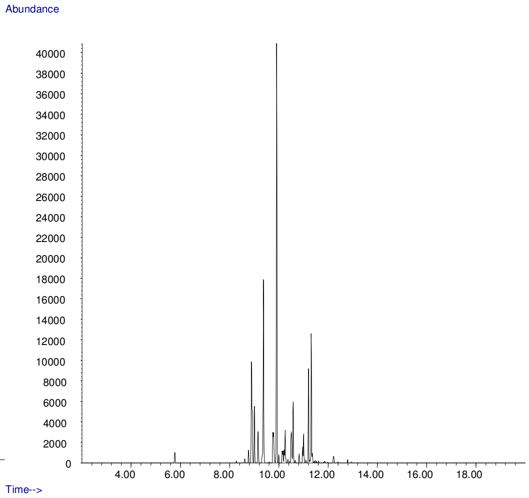
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

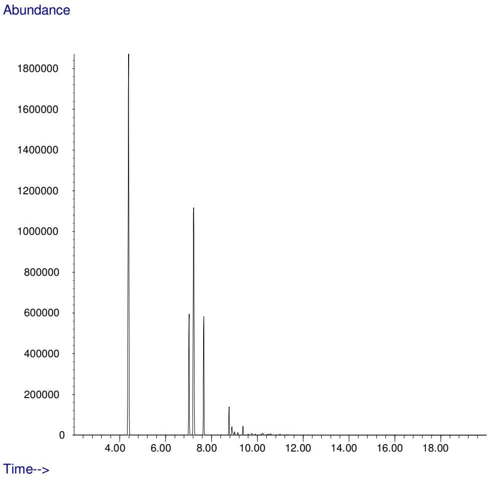


**Figure G.24 EIPs of regular leaded petrol (BP).**

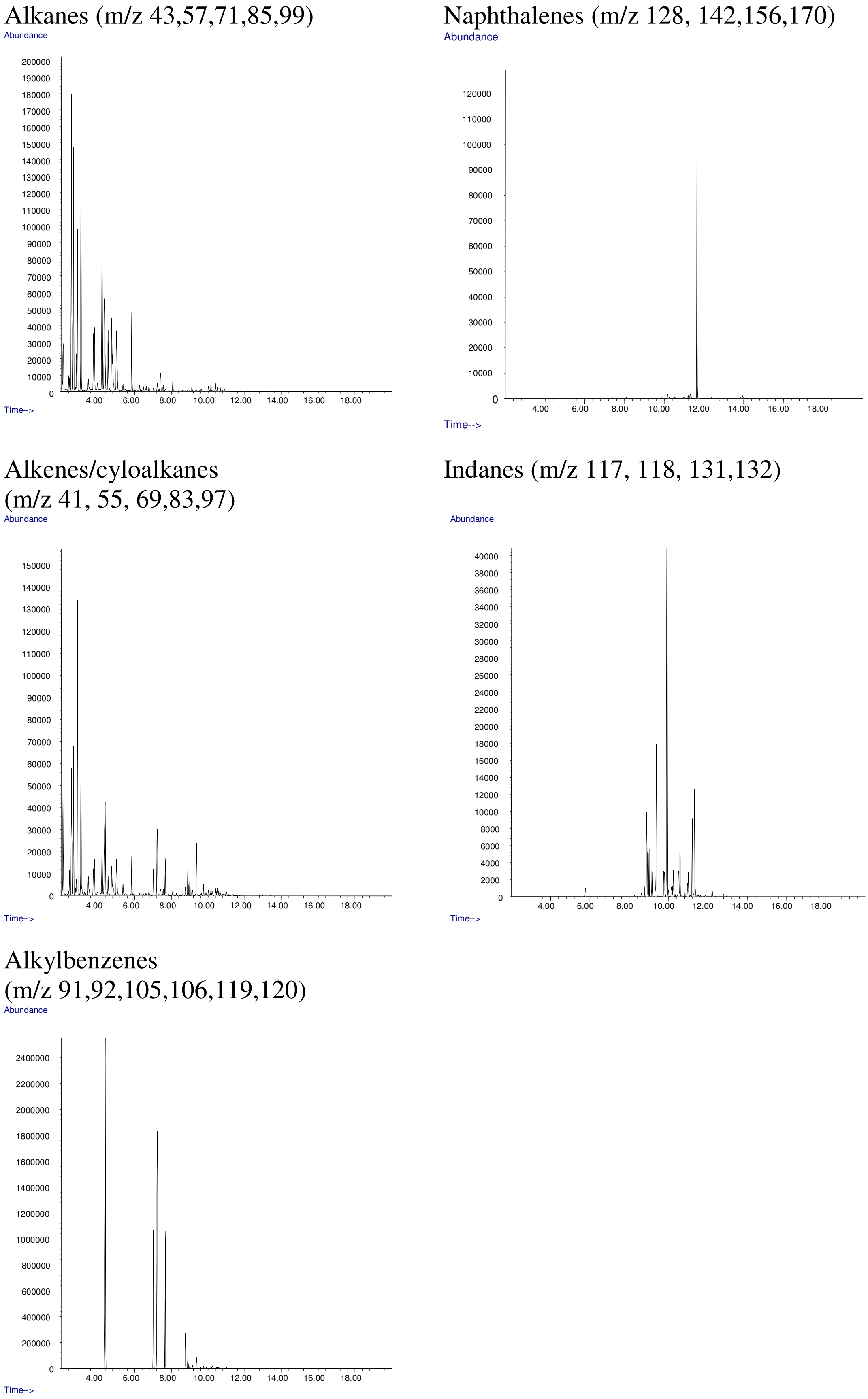
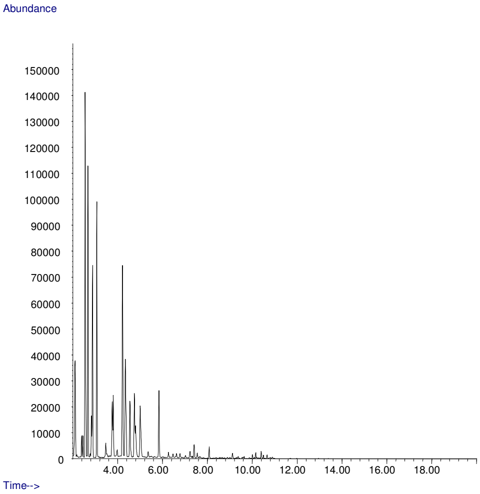
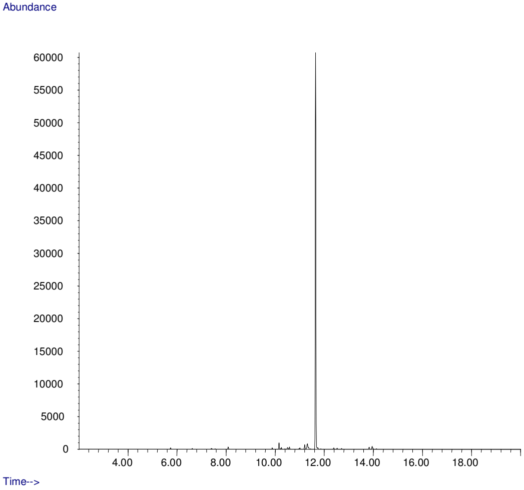


**Figure G.25 EIPs of regular leaded petrol (Esso).**

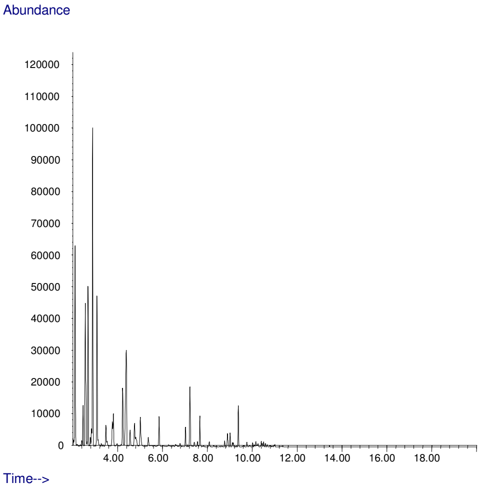
Alkanes (m/z 43,57,71,85,99)



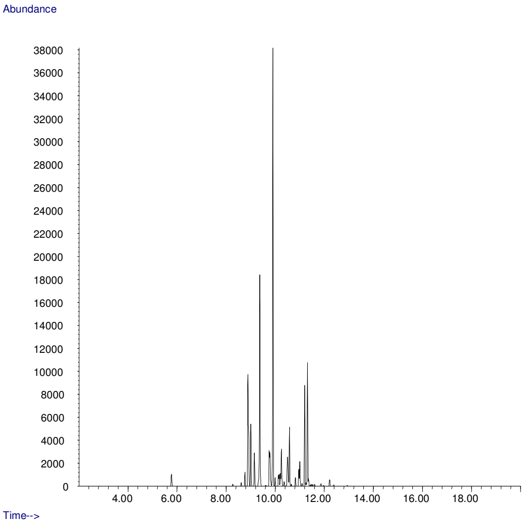
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

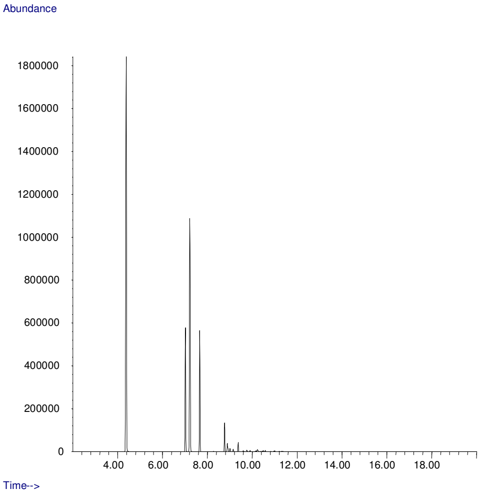
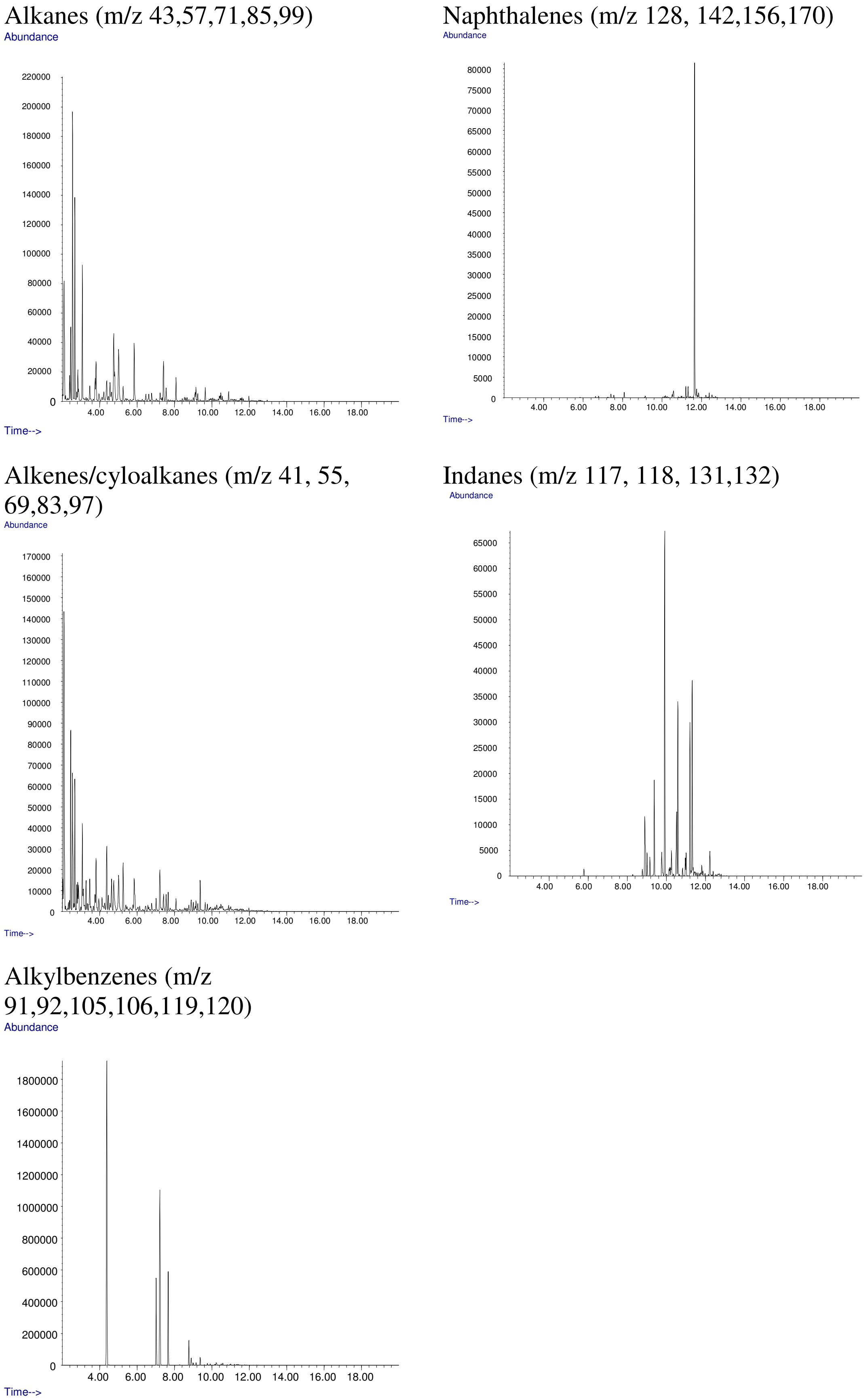


**Figure G.26 EIPs of regular leaded petrol (Jet).**


Alkanes (m/z 43,57,71,85,99)

Naphthalenes (m/z 128, 142,156,170)

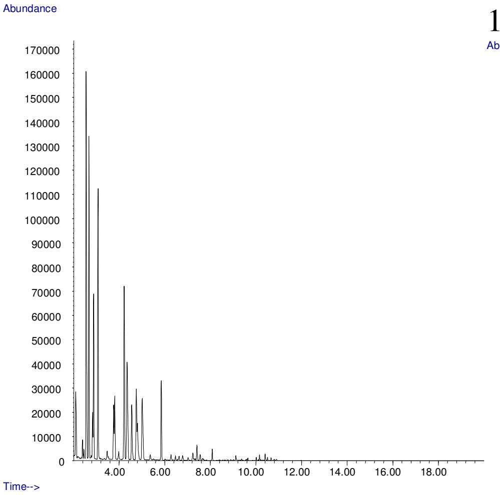
Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)

Indanes (m/z 117, 118, 131,132)

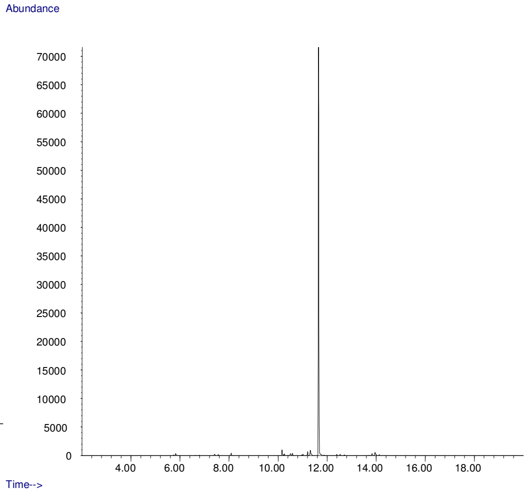
Alkylbenzenes (m/z 91,92,105,106,119,120)

**Figure G.27 EIPs of regular leaded petrol (Morrison).**

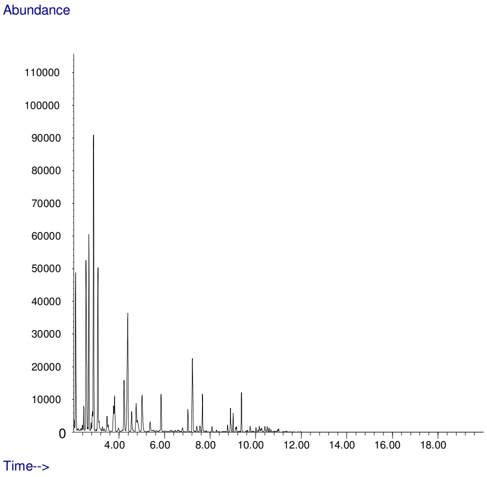
Alkanes (m/z 43,57,71,85,99)



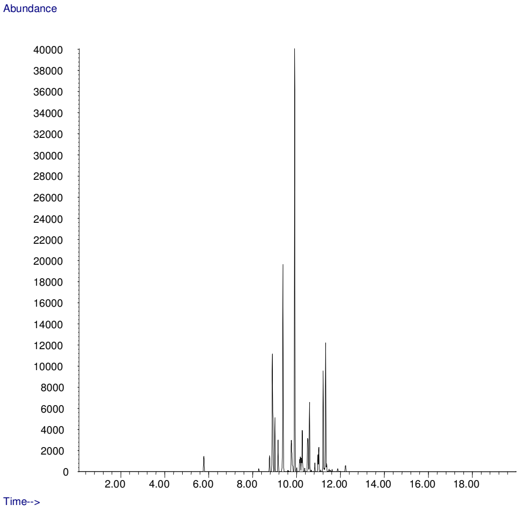
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

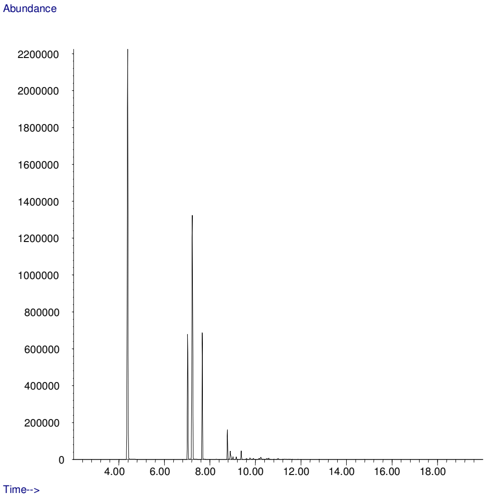
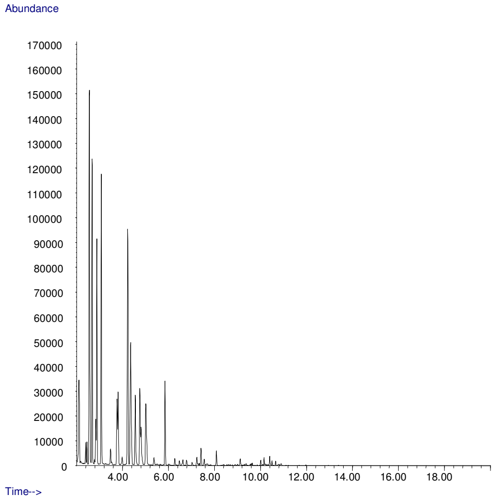
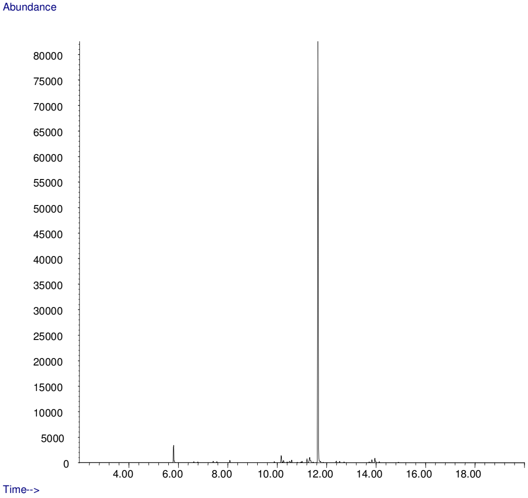


**Figure G.28 EIPs of regular leaded petrol (Sainsbury).**

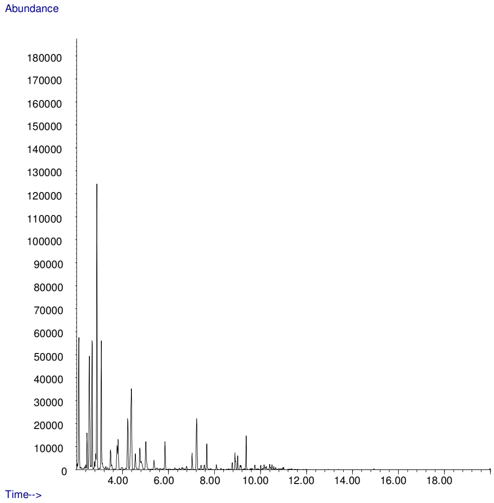
Alkanes (m/z 43,57,71,85,99)



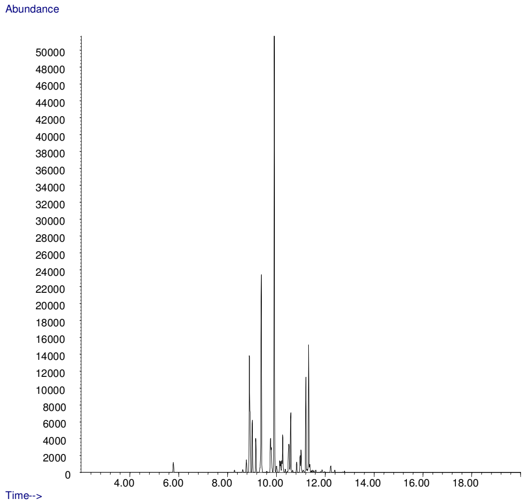
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

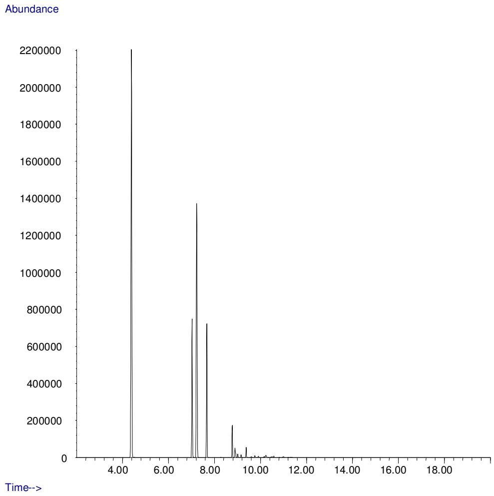
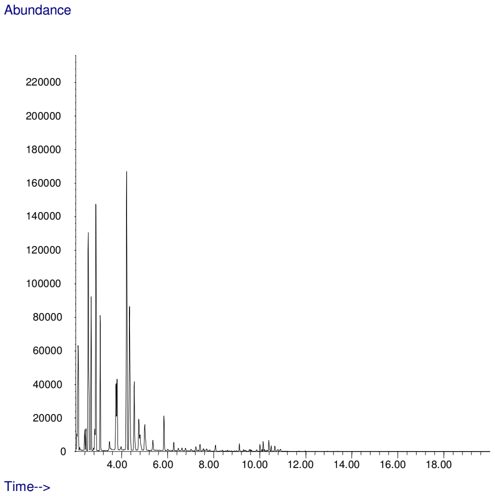
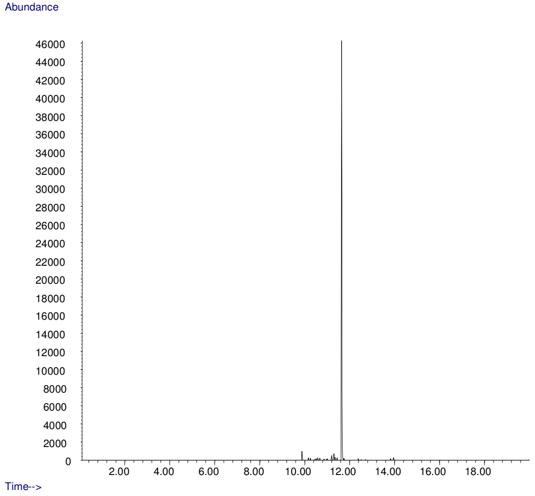


**Figure G.29 EIPs of regular leaded petrol (Shell).**

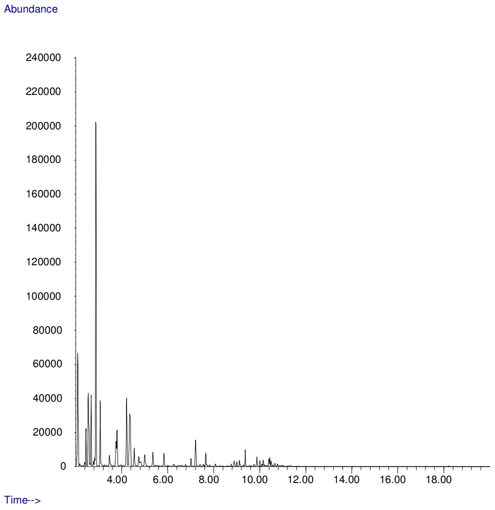
Alkanes (m/z 43,57,71,85,99)



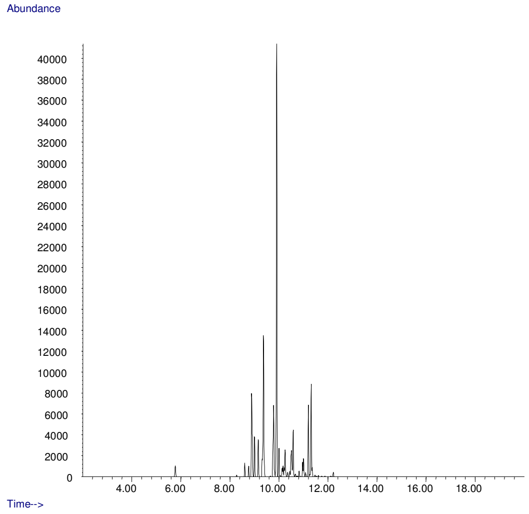
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

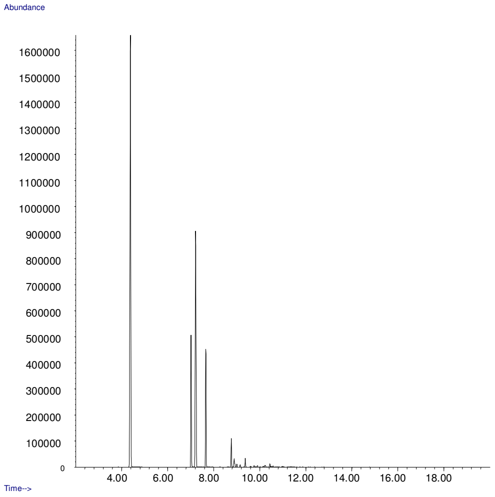
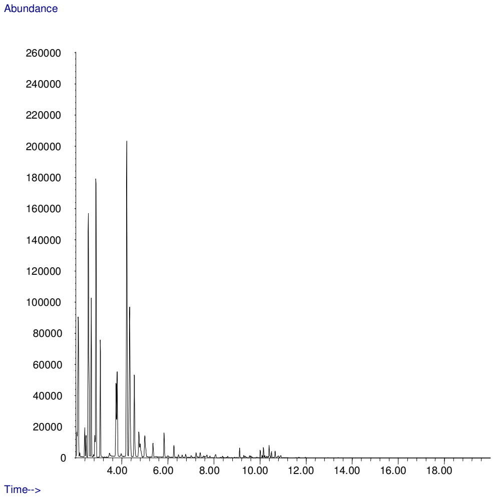
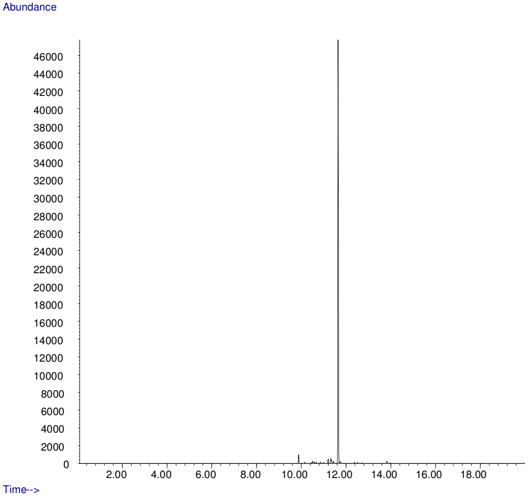


**Figure G.30 EIPs of premium leaded petrol (BP).**

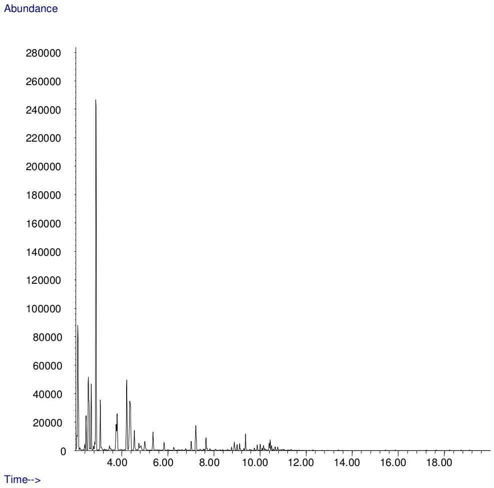
Alkanes (m/z 43,57,71,85,99)



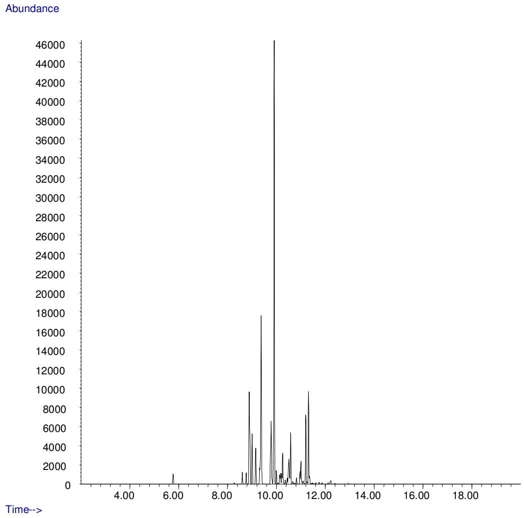
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

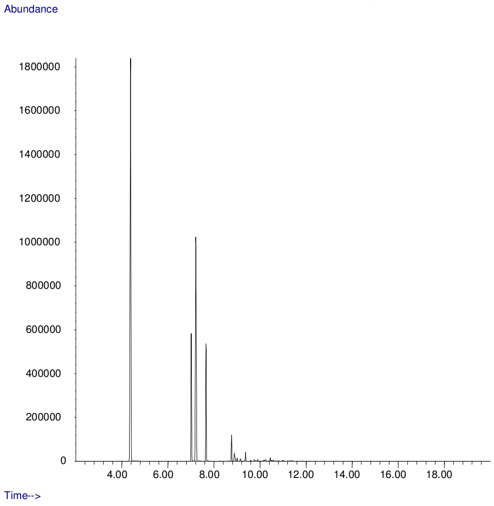
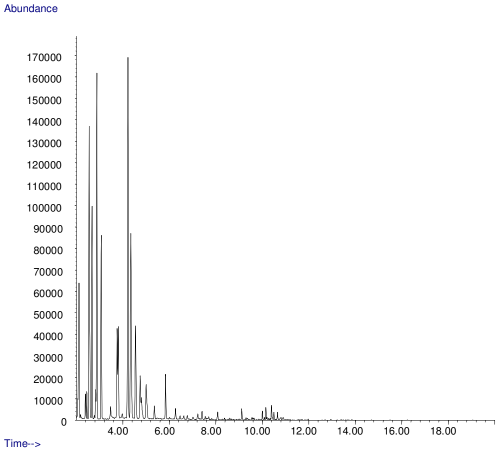
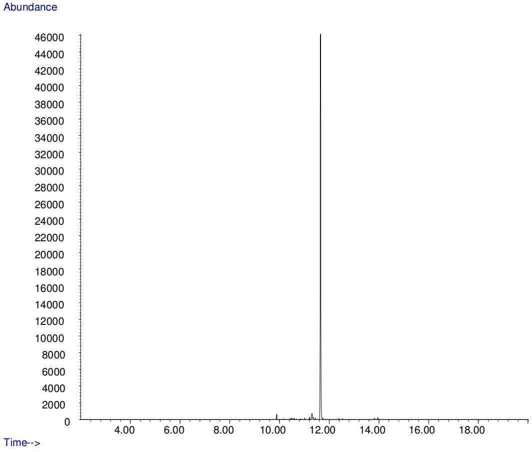


**Figure G.31 EIPs of premium leaded petrol (Esso).**

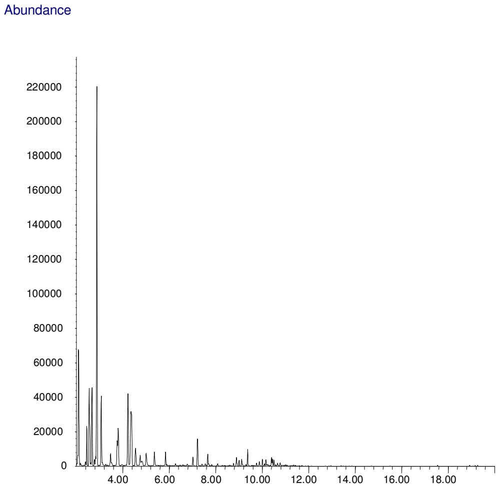
Alkanes (m/z 43,57,71,85,99)



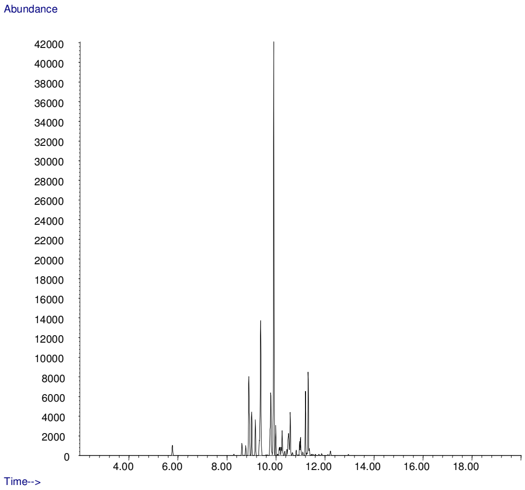
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

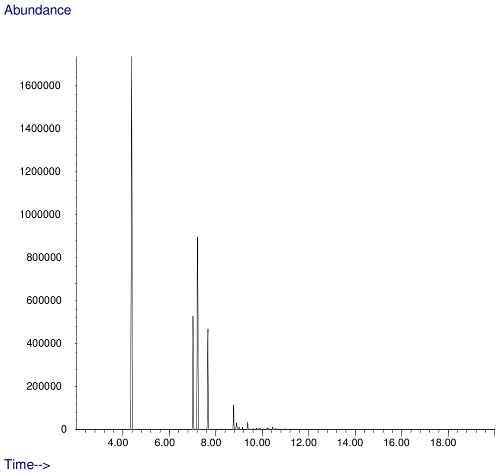
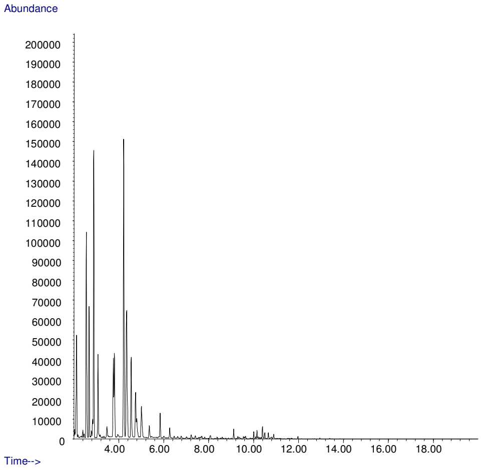
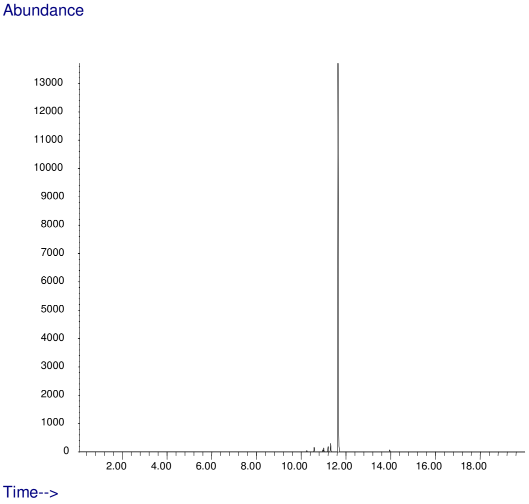


**Figure G.32 EIPs of premium leaded petrol (Sainsbury).**

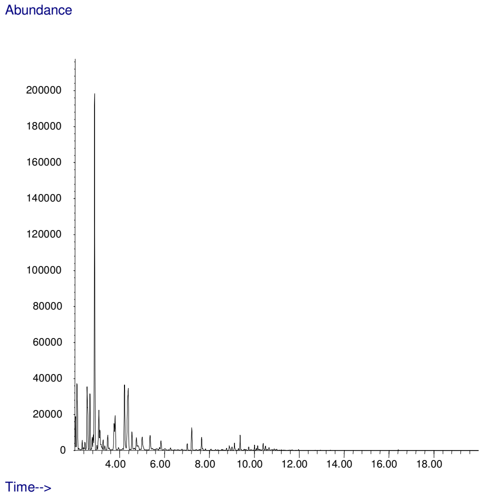
Alkanes (m/z 43,57,71,85,99)



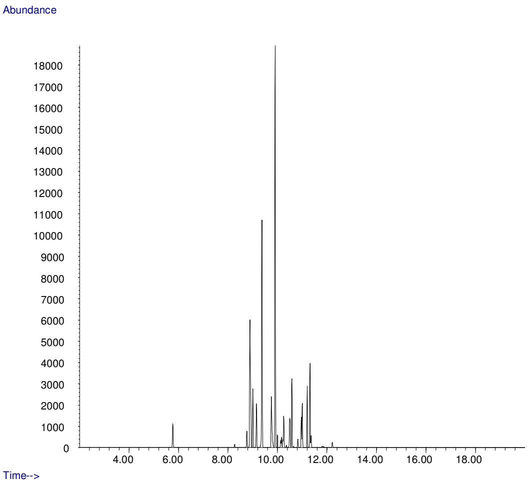
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes(m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

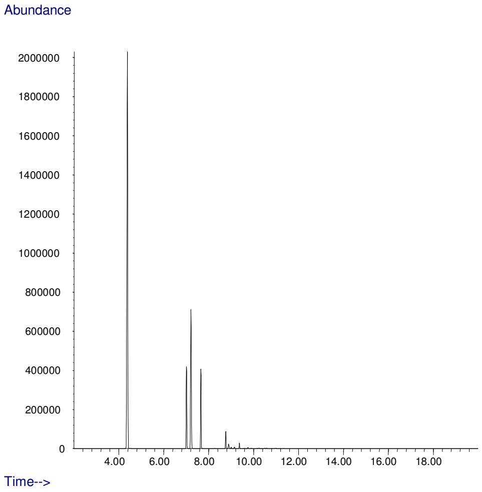
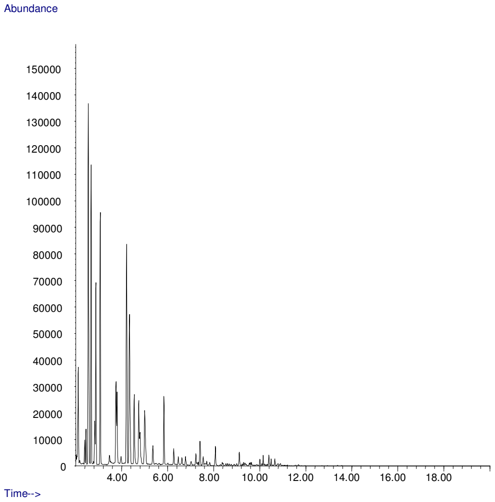
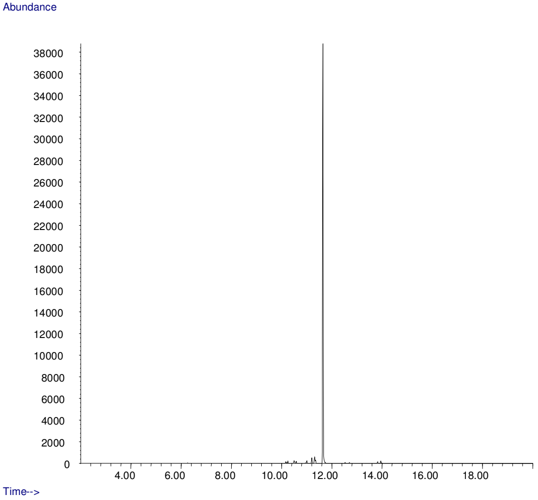


**Figure G.33 EIPs of premium leaded petrol (Shell).**

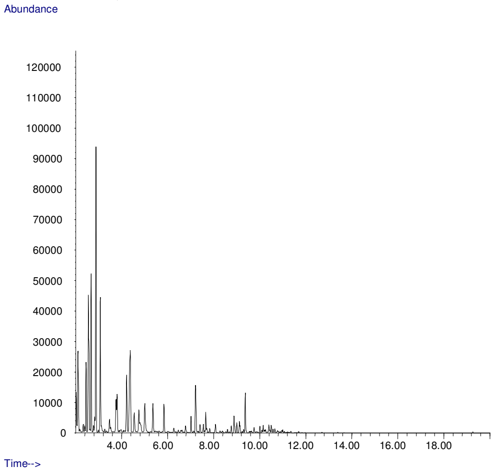
Alkanes (m/z 43,57,71,85,99)



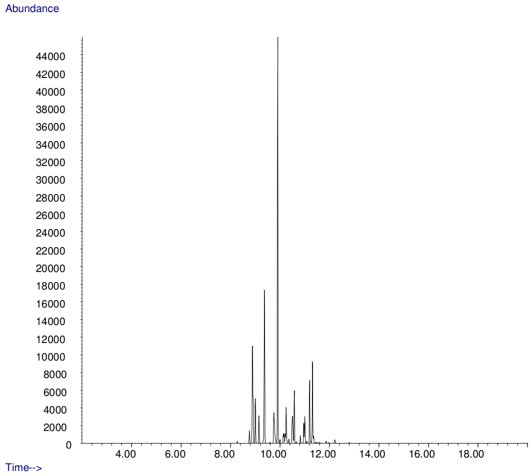
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes(m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

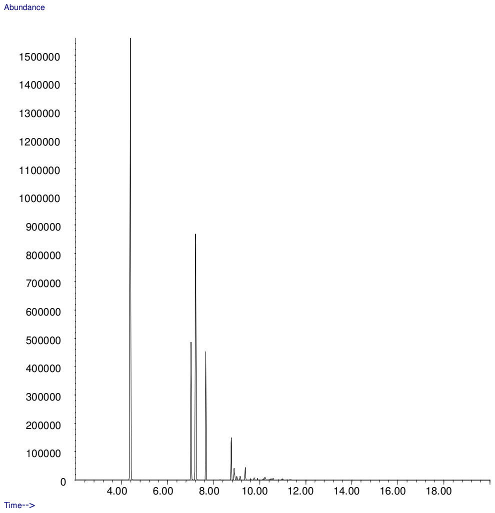
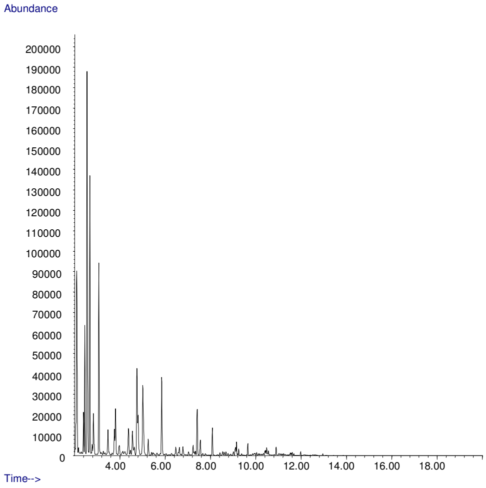
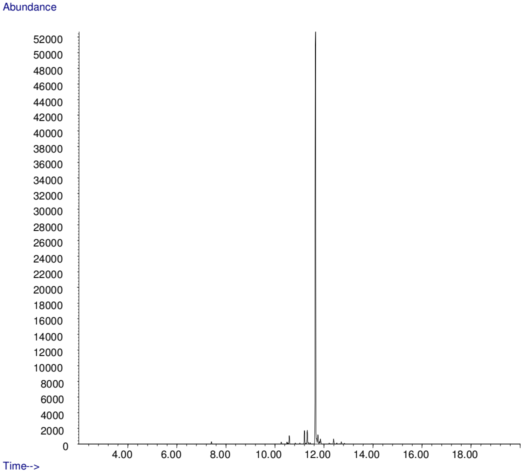


**Figure G.34 EIPs of premium leaded petrol (Tesco).**

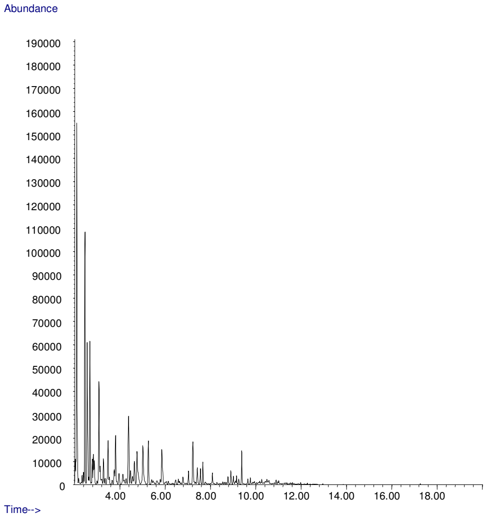
Alkanes (m/z 43,57,71,85,99)



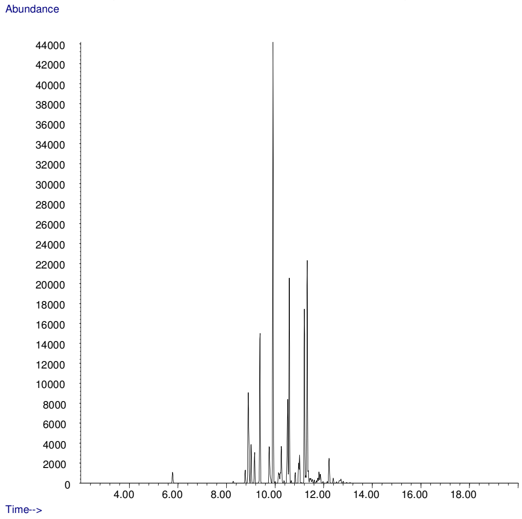
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

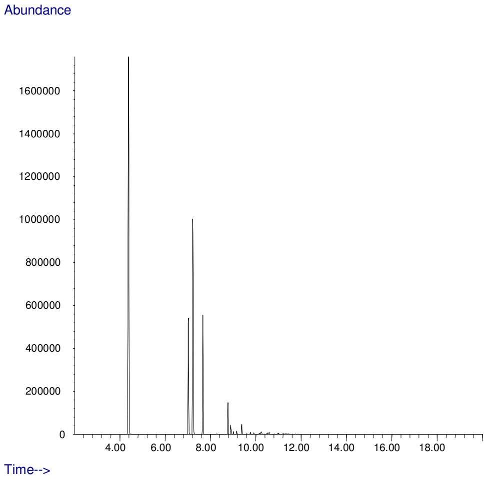
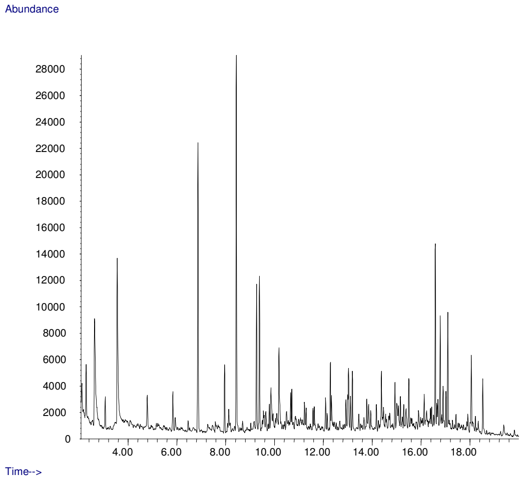


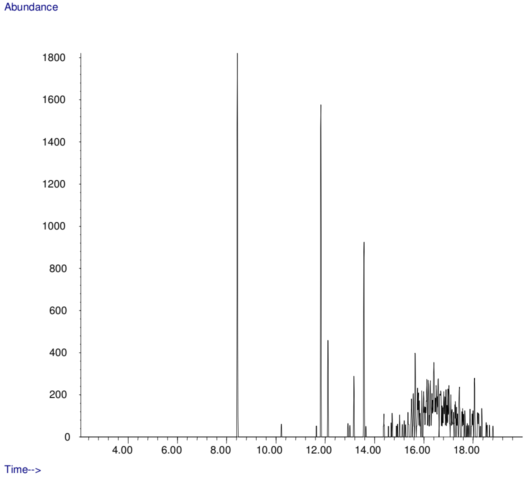
**Figure G.35 EIPs of super leaded petrol (Tesco).**

# Appendix H: Extracted Ion Profile of Burnt Substrates

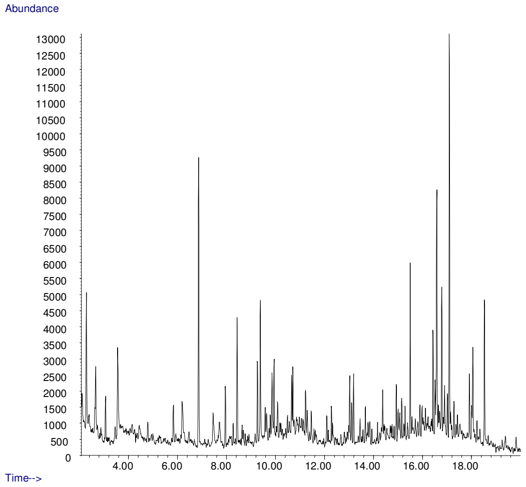
Alkanes(m/z 43,57,71,85,99)



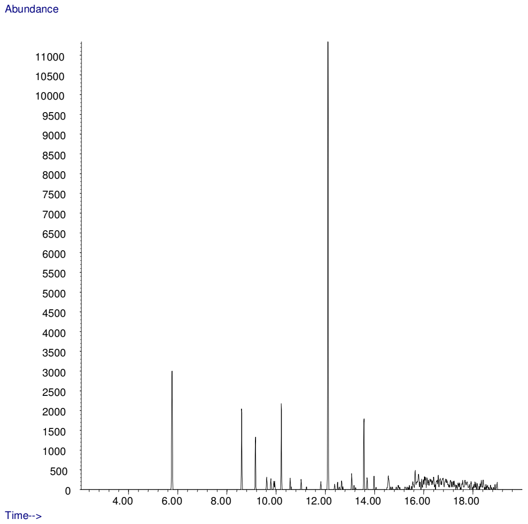
Naphthalenes(m/z 128, 142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

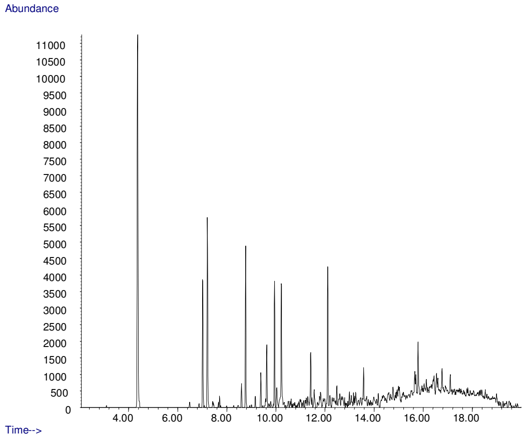
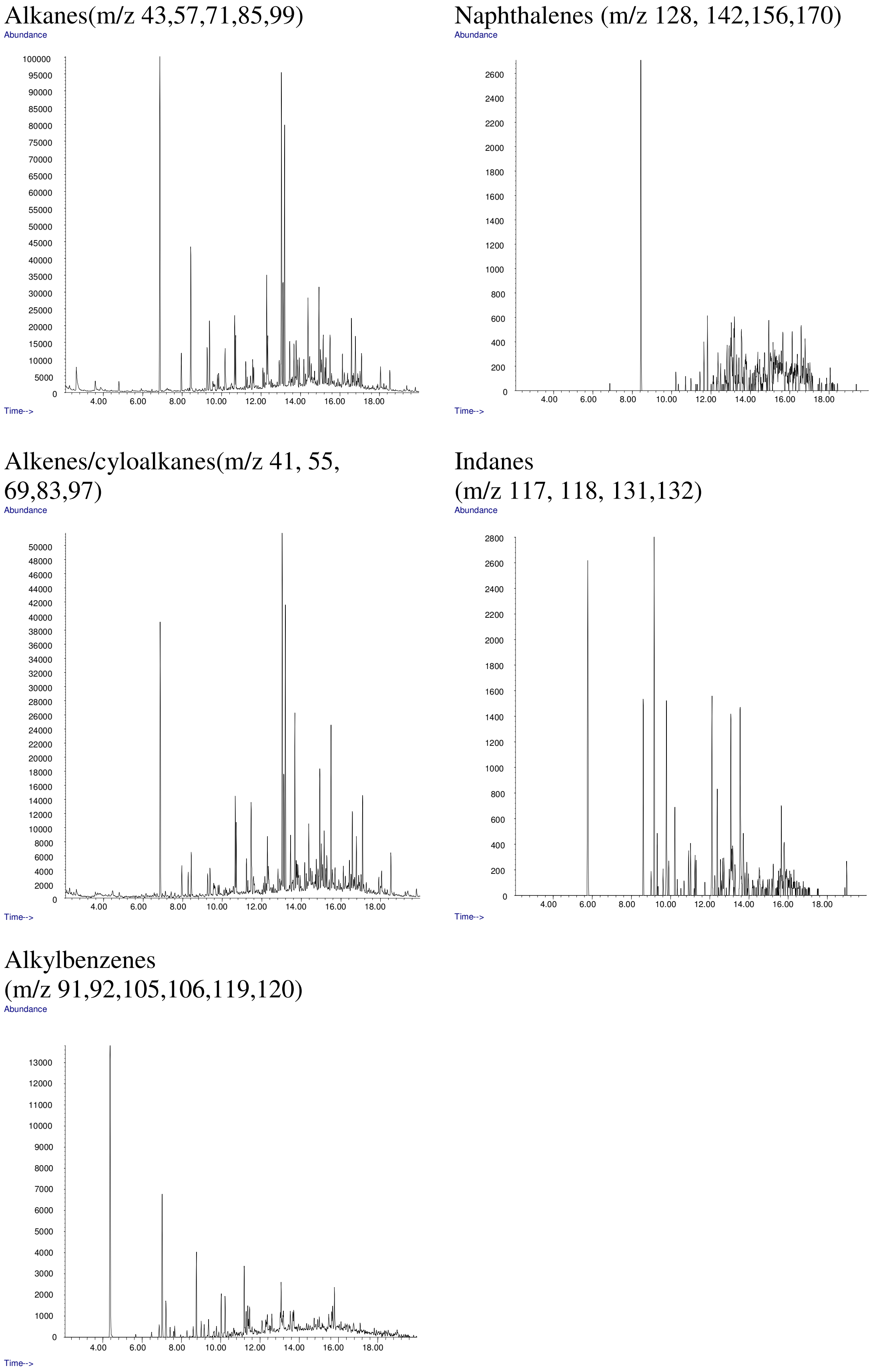


**Figure H.1 EIPS of 100% Polypropylene carpet (S1).**


Alkanes(m/z 43,57,71,85,99)

Naphthalenes (m/z 128, 142,156,170)

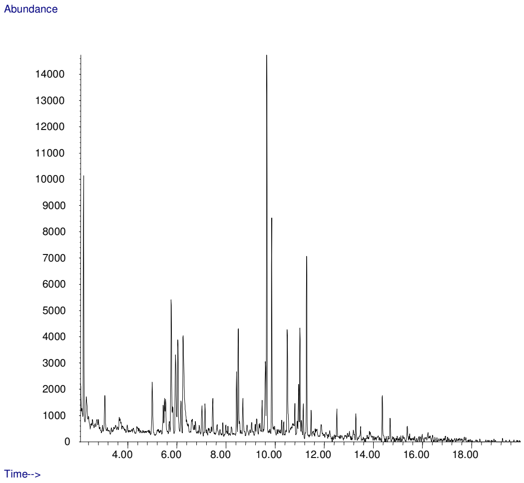
Alkenes/cyloalkanes(m/z 41, 55, 69,83,97)

Indanes (m/z 117, 118, 131,132)

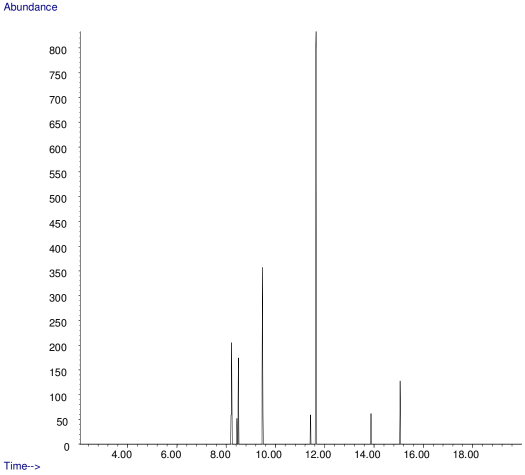
Alkylbenzenes (m/z 91,92,105,106,119,120)

**Figure H.2 EIPS of 100% Polypropylene carpet-jute backing (S2).**

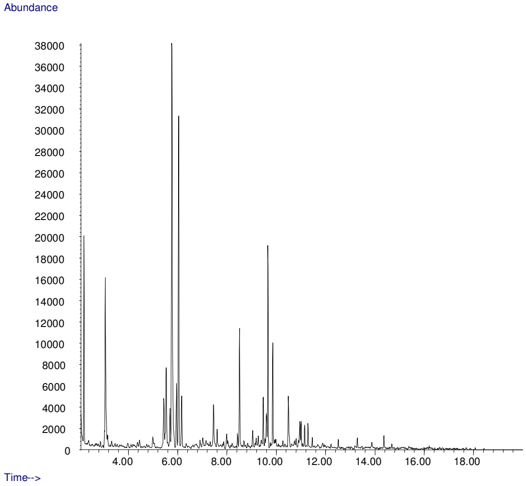
Alkanes(m/z 43,57,71,85,99)



Naphthalenes(m/z 128, 142,156,170)

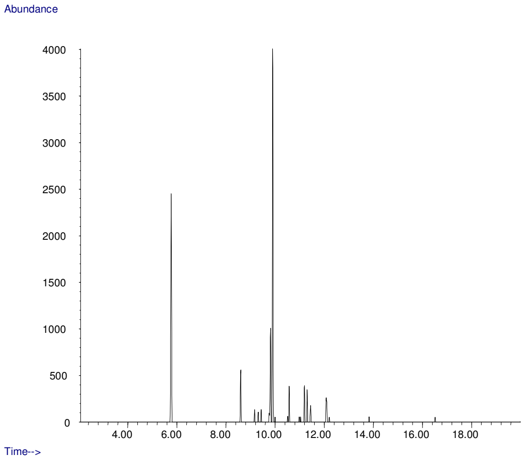


Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes

(m/z 117, 118, 131,132)



Alkylbenzenes

(m/z 91,92,105,106,119,120)

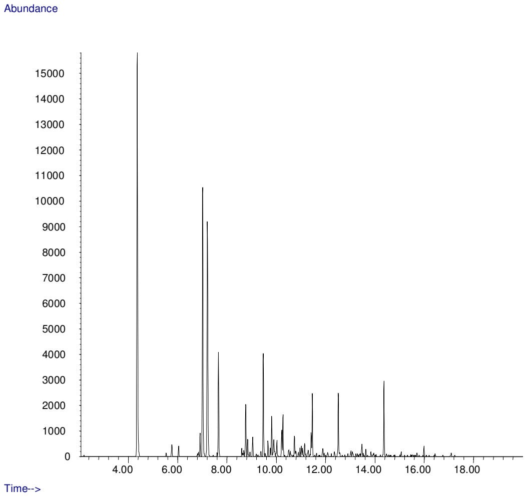
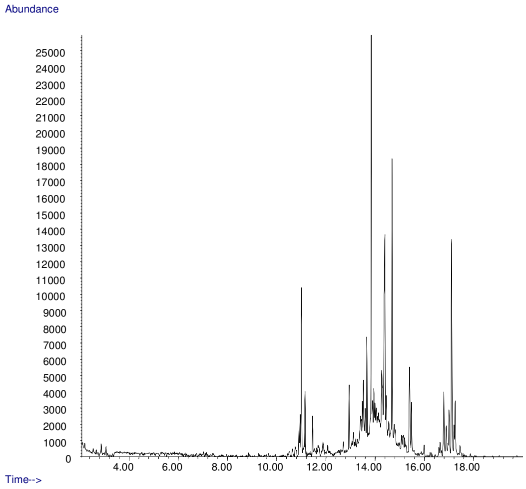
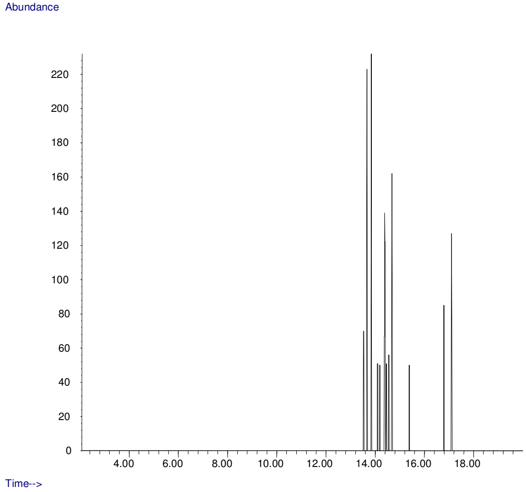


**Figure H.3 EIPS of vinyl sheet (S3).**

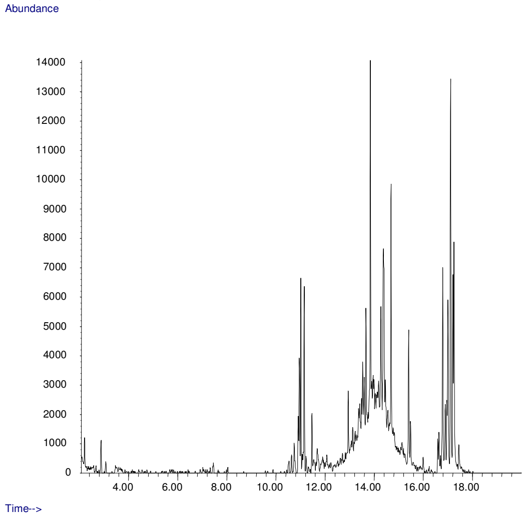
Alkanes(m/z 43,57,71,85,99)



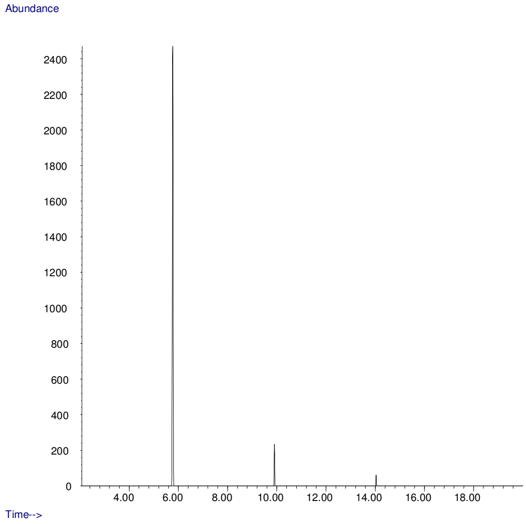
Naphthalenes(m/z 128, 142,156,170)



Alkenes/cyloalkanes(m/z 41, 55, 69,83,97)



Indanes
(m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

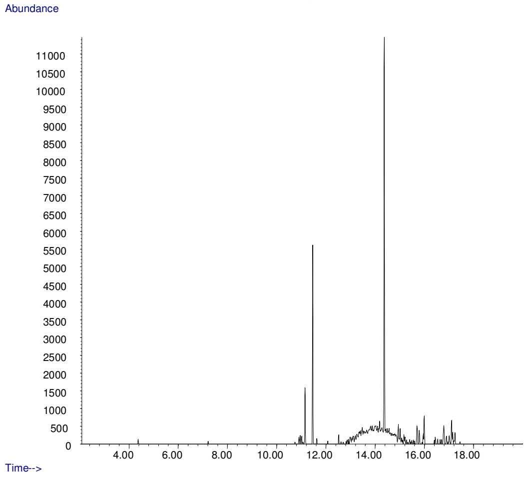
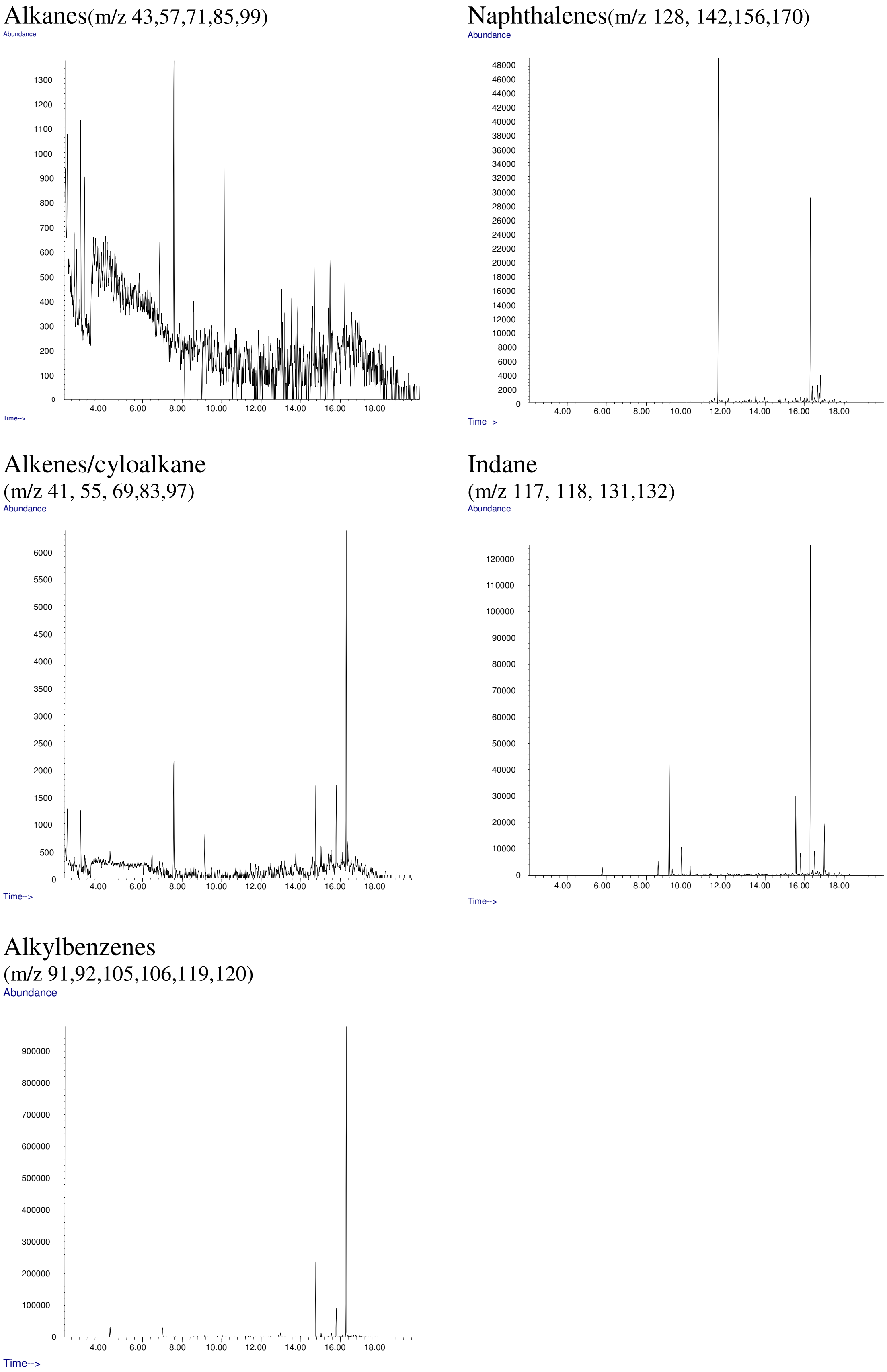


**Figure H.4 EIPS of vinyl tiles (S4).**



Alkanes(m/z 43,57,71,85,99)

Naphthalenes(m/z 128, 142,156,170)

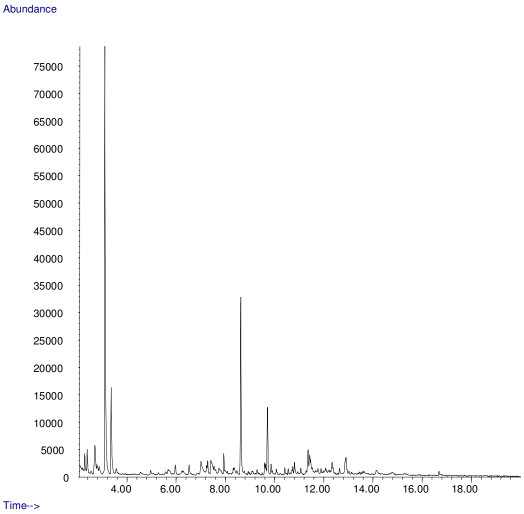
Alkenes/cyloalkane (m/z 41, 55, 69,83,97)

Indane (m/z 117, 118, 131,132)

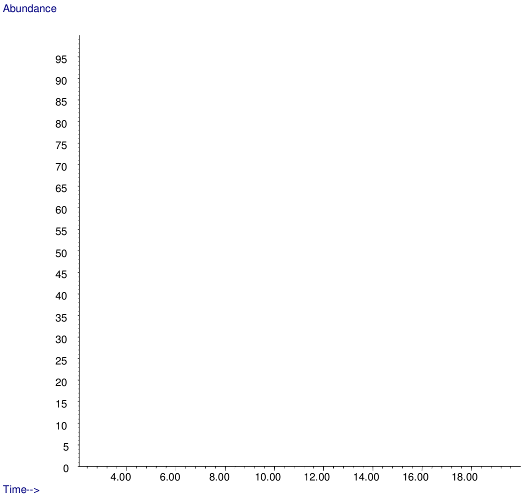
Alkylbenzenes (m/z 91,92,105,106,119,120)

**Figure H.5 EIPS of CD casing (S5).**

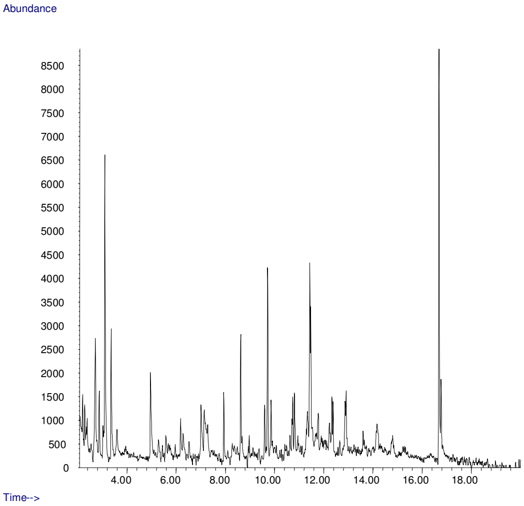
Alkanes(m/z 43,57,71,85,99)



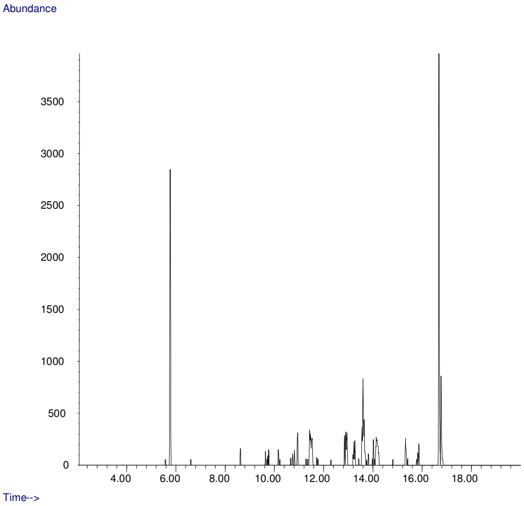
Naphthalenes
(m/z 128, 142,156,170)



Alkenes/cyloalkanes(m/z 41, 55, 69,83,97)



Indanes
(m/z 117, 118, 131,132)



Alkylbenzenes(m/z 91,92,105,106,119,120)

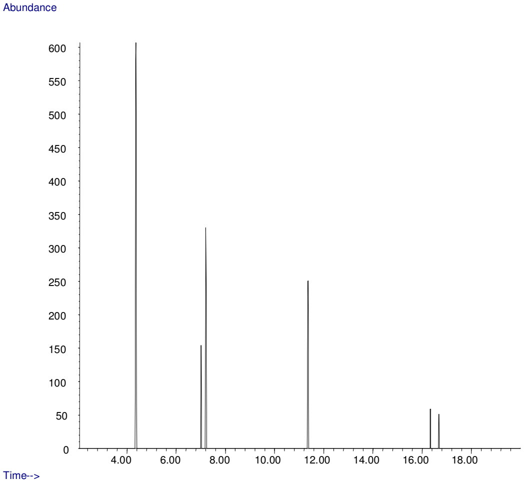
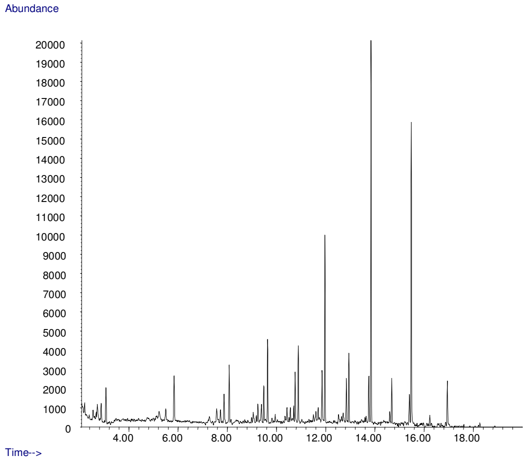
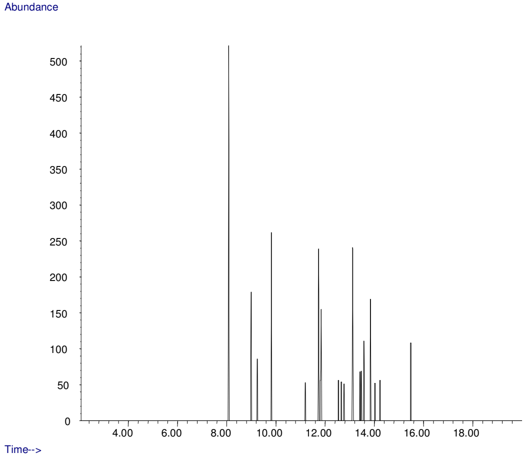


**Figure H.6 EIPS of polyurethane foam (S6).**

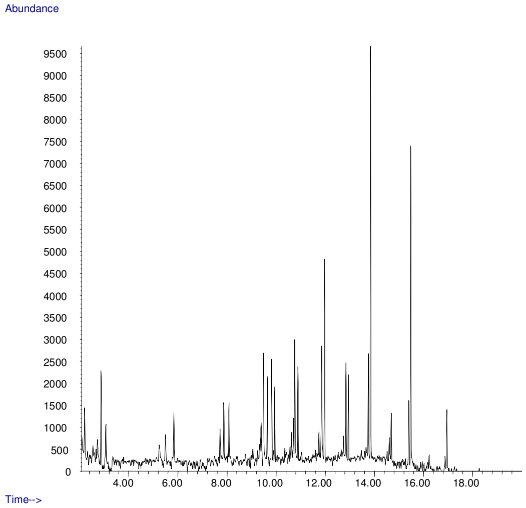
Alkanes (m/z 43,57,71,85,99)



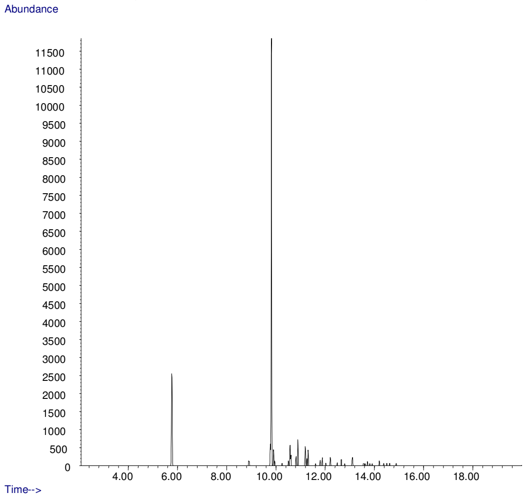
Naphthalene (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

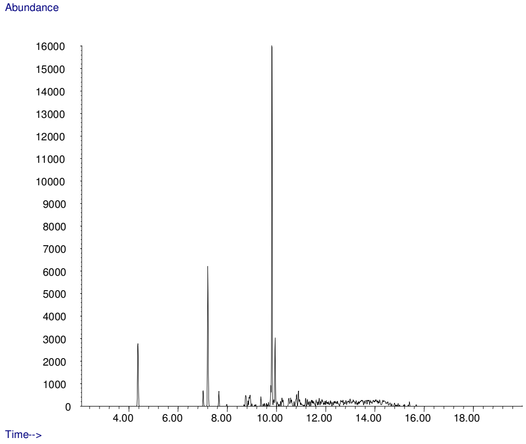
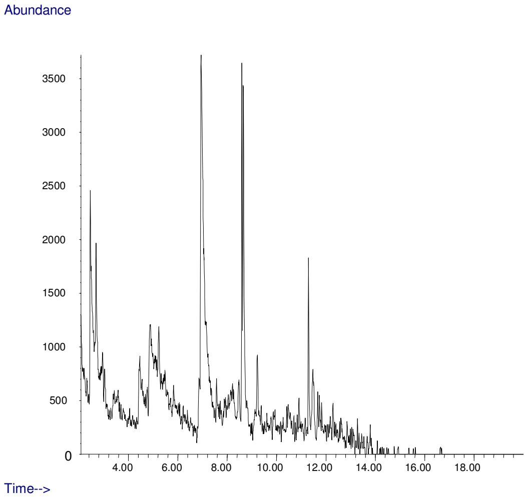
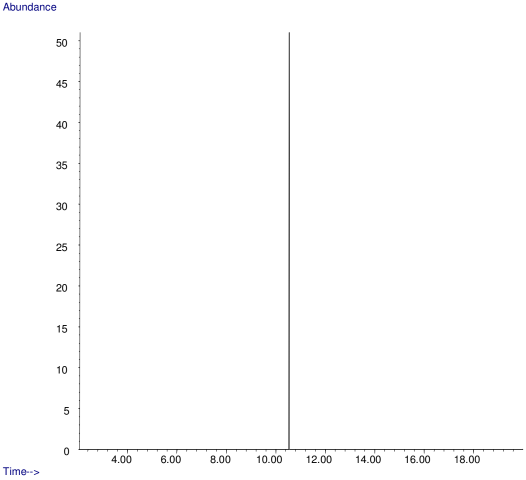


**Figure H.7 EIPS of grocery bags (S7).**

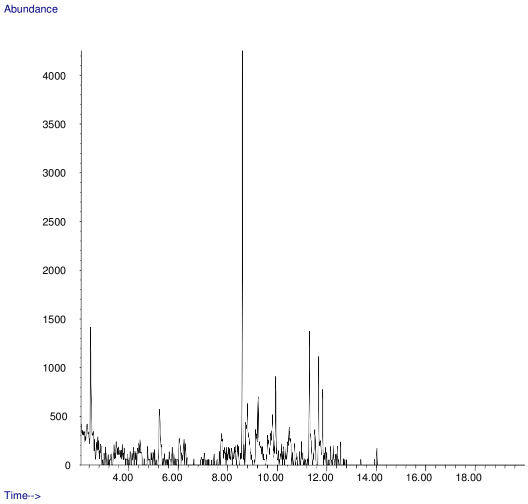
Alkanes (m/z 43,57,71,85,99)



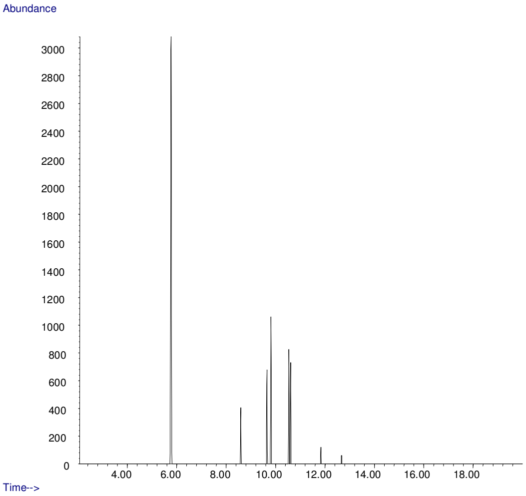
aphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes (m/z 91,92,105,106,119,120)

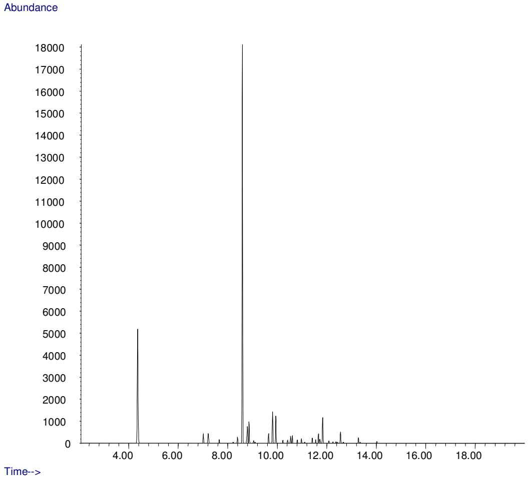
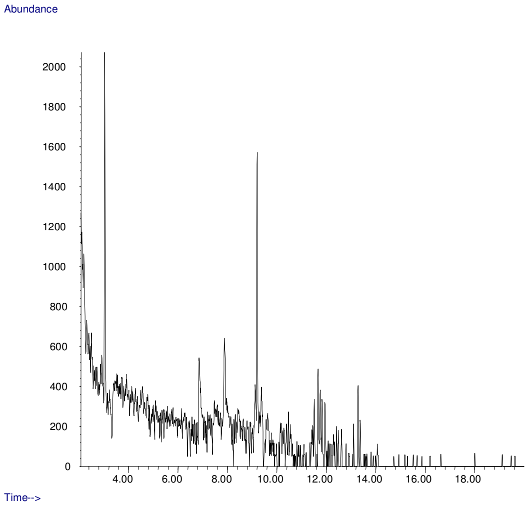
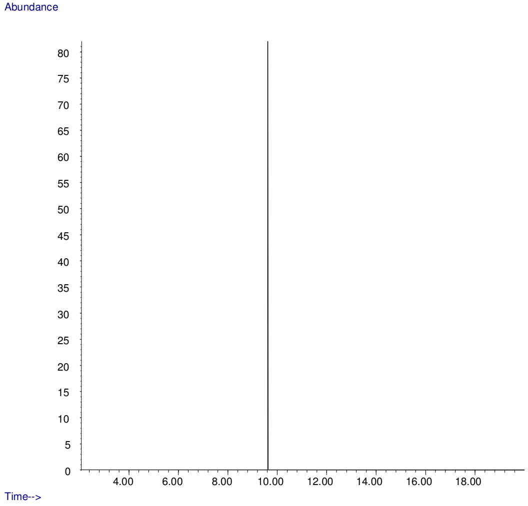


**Figure H.8 EIPS of grocery bags (S8).**

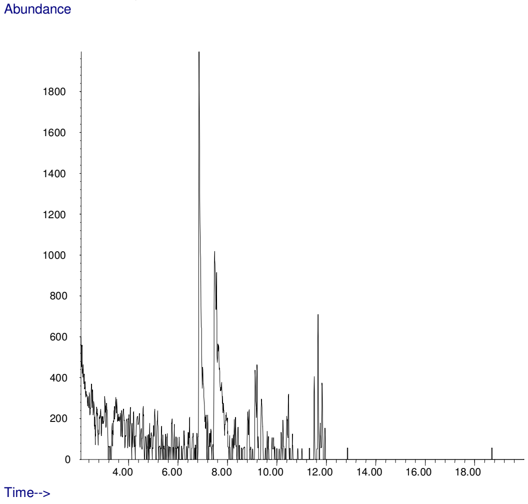
Alkanes (m/z 43,57,71,85,99)



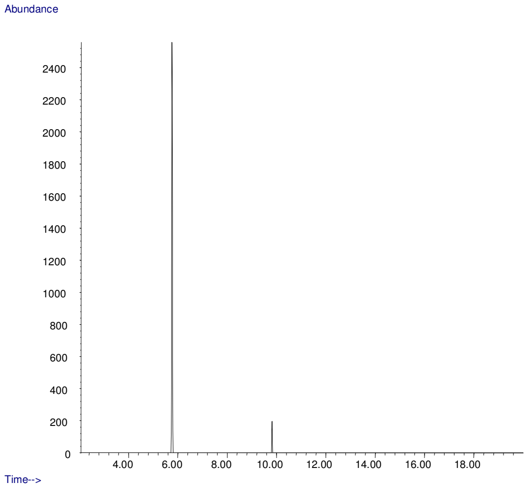
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

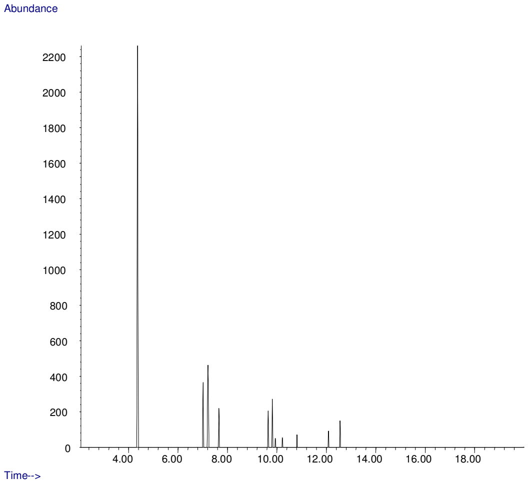
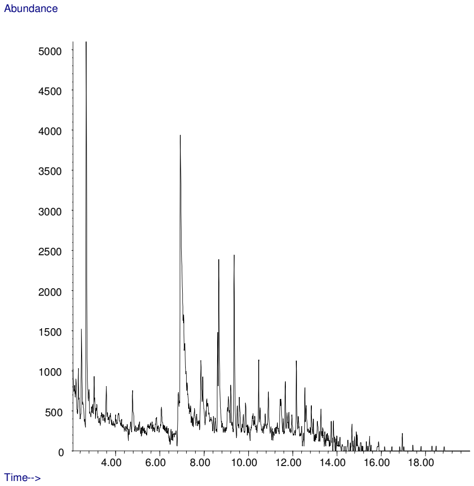
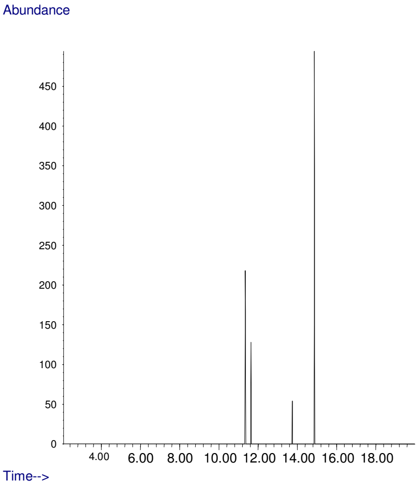


**Figure H.9 EIPS of MDF (S9).**

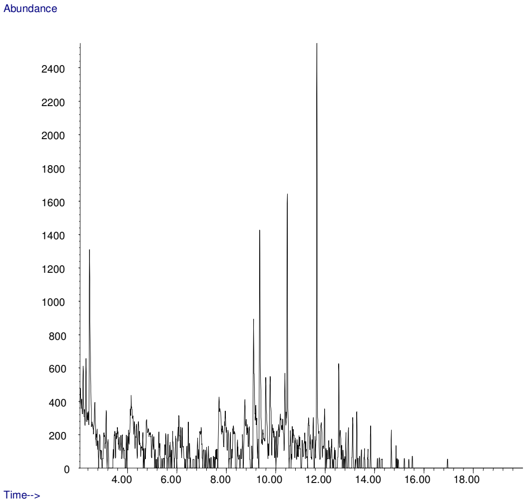
Alkanes
(m/z 43,57,71,85,99)



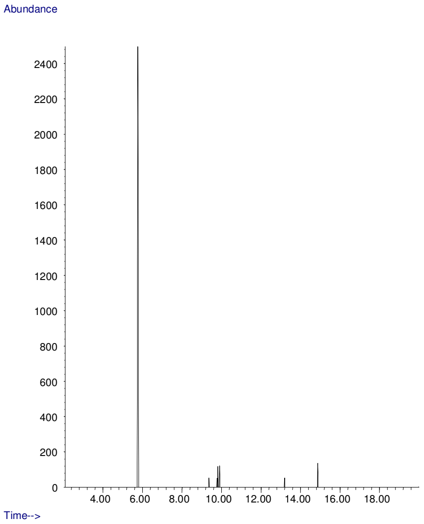
Naphthalenes (m/z 128,
142,156,170)



Alkenes/cyloalkanes
(m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

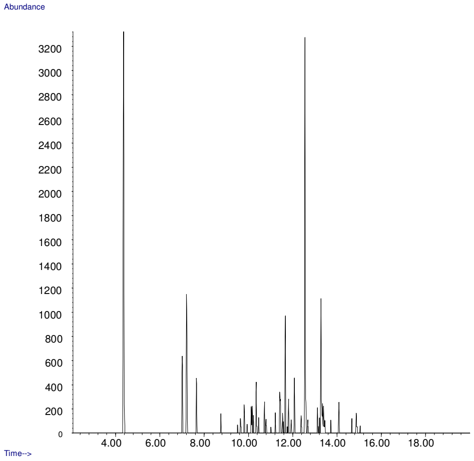
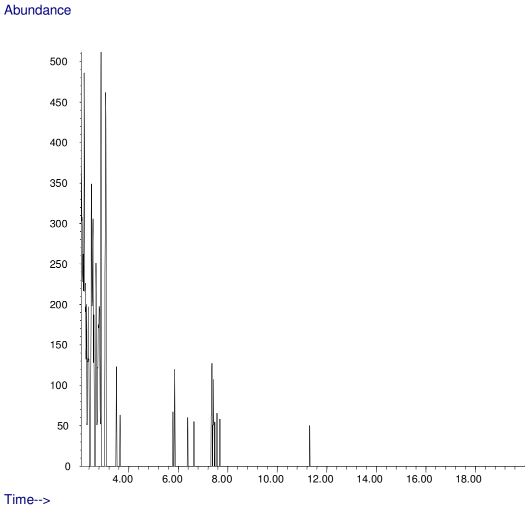
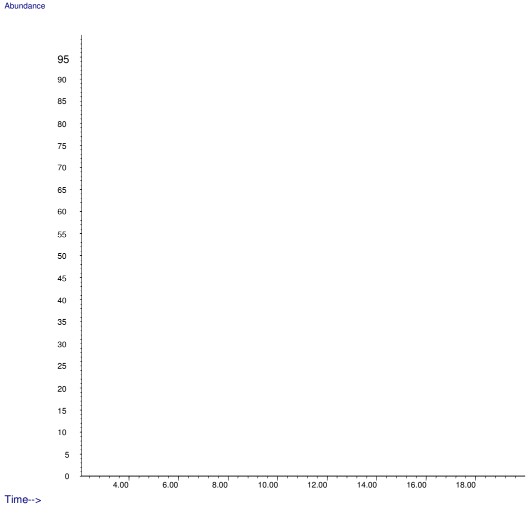


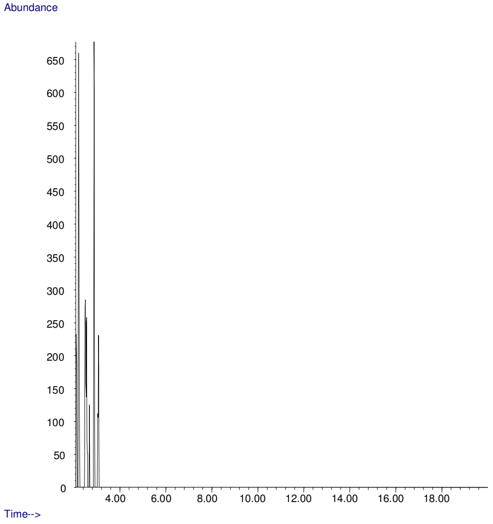
**Figure H.10 EIPS of plywood (S10).**



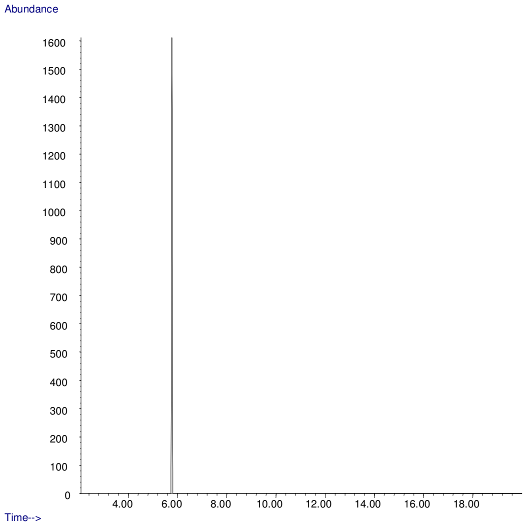
Alkanes (m/z 43,57,71,85,99)



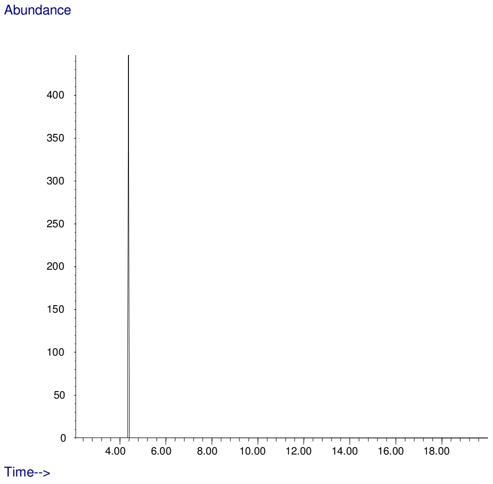
Naphthalenes (m/z 128, 142,156,170)



Alkenes/cyloalkanes (m/z 41, 55, 69,83,97)



Indanes (m/z 117, 118, 131,132)



Alkylbenzenes
(m/z 91,92,105,106,119,120)

**Figure H.11 EIPS of pine (S11).**

# Appendix I: The SOFM Validation Map for Medium Petroleum Distillate Classification.

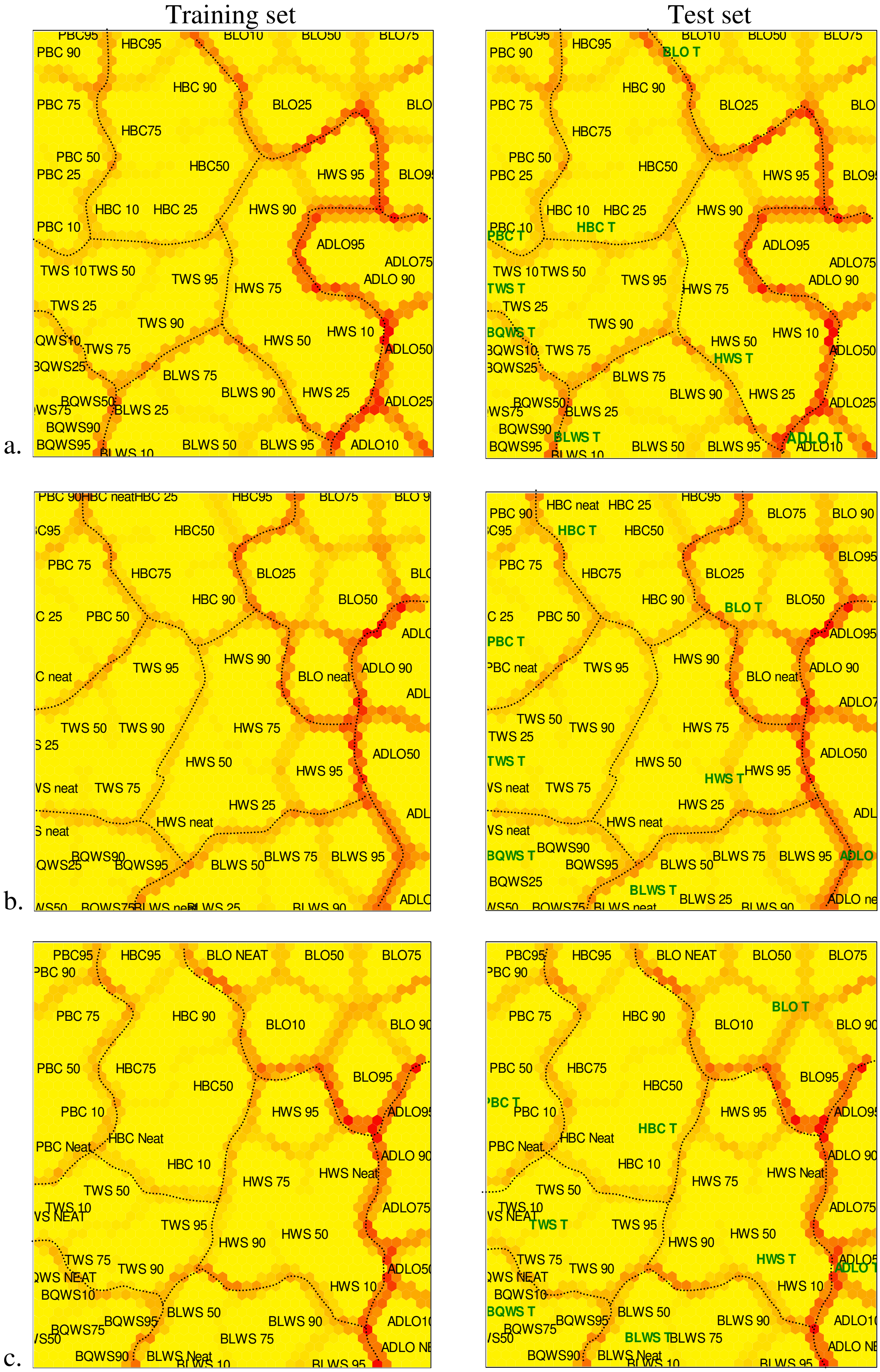


*Figure I1 continued*

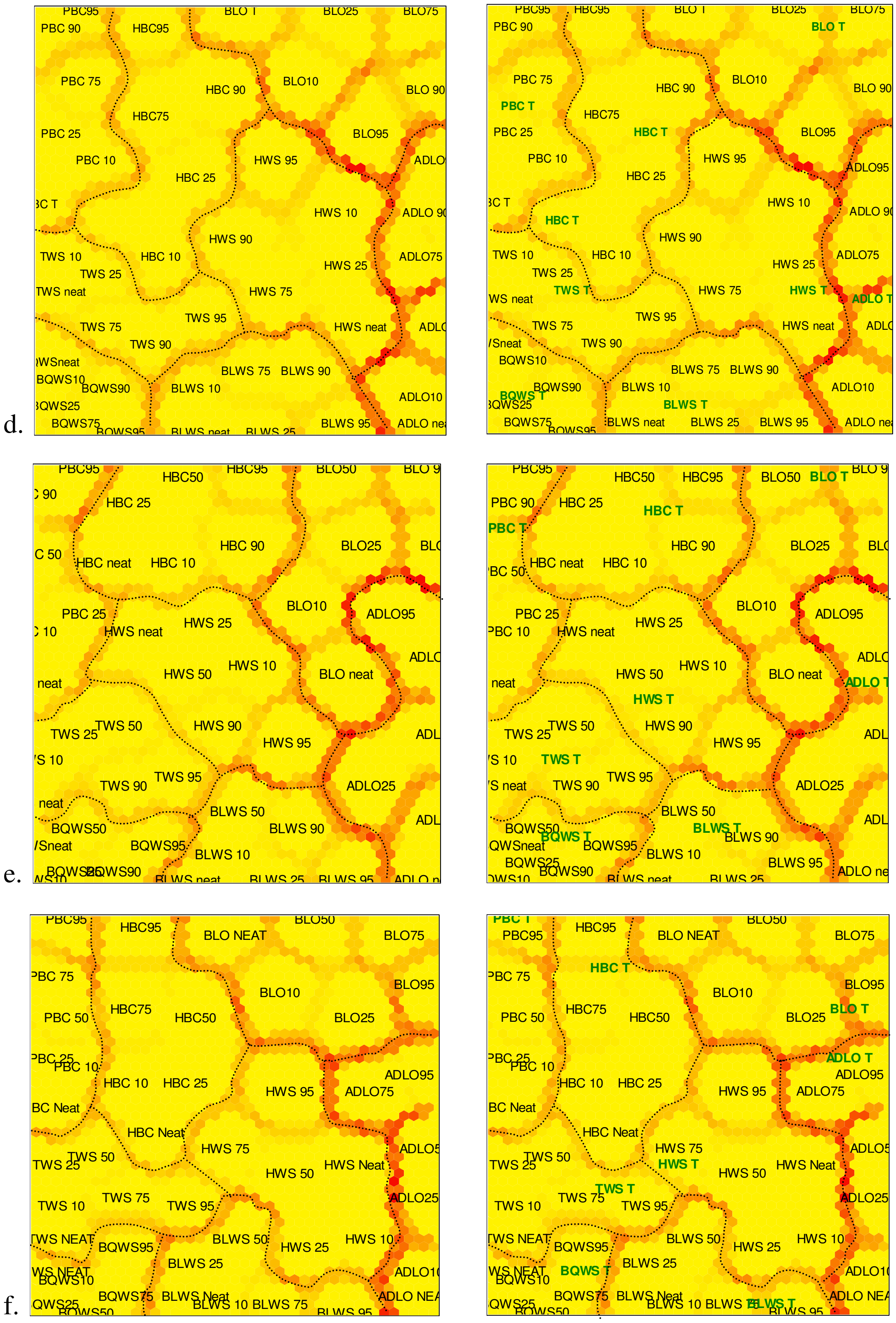


***Figure I1 continued***

g.

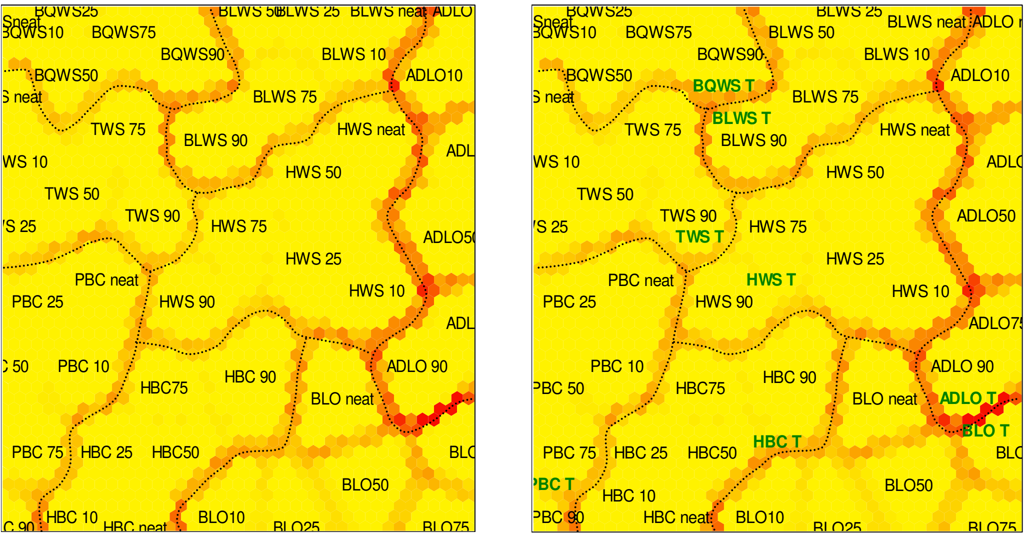


**Figure I.1 Validation of SOFM mapping for medium petroleum distillate samples presented in; a)set Vneat (unevaporated), b) set V10, c) set V25, d) set V50, e) set V75, f) set V90 and g) set V95. Test samples are highlighted in green.**

# Appendix J: The SOFM Validation Map for Heavy Petroleum Distillate Classification

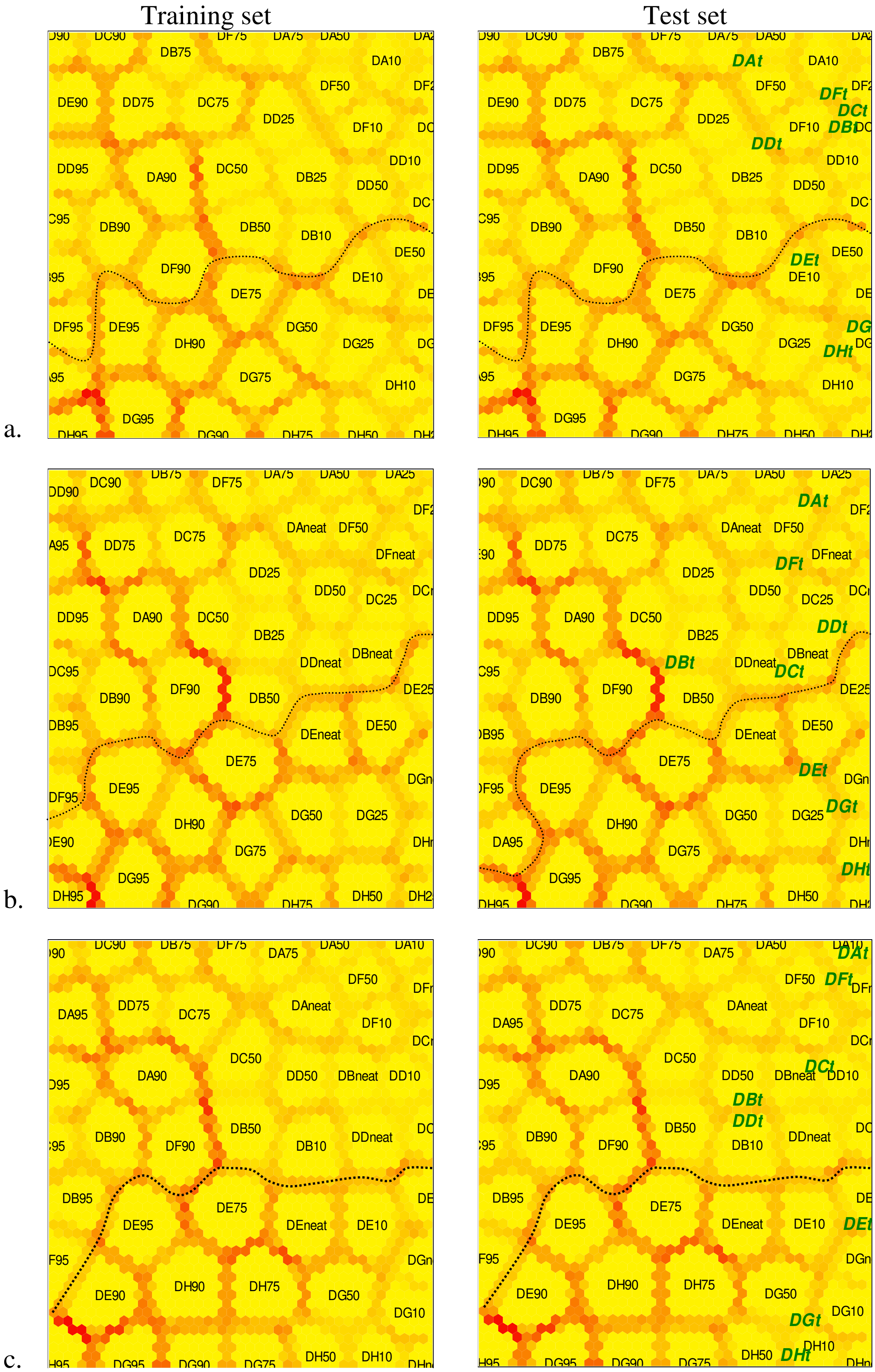
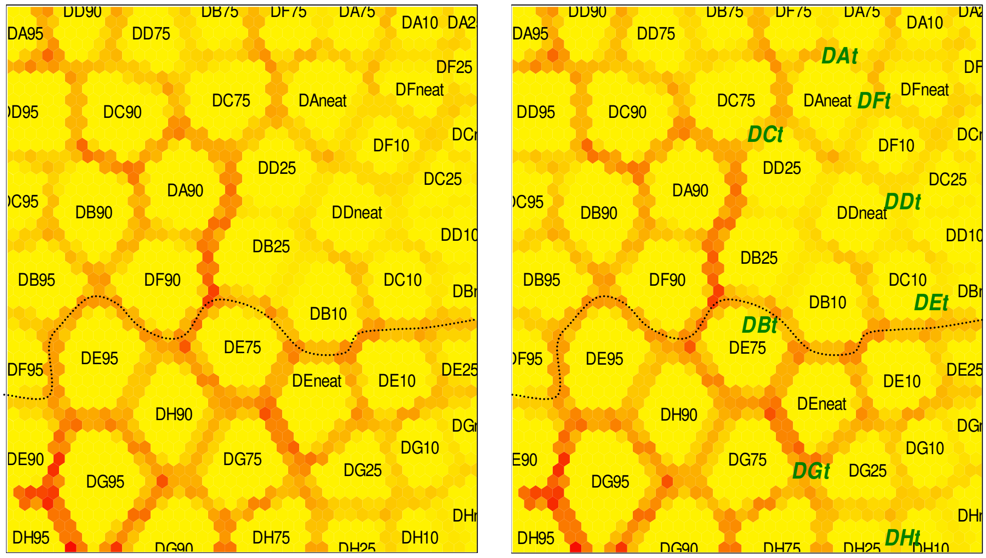
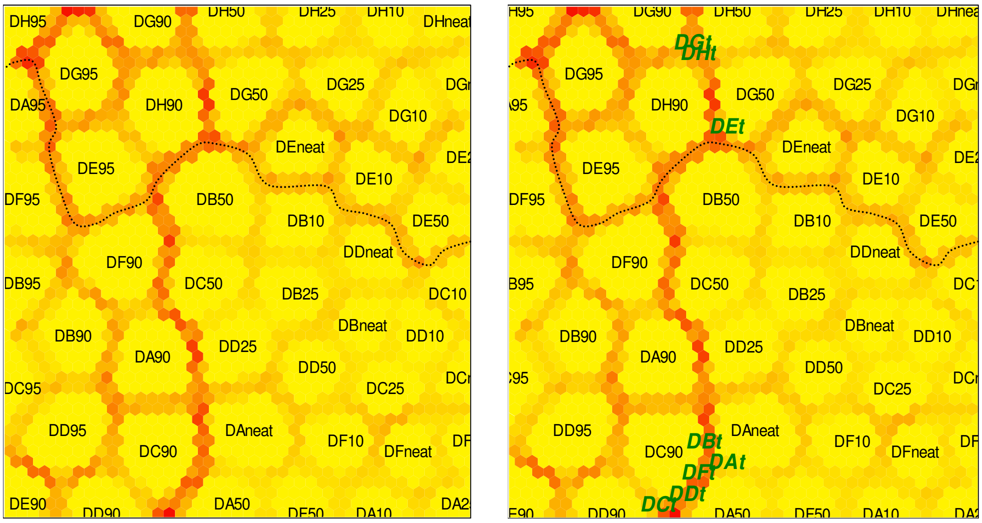


*Figure J1 continued*

d.



e.



f.

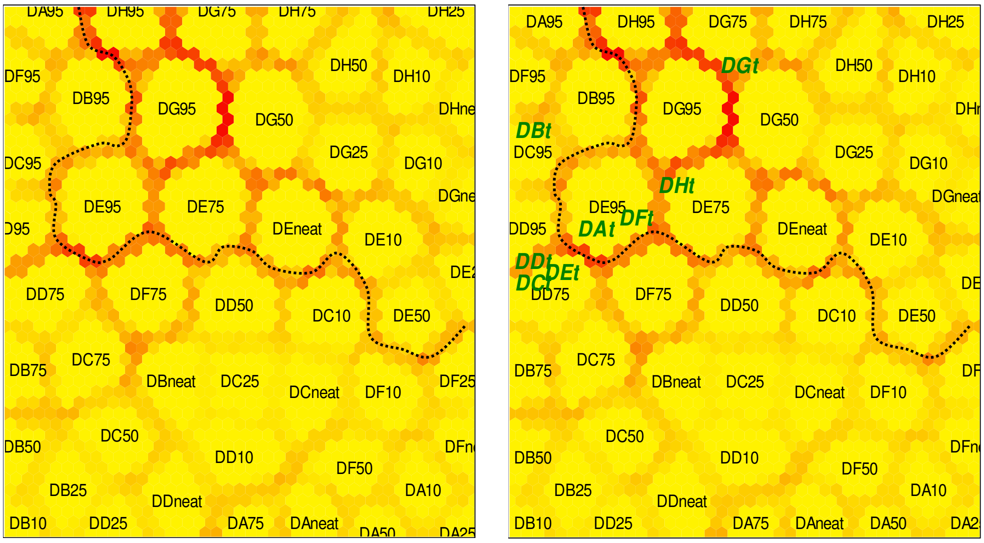


***Figure J1 continued***

g.

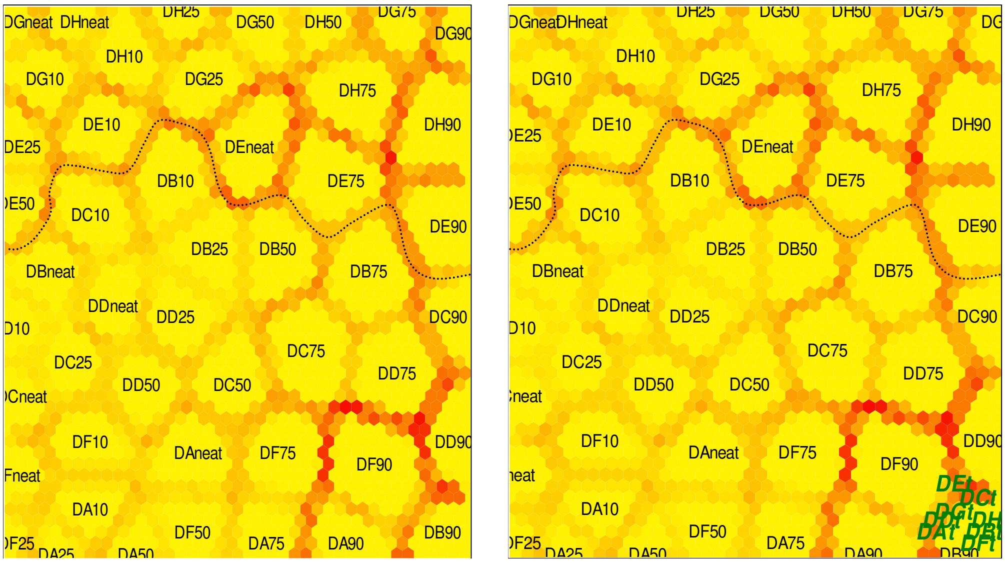


**Figure J.1 Validation of SOFM mapping for diesel samples presented in; a)set Vneat (unevaporated), b) set V10, c) set V25, d) set V50, e) set V75, f) set V90 and g) set V95. Test samples are highlighted in green.**

# Appendix K: The SOFM Validation Map for Petrol Classifications.

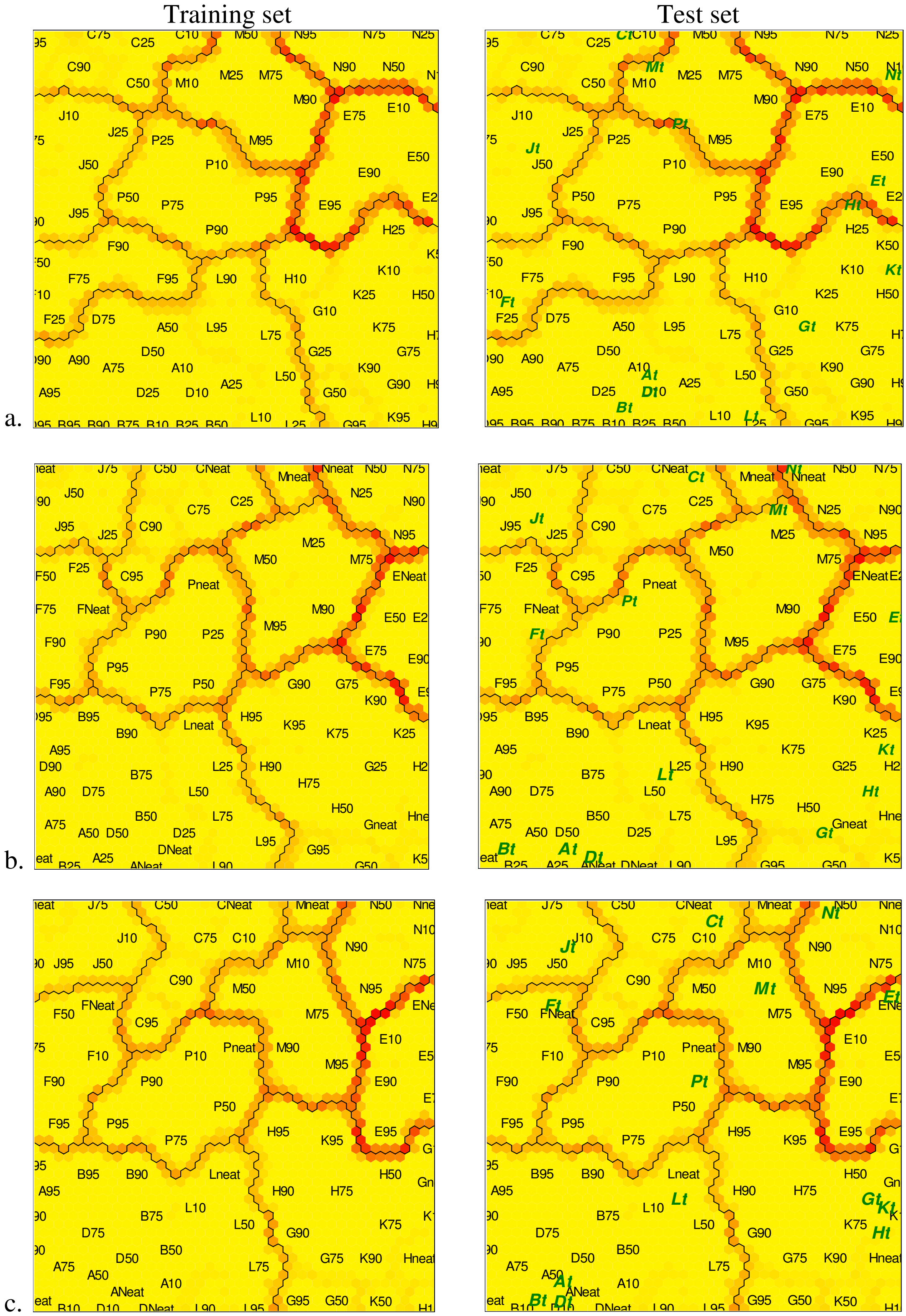


*Figure K1 continued*

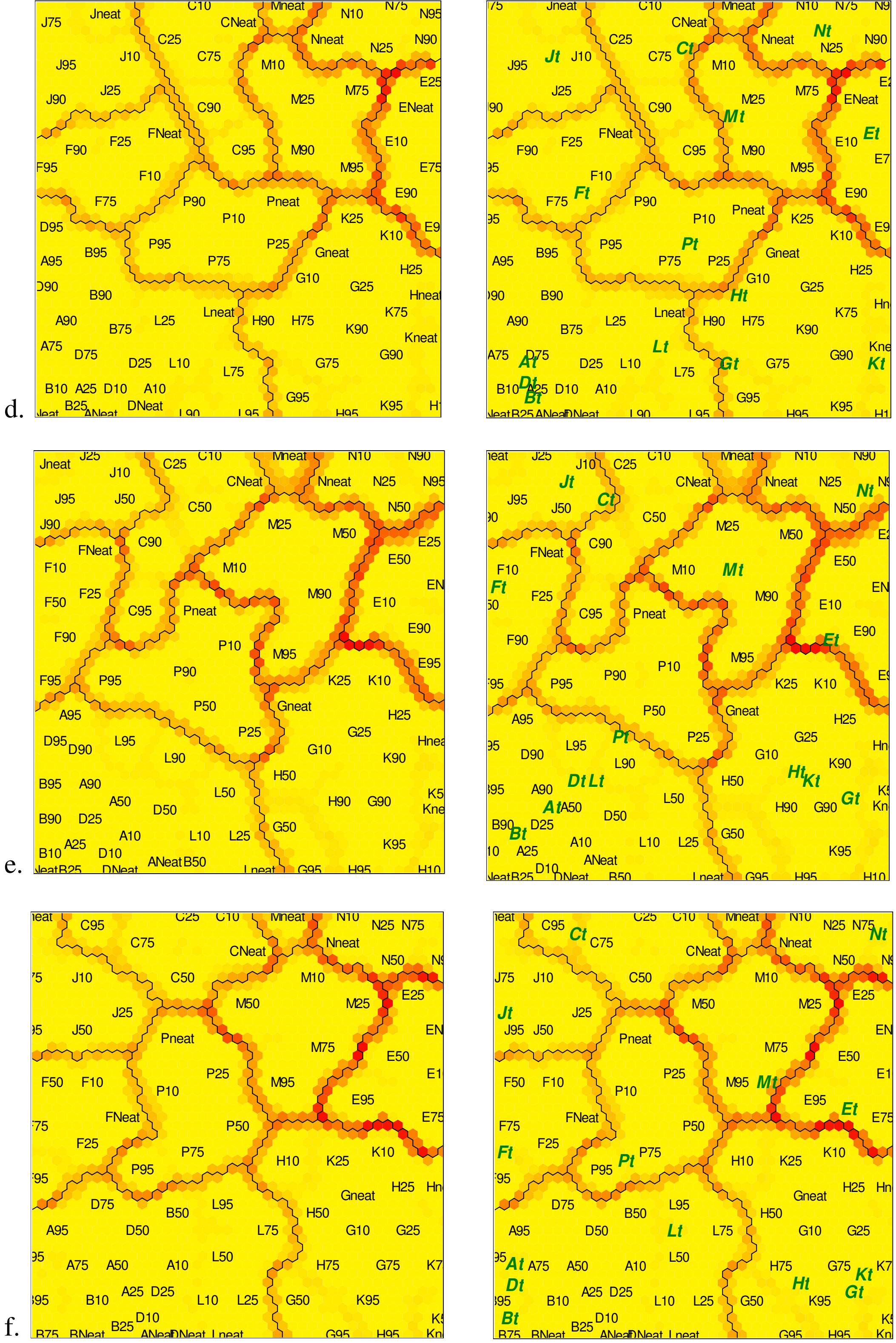


***Figure K1 continued***

g.

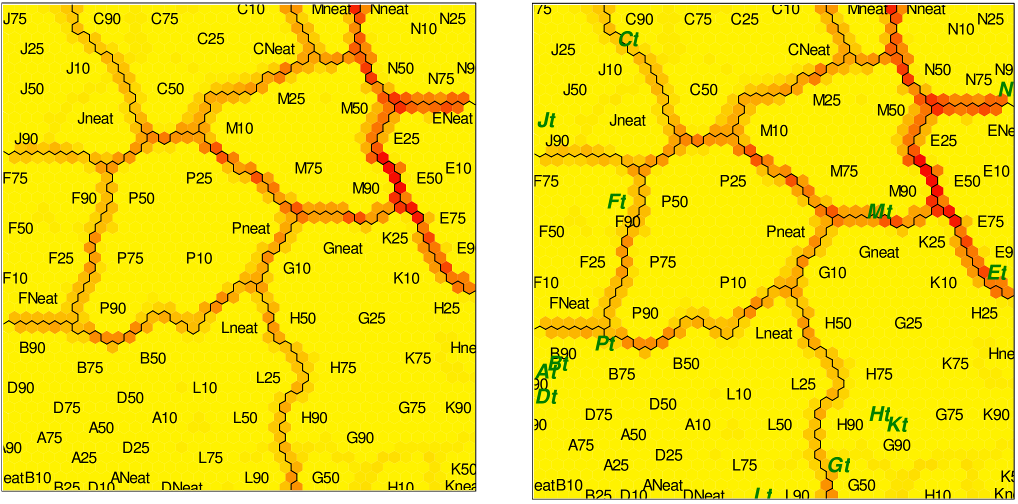


Figure K.1 Validation of SOFM mapping for petrol samples presented in; a)set Vneat (unevaporated), b) set V10, c) set V25, d) set V50, e) set V75, f) set V90 and g) set V95. Test samples are highlighted in green.

# Appendix L: Journal Publications

The following papers were reproduced with permission from:

- *Analytical Chemistry*, **2010,** *82* (15), 6395–640, Copyright 2010 American Chemical Society and
- *Analytical Chemistry*, **2011**, *83* (20), 7745-7754, Copyright 2011 American Chemical Society.

*Anal. Chem.* **2010,** *82,* 6395–6400

# Application of Unsupervised Chemometric Analysis and Self-organizing Feature Map (SOFM) for the Classification of Lighter Fuels

**Wan N. S. Mat Desa,[†] Niamh Nic Daéid,* Dzulkiflee Ismail, and Kathleen Savage**

*Centre for Forensic Science, Department of Pure and Applied Chemistry, University of Strathclyde,*
*204 George Street, Glasgow G1 1WX*

**A variety of lighter fuel samples from different manufacturers (both unevaporated and evaporated) were analyzed using conventional gas chromatography−mass spectrometry (GC-MS) analysis. In total 51 characteristic peaks were selected as variables and subjected to data preprocessing prior to subsequent analysis using unsupervised chemometric analysis (PCA and HCA) and a SOFM artificial neural network. The results obtained revealed that SOFM acted as a powerful means of evaluating and linking degraded ignitable liquid sample data to their parent unevaporated liquids.**

Ignitable liquids are commonly used as accelerants to intensify the rate of fire development in cases of deliberate fire setting. Identification and discrimination of ignitable liquid or ignitable liquid residues within recovered samples are, therefore, of interest and the characterization, identification, and linkage of such ignitable liquids is highly desirable. At present, gas chromatography-flame ionization detector (GC-FID) and gas chromatography-mass spectrometry (GC-MS) are widely accepted as effective methods for the analysis and identification of ignitable liquids.[1−3] Interpretation of the instrumental data and sample classification processes are based mainly on visual comparison of the sample to an ignitable liquid database.[4−6] Other approaches involve selective ion monitoring of the resultant chromatographic data producing a target compound chromatogram (TCC) of the sample which can be compared to TCC of the ignitable liquid from a database.[7−10]

These methods however can be difficult, time-consuming, highly subjective and rely heavily on the skill and experience of the analyst. Petrol for example, consists of a wide range of over 500 hydrocarbon compounds together with other additives.[11] Exposure to heat or aging can result in substantial changes in the liquid's composition, which in turn greatly affects their chromatographic profile. Another common complication encountered in fire debris analysis is the appearance of hydrocarbon byproduct from the combustion and pyrolysis of background matrices.[12−15]

The applications of multivariate pattern recognition to discriminate and classify ignitable liquid samples are suggested as a means of facilitating the pattern matching process and rendering it less subjective. Pattern recognition techniques using chemometric approaches have been used to establish underlying relationships among variables within complex data sets and can be used to differentiate groups within a given data set. Principle component analysis (PCA) and hierarchical cluster analysis (HCA), are both regarded as unsupervised-learning methods which do not require a training set of known categories to derive the classification model. Instead they use the given data to self-establish grouping structures.[16,17]

PCA and HCA have been employed for the classification of ignitable liquid analysis.[18−22]Typically, numerical data sets of selected compounds within the sample are processed by PCA, canonical variate analysis (CVA), and orthogonal canonical variate analysis (OCVA) coupled with linear discriminate analysis (LDA) for discrimination. Petraco et al. demonstrated the use of such methods for the discrimination of 20 gasoline samples, however some misclassification occurred.[22] The authors emphasized the

---

* To whom correspondence should be addressed. Phone: + 44-141-5484700. Fax: +44-141-5482532. E-mail: n.nicdaeid@strath.ac.uk.

[†] Permanent address: School of Health Sciences, Universiti Sains Malaysia, Health Campus, 16150 Kubang Kerian, Kelantan, Malaysia.

(1) American Society for Testing and Materials Method E1618-01. In *Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry*; American Society for Testing and Materials: West Conshohocken, PA, 2001.
(2) American Society for Testing and Materials Method E1387-01. In *Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography*; American Society for Testing and Materials: West Conshohocken, PA, 2001.
(3) DeHaan, J. D., *Kirk's Fire Investigation*, 6th ed.; Brady: New York, 2007.
(4) Almirall, J. R.; Furton, K. G., *Analysis and Interpretation of Fire Scene Evidence.*; CRC Press: Boca Raton, 2004.
(5) Newman, R.; Gilbert, M.; Lothridge, K. *GC-MS Guide to Ignitable Liquids*; CRC Press: Boca Raton, 1998.
(6) Vella, A. J. *J. Forensic Sci. Soc.* **1992**, *32*, 131–142.
(7) Nowicki, J. *J. Forensic Sci.* **1990**, *35*, 1064–1086.
(8) Nowicki, J. *J Forensic Sci.* **1991**, *36*, 1536–1550.
(9) Lennard, C. J.; Rochaix, V. T.; Margot, P. *Sci. Justice.* **1995**, *35*, 19–30.
(10) Keto, R.; Wineman, P. L. *Anal. Chem.* **1991**, *63*, 1964–1971.
(11) Wang, Z.; Fingas, M. *J. Chromatogr., A* **1995**, *712*, 321–343.
(12) Bertsch, W. *J. Chromatogr., A* **1994**, *674*, 329–333.
(13) Dehaan, J.; Bonarius, K. *J. Forensic Sci. Soc.* **1988**, *28*, 299–309.
(14) Lentini, J. J., *Scientific Protocols for Fire Investigation*; Taylor & Francis Gp, CRC Press: Boca Raton, 2006.
(15) Lentini, J. J. *J. Forensic Sci.* **1998**, *43* (1), 97–113.
(16) Everitt, B. S.; Dunn, G., *Applied Multivariate Data Analysis.*; Arnold: London, 2001.
(17) Berrueta, L. A. e. a. *J. Chromatog. A* **2001**, *1158*, 196–214.
(18) Tan, B.; Hardy, J. K.; R.E., S. *Anal. Chim. Acta* **2000**, *422*, 37–46.
(19) Bodle, E. S.; J. K., H. *Anal. Chim. Acta* **2007**, *589*, 247–254.
(20) Doble, P.; al., e., 2003, *132*, 26−39.
(21) Lu, Y.; Harrington, P. B. *Anal. Chem.* **2007**, *79*, 6752−6759.
(22) Petraco, N. D. K.; et al. *J. Forensic Sci.* **2008**, *53*, 1092−1101.

10.1021/ac100381a

importance of statistical methods of pattern recognition for fire debris casework rather than relying on visual comparison alone.

The application of artificial neural networks (ANNs) in forensic data analysis on the other hand, is relatively unusual. ANN has been suggested as an effective data analysis mechanism for various data sets relating to cocaine analysis,[23] toolmark comparison[24] and gasoline identification.[20] Doble et al. demonstrated the application of supervised ANNs using a multilayer perceptron (MLP) arrangement with a back-propagation (BP) algorithm to discriminate between regular and premium gasoline and reported a 97% correct classification-prediction rate.[20] To date no other application of ANN in ignitable liquid analysis has been reported and there is no reported application of self organizing feature map (SOFM) (or Kohonen mapping).[25,26]

SOFM is typically arranged in a two-layer form consisting of an input and output layer. The output neurons of the network are normally arranged as a two-dimensional grid where the multidimensional input vectors, (the variables describing the data), are mapped. The input neurons are fully connected to every neuron in the output layer. Associated with every connection is a weighting, which influences the final output of the network. The network training in SOFM is a competitive process where all the neurons compete to be stimulated by the input vectors. The similarities between the input and output vectors are computed using the Euclidean distance. The neuron with weight vectors which is most similar to the input vector is chosen as the best matching neuron (BMU). The weights of the BMU's and those of neighboring neurons are adjusted so that they will become closer to the input vectors in the next iteration of the algorithm. As the training process continues, the SOFM organizes into a state whereby similar input vectors are mapped onto similar neurons on the output layer. By the end of the training process, the output neuron is labeled according to the input (or data) that has stimulated or mapped onto it in order to reveal if clustering has emerged from the training.

In ignitable liquid analysis, the relevant chromatographic data are isolated by targeting compounds identified as discriminating for that particular sample.[22,27−29] The selected data may also undergo further transformations or data pretreatment (such as normalization, logarithmic transformation and root transformation), which are commonly used to minimize the effect of large peaks or eliminate signal noise in order to make the data distribution more symmetrical and facilitate multivariate analysis.[25,30−33] In this work chromatographic data derived from various brands of unevaporated and partially evaporated lighter fuel was subjected to chemometric analysis using unsupervised methods (PCA, HCA) and an SOFM artificial neural network. The goal was to reveal the most appropriate preprocessing methods for this type of data and to determine the feasibility of using unsupervised classification techniques, particularly SOFM for pattern recognition of chromatographic data with a view to assignation of partially evaporated materials with their corresponding unevaporated source.

## EXPERIMENTAL SECTION

**Chemicals and Materials.** Fifteen refill lighter fluid samples from five different brands (Zippo, Swan, Ronsonol, Perma, and Dunhill) were purchased from commercial outlets. For each lighter fluid brand, a set of partially evaporated samples was generated. This was achieved by gently heating the unevaporated lighter fluid (100 mL) and removing a sub sample at specific intervals when the original liquid had been reduced by 10, 25, 50, 75, 90, and 95 mL in volume. This produced a set of partially evaporated samples for each lighter fluid liquid at approximately 10, 25, 50, 75, 90, and 95% evaporation. Each sample was diluted to 2% in pentane (HPLC grade, WVR International) with 0.5 mg/mL Tetrachloroethylene (Sigma Aldrich, >99%) as internal standard. All samples were stored in screw capped vials and darkness at room temperature until analyzed. An aluminum foil shield was placed inside the screw cap to prevent evaporation of the sample. The prepared samples were at the approximate percentages of evaporation of interest and as such, any additional evaporation which may have occurred during storage was considered to be of little effect to the overall results obtained.

According to ASTM E1618 guidelines, pentane is listed as one of the recommended nonpolar solvents for fire debris analysis and is as efficient as other solvents but relatively less toxic, safer and easier to handle.[1,34] The solvent delay on the MSD was set in order to allow the pentane peak to elute undetected and this had a minimal effect on the overall patterns of interest in the test samples, particularly in relation to the evaporated samples.

The application and efficiency of using volatile chlorinated compound as the internal standard for fire debris analysis, such as Tetrachloroethylene has been reported.[35,36] A chlorinated compound was used mainly because it is not commonly encountered in ignitable liquid samples and is cost-effective and easily identifiable.

**Instrumentation.** Gas chromatographic analysis was performed using a Hewlett-Packard (HP) 6890/5973 gas chromatograph with a mass selective detector (GC-MSD). Data acquisitions were performed by MS ChemStation (version B.00.01, Hewlett-Packard, Agilent Technologies). Chromatographic separation was achieved using a DB1-MS fused silica capillary column (25.0 m × 0.20 mm i.d. × 0.33 $\mu$m film thickness). The injection port temperature set at 250 °C. The oven temperature was set at 40 °C for 5 min and ramped at a rate of 15 °C/min to 280 °C, and

---

(23) Casale, J. F.; Watterson, J. W. *J. Forensic Sci.* **1993**, *38*, 292–301.
(24) Kinston, C. *J. Forensic Sci.* **1992**, *37*, 252–264.
(25) Brereton, R. G., *Chemometrics for Pattern Recognition.*; John Wiley and Sons: West Sussex, U.K., 2009.
(26) Kohonen, T. *Self-Organising Maps*; Springer-Verlag: Heidelberg, Germany, 1995.
(27) Borusiewicz, R.; Zadora, G.; J., Z. b.-P. *J. Chromatogr. (Supplement)* **2004**, *60*, S133–S142.
(28) Sandercock, P. M. L.; Pasquier, E. D. *Forensic Sci. Int.* **2003**, *134*, 1–10.
(29) Sandercock, P. M. L.; Pasquier, E. D. *Forensic Sci. Int.* **2004**, *140*, 43–59.
(30) Wold, S.; Sjostrom, M.; Erikksson, L. *Chemom. Intell. Lab. Syst.* **2001**, *58*, 109–130.
(31) Rietjens, M. *Anal. Chim. Acta* **1995**, *316*, 205–215.
(32) Andersson, K. e. a. *Forensic Sci. Int.* **2007**, *169*, 86–99.
(33) Stauffer, E.; Dolan, J. A.; Newman, R. *Fire Debris Analysis*; Academic Press: New York, 2008.
(34) Stauffer, E. *Sci. Justice* **2003**, *43* (1), 29–40.
(35) Locke, A. K.; Basara, G. J.; Sandercock, P. M. L. *Journal Forensic Science* **2009**, *54* (2), 320–327.
(36) *NIST/EPA/NIH Mass Spectral Library (NIST 08) and NIST Mass Spectral Search Program (Version 2.0f)*: U.S. Department of Commerce, National Institute of Standards and Technology (NIST), Standard Reference Data Program, Gaithersburg, MD 20899: 2008.

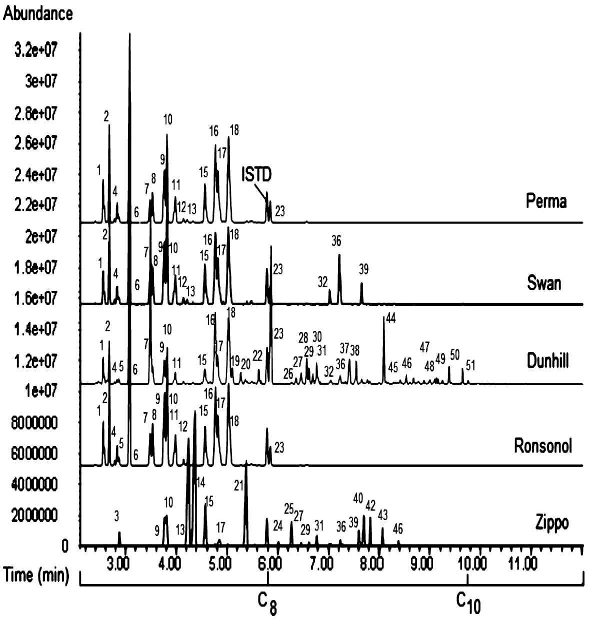


**Figure 1.** Chromatograms of pure lighter fluid samples (2% in pentane with 0.5 mg/mL Tetracholoroethylene as ISTD).

maintained at this temperature for 2 min. Helium was used as the carrier gas and was maintained at a constant flow rate of 1.0 mL/min. The temperatures of the ion source and the quadrupole were set at 150 and 280 °C, respectively. The MS analyses were performed at full scan mode (from 30 to 300 amu) with two minutes solvent delay. Injections were carried out using a 7673A Hewlett-Packard automatic liquid sampler. Each sample was analyzed in triplicate and the injection volume for each sample was 1 $\mu$L with a 20:1 split ratio.

**Data Collection and Preprocessing.** The chromatograms were visually compared and components of similar retention time and relative standards deviation of less than 5% on triplicate analysis were selected. Peak response data was acquired as comma separated values (CSV) files and converted into an Excel (version 10) spread-sheet for ease of use. In total, 51 components were selected as variables from the pure and evaporated samples. Missing components in any individual sample were given a zero value. The peak area response were normalized against the internal standard. Further data pre processing was undertaken by applying a square root transformation and a fourth root transformation to the normalized data set. The four resultant data sets (i.e., raw and processed) were inputted to MATLAB 2008a (version 7.6, Mathwork Inc.) where principal component analysis (PCA) and hierarchical cluster analysis (HCA) were performed. SOFM-artificial neural network analysis was performed using ViscoverySOMine (version 5.0.2, Viscovery Software GmbH).

## RESULTS AND DISCUSSION

**Chromatographic Analysis.** Initial examination of the chromatographic pattern of each lighter fluid sample from each of the five brands revealed compositional differences for Swan, Dunhill, and Zippo samples. By contrast Perma and Ronsonol revealed chromatographic patterns which were very similar to each other as shown in Figure 1. Identification of the components common in the various lighter fluid samples is presented in Table 1. Identification is made based on NIST mass spectral database using AMDIS software (version 2.0).[37]

**Table 1. List of Components Identified in Lighter Fuel Samples**

| no. | RT | peak identification |
|---|---|---|
| 1 | 2.55 | 2-methylhexane |
| 2 | 2.68 | 3-methylhexane |
| 3 | 2.84 | 3-ethylpentane |
| 4 | 2.89 | 2,2,4-trimethylpentane |
| 5 | 3.08 | heptane |
| 6 | 3.47 | 1,2-dimethylcyclopentane |
| 7 | 3.48 | cyclomethylhexane |
| 8 | 3.53 | 2,2-dimethyl-3-hexene |
| 9 | 3.77 | 2,5-dimethylhexane |
| 10 | 3.81 | 2,4-dimethylhexane |
| 11 | 3.99 | 3,3-dimethylhexane |
| 12 | 4.15 | 1,2,3-trimethylcyclopentane |
| 13 | 4.23 | 2,3,4-trimethylpentane |
| 14 | 4.37 | 2,3,3-trimethylpentane |
| 15 | 4.56 | 2,3-dimethylhexane |
| 16 | 4.77 | 2-methylheptane |
| 17 | 4.82 | 4-methylheptane |
| 18 | 5.03 | 3-methylheptane |
| 19 | 5.11 | 1,4-dicyclohexane |
| 20 | 5.28 | 1,1-dicyclohexane |
| 21 | 5.37 | 2,2,4-trimethylhexane |
| 22 | 5.64 | 1,2-Dicyclohexane |
| 23 | 5.85 | octane |
| 24 | 6.01 | 2,4,4-trimethylhexane |
| 25 | 6.28 | 2,3,5-trimethylhexane |
| 26 | 6.36 | 2,2-dimethylheptane |
| 27 | 6.47 | 2,4-dimethylheptane |
| 28 | 6.58 | ethylcyclohexane |
| 29 | 6.63 | 2,6-dimethylheptane |
| 30 | 6.70 | 1,1,3-trimethylcyclohexane |
| 31 | 6.78 | 2,5-dimethylheptane |
| 32 | 7.02 | 2,3,4-trimethylhexane |
| 33 | 7.04 | 3-methylheptane |
| 34 | 7.06 | 1,3,5-trimethylcyclohexane |
| 35 | 7.21 | *m*-xylene |
| 36 | 7.23 | 2,3-dimethylheptane |
| 37 | 7.43 | 2-Methyl octane |
| 38 | 7.56 | 3-methyl octane |
| 39 | 7.66 | *p*-xylene |
| 40 | 7.71 | 2,3,6-trimethylheptane |
| 41 | 7.78 | 1-ethyl-4-methylcyclohexane |
| 42 | 7.83 | 2,2,4-trimethylheptane |
| 43 | 8.07 | 3,3-dimethyloctane |
| 44 | 8.09 | nonane |
| 45 | 8.30 | 3,4-dimethyloctane |
| 46 | 8.41 | 2,4-dimethyl-3-ethylpentane |
| 47 | 8.54 | cis-1,1,3,5-tetramethylcyclohexane |
| 48 | 8.69 | 2,6-dimethyloctane |
| 49 | 9.12 | 1-ethyl-1,3-dimethylcyclohexane |
| 50 | 9.15 | toluene |
| 51 | 9.65 | decane |

The effect of evaporation of an ignitable liquid is 2-fold - lower boiling compounds diminish or are lost completely while higher boiling compounds increase in their abundance relative to neighboring compounds, and as such the chromatographic profiles of the evaporated samples are different to those of pure samples,[5 38]. The exemplar of this is illustrated in Figure 2 which clearly demonstrates substantial changes in peaks abundance.

**PCA Classification.** PCA was performed on each data set (raw data, normalized data only, normalized square root and normalized

---

(37) Newman, R. *Modern Laboratory Techniques Involved in the Analysis of Fire Debris Samples*; CRC Press: Boca Raton, 2004.

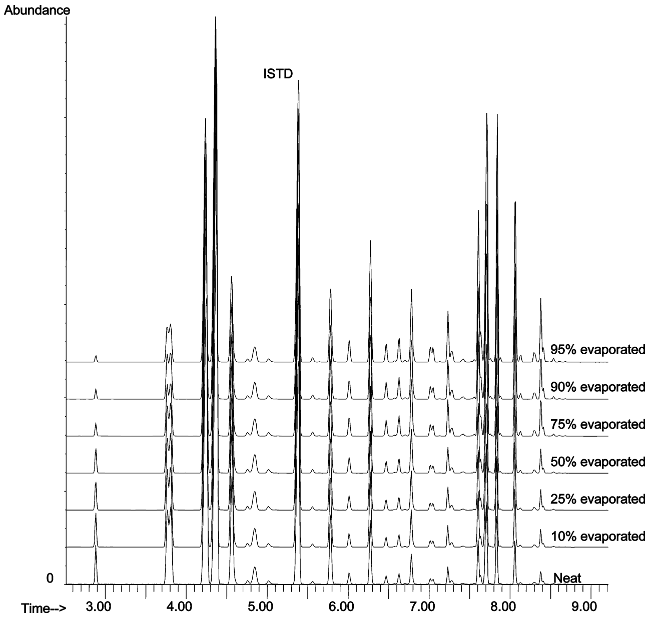


**Figure 2.** Chromatograms of the pure Zippo lighter fluid and evaporated Zippo lighter fluid to demonstrate gradual changes in major peaks abundance as the sample evaporated.

fourth root) to assess the effectiveness of the method to distinguish between the various lighter fluid brands and whether it was possible to establish a link between the pure and evaporated samples of a specific lighter fluid brand. The score plots obtained when all data sets were subjected to PCA analysis are given in Figure 3. Each score plot obtains a series of principal components (PC) where these values represent variances within the data sets.

For all of data sets analyzed only two brands of lighter fluid were successfully resolved irrespective of the data pretreatment method used.

**HCA Classification.** HCA was performed using the same four data sets used in PCA. Similarities between the samples were measured using complete linkage and the results are shown in Figure 4.

Like PCA, HCA did not correctly classify the samples by brand when using the raw data, normalized or normalized square root data sets. However, in contrast to PCA, the normalized fourth root data set produced a HCA classification which was capable of separating all of the pure and evaporated samples by brand and is shown in Figure 4 (D). The HCA classification suggests similarities between Swan and Perma brand samples as well as similarities between both of these samples and those of the Dunhill and Zippo brands, however this was not reflected in the visual comparison of the chromatographic profiles of these samples where clear differences were in evidence. The Ronsonol sample set was clustered away from all other sample sets including

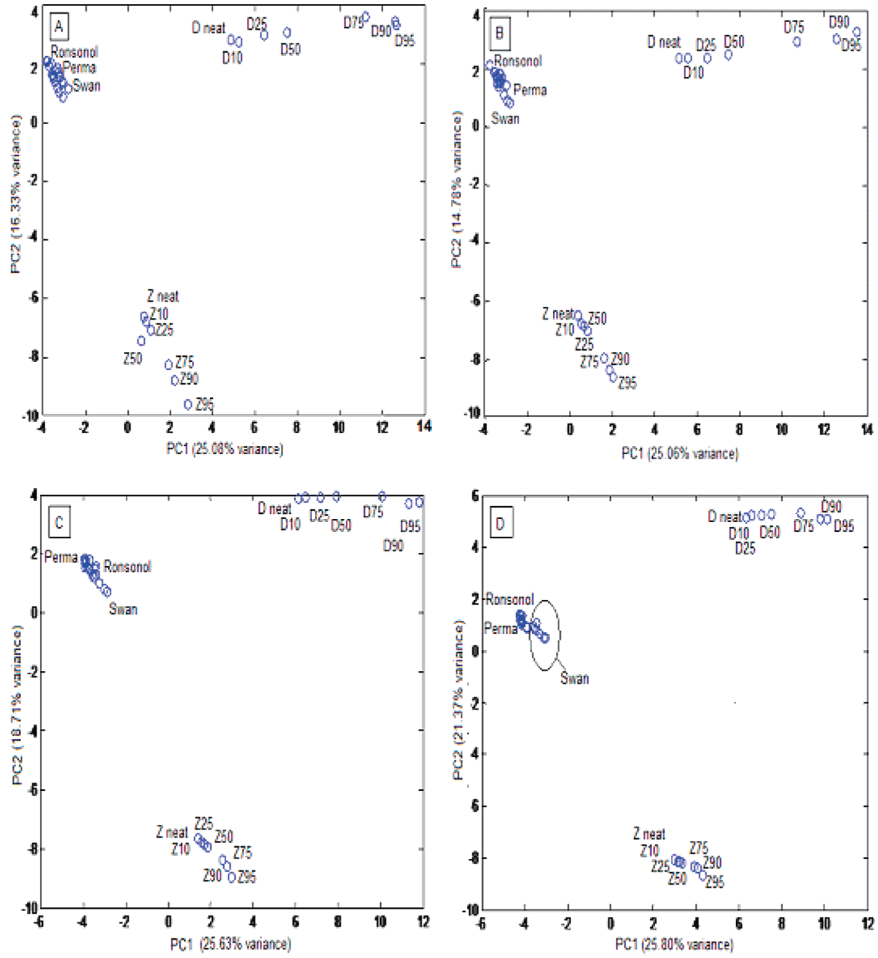


**Figure 3.** Principal component score plots of pure and evaporated samples. A, B, C, and D represent plots of raw data, normalized, normalized square root and normalized fourth root transformation data sets respectively. (*D* = Dunhill, *P* = Perma, *R* = Ronsonol, *S* = Swan, and *Z* = Zippo. Numbers represent degree of evaporation).

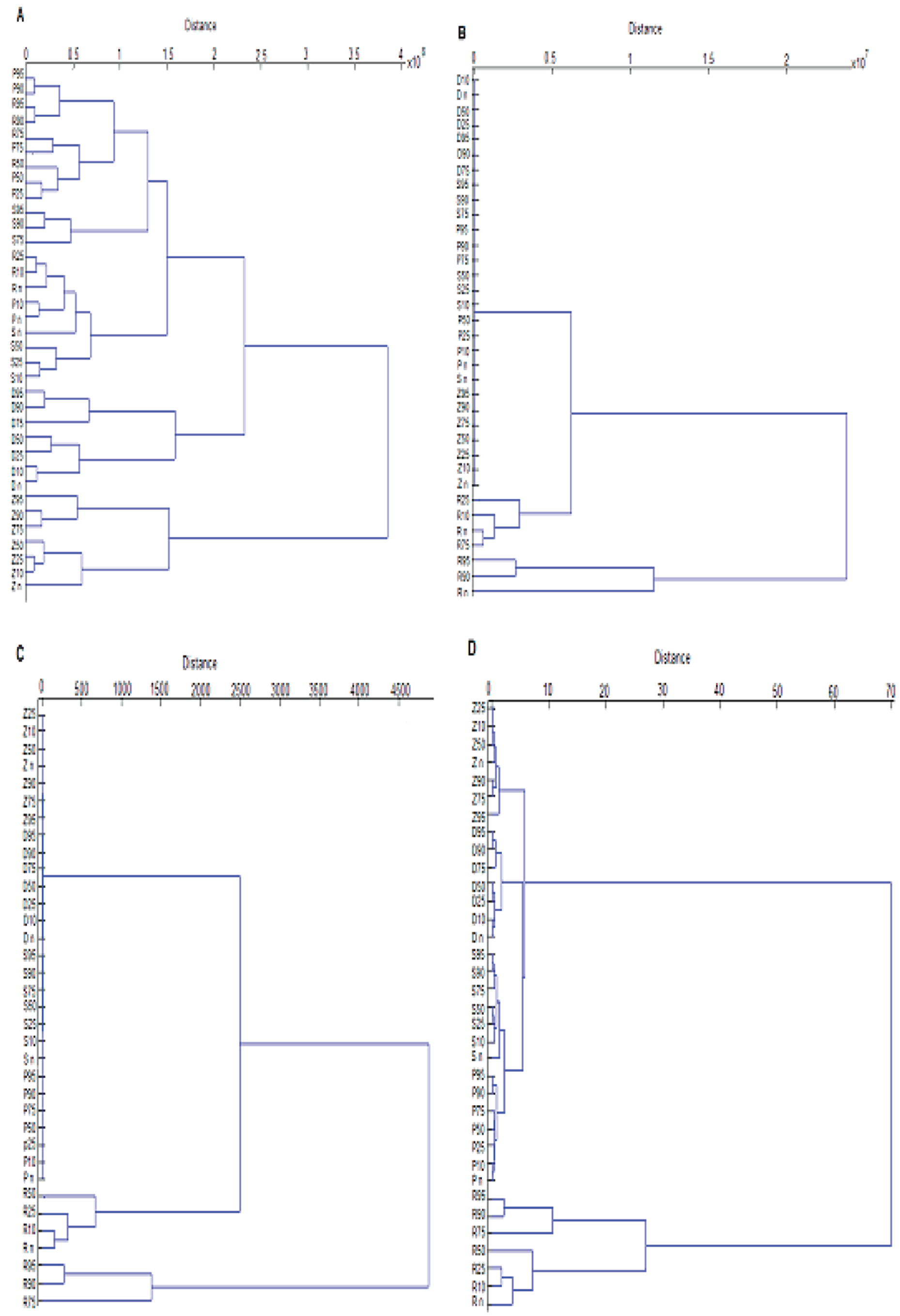


**Figure 4.** Hierarchical clustering of pure and evaporated samples. A, B, C, and D represent dendrograms of raw data, normalized, normalized square root and normalized fourth root transformation data sets respectively. (*D* = Dunhill, *P* = Perma, *R* = Ronsonol, *S* = Swan, and *Z* = Zippo. Numbers represent degree of evaporation).

the Perma sample set even though their chromatographic profiles were visually similar.

**SOFM Classification.** The ability of SOFM to cluster related samples using the four data sets is shown in Figure 5. Data visualization in SOFM can be accomplished by a number of techniques which can be a hit histogram, component planes and the U-Matrix display.[25] The one that is shown in this paper follows the U-Matrix display where the groupings and the degree of dissimilarity between groupings are shown by the more intensely colored boundary lines, where darker boundary lines reflect a greater distance between the adjoining samples.

As a result of using the U-Matrix visualization method, groupings within and between sample brands and the cluster presentation was straightforward and easy to understand. The effectiveness of SOFM over both PCA and HCA is demonstrated by its ability to correctly classify samples using the normalized and preprocessed data sets, although as with HCA the best result was observed with normalized forth root data. In addition SOFM clearly illustrates samples that have similar chromatographic profiles (such as Ronsonol and Parma) by placing these sample clusters in close proximity with each other. This was not achievable using HCA.

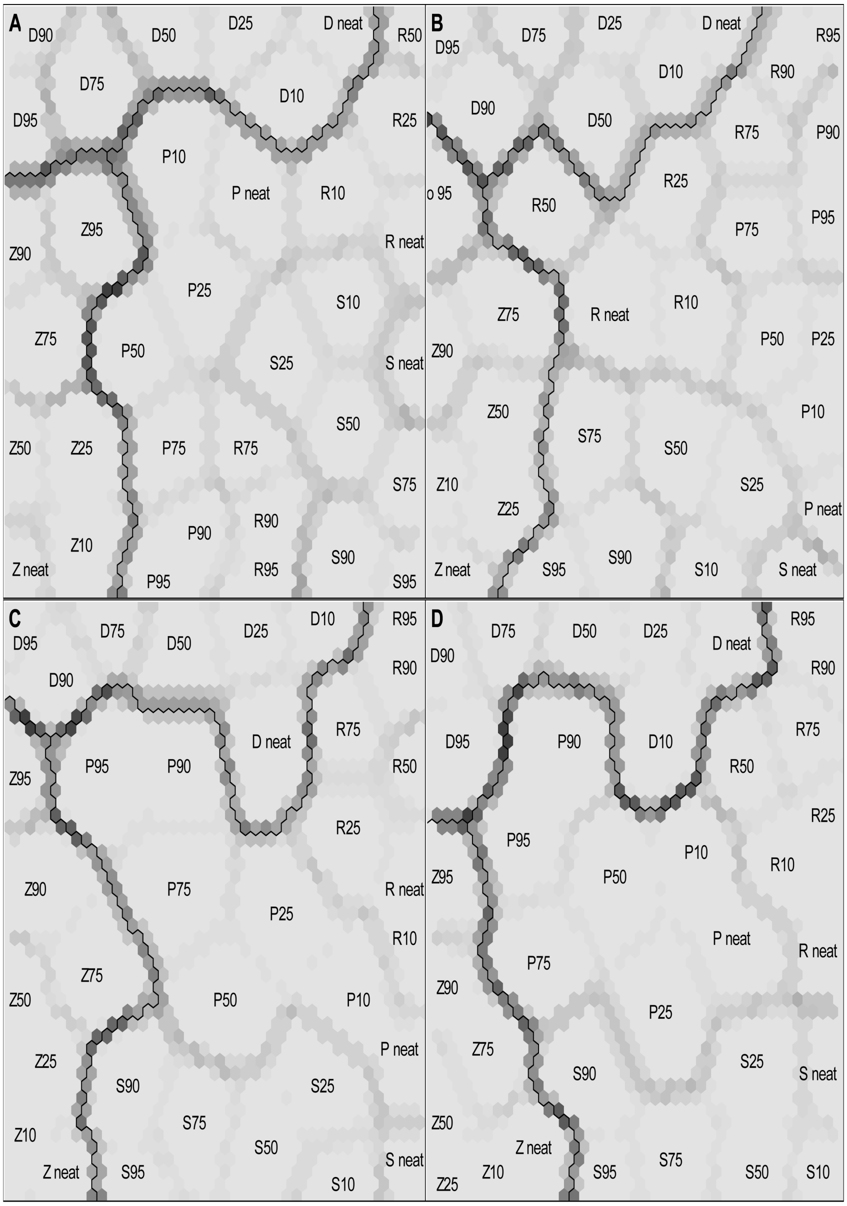


**Figure 5.** SOFM topographic maps of pure and evaporated samples. A, B, C, and D represent the maps of raw data, normalized, normalized square root and normalized fourth root transformation data set respectively. (*D* = Dunhill, *P* = Perma, *R* = Ronsonol, *S* = Swan, and *Z* = Zippo. Numbers represent degree of evaporation).

## CONCLUSIONS

The results of this study demonstrate that pretreated chromatographic data from analyzed lighter fuel samples which have been evaporated to varying degrees can be interrogated using chemometric methods and successfully linked back to their parent pure ignitable liquid sample. Data pretreatment was essential in order to obtain accurate classifications. Three methods of data pretreatment were applied and the best overall discrimination within and between samples was achieved with a normalized fourth root transformation data. It was determined that successful sample classification (by brand) was only achieved using HCA and SOFM where SOFM proved to have a more robust sample linkage capacity and confirmed visual similarities and differences between the samples in evidence in the chromatograms. This has demonstrated a potential means whereby pure and evaporated ignitable liquid samples can be linked successfully by brand and as such presents a powerful new means of interpreting chromatographic data retrieved from fire debris samples. Further studies in this area are ongoing within our laboratory.

## ACKNOWLEDGMENT

We acknowledge the Ministry of Higher Education of Malaysia (SLAB Grant) which provided studentship to W.M.-D. and D.I.

Received for review February 10, 2010. Accepted June 23, 2010.

AC100381A

analytical chemistry

ARTICLE

pubs.acs.org/ac

# Classification and Source Determination of Medium Petroleum Distillates by Chemometric and Artificial Neural Networks: A Self Organizing Feature Approach

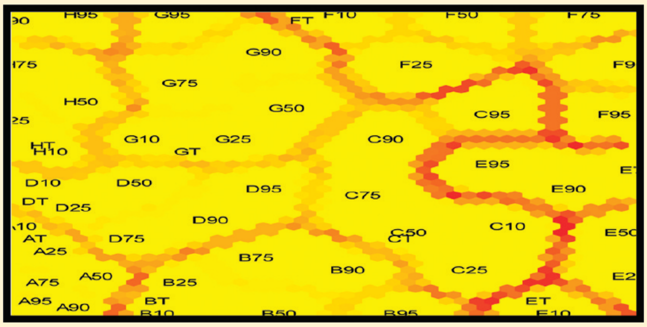
Wan N.S Mat-Desa,[†,‡] Dzulkiflee Ismail,[†,‡] and Niamh NicDaeid[†,*]

[†]Centre for Forensic Science, Department of Pure and Applied Chemistry, University of Strathclyde, 204 George Street, Glasgow G1 1WX

[‡]School of Health Sciences, Universiti Sains Malaysia, Health Campus, 16150 Kubang Kerian, Kelantan, Malaysia

S *Supporting Information*

**ABSTRACT:** Three different medium petroleum distillate (MPD) products (white spirit, paint brush cleaner, and lamp oil) were purchased from commercial stores in Glasgow, Scotland. Samples of 10, 25, 50, 75, 90, and 95% evaporated product were prepared, resulting in 56 samples in total which were analyzed using gas chromatography−mass spectrometry. Data sets from the chromatographic patterns were examined and preprocessed for unsupervised multivariate analyses using principal component analysis (PCA), hierarchical cluster analysis (HCA), and a self organizing feature map (SOFM) artificial neural network. It was revealed that data sets comprised of higher boiling point hydrocarbon compounds provided a good means for the classification of the samples and successfully linked highly weathered samples back to their unevaporated counterpart in every case. The classification abilities of SOFM were further tested and validated for their predictive abilities where one set of weather data in each case was withdrawn from the sample set and used as a test set of the retrained network. This revealed SOFM to be an outstanding mechanism for sample discrimination and linkage over the more conventional PCA and HCA methods often suggested for such data analysis. SOFM also has the advantage of providing additional information through the evaluation of component planes facilitating the investigation of underlying variables that account for the classification.



Ignitable liquids are commonly used as liquid accelerants to assist, increase, and intensify the rate of fire in cases of deliberate fire setting. Subsequent chemical analysis of debris recovered from fire scenes typically involves experimental procedures involving extraction, instrumental analysis and data interpretation in order to classify or possibly identify any ignitable liquid residues which may be present. Chromatographic analysis of ignitable liquids is widely accepted and regarded with GC−MS increasingly recognized as the standard practice.

A classification scheme for ignitable liquids (presented in Table 1) has been defined by the American Society for Testing and Materials (ASTM) and is embodied in ASTM E 1618-06.[1,2] According to this scheme, ignitable liquids are categorized by their chemical composition and boiling point. This leads to classes of products such as gasoline, petroleum distillate products, isoparaffinic products and so on. Each class (excluding gasoline) is further described according to a light, medium or heavy boiling point range.[2]

Medium petroleum distillate (MPD) in particular has been reported in arson cases because of the ready availability of such materials.[3−5] MPD is produced from a straight run distillation of crude petroleum oil and are chemically characterized as a mixture of C8−C13 aliphatic hydrocarbons with a lesser comparative abundance of alicyclic and aromatic hydrocarbons.[6]

Interpretation and classification of such samples are achieved using visual chromatographic pattern comparison against reference samples and associated interrogation of the mass fragmentation of target compounds.[7−13] This is, however, a subjective process, relying heavily on the skill and experience of the analyst. The interpretation can be further complicated by the presence of pyrolysis and combustion products of matrix materials.

**Pattern Recognition.** Pattern recognition refers to all stages of data investigation including problem formulation, data collection, discrimination, and interpretation.[14] The main objective is the classification of a set of objects given a set of associated measurements.[15] This can be achieved by using either an unsupervised or a supervised pattern recognition scheme where the former searches for natural groupings within a given data set and the latter works by assigning the objects into predetermined groups.

The most common pattern recognition techniques reported in the forensic science literature are principal component analysis (PCA) and hierarchical cluster analysis (HCA). Both techniques are based on unsupervised schemes. In this work we introduce a

**Received:** May 21, 2011
**Accepted:** September 15, 2011
**Published:** September 15, 2011

dx.doi.org/10.1021/ac202315y | *Anal. Chem.* 2011, 83, 7745–7754

Table 1. ASTM International Flammable and Combustible Liquid Classification Systems for Forensic Fire Debris Analysis Showing Class and Subclass Examples

| class name | light (C4−C9) | medium (C8−C13) | heavy (C8−C20) |
|---|---|---|---|
| gasoline/petrol | fresh gasoline typically falls in the range of C4−C12, including gasohol | | |
| petroleum distillates | lighter fuels | charcoal starters, white spirit | Diesel, kerosene |
| isoparaffinic products | aviation gas | copier toners | Specialty solvents |
| aromatic products | xylene/toluene | fuel additives | Cleaning solvents |
| naphthenic/paraffinic products | solvents | lamp oils | Copier toners |
| normal alkane products | pentane | candle oils | |
| oxygenated solvents | alcohols/ketones | industrial solvents | |
| other/miscellaneous | | turpentine | |

different means of undertaking data analysis facilitated by the application of artificial neural network (ANN) analysis. Although such methods have been known for almost 30 years,[16] they have found limited applications in forensic science particularly the application of self organizing feature map (SOFM) which we advocate has enormous potential in the field.

*Principal Component Analysis (PCA).* PCA is a means of identifying patterns in data which highlights their similarities and differences.[17] The original data set is described using new variables known as principal components (PCs), which are derived from linear combinations of the original variables with specific loadings for each principal component. A score plot of the first two PCs is most commonly used to display the cluster outcomes of a given data set where samples having similar scores are positioned closely together. This plot provides an important means of visualizing and summarizing the original data set and often reveals patterns that were previously elusive.

*Hierarchical Cluster Analysis (HCA).* HCA uses either agglomerative or divisive methods to identify clusters in a given data set. In the agglomerative method,[17,18] clustering begins with all observations being separate, each forming its own cluster. In the first step, two samples or objects which have close proximity are linked together. In the next step, either a third object is linked to the first set, or another two objects join together into a different cluster. This process continues until all clusters are joined into one large group. In the divisive method, all observations are considered as one large group and successively divided into smaller groups until each group contains only one sample.[17,18] The outcomes of HCA are visualized graphically by a two-dimensional tree diagram known as dendrogram.

*Self Organizing Feature Maps (SOFM).* Self organizing feature maps (SOFM), also known as Kohonen Neural Networks (Kohonen-NN) are an unsupervised neural network. SOFM architecture consists of an input layer and an output layer where each layer is made up of neurons. The input layer is the receiving point for a given data set and displays the arrangement of variables within the data set in an object or sample space. The neurons in the input layer are fully connected to neurons in the output layer and each neuron connection is given a weight which is iteratively adjusted (by means of a learning algorithm) to determine the final arrangement or output of the variables on the output neurons.

The output layer or output map is a powerful means of visualizing complex multidimensional data with a clever use of spatial arrangement and color coding that presents general clustering inherent within the data set. Apart from the output map, there are other multiple visualization methods offered by SOFM depending on what information is acquired, for example various types of distance matrix maps, 2D and 3D projections of hit histograms and the individual component planes associated with each input variable.[19,20] Multiple visualization techniques allow the analyst to view the results in a variety of perspectives increasing the interpretative value of the data. The distance matrix provides a general idea of any trends within the data set and the component plane facilitates the examination of the characteristics of the clusters and explores the correlation between the variables within the data set.[20,21] Furthermore, the SOFM matrix is trained using a training set to correctly classify the members of that set. Once trained, the ability of the specific SOFM algorithm to correctly classify novel samples can be revealed and validated by using a test set of known data.

Table 2. MPD Samples of Different Types and Brands Analysed in This Study

| code | sample | sample name |
|---|---|---|
| A | BQWS | B&Q White Spirit |
| B | BLWS | Bertoline White Spirit |
| C | HWS | Home Base White Spirit |
| D | TWS | Tesco White Spirit |
| E | ADLO | After Dark Lamp Oil |
| F | BLO | Bertoline Lamp Oil |
| G | HBC | Home Base Brush Cleaner |
| H | PBC | Poly Cell Brush Cleaner |

The aim of this study was to classify different brands of MPD samples collected from retail outlets within a relatively small geographical area and space of time. Using the chromatographic patterns generated from these samples and a series of evaporated standards prepared from them, the applicability of unsupervised pattern recognition techniques using PCA, HCA, and an SOFM neural network to classify samples from a similar ignitable liquid subclass has been evaluated. The potential of linking samples that have undergone compositional change (through evaporation) to their fresh counterpart was also examined. The potential of using the component maps derived from the SOFM results to investigate which specific variables were responsible for clustering the given data set is also be demonstrated and discussed.

## ■ METHODOLOGY

**Chemicals and Materials.** Eight medium petroleum distillate products were purchased locally from and included white spirit, paint brush cleaner and lamp oil of different brands. Each liquid was given a code to facilitate data interpretation and the codes are defined in Table 2.

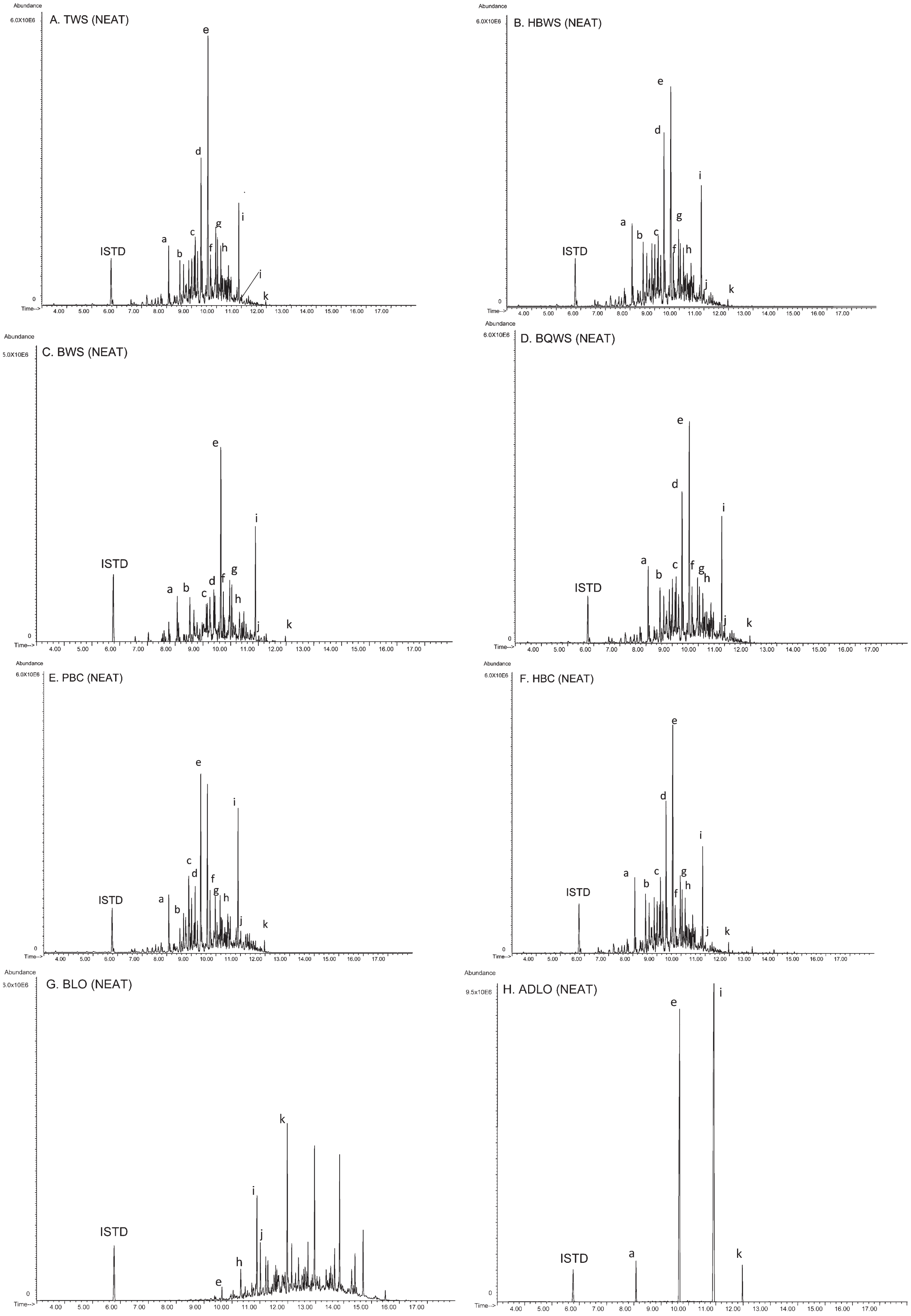


Figure 1. TICs pattern of neat (unevaporated) MPD samples. Samples acronym is listed as in Table 2.

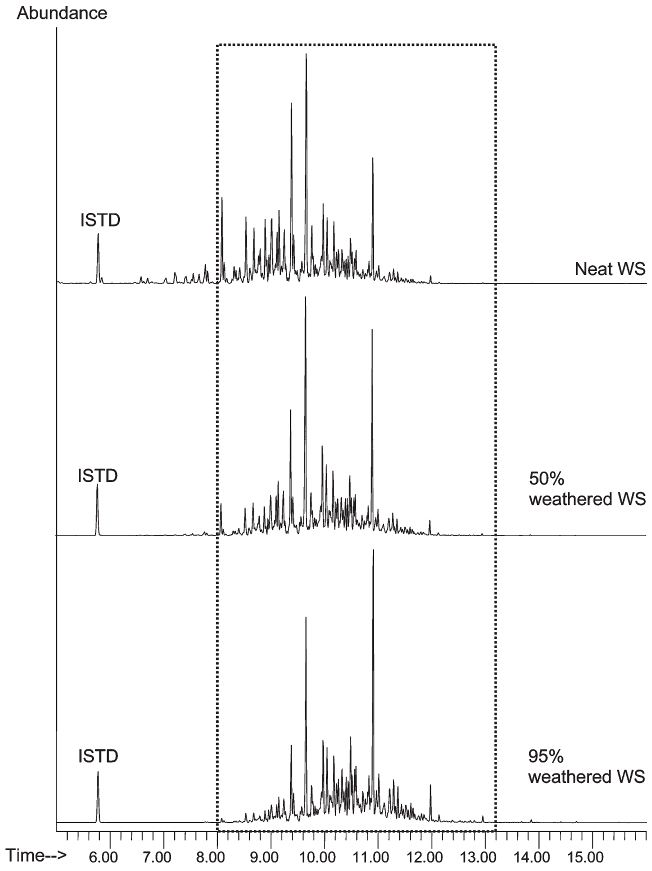


**Figure 2.** Chromatographic pattern of fresh to highly weathered MPD using white spirit as an example. Identified peaks are the characteristic compounds which were listed as target compounds for MPD class.[2] Partial chromatographic profile (in boxed area) showed the peaks selected for multivariate analysis.

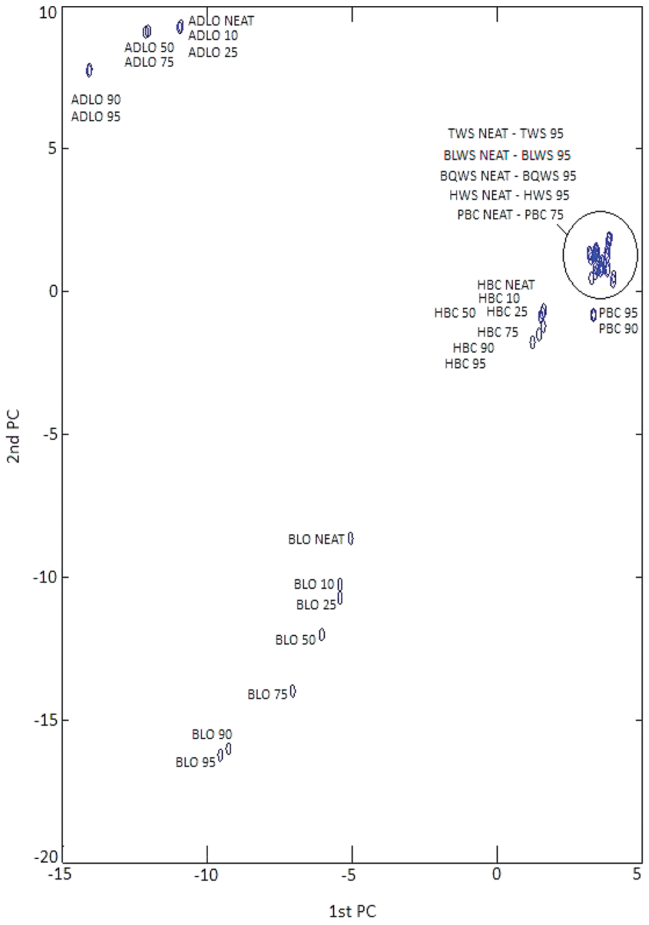


**Figure 3.** PCA score plot of MPD samples. PC1 and PC2 explain 55.6% of total variance in the data set.

For each sample, a set of evaporated products were generated. This was achieved by gently heating 100 mL of the appropriate MPD fluid and removing a sub sample at specific intervals when the original liquid had been reduced by 10, 25, 50, 75, 90, and 95 mL in volume. This produced a set of partially evaporated samples for each liquid at approximately 10, 25, 50, 75, 90, and 95% evaporation, providing 56 samples in total. Samples were placed in glass vials, capped using aluminum foil and tightly sealed with screw caps. All samples were stored in darkness at room temperature until analyzed. Prior to GC−MS analyses, an aliquot of each sample (0.2 mL) was diluted in pentane (100 mL, HPLC grade, WVR International) containing 0.5 mg/mL Tetrachloroethylene internal standard (Sigma Aldrich, >99%) to produce a 2% analytical sample as described in previous work.[22] All samples were prepared immediately prior to analysis using the same LOT number of Pentane and by the same operator in order to minimize any potential influence on the analytical results. Samples were prepared in class A volumetric glassware and subsequently transferred to certified clear vials fitted with Red PTFE/white silicone septa and screw caps (both from Agilent Technologies, UK)

**Instrumentation.** The GCMS instrument used was an Agilent 6890 gas chromatograph (Agilent Technologies Incorporated, Palo Alto, California), mass spectrometer model 5973, Agilent ALS G2614A autosampler, and a 7683 Series injector. Data acquisitions were performed by MS ChemStation (version B.00.01, Hewlett-Packard, Agilent Technologies). Chromatographic separation was achieved using a DB1-MS fused silica capillary column (25.0 m x 0.20 mm i.d. x 0.33 $\mu$m film thickness). The injection port temperature was set at 250 °C and the oven temperature was set at 40 °C for 5 min and ramped at a rate of 15 °C/min to 280 °C, and maintained at this temperature for 2 min. Helium was used as the carrier gas and was maintained at a constant flow rate of 1 mL/min. The temperatures of the ion source and the quadrupole were set at 150 and 280 °C respectively. The MS analyses were performed at full scan mode (from 30 to 300 amu) with a two minutes solvent delay. Each sample was analyzed in triplicate with a blank (pentane) analyzed in between each sample. The injection volume for each sample was 1 $\mu$L with a 20:1 split ratio and the injection needle was programmed to flush out both before and after each injection three times with two independent wash samples of the same pentane used in the blank .

**Data Collection and Preprocessing.** Total ion chromatograms (TICs) of the 56 samples were manually aligned and visually compared for peak selection as detailed in previous studies.[22] The criteria used for peak selection were prominent peaks of matching retention time yielding a relative standard deviation of less than 5% on triplicate analysis. A total of 85 components based on those criteria were selected as variables from the fresh and evaporated MPD samples. Compound identification

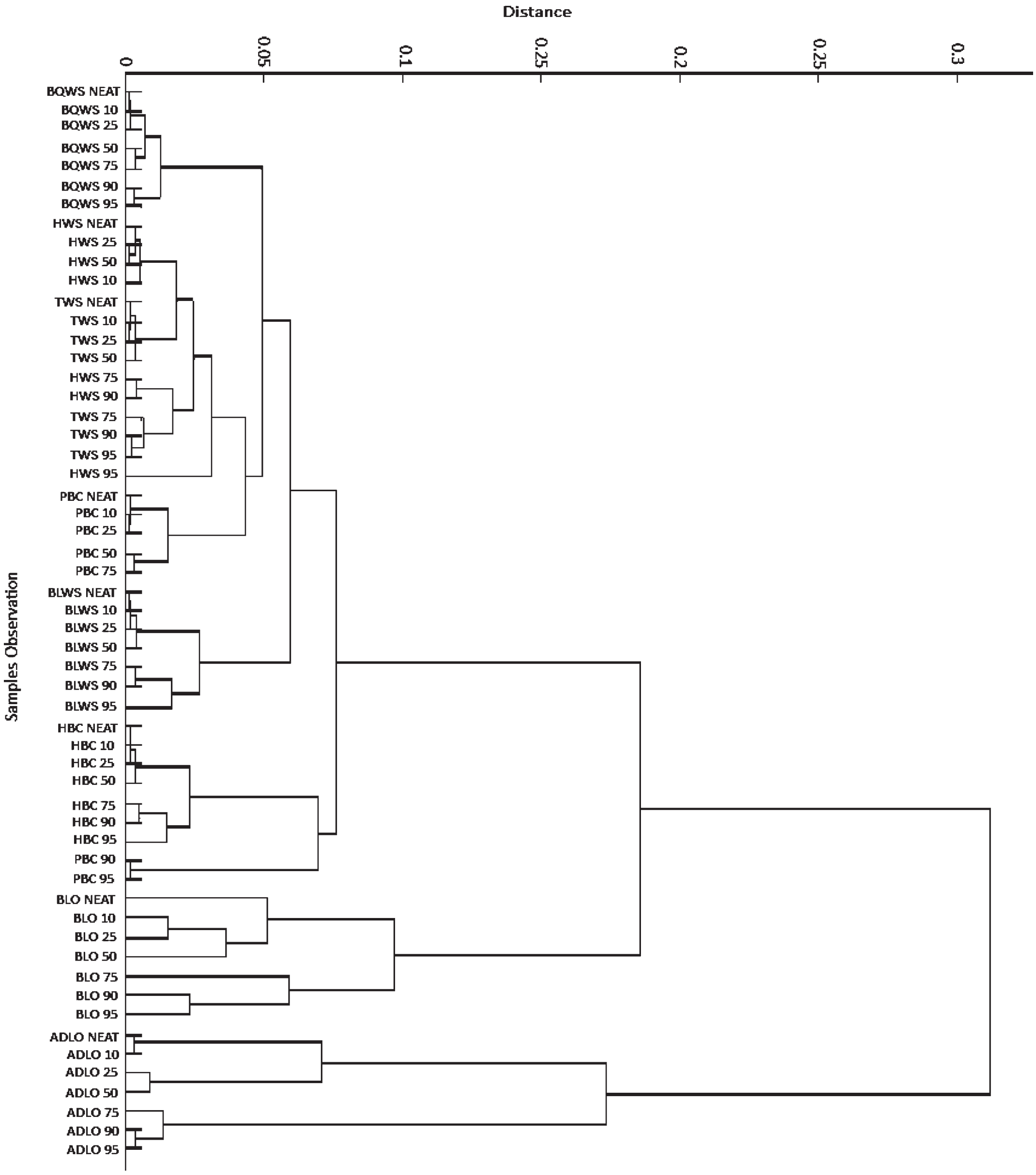


**Figure 4.** Dendrogram of HCA analysis for MPD samples.

was obtained by matching the mass spectra of the sample peak with a NIST08 mass spectral library database (NIST mass spectrometry database V.2.0f, Gaithersburg, MD)[23] and are listed in Table S1 of the Supporting Information.

Peak response data was acquired as comma separated value (CSV) files and converted into an Excel (version 10) spreadsheet for ease of use. Any missing components were given a zero value. The peak area response in all data sets were normalized against the internal standard to eliminate instrumental errors. Further data preprocessing was undertaken by applying a sixteenth root power transformation and row scaling to a range of [0,1] to the data sets to minimize the influence of larger peak areas over smaller peaks.[24]

*Data analysis.* The resultant data sets were inputted to MATLAB 2008a (version 7.6, Mathwork Inc.) where PCA and HCA were performed. SOFM-artificial neural network analysis was performed using Viscovery SOMine software (version 5.0.2, Viscovery Software GmbH).[25]

*PCA and HCA.* PCA was performed with varimax rotation enabled. Hierarchical cluster analysis was undertaken using Euclidean Distance as the proximity measure and Complete Linkage as the amalgamation strategy.

*SOFM.* An output map utilizing the distance matrix technique best demonstrates clusters on SOFM. In this study, we employed a unified distance matrix (U-matrix) output map which becomes more transparent as it shows the similarity of a unit to its neighbor thus revealing clusters within the data set. In the validation phase of this work 40 iterative cycles were used.

## ■ RESULTS AND DISCUSSION

**Chromatographic Analysis.** Visual examination of the chromatographic profiles of the samples are presented in Figure 1 and demonstrate typical patterns for medium petroleum distillates products such as white spirit, paint brush cleaner and lamp oil.[26]

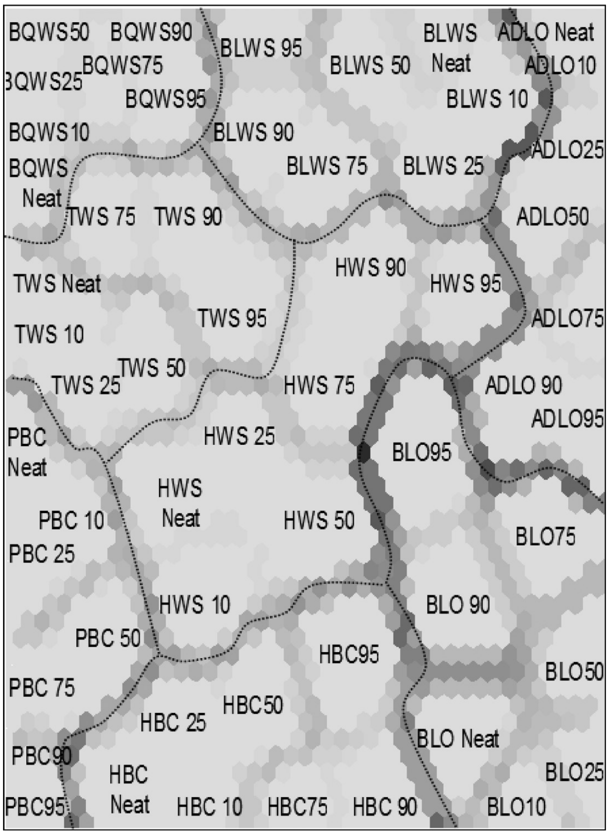


**Figure 5.** U-matrix output map of MPD samples. Dotted lines are drawn to emphasize the boundaries between the samples.

Apart from After Dark Lamp Oil (ADLO) and Bertoline Lamp Oil (BLO) samples, both of which are lamp oils, similar chromatographic profiles were evident between paint brush cleaner and white spirit. Both lamp oils were included in the overall sample set as these liquids are widely regarded as members of the medium petroleum distillate class within the United Kingdom, even though they are predominantly *n*-alkane products. Their inclusion also provided a means of testing the clustering abilities of the statistical approaches employed.

Ignitable liquids, including MPD generally undergo compositional changes when thermally degraded or aged. An example of the effect of white spirit evaporation is clearly demonstrated in Figure 2.

The identification of target compounds within a sample in tandem with mass fragmentation data is used to characterize a particular sample to its class.[10,13,27,28] Thirteen target compounds have been listed specifically for MPD samples as described by ASTM 1618−06, and the majority of these samples were incorporated into the generated data matrix. As the evaporation progresses, lower boiling point hydrocarbon compounds diminish and higher boiling point hydrocarbon compounds begin to predominate with a higher relative abundance. The effect of gradual evaporation on similar samples was examined further by employing a partial selection approach on the chromatographic profiles in order to reduce the number of zero values in the data matrix. This was completed by manually selecting consistent chromatographic peaks, that is, peaks that were present in all samples within a brand (fresh samples through to the most weathered sample). This resulted in the selection of chromatographic peaks from 8.00 min and above (see Figure 2) which were used to construct the data matrix for PCA, HCA and SOFM analysis. This produced a data matrix of 56 × 85 variables for subsequent data preprocessing and mathematical analysis.

**Multivariate Analysis.** *PCA Results.* The plot of the first versus second principal component (accounting for 56% of the total variance) is displayed in Figure 3. BLO, ADLO, and HBC were successfully discriminated however TWS, BWS, BQWS, HWS and PBC combined into one larger convoluted cluster. Within the BLO, ADLO, and HBC cluster, samples are closely arranged according to their degree of weathering. This is illustrated in Figure 3.

*HCA Results.* The HCA dendrogram is revealed in Figure 4. Samples of BQWS, BWS, BLO, and ADLO were successfully grouped and linked close to each other. HCA however, failed to link all HWS and PBC samples and those with a higher degree of weathering were linked to the TWS and HBC cluster respectively.

*SOFM Results.* In Figure 5, very distinctive clustering of MPD samples is shown where the samples are clustered according to both their type and brand in every case.

The representation of the samples is clear and can be easily interpreted. The intensity of the borders between units signifies the level of similarity of the unit with its neighbor and is particularly obvious with the lamp oil samples (ADLO and BLO) as would be expected given that they are medium range normal alkane products. The white spirits samples are clustered on the upper left and central part of the map whereas the paint brush cleaner samples are clustered together at the lower portion of the output map. Vague borders within the units from the same brand are inevitable and signify the compositional changes that have occurred as the sample has weathered. The results also suggest that, even though there have been some substantial changes in the chromatographic pattern due to sample weathering, samples with a common origin still share sufficient features, and are consequently clustered together using SOFM. This information is particularly useful when one tries to relate MPD residues to their original product source.

Associated with the output map are component maps whose number corresponds to the number of input variables of the given data set. Unlike the output map which only shows a general distribution of the objects/variables of the given data set, the component map demonstrates the relationship (both linear and nonlinear) of the variables in the given data set and can be use to find the variables which demonstrate the most significant groupings. Data obtained from component maps may allow detailed comparisons of MPDs of differing types as well as comparisons between brands.

In the component maps, hexagons represent each neuron and their position remains unchanged from one component map to another. Using this technique, the interpretation of variables is normally accomplished by shading the hexagons within the component maps according to the intensity of the weights.[20,21,29] Color coding (below each component map), for example in Figure 5, reveals the relationships between the variables and its associated weight for a particular neuron. Blue indicates a small weight (which can also mean absence); red indicates a large weight (presence) while intermediate colors on the color bar, such as green and yellow, indicate intermediate weights. For the MPDs, 85 component maps were available which corresponded to the 85 variables in the data set. In Figure 6 we briefly highlight some of the crucial component maps as examples of those that

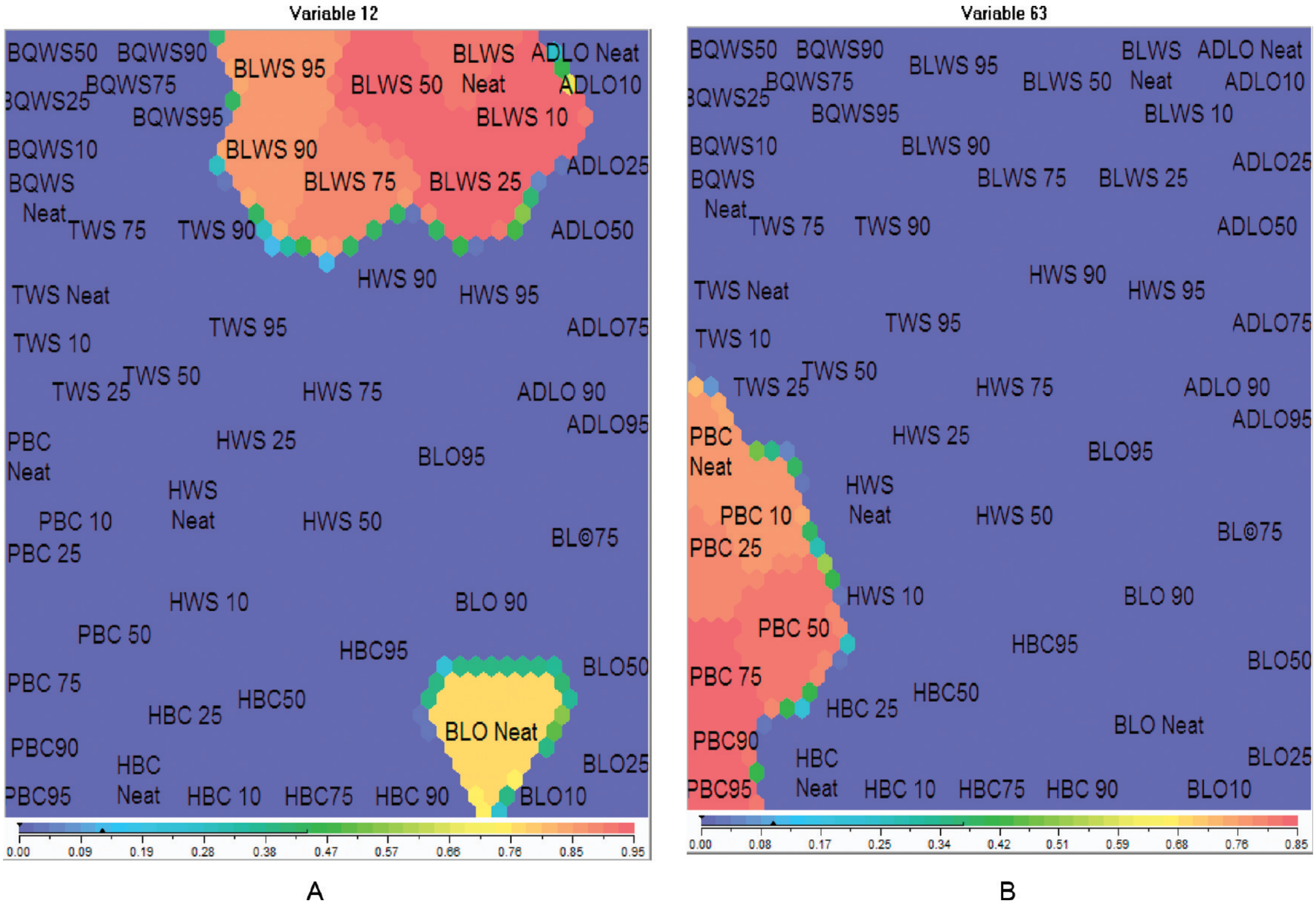


**Figure 6.** TICs of neat, 50% and 95% weathered MPD samples illustrating the visualization of the component map for representative variables for example variable 12 (*n*-propylbenzene) and variable 63 (2,6-dimethylundecane).

best define the characteristics of the MPD samples in order to demonstrate SOFM clustering.

Figure 6A reveals the distribution of variable 12 (identified as *n*-propylbenzene) which can be used to characterize the BLWS samples. The red to orange color indicates higher values of *n*-propylbenzene within the BLWS samples as opposed to other samples coded in blue. It also shows that this compound is present to a greater degree (indicated by the yellow color) in the BLO neat sample but diminishes and is no longer detected as the sample progressively weathers. PBC can be distinguished from the rest of the MPDs by the presence of variable 63 (2,6-dimethylundecane) in high amounts indicated by the red color which covers only the PBC region in Figure 6B.

Figure 7A demonstrates the distribution of variable 31 (2,5-dimethylethyl benzene). The compound is present at higher values in the white spirit and paint brush cleaner samples relative to the lamp oil samples. The intense blue color covering the BLO region indicates lower values or the absence of the compound in these samples. BLO can be further distinguished from the rest of the MPDs by the obvious presence of *n*-dodecane (Figure 7B). Further distinguishing data is shown in Figure 7C where the presence of 2,6,7-trimethyldecane in HBC and BLO samples, and the absence of *n*-dodecane in HBC distinguishes the samples from each other.

In Figure 7D, the lower values or absence of the 2-phenyl-2-methylbutane compound can be seen in both the BQWS and ADLO samples. This has discriminated the BQWS brand from the other white spirit brands and the other MPD samples. By observing the component maps closely (for example in Figure 7D), the relationship between the abundance of this compound and the degree of evaporation is evident. As the weathering progresses, the compound has increased in abundance for TWS, HWS, BLWS, PBC, and HBC samples and decreased for the BLO samples.

*Validation of the SOFM Approach.* One of the critical issues in the use of neural networks as opposed to simple multivariate clustering techniques such as HCA and PCA is the validation of the method. This is particularly important when utilizing the technique for classification based upon pattern recognition as in this case. The SOFM algorithm requires to be optimized or trained for a particular set of inputs. In order to further expose both the predictive nature of the SOFM approach as well as provide reassurance that unknown samples would indeed cluster within their source group, a second set of SOFM calculations were undertaken.

In this case a bespoke training set consisting of all samples in the database with the exclusion of a test set of data were used to produce the predictive algorithm. For example, where the neat samples were used to test the system, the SOFM network was trained with all of the weathered samples and none of the unweathered samples from all of the MPD sources examined. The unweathered samples were then introduced into the SOFM

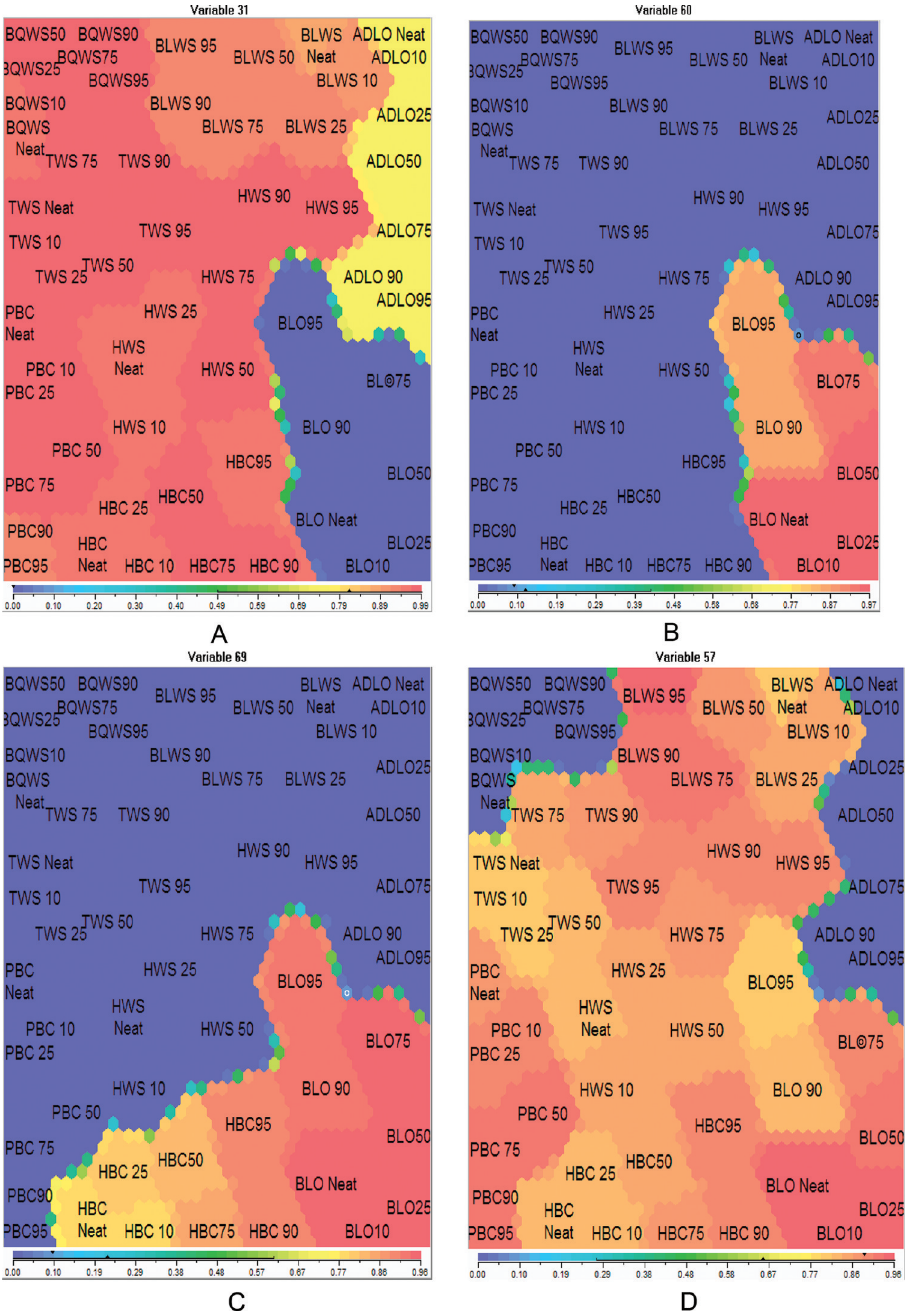


**Figure 7.** Visualization of the component map for 7A: variable 31 (2,5-Dimethylethyl benzene), 7B: variable 60 (*n*-dodecane), 7C: variable 69 (2,6,7-trimethyldecane) and 7D: variable 57 (2-phenyl-2-methylbutane respectively).

**Table 3. Training Strategy Devised to Determine the Predictive Abilities of the SOFM Network**

| set | training set | test set |
|---|---|---|
| neat | all samples except neat | neat sample |
| 10% | all samples except 10% weathered | 10% weathered |
| 25% | all samples except 25% weathered | 25% weathered |
| 50% | all samples except 50% weathered | 50% weathered |
| 70% | all samples except 75% weathered | 75% weathered |
| 90% | all samples except 90% weathered | 90% weathered |
| 95% | all samples except 95% weathered | 95% weathered |

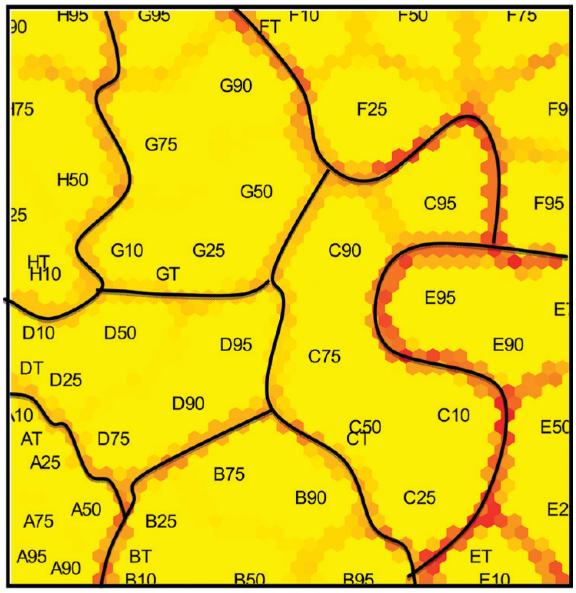


**Figure 8.** Visualization of the component map for the correct association of the neat samples to their weathered group by brand. (NB the coded labels as presented in Table 2 are used for clarity).

network as a test set and the samples classified into the output layer. The training strategy is exposed in Table 3 and an example output revealed in Figure 8. The complete set of outputs for each validation set is presented in the Supporting Information.

In each case and for each sample set tested the SOFM network completely resolved the samples by brand. This clearly demonstrates the powerful potential for SOFM neural networks to provide brand association of even heavily evaporated medium petroleum distillates.

## ■ CONCLUSIONS

In this study, SOFM accurately classified fresh and progressively weathered MPD samples according to type and brand on the basis of GC—MS descriptors. Variable selection and preparation of the data set was crucial to ensure success in the multivariate analysis. This facilitated the successful classification of samples using SOFM even when there was a significant change in the chromatographic profiles. Manual peak comparison and examination of mass spectra for peak selection was carried out and was sufficient for the data analysis undertaken. Although this process is relatively slow and automated peak alignment can be considered for future work, it has demonstrated impressive classification results with the SOFM approach exceeding that of either PCA or HCA in sample linkage. Selective introduction of portions of the data set novel to a trained SOFM model correctly assigned the test set and demonstrated the required validation of the approach.

SOFM presents a viable mathematical technique for linking highly weathered MPD back to its original sample type and brand providing a clustering capability which is both robust and transparent. Moreover, SOFM benefits from the availability of a number of visualization techniques which are particularly useful in revealing the correlations between variables that characterized the grouping. This study has presented a potentially useful method for ignitable liquid identification which can be implemented into an ignitable liquid analysis regime.

## ■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*Phone: + 44-141-5484700; fax: +44-141-5482532; e-mail: n.nicdaeid@strath.ac.uk.

## ■ ACKNOWLEDGMENT

We acknowledge the Ministry of Higher Education of Malaysia (SLAB Grant) which provided studentships for Wan N.S Mat Desa.

## ■ REFERENCES

(1) American Society for Testing and Materials Method E1387-01. In *Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography*; , American Society for Testing and Materials: West Conshohocken, PA, 2001.

(2) American Society for Testing and Materials Method E1618- 01. In *Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry*; American Society for Testing and Materials: West Conshohocken, PA, 2001.

(3) Tranthim-Fryer, D. J. *J. Forensic Sci.* **1990**, *35* (2), 271–280.

(4) Jackowski, J. P. *J. Forensic Sci.* **1997**, *42* (5), 828–832.

(5) http://www.hamilton-co.org/coroner/ARSON%202006.htm (accessed May 1, 2010).

(6) Larsen, P. B. 1996. Retrieved May 28, 2009 from http://www.inchem.org/documents/ehc/ehc/ehc187.htm (accessed May 28, 2009).

(7) Almirall, J. R.; Furton, K. G. *Analysis and interpretation of Fire Scene Evidence*; CRC Press: Boca Raton, FL, 2004.

(8) Newman, R.; Gilbert, M.; Lothridge, K. *GC-MS Guide to Ignitable Liquids*; CRC Press: Boca Raton, FL, 1998.

(9) Vella, A. J. *J. Forensic Sci. Soc.* **1992**, *32*, 131–142.

(10) Nowicki, J. *J. Forensic Sci.* **1990**, *35*, 1064–1086.

(11) Nowicki, J. *J. Forensic Sci.* **1991**, *36*, 1536–1550.

(12) Lennard, C.; Rochaix, V. T.; Margot, P.; Huber, K. *Sci. Justice* **1995**, *35*, 19–30.

(13) Keto, R.; Wineman, P. L. *Anal. Chem.* **1991**, *63*, 1964–1971.

(14) Webb, A. *Statistical Pattern Recognition*, 2nd ed.; John Wiley and Sons Ltd.: West Sussex, 2002.

(15) Lavine, B. K. *Anal. Chem.* **2000**, *72*, 91R–97R.

(16) Wasserman, P. D. *Neural Computing Theory and Practice*; Von Nostrand Reinhold: New York, 1989.

(17) Everitt, B. S.; Dunn, G. *Applied Multivariate Data Analysis*; Arnold: London, 2001.

(18) Everitt, B. *Cluster Analysis*. 3rd ed. ed.; Arnold: London, 1993.

(19) Kohonen, T. *Self-Organising Maps*; Springer-Verlag: Heidelberg, 1995.

(20) Vesanto, J. *Intell. Data Anal.* **1999**, *3*, 111–126.

(21) Lloyd, G. R.; Wongravee, K.; Silwood, C. J. L.; Grootveld, M.; Brereton, R. G. *Chemom. Intell. Lab. Sys.* **2009**, *98*, 149–161.

(22) MatDesa, W. N. S.; NicDaeid, N.; Ismail, D.; Savage, K. *Anal. Chem.* **2010**, *82*, 6395–6400.

(23) *NIST/EPA/NIH Mass Spectral Library (NIST 08) and NIST Mass Spectral Search Program (Version 2.0f)*; U.S. Department of Commerce, National Institute of Standards and Technology (NIST), Standard Reference Data Program: Gaithersburg, MD, 2008.

(24) Brereton, R. G. *Chemometrics for Pattern Recognition*; John Wiley and Sons: West Sussex, 2009.

(25) VSOMine5. *Viscovery SOMine User's Manual*, Ver. 5.0.2; Viscovery SOMine.Ink Gmb H, 2008.

(26) Stauffer, E.; Dolan, J. A.; Newman, R. *Fire Debris Analysis*; Academic Press: Burlington, 2008.

(27) Sandercock, P. M. L.; Pasquier, E. D. *Forensic Sci. Int.* **2003**, *134*, 1–10.

(28) Frank, H. A. *J. Forensic Sci. Soc.* **1980**, *20*, 285–292.

(29) Fei, B. K. L.; Eloff, J. H. P.; Oliver, M. S.; Venter, H. S. *Forensic Sci. Int.* **2006**, *162*, 33–37.

(30) Einax, J. W.; Zwanziger, H. W.; Geiss, S. *Chemometric in Environmental Analysis*; VCH: Weinheim, 1997.