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# Environmental Forensics of Coal Tar using Two Dimensional Gas Chromatography Time-of-Flight Mass Spectrometry (GCxGC-TOFMS)

A Thesis presented for the Degree of
Doctor of Philosophy
By

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Declaration
‘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

Coal tars are complex mixtures of inorganic and organic compounds, which are dominated by PAHs and were produced as a by-product of the former manufactured gas industry. Forensic analysis of coal tar samples was carried out using two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC-TOFMS).

This thesis first presents the application of existing multivariate statistical models developed using UK tar samples to tar samples from the USA as well as identifying 947 individual compounds present within the tars. This has important implications as this study demonstrated that statistical methods developed using UK tar samples can be successfully applied to non-UK tars. The thesis then presents the application of post extraction derivitisation to a creosote samples allowing for the detection of 255 compounds, the majority of which would not be detected without derivitisation. The analysis also detected 1505 individual compounds within the Creosote and provides the most comprehensive list of compounds detected within Creosote that has been produced. The analysis was also able to suggest the production process for the tar from which the Creosote was distilled. The use of both derivitisation and GCxGC were vital in providing this forensic information.

The thesis then presents the analysis of 16 tar samples using GCxGC and post extraction derivitisation and the production of a database of 2373 individual compounds detected within the tar samples. The study showed that 163 individual compounds were present within all tar samples regardless of the production process used. This has important implications as environmental assessment usually focuses on a limited number of compounds, which could be expanded using the database presented within this thesis. Finally the thesis presented a study that analysed a sample of Pintsch Gas tar, which has never previously been analysed using a mass spectrometer and produced a unique dataset.

## Acknowledgements

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## Preface

The main body of this thesis consists of four self-contained chapters written in the form of journal publications with their own introductions, methodology, results, discussions and conclusions. Each chapter has been written with the intent of publishing the content in peer-reviewed journals. Each chapter also contains bridging text to link the individual chapters together. The chapters intended for publication include:

Chapter 4

Gallacher, C., Thomas, R., Hatheway, A., Lord, R., Kalin, R.M., (2016). Ultra Resolution Chemical Fingerprinting for Source Reconstruction of a Complex Former Manufactured Gas Plant DNAPL Waste. Target journal – Environmental Forensics

Chapter 5

Gallacher, C., Thomas, R., Taylor, C., Lord, R., Kalin, R.M., (2016). Qualitative and Quantitative analysis of a highly weathered derivatized Creosote by comprehensive two-dimensional gas chromatography. Target journal – Chemosphere

Chapter 6

Gallacher, C., Thomas, R., Taylor, C., Lord, R., Kalin, R.M., (2016). Comprehensive database of Manufactured Gas Plant tars – Part A Database

Gallacher, C., Thomas, R., Taylor, C., Lord, R., Kalin, R.M., (2016). Comprehensive database of Manufactured Gas Plant tars – Part B Aliphatic and Aromatic compounds

Gallacher, C., Thomas, R., Taylor, C., Lord, R., Kalin, R.M., (2016). Comprehensive database of Manufactured Gas Plant tars – Part C Heterocyclic and hydroxylated PAHs

Target journal – All 3 papers are intended for publication within the journal of rapid communications in mass spectrometry as a 3 part series.

Chapter 7

Gallacher, C., Thomas, R., van Leeuwen, J.A., Lord, R., Kalin, R.M., (2016). Qualitative analysis of a Pintsch Gas Tar using comprehensive two-dimensional gas chromatography. Target Journal – Environmental Science & Technology

In addition the following conference presentations have resulted from this work:

Oral Presentations:

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Poster Presentations:

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Gallacher, C., Thomas, R., Kalin, R.M., (2013). *Environmental Forensics of Coal Tars – Development of new analytical techniques*. Scottish Contaminated Land Forum 2013, Glasgow, UK

Gallacher, C., Thomas, R., Kalin, R.M., (2013). *Environmental Forensics of Coal Tars – Development of new analytical techniques*. 6th Scottish Symposium of Environmental Analytical Chemistry, Glasgow, UK

Gallacher, C., Thomas, R., Kalin, R.M., (2014). *Coal Tar Contaminated Land: Can You Tell the Difference?* Faculty Research Presentation day 2014, Glasgow, UK

Gallacher, C., Thomas, R., Kalin, R.M., (2014). *Coal Tar Contaminated Land: Can You Tell the Difference?* University Research Presentation day 2014, Glasgow, UK

Gallacher, C., Thomas, R., Kalin, R.M., (2014). *Coal Tar Contaminated Land: Can You Tell the Difference?* 8th Annual Environmental and Clean Technology Conference 2014, Glasgow, UK

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# Contents

## Chapter 1 - Introduction

Paper A - Comprehensive database of Manufactured Gas Plant tars – Part A Database

Paper B - Comprehensive database of Manufactured Gas Plant tars – Part B Aliphatic and Aromatic compounds

Paper C - Comprehensive database of Manufactured Gas Plant tars – Part C Heterocyclic and hydroxylated PAHs

Paper - Qualitative analysis of a Pintsch Gas Tar using comprehensive two-dimensional gas chromatography

Thesis Database – A spreadsheet database of all the compound detected with all samples analysed

Thesis PCA+HCA dataset – A spreadsheet of the statistical data for all the samples

**List of figures**

**List of Tables**

# Chapter 1

# Introduction

## 1.1 Research Aims and Objectives

The aim of this research project was to refine and further develop existing methods for the chemical fingerprinting of coal tars using GCxGC-TOFMS and produce a comprehensive database of compounds detected within coal tars. The project aims to achieve the following research objectives:

1. To apply existing coal tar GCxGC analysis methods, including multivariate statistical analysis, to samples produced by production processes that have not been previously analysed.
2. The apply existing coal tar GCxGC analysis methods developed using British based coal tars, including multivariate statistical analysis, to tar samples produced from outside of the UK to expand the scope of the methods.
3. The development of a post extraction derivatization method to increase the number of compounds, particularly hydroxylated PAHs, which can be detected within coal tar.
4. The development of a database of compounds present within coal tars and the evaluation of the differences produced by different production processes.
5. The expansion of the existing coal tar database for the multivariate statistical analysis of coal tar and the assessment of the influence of additional samples on data interpretation.

## 1.2 Thesis Outline

This thesis provides details for the refinement of existing analytical methods for the analysis of coal tar as well as the development of new methods for increasing the potential number of compounds that can be detected with the aim of producing a comprehensive database containing as many compounds as possible.

Chapter 2 provides an in depth looks at the literature surrounding coal tar, and the compounds detected within them. The literature review provides information on the different production processes that produced coal tars as well as the compositions of the tars that are produced. The review also provides information about GCxGC-TOFMS as well as an in depth review of the potential organic compounds of interest that may be found within coal tars.

Chapter 3 provides information on all the methods used to produce the data presented within this PhD thesis as well as providing information on the samples and standards used.

Chapter 4 presents a study of the application of multivariate statistical analysis of coal tar samples obtained from the USA using statistical methods developed using UK based tars. The chapter also presents the results of altering the principle component analysis matrix used to produce the results.

Chapter 5 presents a study of the applications of post extraction derivatization on an extract of coal tar in order to increase the number of compounds of interest that can be detected. The chapter also presents an in depth analysis of Creosote, a coal tar distillate, as well as providing information on the potential contamination of the creosote, and other samples, with carbureted water gas tar.

Chapter 6 presents a series of three papers detailing a database of compounds detected within coal tars produced by varying production processes. The first paper provides a full database of the compounds detected within 16 coal tar samples produced by 5 different production processes. The second paper provides in depth analysis of the aliphatic and aromatic content of the tars samples and the third paper provides in depth analysis of the heterocyclic and hydroxylated PAH content of the tar samples. The chapter also provides details of the analysis an Inclined Chamber Plant tar, which is a tar type that has never previously been analysed.

Chapter 7 presents a study of a Pintsch Oil Gas tar, a type of tar that has never been previously analysed, obtained from the Netherlands. An in depth analysis of a Pintsch Gas tar has tar has never been published and no papers have been previously published using GC-MS, or GCxGC-MS to analyse a Pintsch gas tar. The chapter also includes the multivariate statistical analysis of several other samples.

Chapter 8 summarizes the major findings of the PhD projects and suggests recommendations for future work.

# Chapter 2

# Literature Review

## 2.1. Introduction

## 2.1 Introduction

### 2.1.1 Environmental Forensics and Coal Tar

Environmental forensics is the study of the source, release, distribution in the subsurface and fate of contaminants within the environment (Morrison, 2000). There are two separate motivations for environmental forensic study the first of which is from a purely academic research perspective and the second of which is to determine liability in a variety of contexts (Murphy and Morrison, 2007). Within Europe the Environmental Liability Directive 2004/35/EC was created around the concept of the polluter pays principle, which means that the polluter is both liable for the prevention and remediation of environmental damage. The directive defines environmental damage as damage to any natural habitat, protected species, water or soil. In 1980 the US enacted CERCLA (Comprehensive Environmental, Compensation, and Liability Act (Superfund) with the aim to clean up sites contaminated with hazardous substances (Tarr and McMichael, 2015). This law was also based on the polluter pays principle and set up a superfund to pay for the remediation of sites where no responsible party could be identified.

Coal tar waste is a by-product of former manufactured gas plants (FMGP) and coal tar contamination is a common occurrence at FMGP sites. Coal tars are a complex mixture of organic and inorganic compounds, of which many can be toxic or carcinogenic and pose a complex challenge for remediation. China is currently considering coal tar as a potential energy alternative because of dwindling supplies of petroleum (Shi et al, 2012). Potential contamination from the ongoing international coking industry as well as proposed underground coal gasification (UCG) projects are potential modern sources of coal tar and so contamination with coal tar is still an important modern day as well as a historical environmental problem. Environmental forensic analysis of coal tar can be purely academic in focus or can also be to establish legal liability for remediation.

### 2.1.2 **History of Coal Tar production**

Manufactured gas is a process by which solid or liquid fuels, such as coal and oil, are converted into gas. In the US several thousand manufactured gas plants existed between the early 1800's to the 1950's (U.S. EPA, 1993). Estimates of the specific number of US FMGP sites vary widely from 1500 to 50,000 depending on the function of the type of facilities considered (U.S. EPA, 2004). The first EPA survey identified 1500 sites, which mostly included facilities that were members of gas associations (Eng, 1985). Higher estimates are obtained by considering the wide variety of facilities that used coal or coal tar (U.S. EPA, 2004) and it is estimated that substantial amounts of coal tar residuals are expected to be encountered at between 33,010 and 50,308 sites in the US (Hatheway, 2012). It is estimated that 11.5 billion gallons of tar were produced in the U.S. from 1820 to 1950 (Eng, 1985).

Manufactured gas plants were extensively used in the early part of the 20th century to produce gas from coal or oil. In 1812 the first commercial gas works was established in London to provide street lighting (Birak and Miller, 2009). In the US the first commercial gas works was established in Baltimore in 1816 (Birak and Miller, 2009). The gas industry gradually expanded across the entire continental USA, initially using coal as a feedstock but as indigenous oil feedstock and the appropriate technology became more widely available, some regional variations developed (Thomas, 2014). Within the USA FMGP sites exist where only CWG processes existed, this became the trend within North Eastern USA. On the West Coast of the USA, a group of technologies called the 'Pacific Coast Oil Gas Processes' were used to manufacture gas from oil (Thomas, 2014). After World War II the rise in increased availability of American natural gas through the development of national gas transmission pipelines led to a decline in manufactured gas and by the 1960's manufactured gas was essentially obsolete in the U.S (Birak and Miller, 2009).

Manufactured gas was produced in the UK from 1792 until 1981, when the last gasworks in the UK closed, leaving the only current source of tar within the UK as tar produced by the coking industry (Thomas, 2014). The size of gasworks in the UK varied greatly from the hundreds of small country house gasworks to the many large town and city gasworks found in most large towns or cities (Thomas, 2014). By the mid 19th century every town in the UK with a population over 10,000 was lit by gas and many villages also had their own gasworks (Thomas, 2014). For this reason it is estimated that there are more than 3000 (+-1000) former manufactured gas plant sites, with the upper limit likely to be 5000, within the UK (Thomas and Lester, 1994).

The most widely used early retorts were horizontal retorts and were originally circular and made from cast iron, although this was eventually superseded by fireclay and later silica due to the low durability of cast iron (Thomas, 2014) as well as their inability to resist high temperatures and prohibitive costs of replacement (Butterfield, 1904). Early low temperature horizontal retorts (LTHR) were directly heated by a shallow beds of coke lit beneath the furnace. The direct heat radiating from the furnace and the hot waste gases produced were used to heat the retort. These early LTHR only heated the coal within the retort to temperature of around 600°C (Harkins et al, 1988) and as a result the amount of gas produced by LTHR was fairly low and only limited decomposition of organic compounds took place within the tar. This leads to tar being produced during the LTHR process that is similar in nature to the parent coal from which it was produced (Soule, 1922). Later horizontal retort designs (HR) allowed for higher operational temperatures capable of exceeding 1000°C (Butterfield, 1904) and so greater decomposition of the organic compounds within the tar. The larger surface area present within horizontal retorts allowed for a greater opportunity for contact of the gases with the heated retort sides and so allowed for a greater degree of thermal cracking (Young, 1922). Horizontal retorts were primarily D-shaped vessels around 6.7m long, 0.55m wide and 0.45m high in which the coal was heated for a period of between 8 and 12 hours (Thomas, 2014). An example of a Horizontal Retort is shown in figure 2.1.

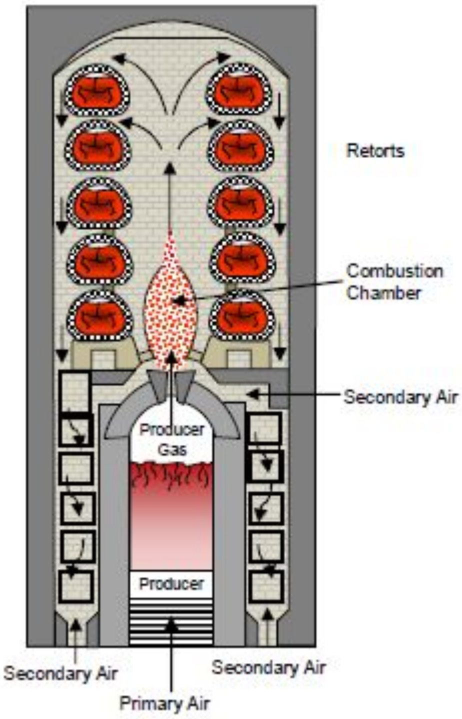


Figure 2.1 – Cross section of a gas-fired Horizontal Retort (Copied from Thomas, 2014)

Vertical retorts (VR) were later developed, which were first patented in 1902 (Thomas, 2014), and rotated the retort by 90$^{o}$ and allowed for the continuous production of gas as coal could be continuously fed into the retort (Thomas, 2014). Vertical retorts generally operated as a high temperature process similar to, but still lower than, horizontal retorts however because of the design of the retort significantly different tars were produced. In a continuous VR the coal was fed down, by gravity, through the retort vessel by gravity and as the coal pass down the retort it was gradually carbonized until it was removed as coke at the base of the retort (Thomas, 2014). The tarry fog generated during the process could also escape vertically up through the coal without carbonizing on the hot surface of the retort and so secondary degradation may be reduced. As the VR process generally operates at a lower temperature than the HR and coke oven (CO) processes and had lower contact time with the retort VR tars contain more paraffins (10%) and tar acids (25%) than CO and HR tars which generally contain only 1-2% paraffins and no more than 10% tar acids (McNeill, 1952). An example of a Vertical Retort is shown in figure 2.2.

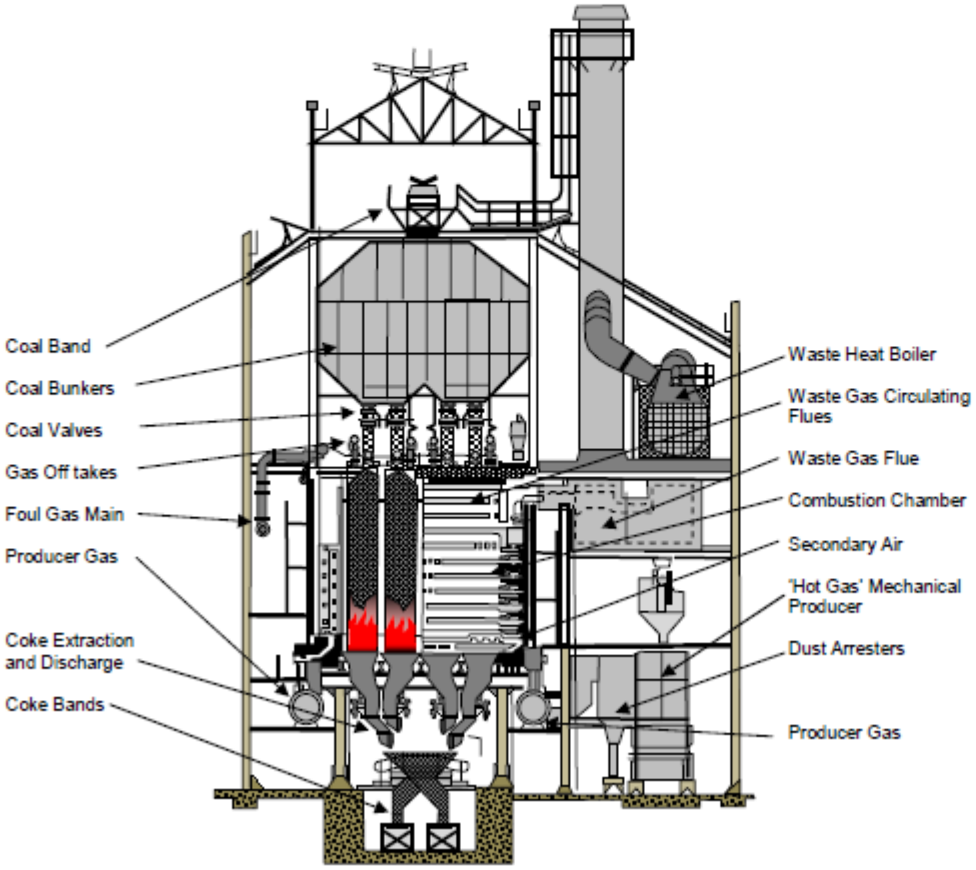


Figure 2.2 – Cross section of a Glover-West vertical retort (Copied from Thomas, 2014)

While coke ovens were of limited importance on gasworks in the UK (Thomas, 2014) they still produced significant amounts of tar. In 1900 the total amount of tar produced in the UK was estimated at 927,000 tons with 692,000 tons in the form of gas-tar and 85,000 in the form of coke-oven tar (Lunge, 1909). In 1901 the total amount of tar produced increased to 965,000 tons with 742,000 tons of gas tar and 95,000 tons of coke-oven tar (Lunge, 1909). Finally in 1902 the total amount of tar produced was 1,033,900 tons with 755,000 tons of gas-tar and 122,000 tons of coke-oven tar (Lunge, 1909). This trend was reversed in Germany with 480,000 tons of tar produced in 1900 with only 180,000 tons of gas-tar and 300,000 tons of coke-oven tar (Lunge, 1909). Estimates of coke oven tar production in the US vary greatly from an estimated 75,000 tons in 1903, 125,000 tons in 1904 and 131,117 tones in 1905 (Lunge, 1909). Another estimate found in Lunge, 1909 provided by a

Dr Kohler is that 300,000 tons of coke oven tar were produced from 2286 United-Otto ovens and 1320 Semet-Solvay ovens although the year for this production is not stated it is significantly higher than the other estimates, but must be from prior to 1909, the year in which Lunge published his book.

Coke ovens were mainly found on iron and steel works and are the only remaining example of coal carbonization within the UK (Thomas, 2014). The temperature of the coke oven has a great influence on the tar produced by coking ovens with coke ovens operating over a wide range of temperatures but roughly falling into two classes. Low temperature coke ovens, <700$^{o}$C, produced tars containing phenolic and heterocyclic nitrogen compounds similar to LTHR tars (Hamper, 2006). High temperature coking ovens operated at temperatures exceeding 700$^{o}$C and produced tars with high PAH content and the conversion of PANHs into ammonia, hydrogen cyanide, pyridine bases and nitrogen (Hamper, 2006). This suggests that the presence of pyridine compounds may be related to the temperature of the coking oven and are a possible forensic marker. As the tar escapes from a coke oven is it forced onto the hot vertical walls and so will have a higher degree of thermal degradation, e.g. cracking, than a HR or VR tar. Metallurgical coke is ideally produced within the temperature range of 900 to 1095$^{o}$C (Lankford et al, 1985)

Other manufactured gas processes were also developed which either used oil as a sole feedstock or added oil into the process to increase gas production. The water gas process involved passing steam over a carbon source (usually heated coke) in order to produce gas (Thomas, 2014). The reaction was extremely endothermic therefore water gas was generally produced by a two-step cyclic process referred to as the run and blow cycle (Harkins, 1988). During the blow stage coke was heated to incandescence by a stream of air and during the run stage steam was injected into the coke. During the run process the fuel would gradually cool due to the endothermic nature of the reaction hence the need for a cyclic process. To improve the calorific and/or illumination value of gas produced by water gas, a spray of oil was introduced to the hot gas steam hence the name Carbureted Water Gas (CWG) (Murphy et al, 2005). The CWG production process can use a variety of solid carbon feedstocks such as coke, anthracite or bituminous coal and initially was carbureted with tar light oils generated at coal gas plants. The normal operational temperature of CWG was between 650°C and 700°C (Hamper, 2006) making it a relatively low temperature process.

The tars produced by CWG plants were largely determined by the feedstock oil used within the production process as water gas without carburation did not produce significant amounts of tar (Hamper, 2006). The primary difference between UK and US CWG plants was the feedstock oils used with UK CWG plants consumed mainly light oils for carburation (Butterfield, 1904), whereas the US tended to use heavier or crude oils, beginning about 1910 because of the increased use of automobiles (Hatheway, 2012). This was especially true in the US after World War I, when light oils such as gasoline were in high demand (Harkins et al, 1988). While coke was generally used as the solid feedstock bituminous coal could also be used. However, the gas producing capacity when using bituminous coal was lower than coke due to uneven heating of the feedstock (Hamper, 2006). Mixing 20% coke into the bituminous coal resulted in gas making capacity equivalent to using coke alone (Furnas, 1942) so it was possible to obtain equivalent gas making capacity with bituminous coal assuming a source of coke was also available. The use of bituminous coal over coke was most likely determined by the economic costs and availability of supply.

Oil gas processes were gas production processes that solely involved the use of oil as a feedstock such as the Pintsch gas process. Pintsch gas was a form of oil gas, which produced distilled naphtha from petroleum or shale oil, and was used extensively in the lighting of railway coached (Egloff and Twomey, 1915) in the late 19th and early 20th century. The overall composition of Pintsch gas varied depending on the temperature of the process and the feedstock oil used to produce the gas with increasing temperatures resulting in higher percentages of benzene and toluene present within the naphtha (Egloff and Twomey, 1915). The process itself operated using a double retort with oil fed continuously in a thin stream into the lower retort falling onto an iron tray (Butterfield, 1904). The oil was vaporized within the lower retort and the vapour passed through the neck of the lower retort into the upper retort and subjected to the high temperatures radiating from the sides of the retort at temperatures up to 1000°C (Butterfield, 1904). The use of a double retort meant that the highest possible temperature acted upon every portion of the vaporized oil, without undue exposure to the heated surface of the retort.

The Hasche (sometime called Koppers-Hasche) process was a gas reforming process developed by Dr. Rudolph Leonard Hasche in the 1950s and was another example of an oil gas process. It provided a synthetic gas manufacturing process, which was very low in investment cost and simplistic in operation. The process converted hydrocarbon gases or vapours (ranging from propane to light naphtha) within a regenerative partial combustion process of high thermal efficiency into a synthetic gas with an energy content similar to natural gas. The process operated at temperatures of between 870ºC and 1455ºC. The Hasche process was particularly popular in Florida (Frink, 1955). As the process use gaseous hydrocarbon as a feedstock it is unlikely that the Hasche process produced significant amounts of tar.

Due to past handling and storage practices it is believed that there is coal tar contamination at most former sites (Brown et al, 2006). The US EPA estimates that release of coal tar or other wastes to the environment is likely to have occurred in over 90% of sites (U.S. EPA, 2004). This means that the forensic analysis of FMGP and other coal tar contaminated sites is important from both a legal and environmental standpoint. The main concern of coal tar contamination is its impact on ground water quality. The equilibrium of the aqueous concentrations of individual PAHs, and other compounds of interest, can be calculated using Raoult's law. This can help give an idea of the possible ground water contamination risks at FMGP sites. However, Birak and Miller, 2009 found that both data and modeling indicate that subsurface tars at FMGPs have aged little. Compositional data also seems to contradict the understanding of aging described by Raoult's law. This specifically applies to naphthalene, the most abundant and most soluble PAH in un-weathered samples, as it is still the most abundant compound in some of the most weathered samples reported in the literature (Birak and Miller, 2009). Birak and

Miller, 2009 suggests the apparent discrepancy may be due to diffusional limitations within the DNAPL phase associated with increasing viscosity.

When DNAPL is spilled into the sub surface it will migrate through the vadose zone and migrate below the water table and can form a deep plume that is a persistent long-term sources of contamination. Although the rate at which contaminant mass transfer in the flowing groundwater takes place is slow the contamination may still pose a risk to human health or the environment (D'Affonseca et al, 2008). D'Affonseca et al. 2008 modeled the long term degradation of coal tar contamination and found that even after 1000 years source depletion of phenanthrene was low with 89% of the original mass still being available. The moderately and sparingly soluble composite constituents were also predicted to have 60% and 98% of the original mass available. These values highlight a key contamination issues of FMGP sites as the coal tar will take an extremely long time to degrade in the environment and can form a long term persistent hazard to human health and the environment.

Coal tar has been used as a feedstock for the chemical industry, such as production of dyes or creosote for wood treatment (McGregor et al, 2012). This adds an additional complication factor when considering coal tar contamination, as it is possible to find coal tar contamination in sites other than FMGPs. By the late 1800's, coal tar was used in the synthesis of a wide array of materials including: dyes, perfumes, explosives, pharmaceuticals and many more (Harkins et al, 1988). Light water-gas tars were used mostly for fuel and road constructions whereas heavy water-gas and oil-gas tars were more difficult to use for these applications due to their variable chemical composition and higher viscosity (Birak and Miller, 2009). Tars that were not sold to refiners were either landfilled or disposed of in open pits (Murphy et al, 2005). This means that there is potential for coal tar contamination at many former landfill sites. From a modern perspective in China coal tar has been considered as a possible energy alternative because of dwindling supplies of petroleum (Shi et al, 2012).

### 2.1.3 Brief overview of composition

Coal tars are a complex mixture of organic and inorganic compounds, of which many can be toxic or carcinogenic and pose a complex challenge for remediation. The organic compounds found on FMGP sites can be divided into three classes that indicate their mechanism of formation and potential sources (Saber et al, 2006): 1) those derived from high-temperature processes such as partial combustion and/or pyrolysis (pyrogenic sources); 2) those derived directly from petroleum, petroleum distillates, or coal (petrogenic sources); and 3) those derived from recent biological transformation of natural organic matter (diagenic sources). Pyrogenic compounds are the organic compounds produced from oxygen-depleted, high-temperature processes such as incomplete combustion or pyrolysis and are primary composed of monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs). Petrogenic compounds originate from petroleum, including fuels, lubricants, and the derivatives of those materials and example of petrogenic compounds include alkanes, isoprenoid hydrocarbons and alkylated PAHs. Diagenic substances include hydrocarbons from recent biological transformations of natural organic matter. Diagenic sources are unlikely to contribute measurably to the levels of PAHs near a FMGP (Saber et al, 2006).

Coal tar composition varies depending on the raw materials and operating temperature of the manufactured gas process used as well as several other factors. A lower operating temperature results in tars containing relatively more acids and heterocyclic compounds (Birak and Miller, 2009). Higher operating temperatures resulted in tars containing more un-substituted aromatic compounds. In Germany and other parts of Europe large quantities of brown coal were available. This type of coal was generally carbonized by low temperature methods not used in the US and produced relatively low-density coal tars with more phenolic compounds and bases (Rhodes, 1966). Tar was produced from the carbonization process and on average was produced equivalent to 5 per cent of the weight of coal carbonized (McNeil, 1952).

The main factors affecting the composition of tar produced during the various production processes are: The temperature of carbonization; The length of carbonization process and the free space within the retort (Forsdike, 1952). Other factors that affect the composition of tar produced include the feedstock used, as well as the quality of any coal/oil used, and the retort type used during the production process. As a general rule the higher the temperature and the greater amount of time that the tar was in contact with the hot surfaces of the retort the greater the degree of aromaticity of the tar (Forsdike, 1952). The influence of free space within the retort results in light oils being found in HR tars to a far greater degree than other production processes, most likely due to the greater amount of cracking and the greater proportion of free space within the retort (Forsdike, 1952). The amount of free space within a HR changed over time as technologies improved leading to decreases in free space and increases in the paraffin (alkane) content of tars (Forsdike, 1952). This suggests that HR tars may be expected to contain more alkanes than LTHR tars as LTHR tars were likely produced within retorts with a higher degree of free space, although this would be dependent on when exactly the higher temperature HR tar was produced.

The various different production processes used produced tars with different chemical signatures. For example, the naphtha fraction of VR tars contained relatively more paraffin's than HR tars and significantly more than CO tars (Forsdike, 1952). This general rule also applies to paraffin's present within the oil fraction that boil above the naphtha range with this oil fraction of VR tars typically containing 12% of its composition as paraffin's while HR and coke oven tars contain 0.9% and 0.3% respectively (Forsdike, 1952). The tar acids (phenolic) composition of VR tar also varied greatly from other tars with VR tars containing 6-7 times more tar acids than CO tars and 3-4 times more tar acids than HR tars (Forsdike, 1952). The compounds present within the tar acids were also very different with HR and CO tars containing significantly more phenol and cresols than VR tars, with phenol making up 25% of HR tar acids and 18% of CO tar acids (Forsdike, 1952). VR tars acids on the other hand contain only 6% phenol, with cresols only making up a small proportion, with high boiling tar acids dominating (Forsdike, 1952). This is further reinforced by the compounds present within creosote, which is a distillate product of coal tar, with VR tar produced creosotes being noted for their high tar acid content and the relative abundance of high boiling tar acids (McNeil, 1952). The main distinction between coke coal tars and other samples is the high parent PAH content (McGregor et al, 2012).

### 2.1.4 Brief overview of GCxGC

Traditional GC analysis allows for the separation of organic compounds in a single dimension. This often causes difficulties when analyzing coal tars as the complex mixture of organics found in coal tars leads to large numbers of compounds co-eluting and generally poor chromatography making fingerprinting difficult. GCxGC-TOFMS runs the sample on the same primary column as traditional GC with the addition of a secondary column of a different polarity the primary column and this allows for an extra degree of vertical separation, which provides for a much wider range of compounds to be separated and identified.

Different column setups allow for the separation of different compounds of interest. Normal phase column sets are the most commonly used setup for analysis of environmental samples (McGregor et al, 2011); this involves a non-polar primary column combined with a mid-polarity secondary column. Reversed polarity sets however give better resolution when analyzing coal tars and allow for the elution of higher molecular weight compounds present in the DNAPL while remaining within the temperature limits of the columns (McGregor et al, 2011). An example of a reversed phase GCxGC chromatograph is shown in figure 2.3. The figure clearly shows the separation of aliphatic from aromatic compounds with the aliphatic compounds having relatively higher secondary separation times. This is due to the aliphatic compounds being more attracted to the secondary phase than the aromatic, and heterocyclic compounds. An example of a 3D chromatograph of the same tar sample is shown in figure 2.4. The 3D view allows not only for the separation between aliphatic and aromatic compounds to be seen but also more clearly shows the difference in peak heights, and therefore peak areas, for the individual compounds.

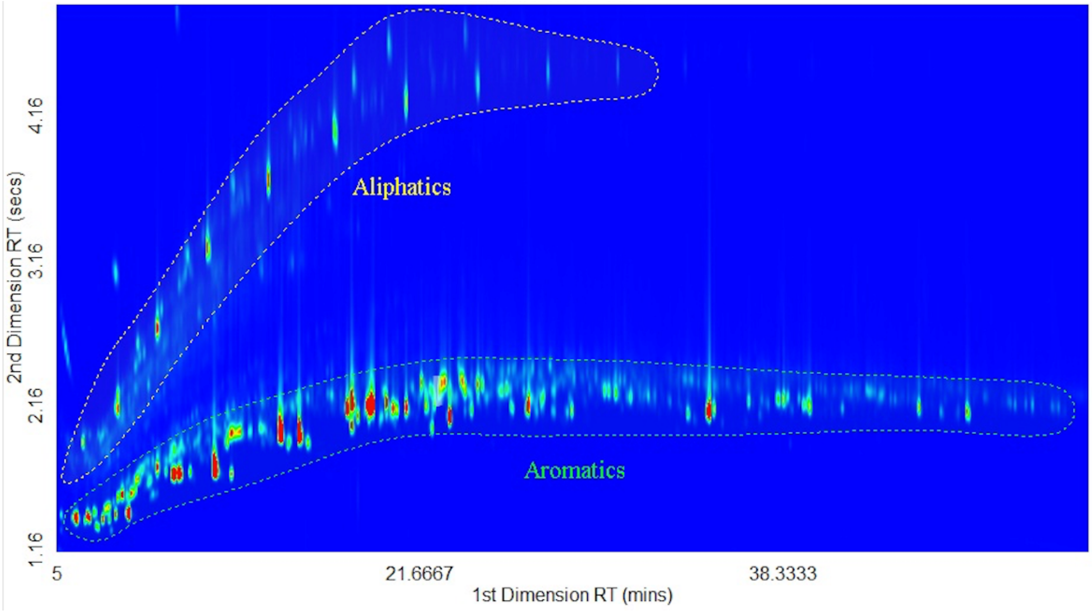


Figure 2.3 Example GCxGC chromatograph

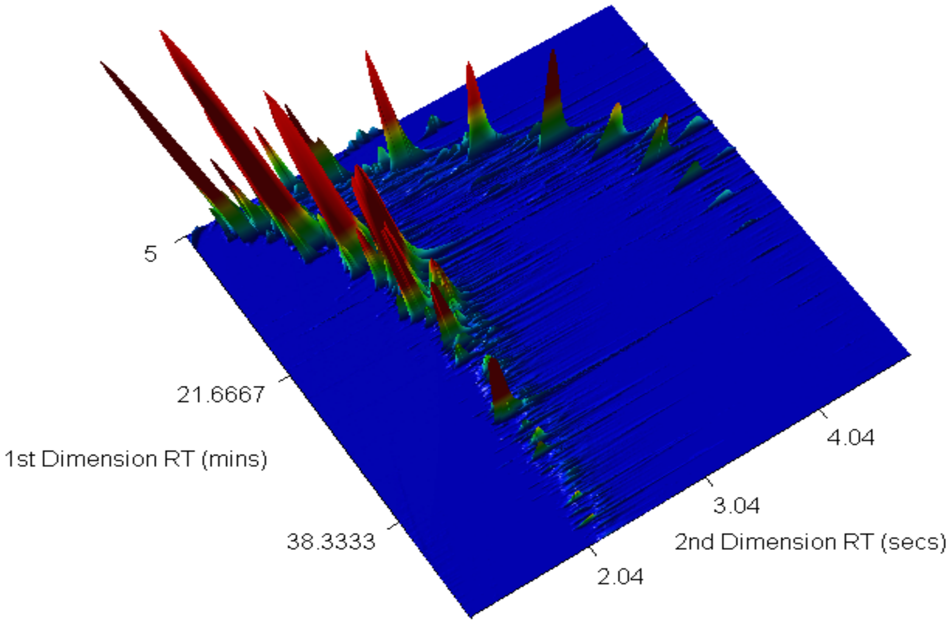


Figure 2.4 Example GCxGC chromatograph 3D view.

There are many factors that can affect the quality of the separation within the primary and secondary phase and column sets are chosen to give the best possible separations and resolution.  The length of the secondary phase in GCxGC will affect the retention time within the second dimension however it can also affect the retention times within the primary dimension. With increasing length of the secondary column, while holding the same flow rate and temperature gradient, the primary retention time will increase. This could be related to the linear velocity of the carrier gas in the first dimension (Adam et al, 2007). This difference in behavior in the first dimension with increasing secondary column length will also have a further knock on affect on the separations within the second dimension. This is due to the fact that the increase in retention time within the primary column will mean that the secondary column temperature may be different for a given analyte as it elutes later in the temperature program (Adam et al, 2007).

GCxGC separation has the advantage over traditional GC analysis that is it able to resolve previously unresolved complex mixtures (UCM), often referred to as a big “hump” in GC (Tran et al, 2010). Because UCMs are believed to consist of many thousands of compounds tradition GC-MS does not provide sufficient resolution leaving most UCM hydrocarbons unidentified. GCxGC allows for the separation of these thousands of compounds and can dramatically increase the number of compounds that can be identified.

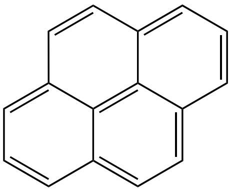
The time-of-flight mass spectrometer (TOFMS) gives structural information and provides clean spectra even within partially co-eluting peaks through mass spectral de-convolution. The high quality of spectra achieved by TOFMS is due to the high acquisition rate of the detector, which can go up to 500 spectra/s. When using the Leco TOF-MS there are several important considerations when interpreting the spectra obtained. The similarity number given by the software of above 800 usually indicates that an acquired mass spectrum shows a good match with the library search (Lu et at, 2003). A probability value of above 9000 means that the mass spectrum is unique and the identification based on mass spectra is logical. It is important to remember that isomers have similar mass spectra and this is especially important when considering such as complex mixture of organics as coal tar. For large molecular weight compounds, and longer chain compounds, that have low intensity (or non detectable) molecular ions the wrong structural information will be given, according to the peak table, even if the similarity value is high (Lu X. et al, 2003).

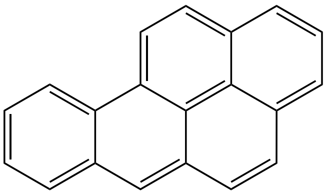
The sensitivity of a detector to different mass ranges also influences the analysis for example Leco systems gives poorer quality spectral data for heavier ions with a sharp decrease in ion intensity (Jover et al, 2005). This decrease is likely down to the tuning of the mass spec as the Leco system was initially designed for analysis of low molecular weight volatile compounds and this could inaccurate compound identification since heavier ions are usually more selective and allow for the identification of the molecular ion (Jover et al, 2005). Jover et al. 2005 gives the example of cholesterol with the m/z of 368 being three times lower than expected (compared to the NIST library) and m/z 458 (molecular mass) four times lower. The Leco model used by Jover et al. 2005 was an older Pegasus II whereas the setup used by McGregor et al. 2011, and for the data present in this PhD thesis, is a newer Pegasus 4D. This may be less of an issue on the 4D system, however it is still an important factor to note.

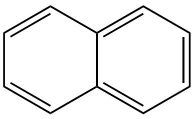
## 2.2 Compounds of interest

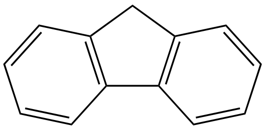
There are many different potential groups of compounds of interest found within coal tar. Since coal tar is such a complex mix of organic and inorganic compounds they can often consist of tens of thousands of different organic compounds from different chemical classes. Several of these classes are of interest from both a remediation and a toxicological viewpoint. There is also the possibility of organic molecules from biological activity within the coal tar as it is slowly weathers over time.

### 2.2.1 Polycyclic Aromatic Hydrocarbons (PAHs)


Pyrene


Benzo[a]pyrene


Naphthalene


Fluorene

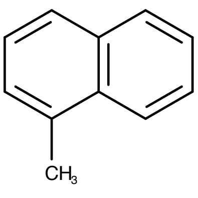
Polycyclic aromatic hydrocarbons (PAHs) form an important group of compounds that have been extensively studied as they persist within the environment and can form a threat to human health and the environment. PAH consist of fused aromatic rings with biochemical persistence arising from dense clouds of π-electrons on both sides of the ring structure (Wang et al, 2012). The toxicity of PAHs can vary greatly with the number of fused rings. For example, the 4 and 5-ring PAHs have a strong tendency to be carcinogenic and/or mutagenic, while PAH's composed of 6 or more rings have substantial mutagenicity in human cells (Yu et al, 1998). A carcinogenic compound is a compound that has the potential to cause cancer, whereas a mutagenic compound is a compound that induces or increases the frequency of mutation of an organism, usually through DNA damage. The EPA specifies 16 priority parent PAHs to be of concern and these are usually the main focus of research into PAHs, although there are many more different possible PAHs of interest the EPA 16 is considered to be the dominant list of PAHs of interest. Two extra PAH's have been added to the list from the EU REACH regulations (EC 1272/2013) that do not appear on the original EPA list, benzo[j]flouranthene and benzo[e]pyrene, to create a list of 18 parent PAH's of interest. The US agency for toxic substances and disease registry combines the EPA priority list and the EU REACH lists to create the 18 PAH's list often cited within the literature.

The PAH composition of coal tars can vary greatly depending on the production process used to produce the tar, as well as various other factors previously mentioned. For example, the naphthalene content of VR tars is very low making up between 0 and 3% of the total tar (Forsdike, 1952). This is not the case in HR or CO tars were naphthalene can be found to represent 7% and 5% respectively of the total composition of the tar (Forsdike, 1952). The yields of other PAHs such as anthracene and phenanthrene also follow the same general trend (Forsdike, 1952).

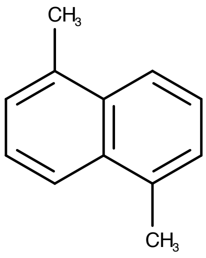
PAHs can come from either pyrolytic, petrogenic or biogenic sources. PAHs are introduced into the environment through contamination by crude oils, coal and coal tar or various refinery products. They can also occur naturally and are derived from biogenic precursors like terpenes, pigments and steroids (Budzinski et al, 1997). The distribution of PAHs found in sediments can give information on the precursor sources and a multitude of diagnostic ratios relating to PAHs exist. The ratios of phenanthrene to anthracene and flouranthene to pyrene can be used to distinguish between sources of PAH contamination. As phenanthrene is the most thermally stable tri-aromatic isomer it is much harder to break down at high temperature. This means that a P/A ratio of >10 mainly comes from petrogenic sources whereas a P/A ratio of <10 is predominantly pyrolytic in nature (Budzinski et al, 1997). Borderline values can be less precise in determining source and lower ratios of P/A <15 are related to incomplete combustion of organic matter like coals, fuel or crude oils (Budzinski et al, 1997). A flouranthene/fyrene ratios of >1 shows that PAHs are pyrolytic in origin, namely from the combustion of coal although this only applies to European and American coals as Australian coals have been found to favour the production of pyrene (Fluo/Pyr between 0.3 and 0.7). Pyrene can also predominate over flouranthene in urban atmospheric aerosols (Budzinski et al, 1997).

Several other PAH ratios can be used to differentiate pyrogenic and petrogenic contamination including anthracene/(anthracene + phenanthrene), fluoranthene/(fluoranthene + pyrene) and benzo[a]anthracene/(benzo[a]anthracene + chrysene) (McGregor et al, 2011). The ratio of flouranthene to pyrene (Flt/Pyr) in pyrogenic substances correlates to the temperature of formation (Saber et al, 2006). FMGP operating the relatively low-temperature carbureted water gas process have a Flt/Pyr ratio that typically range from about 0.6 to 0.8. In contrast this ranges from about 1.0 to 1.4 or higher in coke oven tars and other pyrogenic material generated at relatively high temperature (Saber et al, 2006).

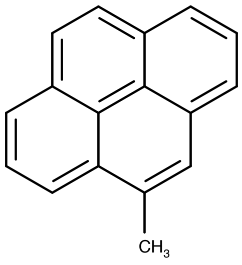
### 2.2.2 Alkylated Poly Aromatic Hydrocarbons (Alkyl-PAH's)



Methyl Naphthalene



Dimethyl Naphthalene



Methyl Pyrene

Alkylated PAHs form an important group of compounds that are often ignored in environmental analysis due to difficulties in accurate measurement. The EPA has created a list of 16 groups of prominent C1 to C4 alkyl PAHs derivatives and combined that with the 18 parent PAH's to create the so-called 34 EPA PAHs (Arp et al, 2011). Alkylated PAHs can serve as useful indicators for petroleum, coal tar and creosote weathering in the environment. Investigators can use alkyl PAHs to study PAH transport and migration pathways as well as the rate the pollutants degrade (Zeigler and Robbat, 2012). The ratio of alkylated 2-ring and 3-ring PAHs to 4-ring and 5-ring PAHs can be used to suggest the extent source materials have weathered in the environment and whether it is likely the remaining compounds will evaporate, dissolve, or degrade due to the environmental conditions (Zeigler and Robbat, 2012). Parent PAH's degrade faster in the environment than their alkylated homologues therefore weather pyrogenic samples will generally have a characteristic PAH pattern of C0 <C1 <C2 <C3, while parent PAH's are dominant in fresh pyrogenic samples (McGregor et al, 2012).

Alkyl PAHs have a large number of possible isomers with alkyl naphthalenes having the lowest possible number of isomers compared to the higher molecular weight PAHs. One important point of note is that due to the co-elution of the alkyl PAHs in GC the EPA34 PAH method actually represents several hundred individual alkylated PAH compounds (Hawthrone et al, 2006). The use of GCxGC allows for the separation of alkylated PAHs with McGregor et al. 2011 reporting the separation of 12 C2 alkyl naphthalenes into 10 peaks and only 2 pairs of alkyl naphthalenes still co-eluting. The type of column setup used in the GCxGC method is important with normal phase column setups only separating 9 out of a possible 34 C3-naphthalene isomers and 14 of the 112 possible C4-naphthalene isomers, while reserved phase columns setups separate 14 C3-naphthalene and 20 C4-naphthalene peaks within the same DNAPL (McGregor et al, 2011).

Alkylated PAHs have been shown to contribute substantially to the toxicity of PAH mixtures, in some cases accounting for 80% of the toxic burden (Zeigler and Robbat, 2012). In crude oil parent PAH's only make up roughly 1% of the total toxic burden with alkyl PAHs making up 99% (Hawthorne et al, 2006). In Benthic organisms affected by crude oil contamination only 1.4% of the TU (Toxic units available to benthic organism) is made up of the parent PAHs and the remaining 98.6% is made up by alkyl PAHs (Hawthorne et al, 2006). Historical studies, and many modern studies, focus only on the 18 (or 16) parent PAH's and this means that the risks associated with crude oil contaminated sites may be been greatly underestimated. In diesel fuel contaminated sites the parent PAHs account for 2.2% of the composition and 2.7% of the TU. In contrast the PAHs in pyrogenic FMGP samples account for 35 to 42% of the total PAH concentrations and TU (Hawthorne et al, 2006), although this will vary depending on the type of coal tar and the processes that produced it.

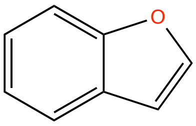
Hawthrone et al. 2006 give an example of FMGP site contaminated with PAH's. Using the EPA priority PAH method the estimate would be fairly reasonable and would estimate 350mg/kg of PAHs versus the true value of 1000mg/kg. However in a site contaminated with the same level of oil or diesel the reported value would be 10 to 20mg/kg rather than the true value of 1000mg/kg. These results support the idea that using only the parent PAHs in petroleum-contaminated underestimates the ecological risks due to the reliance on PAH data based only on the US EPA 16 priority pollutants PAHs (Barron and Holder, 2003). It also suggests that the risk from FMGP sites has also been underestimated in the past although not to the same degree that crude oil contaminated sites have. This may apply to a greater degree in CWG and oil-gas tar contaminated sites as the tar produced by these processes comes from the petroleum feedstock used rather than coal.

### 2.2.3 Heterocyclic compounds

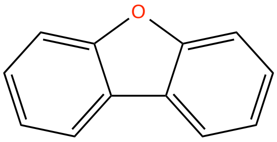
A heterocyclic compound is a compound that has at least two different elements as members of its ringed structure. Of particular interest in samples of coal tar, or coal tar contaminated soils, are those containing oxygen (PAOH), sulphur (PASH) and nitrogen (PANH). The O, S and N heterocycles in tar are generally determined by the sulphur, oxygen and nitrogen content of the coal carbonized (McNeil, 1952) although with some temperature-dependent alteration (Gauchotte-Lindsay et al, 2012).

Historically these compounds were considered major components of low temperature coal tars, like those produced in Germany (Birak and Miller, 2009). However, these compounds have also been detected in US coal tars and water-gas tars, although at concentrations one to two orders of magnitude lower than naphthalene (Birak and Miller, 2009). Heterocyclic compounds are difficult to determine analytically (Johansen et al, 1996) however there is much published literature attempting to refine identification and quantification of heterocyclic compounds. Heterocyclic compounds can leach into water and contaminate both groundwater and drinking water (Zamfirescu and Grathwohl, 2001). Unlike MAH's and PAH's heterocyclic compounds do not appear to have any trends in concentration related to the degree of weathering (Birak and Miller, 2009). Heterocyclic compounds with more than a single non-carbon element within the aromatic ring have previously been reported in coal tar derived materials. For example thieno[2,3-c]pyridine has been previously reported in anthracene oil (Burchill et al, 1982) and azadibenzothiophenes have been previously reported in anthracene oil (Burchill et al, 1982) and solvent refined coal heavy distillate SRCII (Nishioka et al, 1985)

### 2.2.3.1 Oxygen containing PAHs (PAOH)



benzofuran

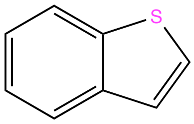


Dibenzofuran

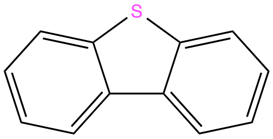
Phenolics (see OH-PAHs) form the major group of oxygen containing compounds in coal tar and brown coal derived liquids, of which the alkyl phenols are dominant (Shi et al, 2010). Other oxygen containing compounds have been found including tetralinol, indanol, hexahydroflourenol, flourenol, hydroxybiphenyl and dihydroxybenzene (Shi et al, 2010). Benzofuran and dibenzofuran are two important oxygen containing PAHs that are derived from coal tar and are important biomarkers for coal tar contamination. Oxygen containing compounds can be toxic, mutagenic and carcinogenic and are more mobile within the environment than their parent PAHs due to their increases solubility in water. This makes them of special concern in ground water as they can leach out for coal tar plumes and contaminate drinking water.

In terms of the composition of the oxygen containing compounds in coal tars 45% of oxygen in brown coal tars and 80% in bituminous coal tars occurs as reactive groups, such as carboxyl groups (Surgala and Sliwka, 1994). This suggests that brown coal derived coal tars are like to have more heterocyclic oxygen containing PAH (Oxy-PAHs) than bituminous coal tars. Carbureted water gas tars are generally low in oxygen-containing compounds (Saber et al, 2006). The ratio of dibenzofuran to fluorene (D/F) in carbureted water gas residue ranges from less than 0.1 to 0.4, while the ratio in coal tars ranges from about 0.4 to more than 1.0 (Saber et al, 2006).

### 2.2.3.2 Poly aromatic Sulphur hydrocarbons (PASHs)



Benzothiophene



Dibenzothiophene

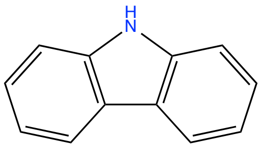
The sulphur content within coal is present either as inorganic compounds, such as pyrite and sulphides or organic sulphur compounds, such as poly aromatic sulphur hydrocarbons (PASHs). The organic Sulphur content (OSC) of coal is determined by the original organic matter that formed the coal deposits and takes the form of aliphatic and aromatic thiols, sulphides, disulphides and heterocyclic combinations of thiophenes and dibenzothiophenes (Diez et al, 1994). Due to the low concentration of organic Sulphur compounds and the fact they co-elute with PAHs the identification usually requires either a fractionation or isolation step (Andersson and Schmid, 1995). The use of GCxGC can overcome the need for a fractionation step as the PASHs and PAHs will separate in the 2nd dimension.

The occurrence of PASHs (also known as thiaarenes) in environmental samples and fossil fuels as well as their mutagenic and carcinogenic potential has been reported (Mössner et al, 1999). PASHs exist in an even greater variety of structures compared to PAHs due to the presence of sulphur therefore the number of isomers and alkylated isomers can be extremely high and quantitation and identification of individual PASHs isomers in environmental samples can be difficult (Mössner et al, 1999). In general the use of DB-17MS 50% phenyl methypolysiloxane phase gives

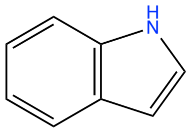
better separations for PASH isomers than a 5% DB-5MS (Mössner et al, 1999) this suggests that reversed phase column setups may provide better horizontal separation of PASHs over normal phase setups. Budzikur et al. (2012) studied the mutagenic properties of two aryl thiophenes on Salmonella. Out of the compounds tested only 2,4-diphenylthiophene showed little mutagenic effect with 3,6-dimetoxyphenanthro[9,10-c]thiophene showing no mutagenic potency.
Many thiaarenes have been shown to be mutagenic and the level of mutagenicity varies between different compounds. Among the 3-ring containing thiaarenes only naphtha[1,2-b]thiophene has been shown to be mutagenic (Jacob, 1990) and methyl-substitution in the inactive dibenzothiophenes does not alter their mutagenic activity. Among the 4-ring containing thiaarenes various actively mutagenic compounds have been found with the most mutagenic being phenanthro[3,4-b]thiophene. The isomeric phenanthro[4,3-b]thiophene exhibits only a low activity in TA 100 indicating that the position of the Sulphur plays a key role in the biological effect (Jacob, 1990). Benzo[2,3]phenanthro[4,5-bcd]thiophene has been shown to be an extremely powerful mutagen, which is even stronger than that of benzo[a]pyrene to which it is the homocylic isoster (Jacob, 1990). As well as being mutagenic many thiaarenes also have carcinogenic properties.

Williams. (2013) studied the comparison of the metabolism of highly mutagenic phenanthro[3,4-b]thiophene (P[3,4-b]T) and its weakly mutagenic carbon analogue, benzo[c]phenanthrene (B[c]P). Metabolism studies were conducted using liver microsomes from induced rats, un-induced rats, as well as lung microsomes from smokers and non-smokers. While all of the microsomes metabolized B[c]P to ring oxidation products (predominantly K-region B[c]P 5,6-diol), P[3,4-b]T is metabolized to both ring oxidation products (predominantly benzo-ring P[3,4-b]T 8,9-diol) and S-oxidation products (predominantly P[3,4-b]T sulfone). P[3,4-b]T is a more potent mutagen than its homocyclic analog B[c]P. Previous studies have shown that, like many carcinogenic PAHs, B[c]P is metabolically activated to B[c]P 3,4-diol to produce mutagenic and carcinogenic effects. Recent studies with P[3,4-b]T, have shown that, in contrast to P[3,4-b]T 8,9-diol, a corresponding sulfur analog of B[c]P 3,4-diol, P[3,4-b]T-sulfone exhibited significantly higher mutagenic activity compared to P[3,4-b]T. This earlier finding along with the present study, lends support to the hypothesis that unlike B[c]P, P[3,4-b]T exhibits its mutagenic and possibly carcinogenic activity predominantly via sulfoxidation pathway. This means that the study of the metabolic products of PASH metabolism are also important compounds of interest from both an environmental and human health viewpoint.

### 2.2.3.3 Poly aromatic Nitrogen Hydrocarbons (PANHs)



Carbazole



Indole

Nitrogen is present in all fossil fuels and is associated almost exclusively with the organic portion of the crude material (Burchill et al, 1983). It usually makes up around 0.5% of crude petroleum but is found in higher concentrations (1-2%) in shale oils and coal (Burchill et al, 1983). The toxicity of aromatic compounds greatly depends on the structure and number of fused rings. Several studies have found that nitrogen-containing substituents, such as nitro- and amino- functional groups can enhance toxicity by up to 100-fold (Yu et al, 1999). This means that even though the nitrogen content of the parent coal may be low the possible health effects from nitrogen containing polycyclic aromatic compounds (PANH) cannot be ignored.

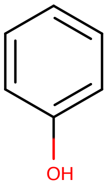
The use of GCxGC dramatically improves the separation of PANHs with the implementation of a polar secondary column with free electron pairs (Adam et al, 2007). Traditional GC suffers from a lack of resolution of PANHs leading to co-elution of basic and neutral nitrogen compounds that cannot be resolved by MS alone (Adam et al, 2007). For example indole and quinoline co-elute and fragment into the same ions. The second dimension in GCxGC allows for the separation of these compounds. Another way to separate the neutral and basic compounds prior to analysis is the use of a neutral-basic liquid liquid separation. When this is carried out the aniline and quinolone derivatives are separated into the basic fraction whereas indole and carbazole derivatives go into the neutral fraction (Adam et al, 2009).

The mechanisms affecting the structures of nitrogen containing compounds during pyrolysis is poorly understood (Yu et al, 1999). Nitrogen containing compounds are devolatilized from coals during primary pyrolysis and will be contained within the coal tar. During secondary pyrolysis nitrogen content in coal tars can also undergo secondary reactions including: conversion of tar into soot, expulsion of non-condensable gases (such as HCN) and structural rearrangements among the condensable organic products (Yu et al, 1999). During the condensed phase benzene and naphthalene are more stable than their corresponding heterocyclic PANH's (pyridine and quinolone), while in the vapour phase PANHs appear to be slightly more stable (Johns et al, 1962). PANHs are highly stable relative to neutral PAH's and can persist through severe thermal conditions and so are possible compounds of toxicological interest (Yu et al, 1999).

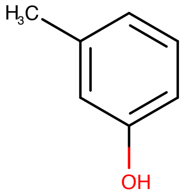
While in general PANH compounds are present in lower concentrations than their non-substituted PAH-analogues their higher water solubility leads to a higher bioavailability and potential toxic effects (Neuwoehner et al, 2009). The toxicity of dimethyl quinolines can span over two orders of magnitude and is affected by the relative position of the nitrogen within the ring as well as the relative positions of the methyl groups to the nitrogen (Birkholz et al, 1990). For example compounds with a methyl group at the 2 position (and another group at 4, 6, 7 or 8 positions) show the lowest toxicity among the range of toxicities for isomers involving other positions (Birkholz et al, 1990). This suggests that the methyl group adjacent to the ring nitrogen reduces the toxic effect.

Microbial degradation of quinoline compounds results in the formation of stable hydroxylated compounds and this leads to detoxification and a decrease in genotoxicity and mutagenicity, although the ecotoxic affects of these metabolites are still relevant from an environmental risk perspective (Neuwoehner et al, 2009). Acridine, aniline and quinoline all have toxic and teratogenic effects at sufficiently low concentrations to make them potential environmental hazards (Davis et al, 1981). The environmental impacts of these compounds may be greater than their reported LC50 values because of sub lethal effects such as decreased growth rate that may render surviving organisms incapable of coping with environmental stress (Davis et al, 1981).

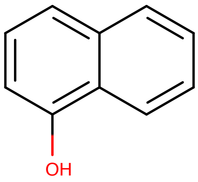
### 2.2.4 Hydroxy Poly aromatic hydrocarbons (OH-PAHs)



Phenol



m-Cresol



Naphthalen-1-ol

Oxygen containing compounds form an important diagnostic component within coal and of particular interest are the hydroxyl- and dihydroxy- PAH's. Ether linkages in coal can be readily broken under pyrolytic conditions and break down into phenolic fragments. These phenolic fragments undergo secondary reactions producing a range of chemicals from PAH's, cyclic alkanes, furans, ketones and other phenolic species (Gauchotte-Lindsay et al, 2012). The chemical composition of the coal, the temperature of pyrolysis, the shape and type of retort, catalysis by retort surfaces and inorganic coal components affect the reaction rates and mechanisms (Gauchotte-lindsay et al, 2012). The production of phenols and alkylphenols is significantly different between vertical and horizontal retort types (McGregor et al, 2012). This means that OH-PAHs may form an important group of analytes that can be used to potentially determine the retort type used to produce the tar. The analysis of OH-PAH's by GC-MS or GCxGC-TOFMS is enhanced by the use of silylation in order to improve limits of detection and chromatographic separations.

High phenolic content is a major characteristic of Low temperature coal tars (650°C) and Medium temperature coal tars (800°C)(Shi et al, 2012). Phenolics with 1-2 aromatic rings, including phenols, indanols, fluorenols, and phenyl phenols have been reported as major oxygen containing compounds in coal tar and brown coal derived-liquids (Shi et al. 2012). The aromatic hydrocarbons in coal tar appear to have corresponding phenolic compounds with the same carbon skeleton (Shi et al, 2012). Surgyala & Sliwka et al. 1994 found that phenolic oxygen accounted for 68-71% of the total oxygen in bituminous coal oils and 31-33% in brown coal oils. No difference was found for oil components from Australian coal tars with subbituminous coal containing 67-76% of their oxygen as hydroxyl groups compared to 57% and 75% in oils from Yallourn and Loy Yang brown coals respectively (Surgyala and Sliwka, 1994). This means that the type of feedstock coal used will also affect the overall composition of the oxygen containing compounds in the product tar.

Hydroxy PAHs can also be formed by biological activity from the metabolism of parent PAHs and this will have relevance to not only human health but also the wider environment. Following PAH exposure in human the PAHs are first oxidized in phase I metabolism by P450 enzymes and then reduced or hydrolyzed to hydroxylated metabolites (Campo et al, 2008). In phase II metabolism, the hydroxyl PAHs are reacted to form glucoronate and sulphate conjugates to facilitate excretion through urine or faeces (Campo et al, 2008). Urinary 1-hydroxypyrene, a metabolite of Pyrene, has been proposed as a biomarker of PAH exposure (Jongeneelen et al, 1988). However, since multiple exposures to different PAHs continuously occurs measurement of a wide range of hydroxylated parent PAH metabolites is required. Most studies report the simultaneous quantification of pyrene, naphthalene and phenanthrene metabolites, which very few studies report quantification of metabolites of other compounds such as fluorene, fluoranthene, chrysene and benzo[a]pyrene (Campo et al, 2008).

Flouranthene is of particular interest in marine environments as it is one of the most abundant PAHs in marine sediments (Palmqvist, 2003). It has been shown to be highly toxic to marine invertebrates (Swartz et al, 1990) and is as potent a mutagen as the extensively studied PAH benzo[a]pyrene. Fish are usually exposed to parent PAHs from contaminated sediments and bio transform PAHs to hydrophilic metabolites in the liver, using an active oxidative enzymatic system (Johnson-Restrepo et al, 2008). Therefore parent PAHs are not often found in fish and so analysis of hydroxylated metabolites of PAHs in fish bile is a more appropriate approach to understanding their exposure to PAHs (Da Silva et al, 2006). Although the parent PAH's themselves may not be actively carcinogenic their metabolites may be carcinogenic. In fact metabolites of PAHs found in benthic fish are strongly associated with hepatic lesions and liver neoplasm (Johnson-Restrepo et al, 2008). Johnson-Restrepo et al. 2008 was able to identify and quantify OH-PAH metabolites in fish bile and the concentration of the OH-PAHs correlated with the extent of PAH contamination within the sediments from the sampling location.

Hydroxylated PAHs, such as 1-hydroxy pyrene can also be used as a biomarkers to evaluate human exposure to PAHs and potential toxicity. This is important as the presence of carcinogenic PAHs in the environment poses a potential risk to human health (Wang, X et al, 2012). Several parent PAHs are metabolized to active and potent carcinogens and there is also evidence from bacteria to humans that indicates that PAH metabolites can be considerably more genotoxic than the untransformed parent compounds from which they are derived (Wang, X. et al, 2012).

In cases of sites contaminated by coal tar there are two main exposure routes relating to hydroxylated PAHs. The first is primary exposure from hydroxylated PAHs present within the coal tar itself or contaminated ground water. Hydroxylated PAHs are much more soluble than their corresponding parent PAH and are more likely to leach into ground water, for example phenol has a water solubility of 91.7 g per kg $H_2O$ at $25^oC$ whereas benzene has a water solubility of 1.83 g per kg $H_2O$ at $30^oC$ (Haynes et al, 2015). This could increase the potential for exposure to hydroxylated PAHs in ground water from sites contaminated with coal tar. The increased solubility will make the hydroxylated PAHs more environmentally mobile than their corresponding parent PAH. The second exposure route would be exposure to the parent PAHs themselves and so metabolism to hydroxylated PAHs within the body.

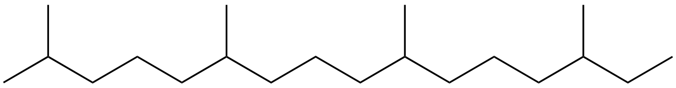
Bacterial degradation of PAHs can also lead to the generation of hydroxylated PAHs by co-metabolism. Co-metabolism is an important process that transforms non-growth substrate PAHs, in the presence of a suitable growth substrate, to their hydroxylated metabolites. Co-metabolic degradation of recalcitrant high molecular weight PAHs combined with the degradation of readily utilized PAHs has been reported (Zhong et al, 2007). The co-metabolic degradation rates of PAHs are linked to the consumption of growth substrate. The availability of a suitable growth substrate will limit the potential for PAH degradation by co-metabolism. Within heavily coal tar contaminated soil microbial breakdown of PAHs is unlikely as suitable growth substrate is likely to be limited (and other components of the coal tar are likely to inhibit microbial growth). Metabolism of PAHs may be possible around the boundary of the coal tar plume and any of the PAHs that are dispersed into the environment.

The toxicity of phenolic compounds varies greatly for example p-cresol is the most toxic cresol isomer with a 5 to 10 fold higher concentration of o-cresol or m-cresol being required to observe the same degree of toxicity of p-cresol (Thompson et al, 1994). p-Cresol has the lowest water solubility of the cresol isomers, however due to it's significantly higher toxicity it is still the highest risk cresol isomer that may contaminated groundwater. P-Cresol and phenol have the ability to change bacterial membrane lipid structure, increasing the degree of saturation of the lipids, as the phenols alter the cell membrane permeability and increase their fluidity (Keweloh et al, 1991).

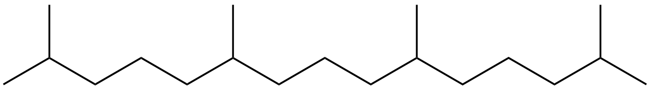
The environmental effects of the 3 cresol isomers do not only extend to their direct toxicity. Low concentrations of o-cresol can increase the carcinogenicity of benz(a)pyrene, whereas high concentrations can inhibit the carcinogenic effect (Yanysheva et al, 1993). p-Cresol can be utilized by bacteria as a sole energy source (Yu and Loh, 2002) and the presence of p-cresol can inhibit the degradation of carbazole with incomplete degradation of carbazole at p-cresol concentrations above 20mg/L and complete removal of carbazole can only occur when p-cresol concentrations are below 10mg/L (Yu and Loh, 2002). When the concentration of p-cresol is higher than 120mg/L carbazole degradation is completely inhibited (Yu and Loh, 2002). This means that the concentrations of p-cresol within a tar may be important for the potential biodegradation of the tar. p-Cresol also inhibits the degradation of phenanthrene (Millete et al, 1995) and phenol (Kar et al, 1997).

### 2.2.5 Other compounds of interest

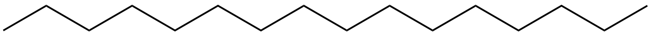
#### 2.2.5.1 *n*-Alkanes



Phytane



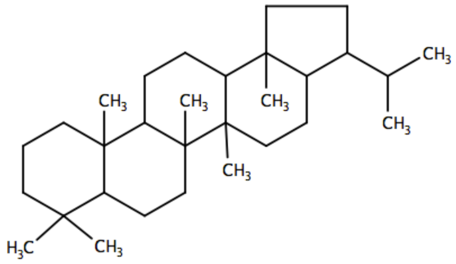
Pristane



Hexadecane

*n*-Alkane distributions can give a large amount of diagnostic information from environmental samples. Two different indexes are of particular importance for coal tar analysis. The High molecular weight versus low molecular weight HMW:LMW index and the carbon preference index (CPI) can tell you what the source of the *n*-alkanes within a sample is. Samples that are dominated by long chain *n*-alkanes with a strong odd over even predominance and a CPI index much higher than 5 are characteristic of higher plant signatures (Faure et al, 2006). The C27 and C29 *n*-alkanes are the dominant *n*-alkanes found within higher plants (i.e. vascular plants). The C23 *n*-alkane is indicative of lower plants (i.e. non-vascular plants). Coal tar *n*-alkane distributions are dominated by short chain *n*-alkanes between the range C15 and C23 with C17-C19 dominating. Coal samples will demonstrate a much wider range of n-alkanes from C14 to C30 with a downward trend that has no clear dominant *n*-alkane. The CPI of coal particles in the Faure et al. 2006 study was found to be between 1.1 and 1.3. Benhabib et al. 2010 found that the n-alkanes in the C25-C35 range presented a CPI of 1.97, which is commonly assigned to organic matter coming from higher plants and this is consistent with the origin of the coal tar analysed.

### 2.2.5.2 Hopanes

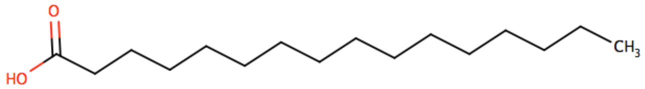


C30 Hopane

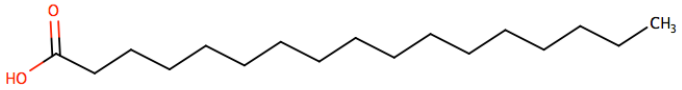
Hopanes are a bacterial membrane biomarker that serve a similar function in bacteria that sterols perform in eukaryotes. Hopanes are useful for not only telling you about modern day bacterial activity but can also give you information about the thermal maturity of the parent coal.

The 18α(H)-22,29,30-trisnorhopane/(18α(H)-22,29,30- trisnorhopane + 17α(H)-22,29,30-trisnorhopane) ratio can be used as a diagnostic ratio to establish the maturity of a sample. Hopane distributions in soils are characteristic of mature fossil organic matter as indicated by the low abundance of less stable compounds such as moretanes and systematic pre-dominance of 22R-homohopanes over 22S-homohopanes (Faure et al, 2006). Differences of maturity can be observed among samples mainly based on the relative abundance of 18α(H)- 22,29,30-trisnorhopane (Ts) with a higher relative thermal stability over 17α(H)-22,29,30-trisnorhopane (Tm) and on the presence or the absence of the thermally stable 18α(H)-30-norneohopane (18αC29). These differences can be ascribed to the relative proportion of coal and coal tar, which display different hopane fingerprints when analyzed separately. Coal tar displays a more mature hopane fingerprint than coal. This can be explained by the fact that coal tar is produced by the destructive distillation of bituminous coal involving a thermal cracking of coal. (Faure et al, 2006). Hopane distributions may also give important information about active microbial activity within coal tar if hopanes that are fresh/thermally immature are detected.

#### 2.2.5.3 Fatty Acids



Hexadecanoic acid



Octadecanoic acid

Fatty acids are an important lipid class which are essential parts of most living cells and cellular fluids (Jover et al, 2005). Fatty acids present a complex chemical class, with varying chain length and number of double bonds. In order to analyse fatty acids it is preferable to derivatize them. This can be done with either BSTFA to add a trimethyl silyl group or with BF3 Methanol to change the fatty acids into fatty acid methyl esters (FAMEs). Due to the complexity of coal tar a multi-step separation of fatty acids may be required prior to analysis. Fatty acids may be an important biomarker for biological activity within FMGP coal tar samples as they are unlikely to survive the production process as they decompose at high temperature (Shi et al, 2010) and so should only be present due to recent biological activity.

### 2.2.6 Microbial activity and coal tar

Most research on microbial activity in relation to coal tars focuses on the use of aerobic bacteria for bio treatment and remediation of coal tar contaminated soils. The limiting factor of biodegradation of DNAPL from coal tar seems to be that PAH phase partitioning and/or sorption limits the rate and extent of microbial degradation processes (Roy et al, 2000). Experimental ex situ studies of biological treatment of PAH's in liquid cultures and solid matrices associated with FMGP site soils have indicated a range of 2-6 ring PAH's may biodegrade when present in aqueous solution, but removal from a solid-NAPL matrix is less predictable and generally will be much less efficient (Roy et al, 2000). This can make the bio treatment of coal tar plumes in-Situ problematic.

The rate at which PAHs are removed by bio treatment is more limited by mass transfer (Raoult's law) than the explicit aqueous-phase biodegradation kinetics. In such laboratory tests freshly added PAH's degrade readily showing that toxicity is not the limiting factor (Roy et al, 2000). As toxicity is not a limiting factor in aerobic microbial breakdown of PAHs it is unlikely to be for anaerobic bacterial breakdown and available substrate is also likely to be the limiting factor.

Bacterial metabolism of PASH's has been demonstrated under laboratory conditions (Saftic et al, 1992) with diones, sulfodixed and sulfones having been observed as bacterial transformation products of thiophenes. There have been several reports of the aerobic co-metabolism of benzothiophene (Saftic et al, 1992). The transformation products show oxidation of the thiophene ring at different positions, but not cleavage of either aromatic ring (Saftic et al, 1992). Bacterial metabolism of PASH's within fresh coal tar samples is unlikely due the anaerobic conditions and the overall composition of coal tar being a very hostile environment for bacteria, although bacterial degradation of PAH's can take place under aerobic conditions were toxicity is not the limiting factor (Roy et al, 2000). The main limiting factor is, as with PAHs, available substrate and the coal tar itself may not have the correct substrate to allow for the co-metabolic breakdown of PASHs.

Fluorenone is another compound, which has been previously reported in coal tar (Benhabib et al, 2010), which may be produced by bacterial metabolism, although it may also be present within tar as a result of the production process. Fluorenone can also be produced by oxidation of fluorene (Korfmacher et al, 1980). Fluorenone can also be produced by the bacterial metabolism of fluorene (Grifoll et al, 1992) and fluoranthene (Kelley et al, 1993). Eriksson et al, (2000) reported increased concentrations of both fluorenone and cyclopenta[def]phenanthrenone within soils contaminated by creosote, a coal tar distillate. Wischmann and Steinhart, (1997) also reported increasing concentrations of fluorenone and 9,10-anthracenedione during the degradation of a coal oil in soil. The detection of these compounds with a tar may be possible indicators of bacterial activity, although they could also be present within the fresh tar prior to its release into the environment.

### 2.3. Extraction

Traditional extraction techniques require long extraction times and large amounts of sample, sorbents and organic solvents (Carro et al, 2013). The costs associated with the purchase of large volumes of organic solvent as well as environmental concerns have led to the development of pressurised liquid extraction (PLE) better known as accelerated solvent extraction (ASE). ASE has the benefits of faster extraction, using lower volumes of organic solvents that requires smaller sample sizes. (Carro et al, 2013). Accelerated solvent extraction can achieve recoveries that are comparable to those obtained from traditional extraction methods (Wang et al, 2012). This makes ASE an excellent choice of extraction technique for the analysis of coal tar and coal tar contaminated samples.

In ASE, the solubility of the target analytes is enhanced by the decrease in viscosity of the solvents at high temperature, which also diminishes the matrix interactions and increases the diffusion of the analytes through the matrix (Carro et al, 2013). The use of high pressure means that the solvents are kept in the liquid phase at elevated temperatures far above their boiling point and this allows for faster extraction. The amount of co-extracted analytes might be greater at higher temperature, decreasing the selectivity of extraction, whereas high temperatures might also affect thermo-labile compounds subjected to decomposition. In the context of coal tar analysis all compounds of interest should be thermally stable enough to survive the extraction process even at temperatures up to $150^{o}$C.

As with other extraction techniques the main limitation of ASE is the low selectivity toward the analytes during extraction and the fact that, depending on the kind of sample, many interferants such as lipids, pigments and cholesterol may be co-extracted (Nieto et al, 2008). This can be reduced by the use of silica gel within the ASE cell and depending on the composition of the sample this may or may not be sufficient to remove all potential interferences. McGregor et al, 2011 developed an ASE method for the extraction of coal tar using ASE and analysis using GCxGC-

TOFMS. Fractionation using this method is not possible as the n-hexane extracts all of the organic compounds into a single fraction even when using an extraction temperature of 40°C (McGregor et al, 2011). Lundstedt et al, 2006 used ASE to fractionate PAHs and PAOHs from coal tar contaminated soils and developed a method that allowed for the fractionation of these classes, using cyclohexane/dichloromethane 9:1 for the first fraction and cyclohexane/dichloromethane 1:3 for the second.

One of the important step of the method development work carried out by Lundstedt et al, 2006 was the water content of the silica and found the following: Several experiments with silica-packed extraction cells were then conducted on both the gasworks soil and a soil spiked with different PAHs and oxy-PAHs. Various combinations of extraction solvents, extraction temperatures, and percentages of water in the silica gel were tested to fine-tune the separation. The choice between activated or deactivated silica was not obvious. When activated silica was used, stronger solvents were needed to elute the target compounds from the extraction cell (also seen during the screening experiments). This ensured that the target compounds were exhaustively extracted from the soil matrix. On the other hand, it also released more interfering substances from the soil and increased the risk that oxy-PAHs would be eluted in the fraction intended for PAHs.

For the gasworks soil and the spiked soil, good results were obtained using a procedure with 2% deactivated silica and *n*-hexane at 150°C to extract the PAHs, whereas many experiments with activated silica and stronger solvents at the same temperature resulted in a significant portion of the oxy-PAHs in the PAH fraction (data not shown). Due to its low polarity n-hexane may have a limited capacity to desorb high molecular weight PAHs from complicated soil matrixes (Björklund et al, 2000). This suggests the use of stronger more polar solvents is preferable to extract the PAHs. To be able to do this without co-eluting the oxy-PAHs among the PAHs, a lower extraction temperature may be used for the first fraction.

The optimal method used in Lundstedt et al, 2006 employed 2% deactivated silica and cyclohexane/ dichloromethane (9:1, v/v) at 120°C to extract the PAHs and cyclohexane/dichloromethane (1:3, v/v) at 150°C to extract the oxy-PAHs. This method was subjected to a subsequent validation process. The water content used for the separation is of particular relevance to the findings in McGregor et al. 2011 were fractionation of compounds in DNAPL could not be achieved as n-hexane extracted all the organic compounds. This may be down to the water content of the silica that was used. In McGregor et al. 2011 the water content was 10% and this may account for why the compounds would not fractionate as they would all go straight through the silica in the first n-hexane fraction without any separation. It could also be related to the relative organic content of pure DNAPL compared to soil with the pure DNAPL obtaining significantly higher concentrations of organics. These higher concentrations, and the larger amount of potential interferents, may result in compounds be extracted using n-hexane which would ordinarily be retained on the silica but are not due to saturation and overloading of the cleanup silica.

Machado et al. 2011 used ASE to identify organic Sulphur compounds in coal bitumen and analysed the extracts using GCxGC. The method used n-hexane then dichloromethane as extraction solvents combined into a single fraction prior to analysis and was compared to both supercritical-fluid extraction and ultrasonic extraction. The ASE was able to extract a wider range of PASHs including thiophene, benzothiophenes, dibenzothiophenes, napthobenzothiophenes and dibenzothiophenes (Machado et al, 2011). These results suggest ASE may be the best extraction technique for extracting PASHs from Coal tar.

Soxhlet is one of the most commonly used traditional extraction techniques (Graham et al, 2006). It was developed in the late 19th century and is still used routinely in laboratories today. Soxhlet is essentially a reflux technique using organic solvents to extract the organic compounds from a solid sample. However Soxhlet requires large volumes of organic solvents and requires a very long extraction time e.g. 24 hours, owing to slow analyte diffusion and desportion from the sample matrix to the extraction fluid (Björklund et al, 2000). Soxhlet also generates dirty extracts that require clean up of the extracts and gives rise to high labour costs (Björklund et al, 2000). Song et al. 2002 preformed a comparative study of different extraction techniques for the determination of PAH’s from contaminated soils and sediments.

They evaluated Mechanical shaking or stirring, soxhlet extraction and ultrasonic extraction and found that the effectiveness of the extraction procedure was only different in high-PAH-polluted samples. Graham et al. 2006 found that for isotope analysis ASE produced results with better re-predictability over soxhlet. This suggests that ASE may be the superior extraction technique for environmental samples that do not require large volumes of sample such as coal tars.

## 2.4. Derivatization

### 2.4.1 What is derivatization?

The aim of using a derivatization method for GC is to improve peak symmetry, resolution, selectivity and sensitivity of the target analytes and improve their thermal stabilities (Segura et al, 1998). Derivatization can increase the sensitivity of detection of a particular compound of interest by several orders of magnitude (Parkinson, 2012) and so allow for more compounds to be identified within a sample. The derivatization techniques generally consist of substitution of the active hydrogen in –NH, -COOH, -OH, or –SH using alkylation, acylation or silylation reagents (Parkinson, 2012). Isotopically labeled derivatization reagents can also be employed to study the fragmentation pattern of the derivative and help in structural interpretation (Carro et al, 2013). The main requirements for a successful derivatization reaction are the formation of a single derivative for each compound, a straightforward and quick reaction, high and reproducible yields of derivatives and the formation of a derivative that is stable during the period of analysis.

The derivatization step can take place before, combined with or after the sample extraction and can be used for metals, nonmetals and organic analytes. Post extraction derivatization is by far the most common method of derivatization. The application of pre extraction derivatization is limited within the literature as a quantitative and reproducible derivatization reaction for standards and analytes in the sample is required (Carro et al, 2013). There is also the issue of matrix effects interfering with the derivatization reaction this may be especially important in the derivatization of coal tars due to the extremely complicated matrix of coal tars. The use of ASE as a “Reaction chamber” has been demonstrated within several studies

(Carro et al, 2013) however this could also be prone to complicated matrix effects and this may make any in cell derivatization method development for coal tars difficult. There is also an issue with the volume of derivatization reagent used as complete derivatization requires the derivatization reagent to be present in excess and this may be difficult to achieve with pre-extraction, or during extraction, derivatization as the concentrations of potentially derivatized compounds is unknown. This is not an issue in post-extraction derivatization as any underivatized products detected within the sample run may suggest more derivatization reagent is required and the samples can be rerun with more derivatization reagent added.

### 2.4.2 Silylation

Silylation derivatization involves the replacement of acidic or active hydrogen within an organic compound with an alkylsilyl group (trimethylsilyl – TMS). Silylated derivatives are generally less polar, more volatile and have increased thermal stability. The increased volatility enhances the chromatographic separation properties of a compound within GC, particularly on nonpolar stationary phases. The order of reactivity for the acidic hydrogen is generally as follows: Alcohols > Phenols > Carboxylic acids > Amines > Amides (Carro et al, 2013). When combined with GC/MS silylation can greatly lower the limits of detection and improve the sensitivity of analysis. Silylated groups give strong ion abundance and clear fragmentation patterns that aid with structural identification.

Silylation is a non-permanent reaction and will readily degrade in the presence of oxygen. Silylated derivatives should be run as quickly as possible and should not be left for more than 48 hours before analyzing as long as they have been stored in a cold environment in sealed vials. TMS derivatives of carboxylic acids are readily formed however these compounds tend to suffer from limited stability and so should be run within 24 hours. Any replicate analysis should be run immediately after each sample as this will reduce the chance of the TMS derivatized compounds loosing their TMS group.

BSTFA is a common silylation reagent and has better silyl donor ability than MSTFA and MTBSTFA and tends to react faster, more completely and has by-products that are usually very volatile and tend not to interfere with the resulting spectrum (Parkinson, 2012). For this reason BSFTA is the most commonly used derivatization reagent. If further reactivity is required MSTFA reagent can be used, which can still give extensive coverage of functional group reactivity similar to BSA (N,O-bis(trimethylsilyl)-acetamide) (Parkinson, 2012). The addition of TMCS to BSTFA or MSTFA catalyzes the reaction and increases its stability allowing for thiol groups to be derivatized.

Wang et al. 2012 used MTBSTFA to derivatize OH-PAH's in sediment samples due to the stability of the *tert*-BDMS derivatives of OH-PAH's and the resulting *tert*-BDMS derivatives producing very characteristic spectra with EI-MS. There are few studies published using BTSFA on coal tars and none could be found using MSTFA or MTBSTFA. Johnson-Restrepo et al. 2008 used MSTFA for the derivatization of OH-PAH's in fish bile samples to form TMS-O-PAHs. The author does not explain why MSTFA was chosen over BSTFA or MTBSTFA. Campo et al. 2008 evaluated the use of three silylation agents for derivatization of several urinary monohydroxy metabolites of PAHs in occupationally exposed subjects. BSTFA, Trisil and Trisil Z were all evaluated in order to access that was best for derivatization of monohydroxy PAHs with BSTFA being found to be the best derivatization reagent.

There is very little published literature using Silylation for the analysis of coal tar. Shi et al. 2010 used BSTFA to derivatize dihydroxy aromatic compounds and analysed them with GC-MS, the BSTFA reaction conditions are not reported. Prior to derivatization dihydroxy benzenes were masked by co-elution with other compounds such as dimethyl phenols and naphthalenes, after derivatization this will no longer be the case. Although this may not be a limitation when using GCxGC using silylation will not only improve separations in the primary phase and reduce the number of compounds eluting at the same time but will also improve the secondary phase separation by reducing the polarity of the dihydroxy aromatics. Shi et al, 2013c used BSTFA for the derivatization of phenolic and acidic compounds within coal tar produced by middle-temperature gasification. Prior to silylation phenolic and 1-ring aromatic hydrocarbons showed similar orders of magnitude on the TIC. Following derivatization the response of the phenolic compounds was greatly enhanced relative to the aromatic hydrocarbons and also give better peak shapes. Gauchotte-Lindsay et al, 2012 published a method for the pre-extraction derivatization of coal tars, however pre-extraction derivatization is not commonly used due to issues with the reproducibility of results (Carro et al, 2013).

### 2.4.3 Alkylation

Alkylation is the replacement of an active hydrogen with an alkyl or aryl group. Carboxylic acids, alcohols, thiols, phenols, primary and secondary amines, amides and sulfonamides are the main functional groups that can be subject to alkylation reactions. Alkyl derivatization adducts give better chromatograms than the corresponding free acids (Parkinson, 2012). Alkyl derivatives are very stable and the reaction is permanent. No papers using of BF3 Methanol as a derivatization reagent for coal tars, or the use of Alkylation at all, could be found within the literature. This could be an important gap within the literature especially when considering any biological activity that may or may not be taking place within the coal tar.

Un-derivatized acids are very reactive and are usually too polar to give proper GC separations as they go through absorption and nonspecific interactions with the column, causing GC peak tailing (Parkinson, 2012). The use of BF3 Methanol to methylate fatty acids improves the sensitivity and resolution of the now fatty acid methyl esters. The use of BF3 methanol allows for the derivatization of fatty acids between C10 and C22 fatty acids (Parkinson, 2012). Short-chain fatty acids are not thermally stable <C8 and so do not give reproducible results when using BF3 Methanol for methylation. In the context of coal tars the fatty acids of above C10 will be of interest with the shorter chain being of little interest. The C16 and C18 Fatty acid are the two most common fatty acids in nature and can give a gauge of biological activity within the coal tar.

Alkylation and Silylation can be used in a dual derivatization method and compliment each other well. When using only methylation distinct tailing occurs for the compounds containing hydroxyl groups such as the *n*-alcohols that are not derivatized. When dual derivatization is used alkylation is always carried out prior to silylation (Jover et al, 2005). The main reason that alkylation takes place prior to silylation is that alkylation is permanent and will only work if the fatty acids do not have TMS groups attached, which would be the case if BSTFA was used first. Two step alkylation then silylation is the most time consuming technique but in principle gives the most rewarded results. When using GCxGC there is the added advantage that silylation will improve the separation of *n*-alcohols, diols and Hydroxy-acids, and any other derivatized compounds, in the second dimension as their polarity is decreased. This decrease in polarity allows for sharper separations within the second dimension and improved overall peak shapes.

### 2.4.4 Acylation

Acylation is another commonly used derivatization method in GC–MS that possesses some features of silylation, such as the creation of more polar and more volatile derivatives (Parkinson, 2012), but does not derivatize most carboxylic acid. Acylation involves the replacement of labile hydrogen with an acyl group and produces thermally stable derivatives suitable for GC analysis. Acylated derivatives can be obtained from a great variety of functional groups: alcohols, amines, amides, thiols, phenols, enols, sulfonamides, unsaturated compounds and aromatic rings (Carro et al, 2013). An example of the use of Acylation for Coal tar analysis was the use of benzene solution with triflouracetic anhydride in the presence of triethylamine in Das et al. 1985 to derivatize nitrogen bases in coal tar samples. The results obtained showed that this technique is useful to the analysis of Azarenes and Amines when followed by column separation, however the use of GCxGC may negate the need for a column separation. The author may have chosen to use Acylation to avoid possible interference from carboxylic acids that would increase in response if silylation was used, although carboxylic acids are unlikely to be a major component of coal tar as they are unlikely to survive the production process.

Acylation reagents can be classified into three main groups: perflouro acid anhydrides, flouracylimidazoles, and non-halogenated groups (Parkinson, 2012). Fluorinated anhydride derivatives of alcohols, phenols and amines are both stable and highly volatile and can be injected onto the GC column without the need to remove the derivatization reagent (Parkinson, 2012). The perflouro acidic anhydrides can produce acidic by-products that must be removed from the mixture before the derivatives can be injected into the GC as they can contaminate the injector port (Parkinson, 2012). The flouracylimadazoles react readily with hydroxyl groups and secondary and tertiary amines to from acyl derivatives and the imidazole produced as a by-product is relatively unreactive and will not usually need to be removed before injection into the GC (Parkinson, 2012). The final method is not commonly used as it decreases the volatility of the compounds and is only used in cases were the retention time of a compound wants to be increased on the GC to avoid interferences (Parkinson, 2012).

# Chapter 3

# Materials and Methods

**3.1 Samples**

**3.2 Standards and Solvents**

**3.3 Extraction**

**3.4 Sample Evaporation**

**3.5 GCxGC-TOFMS**

**3.6 Quality Control**

**3.7 Statistics**

## 3.1 Samples

DNAPL001-006 (D2-D6) samples were taken from the same site that manufactured gas between 1836 and 1971. The site had manufactured gas from a wide range of process from low temperature horizontal retorts, high temperature horizontal retort and later vertical retort. D2 was taken from a borehole near a gasholder on the southern boundary of the site. D3, D4 and D5 were taken directly from a former tar tank on the opposite side of the site. This tar tank had been built at the same time as the vertical retort plant had been constructed. D6 was taken from a borehole located near to the tar tank containing samples D3, D4 and D5. All of the samples were produced by the Vertical Retort process. D2, D3 and D6 are Sandy soil samples heavily contaminated with tar. D4 and 005 are both waterlogged soils that are heavily contaminated with tar. D1 was taken from a borehole downstream of the same former gasholder that D2 was taken and was included within the PCA data produced in McGregor et al., 2012 but was not included in the work for this PhD as it was misplaced during the lab move.

The site initially operated simple horizontal retorts until the gasworks was redeveloped in 1878 and expanded in 1912 to include five continuous vertical retort beds. This was further extended in the 1920's with the addition of an additional five continuous vertical retorts. From the early 1930's until 1952 the plant remained at capacity, with various improvements to increase efficiency, such as the addition of two water gas plants. The site was expanded again in 1952 with the construction of a purification plant, additional vertical retorts and the development of a storage area for primary flash distillate (a type of light petroleum distillate). A CWG plant and microsimplex oil gasification plant operated on the site and so there is the potential for traces of CWG and oil gas tar within the samples.

DNAPL007 (D7) was taken from a site that operated between 1856 and 1969 and initially produced low temperature horizontal retort gas. However, this later switched to higher temperature horizontal retort gas and the tar sample came from this process rather than the earlier LTHR process. The sample is in the form of pure

DNAPL taken at the base of an underground gasholder tank during a remediation project in 2009.

DNAPL008 (D8) was collected from a FMGP, which operated between 1856 and 1971 and may contain traces of CWG tar as the site produced CWG in the later stages of its operation. The majority of the tar would have been produced by the HR process and this was shown in the statistical analysis of the tars (McGregor et al., 2012). The sample is in the form of pure DNAPL in water. The tar sample was taken from a former 250,000 gallon tank associated with the horizontal retort house and was taken from a skimmer pump, which was being used to empty the tar tanks during a remediation process

DNAPL009 (D9) was obtained from a site that ceased production in 1953, with an unknown initial operation date, the site was manufacturing gas using a vertical retorts when it closed, but could also have produced horizontal retort, likely a LTHR, or carbureted water gas. The CWG plant was commissioned in 1902, with vertical retorts being constructed in 1913 and 1931. Statistical analysis showed the samples to have been derived from the LTHR process (McGregor et al., 2012). The sample is in the form of pure DNAPL in water and was taken from inside a former tar well during a remediation process. The sample was taken within a clean glass laboratory sample of 250ml.

DNAPL010 (D10) was obtained from a FMGP, which operated between 1849 and 1981 and mainly operated horizontal retorts, originally using LTHR and later switching to producers fired HR process circa 1890's. The tar samples were collected from a circular concrete tar tank known to be associated with the later HR process. The sample is in the form of pure DNAPL in water. The site also operated a CWG plant so it is possible that CWG tar may also be present within the sample.

DNAPL011 (D11) was recovered using a Low Flow from a sump present on a former wood treatment facility, associated with a former tar distillery in the United Kingdom. The sample is likely to be a distilled fraction of coal tar, such as creosote oil, used for the preservation of timber.

DNAPL012 (D12) was obtained from a former gasworks that opened in 1854 and initially operated low temperature horizontal retorts. By 1957 vertical retorts and CWG processed were also employed on the site and finally a SEGAS plant was located on site for the conversion of oil to gas as well as a number of different tar tanks associated with tar distillation. The sample was taken from a borehole (6.96 mbs) close to the former CWG and SEGAS structures on the site. Statistical analysis of the sample showed that the sample was derived from the CWG process (McGregor et al., 2012). The sample is included in the PCA and HCA analysis but was not included in any of the work presented within this PhD thesis.

DNAPL013 (D13) operated from 1885 until the 1970's, the site manufactured gas using horizontal retort until 1939, taking a bulk gas supply from another source. It did continue to maintain and use its CWG plan to supply peak demand. . The sample of liquid NAPL was removed from a groundwater NAPL plume beneath the site by a skimmer pump.

DNAPL014 (D14) was taken from the same site as DNAPL017 and was taken from an infilled former gasholder and later a tar emulsion storage tank, used for the storage of NAPL emulsions produced by the CWG process and was present in the form of pure DNAPL. This sample was obtained from a remediation system, which used total fluids pumping

DNAPL015 (D15) was taken from a site that operated between 1841 and 1961 as a Tully gas plant, which used a combination of vertical retorts and water gas processes. It is also believed that early horizontal retorts were also located on the site, however the tar sample is thought to have been produced by the vertical retorts from the Tully gas plant. The sample as obtained from a sump of tar/oil and is suspected to have been exposed to significant weathering. The sample is included within the PCA and HCA analysis but was not included in any of the other work presented within this PhD thesis.

DNAPL016 (D16) was obtained from a FMGP which operated between 1854 and 1946 and was a typical small country town FMGP site. The site is known to have operated hand charged directly fired horizontal retorts which would have produced a tar with low temperature characteristics (LTHR), which was shown in the statistical analysis (McGregor et al., 2012). The sample was recovered from the core barrel of a pioneer rotary drilling rig and is in the form of a tar saturated soil.

DNAP017 (D17) and was taken from the same site as DNAPL014 (D14) from a site which operated from 1868 to 1976. The site operated HR, Coke ovens, CWG, gas reforming plant and a by-products works. The samples were obtained from an area of the site where both the CWG and HR had operated. D17 was taken from a tar tank that would have been associated with the HR process.

DNAPL018 (D18) and DNAPL019 (D19) were taken from coke ovens that were still in operation at a steelworks. Both samples were taken on the day of coke production with D18 coming from an oven that has been in operation since the 1930's. D19 was taken from a coke oven that has been in operation since the 1970's. Both samples are in the form of pure DNAPL. The coals used in the manufacture of these tars was a blend of up to 12 non British imported crushed coals.

DNAPL020 (D20) operated from 1885 and ceased production in 1975. The site initially used horizontal retorts until the 1920s before then operating a Vertical retort plant and CWG plant. The coal tar sample was derived from the VR process. The sample is in the form of pure DNAPL. The site also operated a CWG plant so CWG tar may be present in trace amounts.

DNAPL021 (D21) and DNAPL022 (D22) both came from the same site, which ceased operation in 1870. Both samples were taken from the base of a gasholder, with D21 coming from a depth of 1.8m and D22 coming from a depth of 2.3m. Both samples are included in the PCA and HCA analysis but are not included in the other work presented within this PhD thesis.

DNAPL023 (D23) is thought to have been constructed between 1896 and 1915 on the site of a former mill. The site initially operated low temperature horizontal retorts and in 1916 continuous vertical retorts were added to boost gas production. The site was further expanded with the addition of eight more continuous vertical retort benches in 1938 and production ceased in 1972. A CWG plant was also added in the 1950's so traces of CWG tar may be present within the tar. The sample was included in the PCA and HCA analysis but was not included in the other work presented within this PhD thesis.

DNAPL031-039 and DNAPL040 (average) were obtained from a former un-engineered municipal landfill site in Florida US suspected of being used for the disposal of waste from a FMGP located within 5 miles of the landfill. The suspect FMGP was built in 1910, as a purpose built Lowe-type Carbureted War Gas (CWG) plant. In 1955 a Hasche oil-reforming gas plant was added, although this likely did not produce significant quantities of tar. The CWG plant is suspected to have used bituminous coal as a feedstock rather than coke as this variant had been prominent in the American gas industry following the outbreak of WW1. A total of 9 samples (DNAPL031-039) of perched ground water containing a mixture of water and non water-soluble waste DNAPL were collected. DNAPL040 is the average of all of the samples for the purposes of statistical analysis.

DNAPL043 (D43) and DNAPL044 (D44) were obtained from a contaminated site in the Netherlands and were located beside the Amersfoort railway station with the contaminated site covering an area of roughly 15,000m$^2$. The tar is in the form of a dense non-aqueous phase liquid (DNAPL), which was produced at a Pinstch Gas factory that operated from 1910 to 1954. The tar was produced as a byproduct of the Pintsch gas process using gasoil (likely diesel) and was discarded on site, at first in a ditch and later within dug out lagoons. From the ditch and lagoons the tar could freely sink into the subsurface and pure phase tar accumulated at the bottom of an aquifer at around 10-12 meters below ground surface (mbgs). The sample was taken from a fully filtrated monitoring well (A010F) situation near the former lagoons. 6m of tar was present within the well (6-12mbgs) at the time of sampling with the sample obtained from the bottom of the well. As both tar samples were of the same tar, in different bottles, only D43 was used for purposes of this PhD.

DNAPL047 (D47) was obtained from a former gasworks site located in central Scotland that operated between 1824 and 1901. Due to the operational timeframe it is likely to have operated as a Low Temperature Horizontal Retort.

DNAPL048 (D48) was obtained from a former gasworks site located in Arnhem, Holland. The site operated from an unknown date until the 1960's operating several different production processes over its production lifetime. In 1923 the site contained 16 half generator ovens with 8 horizontal retorts 3m in length and 6 full generator chamber ovens with 6 vertical retorts of 5m in length. In 1924 8 of the horizontal retorts were removed with the remaining 8 horizontal retorts removed in 1928. In 1932 the site was expanded with all old ovens replaced with 4 chamber ovens which were neither vertical nor horizontal but somewhere in between. This site history results in tar that may have been produced from horizontal retorts, vertical retorts or chamber ovens.

DNAPL049 (D49) – was obtained from a former manufactured gas works located in central Scotland. The site history for this sample is unknown and the sample is in the form of pure DNAPL tar taken from a tar tank present on the site.

DNAPL050 (D50) was obtained from a former manufactured gas works located in Northern England, UK. The site operated between around 1855 until the 1950's. In 1855 the site consisted mainly of 4 small gas holders and a small retort house with the site expanded in 1878 with 2 larger gas holders and a larger retort house added. Tar and ammonia works as well as tar oil stores and sulphate stores were also added in 1878. The site was significantly expanded in 1927 with the addition of a larger retort house as well as several tar and liquor wells. A CWG plant and gasholder were also added in 1927 as well as an oil tank and a significantly larger sulphate store. The site was further expanded in 1938 with the addition of a coke processing plant and finally a Benzole plant and coke breaking plant were added in 1950. The site mainly operated as an inclined chamber plant, although this was likely added in 1927 with the significant expansion that took place at this time.

### 3.2 Standards and Solvents

All solvents used (n-hexane, methanol and dichloromethane) were of analytical grade purchased from Fisher Scientific (Loughborough, U.K.). $D_{10}$-phenanthrene, D8-naphthalene, D10-fluorene, D10-fluoranthene, D10-pyrene were purchased from Sigma-Aldrich (Gillingham, U.K.). Standards of phenol, p-cresol, 3,5-dimethylphenol, 2,4,6-trimethylphenol, 1-naphthol, aniline, 9-phenanthrol and 1-hydoxypyrene were purchased from Sigma-Aldrich (Gillingham, U.K.). N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) was purchased from Sigma-Aldrich (Gillingham, U.K.). Calibration standards were prepared using a standard mixture containing all 16 USEPA RCRA Appendix VIII Priority Pollutant gasworks PAHs, as purchased from Thames Restek (Saunderton Bucks, U.K.).

### 3.3 Extraction

Accelerated solvent extract (ASE) is a solvent extraction technique that uses high temperatures and pressures in order to extract the organic compounds from a sample. While traditional extraction techniques, such as soxhlet, require long extraction times and relative large volumes of solvents ASE is capable of performing equivalent extraction efficiency while using lower volumes of solvent and with a quicker extraction time (Carro et al., 2013). This makes ASE an excellent choice of extraction technique for the analysis of coal tar and coal tar contaminated soils.

During extraction the solubility of the target analytes is enhanced by the decrease in viscosity of the solvents at high temperatures, which also reduces matrix interactions and increases the diffusion of the analytes through the matrix (Carro et al., 2013). The use of high pressure means that the solvents remaining within the liquid phase at temperatures far above their boiling points and so allows for faster extraction. As the temperature of extraction increases the level of analytes co-extracted increases meaning that higher temperatures decrease the selectivity of extraction. As with other extraction techniques the main limitation of ASE is the low selectivity of the extraction as well as the potential interferents that may be co-extracted.

Extraction is performed using an Accelerated Solvent Extraction system (ASE 350 Dionex, Camberley, UK) using 10 mL stainless steel extraction cells using the following methods:

Approximately 0.5g of tar is mixed with equal amounts of Sodium Sulphate ($NaSO_4$) and diatomaceous earth in a 1:1:1 ratio. This removes any water present within the coal tar and results in a fine powder that can be quantifiably transferred into the extraction cells, ensuring there was no loss of sample. Prior to loading, the samples are spiked with a recovery standard to calculate recovery.

The extraction cells are lined with 2 Dionex glass fibre filter papers (to ensure unwanted particulate matter did not collect in the extract) and packed with 3g of silica gel 60 deactivated with 300μl of water. The sample mixture is then loaded into the cells and excess diatomaceous earth was added until the cell was well packed to ensure that there is no void space.

*n*-Hexane is used as the extracting solvent at 150$^{o}$C and 10 MPa, using one dynamic (7 min) and two static (5 min each) extractions. A flush volume of 150% and purge time of 60 s was used. The extracts were concentrated to 1 mL using a Büchi Syncore Analyst (Oldham, U.K). The extracts are then made up to exactly 10 mL using *n*-hexane. A 1 mL aliquot is then transferred to an auto sampler vial prior to analysis. D10-phenanthrene is added to the sample prior to analysis as an internal standard.

Dichloromethane can also be used as an extracting solvent at 100$^{o}$C and 10 MPa, using one dynamic (7 min) and two static (5 min each) extractions. A flush volume of 150% and purge time of 60 s was used. Analysis was tested using Dichloromethane at 150$^{o}$C but was not used as the high temperature resulted in tar leaking from the cells within the ASE so the extraction temperature was lowered to 100°C.

### 3.4 Sample Evaporation

As the samples are dissolved in a relatively large amount of solvent following extraction sample concentration is required in order to both increase the relative concentration of the sample as well as re-dissolving them in a known volume of solvent. Extract concentration was performed using a Büchi Syncore® Analyst, which allows for the concentrations of up to 12 samples down to a volume of around 1ml. The system operates using a hotplate and vacuum in order to volatilize the extraction solvent and a condenser unit to remove it. *n*-Hexane method + DCM method

Following evaporation samples were transferred into 16ml furnaced glass vials, using dichloromethane in order to recover achieve full recovery. Dichloromethane was removed by the use of a nitrogen blowdown system and the samples were then made up to 10ml with n-hexane prior to analysis. An aliquot of known volume, either 0.5ml or 1ml depending on the application, was transferred into an auto sampler vial and spiked with the internal standard prior to analysis. All extracts were stored at 4°C prior to analysis. All samples the required derivatization were derivatized using 100ul of BSTFA with 1% TMCS placed in an oven at 70°C for 1 hour prior to immediate analysis, although the volume of BSTFA may vary depending on the nature of the sample.

### 3.5 GCxGC-TOFMS:

Traditional GC analysis allows for the separation of organic compounds in a single dimension. This often leads to problems when analyzing coal tars as the complex mixture of organics found in coal tars leads to large numbers of compounds co-eluting and generally poor chromatography making fingerprinting difficult. GCxGC-TOFMS runs the sample on the same primary column as traditional GC with the addition of a secondary column of a different polarity to the primary column and this allows for an extra degree of separation, which provides for a much wider range of compounds to be separated and identified.

The use of different column setups allows for the separation of different compounds of interest. Normal phase column sets are the most commonly used setup for analysis of environmental samples (McGregor et al. 2011), and this involves using a non-polar primary column combined with a mid-polarity secondary column. Reversed polarity sets give better resolution when analyzing coal tars and allow for the elution of higher molecular weight compounds present in the DNAPL while remaining within the temperature limits of the columns (McGregor et al. 2011), and involve the use of a mid-polarity primary column and a non-polar secondary column.

There are many factors that can affect the quality of the separation within the primary and secondary phase and column sets are chosen to give the best possible separations and resolution. The length of the secondary phase in GCxGC affects the retention time within the second dimension however it can also affect the retention times within the primary phase. As the length of the secondary column increases and while holding the same flow rate and temperature gradient the primary retention time will increase. This could be related to the linear velocity of the carrier gas in the first dimension (Adam et al. 2007). This difference in behavior in the first dimension with increasing secondary column length also has a further knock on affect on the separations within the second dimension. This is due to the fact that the increase in retention time within the primary column will mean that the secondary column temperature may be different for a given analyte as it elutes later in the temperature program (Adam et al. 2007).

The use of GCxGC allows for the separation of unresolved complex mixtures (UCM), often referred to as a big “hump” in the GC (Tran et al., 2010), which cannot be separated using traditional GC-MS analysis. Because UCMs are believed to consist of many thousands of compounds, traditional GC-MS is simply not capable of providing sufficient resolution leaving most UCM hydrocarbons unidentified. The combination of the GCxGC with the TOFMS (time-of-flight mass spectrometer) allows for the identification of compounds within the UCM that previously would be unidentifiable within the "hump" and most likely missed using GC-MS. The time-of-flight mass spectrometer (TOFMS) gives structural information and provides clean spectra even within partially co-eluting peaks through mass spectral deconvolution. The use of GCxGC allows for the separation of coal tar without the need for a lengthy separation process.

The high quality of spectra achieved by TOFMS is due to the high acquisition rate of the detector, which can go up to 500 spectra/s. When using the Leco TOF-MS there are several important considerations when interpreting the spectra obtained. The similarity number given by the software of above 800 usually indicates that an acquired mass spectrum shows a good match with the library search (Lu X. et at. 2003). A probability value of above 9000 means that the mass spectrum is unique and the identification based on mass spectra is logical. However it is important to remember that isomers have similar mass spectra and this is especially important when considering such as complex mixture of organics as coal tar. For large molecular weight compounds, and longer chain compounds, that have low intensity (or non detectable) molecular ions the wrong structural information will be given, according to the peak table, even if the similarity value is high (Lu X. et al. 2003).

Because the Leco system was initially thought to be mainly directed towards analysis of volatile compounds it gives somewhat poor-quality spectral data for the heavier ions with a sharp decrease in ion intensity (Jover et al. 2005). This is a potential problem since heavier ions are usually more selective and allow for the identification of the molecular ion. Jover et al. 2005 gives the example of cholesterol with the m/z of 368 being three times lower than expected (compared to the NIST library) and m/z 458 (molecular mass) four times lower. The Leco model used by Jover et al. 2005 was a Pegasus II whereas the setup used within this PhD is a Pegasus 4D. This may be less of an issue on the 4D system, however it is still an important factor to remember.

The GCxGC temperature programs varied throughout the PhD projected depending on the application with longer temperature programs allowed for easier identification of higher molecular weight compounds.

All GCxGC TOFMS analysis was performed using a Leco Pegasus 4D (St. Joseph, Michigan) time of flight mass spectrometer, connected to an Agilent 7890A gas chromatograph equipped with a LECO thermal modulator. The TOF ion source temperature was 200 °C and the mass range 45 and 500u was scanned at a rate of 200 spectra/second. The detector voltage was set at 1700V, although the voltage did vary, with an electron ionisation voltage of 70 eV.

The initial GCxGC-TOFMS work used the following primary oven temperature programme: 60°C isotherm for 2 minute, then ramp at 10°C/min to 110°C, then ramp at 3°C/min to 310 °C, and isothermal at 310°C for 15 minutes with a total run time of 67.8 minutes. The secondary oven and modulator temperatures were programmed at a 10 °C offset relative to the primary oven. The modulation period was 6 seconds with a 1.3 second hot pulse time and a cool time of 1.7 seconds. The injection port temperature was set to 250 °C and set to split injection with a split ratio of 50 and an injection volume of 1µl. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min.

Later GCxGC-TOFMS work used the following primary temperature oven programme: 60°C isotherm for 2 minute, then ramp at 3°C/min to 310 °C, and isothermal at 310°C for 15 minutes with a total run time of 88.6 minutes. The secondary oven and modulator temperatures were programmed at a 10 °C offset relative to the primary oven. The modulation period was 6 seconds with a 1.3 second hot pulse time and a cool time of 1.7 seconds. The injection port temperature was set to 250 °C and set to split injection with a split ratio of 50 and an injection volume of 1µl. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min.

The reversed polarity column set that was used through the PhD comprised of a mid-polarity TR-50 MS supplied by Thermo Scientific (30 m × 0.25 mm i.d. × 0.25 µm film thickness) as the primary column and a non-polar Rtx-5SilMS supplied by

Thames Restek (1.5 m × 0.25 mm i.d. m × 0.25 μm film thickness) as the secondary column, connected via a Thames Restek Press-tight connector.

GCxGC standard calibrations were performed using a mixture of 16 EPA priority PAHs, as well as 4 deuterated PAHs (D8-Naphthalene, D10-Fluorene, D10-Fluoranthene, D10-Pyrene). All calibrations curves obtained were linear and D10-Phenanthrene was used as an injection standard. Other standard calibrations performed include Phenol, p-Cresol, 3,5-Dimethylphenol, 2,4,6-Trimethylphenol, 1-Naphthol, Aniline, 9-Phenanthrol and 1-Hydoxypyrene all of which were run both derivatized and underivatized. Example calibrations can be found in appendix x1.

### 3.6 Quality Control

To ensure the accuracy of the analytical data produced stringent quality control measures were employed including:

- The use of procedural and reagent blanks
- The inclusion of an internal standard (D10-phenanthrene) prior to GCxGC analysis
- Recovery standards were added during extraction (including D8-Naphthalene, D10-Fluorene, D10-Fluoranthene, D10-Pyrene)
- Calibration standards (EPA 16 priority PAHs) for the GCxGC-TOFMS.
- Selected samples were extracted in duplicate and all samples were analysed in duplicate.
- All glassware used was clean and furnaced at 450$^{o}$C for 8 hours prior to use.
- Gloves were changed in between handling of different coal tar samples in order to reduce the potential for cross contamination.

### 3.7 Statistics

The chromatograms from each sample were processed using Leco ChromaTOF software (Version 4.50.8.0) to search for, identify and align all peaks with a signal-to-noise ratio greater than 10. All peak areas were corrected for sample weight and extraction efficiency prior to quantification and all statistical analysis was carried out using either Microsoft Excel (Version 14.3.7) or Minitab version 16 (Principle

Component Analysis (PCA) and Hierarchical cluster analysis (HCA)). The 16 USEPA Priority PAHs were quantified using standard calibrations for each of the individual PAHs.

Principle component analysis was carried out using 156 peaks (McGregor et al., 2012) and the unknown samples were combined with the previously published data set in McGregor et al., 2012. Prior to PCA analysis, all peak areas were normalized by dividing the peak area by the sample weight and then the $D_{10}$-phenanthrene peak area and taking the fourth root of the normalised value. Fourth Root data transformation is required, as without data pre-processing the large range of peak intensities within the dataset results in small peaks contributing less towards the principle components, regardless of their chemical importance. The use of the 4th root allows for the statistical analysis to focus more on the presence or absence of specific compounds rather than their relative concentrations. As the samples may have been in the environment for decades and so environmental processes, such as evaporation or dilution/transport in groundwater may have changed the contaminant ratios (McGregor et al., 2012). Using the 4th root means the PCA results can relate to the primary production methods used to produce the tars rather than changes that may have happened due to environmental factors (McGregor et al., 2012).

For HCA analysis the 8th root data formation was found to give the best results with subsequent transformations giving no extra resolution. A list of the sample information is shown in Table 1 including the information for the previously published British database in McGregor et al., 2012. While taking the 4th root for the PCA and 8th root for the HCA is done to reduce the influence of concentration differences on the results it cannot entirely remove the influence from the dataset. As the HCA analysis focuses on the similarities between the compounds and the PCA focuses on the variance the concentration influence will have more affect on the HCA than the PCA. This could possibly explain why the HCA is not completely able to separate the different production processes whereas the PCA is.

# Chapter 4

# Application of GCxGC coal tar method to non-British tars – A case study

## 4.1 Preface

This chapter contains an original journal article submitted for publication in the journal of Environmental Forensics in September 2016. The paper investigates the use of previously published method for the analysis of coal tar using GCxGC and multivariate statistics developed using UK tars on tars from the USA. C. Gallacher as the main author was responsible for all the analysis, data interpretation and writing of the paper. R. Kalin and R. Lord, as project supervisors, provided support with the research as well as assistance with preparation and review of the manuscript. R. Thomas, as the industrial supervisor, provided expert knowledge in the field of coal tar and manufactured gas as well as reviewing the manuscript. A. Hatheway provided expert knowledge in the field of coal tar research, with particular focus on local knowledge for the site analysed as well as reviewing the manuscript.

Previously research into Coal Tar using GCxGC analysis was performed by McGregor et al., 2012 and developed statistical methods for the source appropriation of coal tar using a database of British tar samples. Chapter 4 presents the expansion of this statistical database with the inclusion of tar produced within the USA. The chapter demonstrates the ability for the method developed in McGregor et al, 2012 to be applied to non-UK tars. The analysis using GCxGC was capable of detecting 947 individual compounds without the need for a separation step prior to analysis. Even with a chemical separation step it is unlikely that GC-MS analysis would have been capable of detecting such a large number of compounds. The chapter clearly demonstrates the separation power of the GCxGC as well as the statistical applications of the data produced using GCxGC. A full list of the compounds found within the sample can be found in Appendix B.

## 4.2 Ultra Resolution Chemical Fingerprinting of a Former Manufactured Gas Plant DNAPL Waste

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### Abstract

Ultra resolution chemical fingerprinting using two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC TOFMS) was performed on 9 tars samples from a former landfill site located in Florida. The tar likely came from a nearby former manufactured gas plant between the 1940's and 1950's that operated both the process (1910-1950) and Hasche Reforming Oil-Gas process (1951-1959). Statistical techniques including univariate analysis, hierarchical cluster analysis (HCA) and principle component analysis (PCA) were employed to identify if the samples were FMGP tar, and demonstrated that the tar was derived from the Carbureted Water Gas process. The results showed that an approach developed using British tars using can be successfully applied to US waste tars.

**Keywords:** Coal Tar, Environmental Forensics, GCxGC, Contaminated Land

### Introduction

Coal tar waste is a residual product of manufactured gas plants (MGP) and coal tar contamination is an expected occurrence at former MGP (FMGP) sites. Coal tars are dense non-aqueous-phase liquids (DNAPL) containing thousands of organic and inorganic compounds of which many can be toxic or carcinogenic, such as Polycyclic Aromatic Hydrocarbons (PAH's) (Birak and Miller, 2009). Coal tar

DNAPLs pose a complex challenge for regulatory-driven remediation of derelict sites (Gilbert et al, 2007). PAHs dominate the organic fraction of FMGP tars, and were produced by the pyrolysis of the feedstock (either in the absence of oxygen or by combustive flame) producing thousands of separate PAH compounds, which are separated from the processed consumer gas.

The term coal tar is generally used as a catch-all to include all tars produced by FMGPs, irrespective of the feedstock used in the gas-making process. Within the North Eastern American States, the Carbureted Water Gas process (CWG) was the predominant post-1900 process used at manufactured gas plant sites. On the West Coast of the USA, a group of technologies called the ‘Pacific Coast Oil Gas Processes’ were used to manufacture gas from oil and so oil-derived gas became the predominant feedstock for gas manufacture, although regional variations did exist such as the Midwest (Brown et al, 2006).

During the period of 1950’s to 1970’s processes which could produce “town gas” gas from oil refinery residuals such as butane and naphtha were developed. These were called gas reforming process and the Hasche Oil-Gas process was an early example of this type of technology. The Hasche Oil-Gas process converted hydrocarbon gases or vapours (ranging from propane to light naphtha) within a regenerative partial combustion process. The resulting synthetic gas had a similar energy content to natural gas and was particularly popular with Florida (Frink, 1955) The Carbureted water gas process involved passing steam over a carbon source (usually heated coke) with oil injected into the resulting produced gas (Thomas, 2014a).

Coal carbonization has been used worldwide for 200 years producing tar, which was derived from the pyrolytic thermal decomposition of coal in the absence of oxygen (Thomas, 2014a). There are many countries, which still use the technology, however the wastes are now considered more of a potential chemical feedstock. For example China is considering use of its coal tar for direct use as a potential energy alternative, because of dwindling supplies of petroleum (Shi et al, 2012). There has also been a shift in Chinese energy policy and a push towards clean coal technology such as integrated gasification combined cycle (IGCC) plants (Chen and Xu, 2010), which could produce significant quantities of residual tar. Additionally, underground coal gasification (UCG), one of the 1960s developments driven by the Middle Eastern energy crisis, is again gaining ground as a way of utilizing otherwise un-exploitable coal reserves lying at considerable depth beneath the ground.

In the US several thousand manufactured gas plants existed between the early 1800's to the 1950's (U.S. EPA, 1993). Estimates of the total specific number of US FMGP and associated tar-generating/tar-utilizing sites vary widely from 1,500 to more than 50,000 and this estimate depends on the function of the type of facilities considered (U.S. EPA, 2004). It is estimated that 11.5 billion gallons of tar were produced and gathered for sale and ongoing industrial use in the USA from 1820 to 1950 (Eng, 1985). Due to past handling, storage and waste disposal practices it has been shown that tar NAPL contamination is expected to be encountered at many former sites. The US EPA estimate that release of coal tar or other wastes to the environment is likely to have occurred in over 90% of sites (U.S. EPA, 2004).

Ultra resolution chemical fingerprinting takes advantage of the separation power of comprehensive two-dimensional gas chromatography to provide a large amount of chemical information for a given tar DNAPL. A full understanding of chemical 'signatures' for environmental forensic apportionment of historical contamination and waste from the ongoing international coking industry, gasification of municipal waste, syngas production, etc. is therefore required to distinguish recent environmental degradation from that of historical-origin. McGregor et al. (2012) developed a multivariate statistical analysis using GCxGC-TOFMS for the source appropriation of coal tar using a database of 23 British coal tar samples from various different production processes.

**Site History**

The study site was a former unengineered municipal landfill (dump) site suspected of being used for the disposal of wastes from a FMGP located within 5 miles of the landfill. The suspect FMGP was built in 1910, as a purpose-built Lowe-type

Carbureted Water Gas (CWG) plant. In 1955 a Hasche oil-reforming gas plant was added, with the purpose of creating synthetic natural gas, in anticipation of the arrival of a regional pipeline natural gas and the plant switched entirely to this process of gas manufacture. This means there are two potential basic forms of tar present at the site.

The Carbureted Water Gas plant is suspected to have used Bituminous coal as a feedstock rather than coke as this variant had been prominent in the American gas industry following the outbreak of the First World War. Unlike some FMGP sites, this site did not produce its own source of coke via coal gasification and would not have had the benefit of a local source of coke from a coking works. This would have also favored the import of low-grade bituminous coals.

A total of 9 samples (DNAPL031-039) of perched ground water containing a mixture of water and non water-soluble waste DNAPL were collected and analyzed. The groundwater was suspected to be contaminated with some form of gasworks process tar waste, from a FMGP located in the same town, as the samples were obtained from natural geologic strata lying below an (to remain unidentified) abandoned municipal landfill site located in the State of Florida, USA. All samples contained water contaminated with free-phase DNAPL and were sealed and stored at 4$^{o}$C prior to analysis.

All sample analysis and data interpretation was performed without specific prior site knowledge in order to test that Environmental Forensic analysis developed for analyzing UK tars was applicable to samples recovered from FMGPs in the USA.

## Materials and Methods

### Analytical Methods

All analytic mobilizing solvents used were of analytical grade purchased from Fisher Scientific (Loughborough, U.K.) and $D_{10}$-phenanthrene was purchased from Sigma-Aldrich (Gillingham, U.K.). Calibration standards were prepared using a standard mixture containing all 16 USEPA RCRA Appendix VIII Priority Pollutant gasworks PAHs, as purchased from Thames Restek (Saunderton Bucks, U.K.) and 4 Deuterated PAHs purchased from Sigma-Aldrich (Gillingham, U.K.).

Extraction was performed using an Accelerated Solvent Extraction system (ASE 350 Dionex, Camberley, UK) using 10 mL stainless steel extraction cells using the following method:

- Approximately 0.5g of tar was mixed with equal amounts of Sodium Sulphate ($NaSO_4$) and diatomaceous earth in a 1:1:1 ratio. This removed any water present within the coal tar and results in a fine powder that can be quantifiably transferred into the extraction cells, ensuring there was no loss of sample. Prior to loading, the samples were spiked with 100ul of 5000ug/ml of a mix of the recovery standards to calculate recovery.
- Extraction cells were lined with 2 Dionex glass fibre filter papers (to ensure unwanted particulate matter did not collect in the extract) and packed with 3g of silica gel 60 deactivated with 300µl of water. The sample mixture was then loaded into the cells and excess diatomaceous earth was added until the cell was well packed to ensure that there is no void space.
- *n*-Hexane was used as the extracting solvent for all extractions. ASE was performed at 150$^{o}$C and 10 MPa, using one dynamic (7 min) and two static (5 min each) extractions. A flush volume of 150% and purge time of 60 s was used. The extracts were concentrated to 1 mL using a Büchi Syncore Analyst (Oldham, U.K). The extracts were then made up to exactly 10 mL using *n*-hexane. A 1 mL aliquot was then transferred to an auto sampler vial prior to analysis. D10-Phenanthrene was added to the sample prior to analysis as an internal standard.

GCxGC TOFMS analysis was performed using a Leco Pegasus 4D (St. Joseph, Michigan) time of flight mass spectrometer, connected to an Agilent 7890A gas chromatograph equipped with a LECO thermal modulator. The TOF ion source was fixed at 200 °C and masses between 45 and 500u were scanned at a 200 spectra/second rate. The detector voltage was set at 1700 V and the applied electron ionisation voltage was set at 70 eV.

All standards and extracts were analysed with the following primary oven temperature programme: 75°C isotherm for 1 minute, then ramp at 12°C/min to 120°C, then ramp at 3°C/min to 310 °C, and isothermal at 310°C for 10 minutes. The secondary oven and modulator temperatures were programmed at a 20 °C offset relative to the primary oven. The modulation period was 6 seconds with a 1.3 second hot pulse time and a cool time of 1.7 seconds. The injection port temperature was set to 250 °C and set to split injection with a split ratio of 50 and an injection volume of 1µl. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min.

The reversed polarity column set that was used comprised of a mid-polarity TR-50 MS supplied by Thermo Scientific (30 m × 0.25 mm i.d. × 0.25 µm film thickness) as the primary column and a non-polar Rtx-5SilMS supplied by Thames Restek (1.5 m × 0.25 mm i.d. m × 0.25 µm film thickness) as the secondary column, connected via a Thames Restek Press-tight connector.

The chromatograms from each sample were processed using Leco ChromaTOF software (Version 4.50.8.0) to search for, identify and align all peaks with a signal-to-noise ratio greater than 10. All peak areas were corrected for sample weight and extraction efficiency prior to quantification and all statistical analysis was carried out using either Microsoft Excel (Version 14.3.7) or Minitab version 16 (Principle Component Analysis (PCA) and Hierarchical cluster analysis (HCA)). The 16 USEPA Priority PAHs were quantified using standard calibrations for each of the individual PAHs.

**Statistical Methods**

Principle component analysis was carried out using 156 peaks (McGregor et al, 2012) and the unknown samples were combined with the previously published data set in McGregor et al. (2012). Prior to PCA analysis, all peak areas were normalized by dividing the peak area by the sample weight and then the $D_{10}$-phenanthrene peak area and taking the fourth root of the normalised value. Fourth Root data formation is required, as without data pre-processing the large range of peak intensities within the dataset results in small peaks contributing less towards the principle components, regardless of their chemical importance. The use of the 4th root allows for the statistical analysis to focus more on the presence or absence of specific compounds rather than their relative concentrations. As the samples have been in the environment for decades and so environmental processes, such as evaporation or dilution/transport in groundwater may have changed the contaminant ratios (McGregor et al, 2012). Using the 4th root means the PCA results can relate to the primary production methods used to produce the tars rather than changes that may have happened due to environmental factors (McGregor et al, 2012).

For HCA analysis the 8th root data formation was found to give the best results with subsequent transformations giving no extra resolution. A list of the sample information is shown in Table 4.1 including the information for the previously published British database in McGregor et al. (2012).

### Quality control

To ensure the accuracy of the analytical data produced stringent quality control measures were employed including: The use of procedural and reagent blanks; the inclusion of an internal standard (D10-phenanthrene); recovery standards (D8-Naphthalene, D10-Fluorene, D10-Fluoranthene, D10-Pyrene); and calibration standards (EPA 16 priority PAHs) for the GCxGC-TOFMS. Recoveries of the recovery standards ranged from 91.18% to 102.53% falling well within US EPA method 8000B requirements (70-130%). Both procedural and reagent blanks were clean and free of contamination and all standard calibrations obtained were linear.

### Results and discussion

Of the 9 samples analysed DNAPL031 was analysed in depth for all the compounds that could be detected within a single GCxGC run. A total of 947 individual compounds were detected with 88 aliphatic compounds, 569 Aromatic compounds, 66 Oxygen containing compounds (PAOH), 180 Sulphur containing compounds

(PASH), 43 Nitrogen containing compounds (PANH) and 1 mixed heterocycle. As the water gas process without carburation does not produce significant amounts of tar (Hamper., 2006) then the organics present within a CWG tar predominantly come from the feedstock oil used in the production process.

The n-alkane distribution of the sample, shown in figure 4.1, is dominated by n-alkanes between C12 and C17 with only minor abundances of n-alkanes between C22 and C33. The presence of abundant n-alkanes and the presence of light-end n-alkanes such as C11, which is the smallest n-alkane that can be detected using the GC method, suggest that the sample is not degraded (Volkman et al., 1984). The ratio of the C17 *n*-alkane to Pristane can also be used to determine how weathered the oil is with a ratio of <1.0 indicating the oil has been highly weathered[25]. The average *n*-C17/Pristane ratio is 2.07 suggesting that the tar sample has not undergone significant biodegradation. The presence of n-alkenes, between C11 and C17, within the sample may also be important, as n-alkenes are not commonly present within crude petroleum (Wang et al., 2006). This suggests that either the oil used as a feedstock was refined prior to use, or the CWG process itself produces n-alkenes. Alkyl-cyclohexanes are commonly associated with being derived from petrogenic sources (Saber et al., 2006) and were detected within the sample between C4- and C18-. The alkyl-cyclohexane distribution is shown in figure 4.2 with only minor abundances of C14- to C18- present within the sample and a maxima at C8-.

CWG tars exhibit a large abundance of low molecular weight *n*-alkanes, alkylated benzenes and sulphur-containing heterocycles and this is clearly shown with DNAPL031 (McGregor el al, 2012). A total of 68 alkylated benzenes between C3 and C8 were detected, making up the largest individual group of compounds. Of the 180 PASHs detected within DNAPL031 178 were present in the form of sulphur heterocycles. Two Naphthalene thiol isomers ($C_{10}H_8S$) make up the remaining sulphur compounds detected within the sample. Only a single compound was detected containing more than 1 sulphur in the form of Thieno[3,2-b]thiophene ($C_6H_4S_2$). The number of potential PASH isomers relative to their corresponding PAH isomers is higher due to the presence of sulphur within the ring resulting in a greater number of isomers (Mössner et al., 1999). A large variety of alkylated PASH isomers were detected within the sample with 17 alkylated thiophene isomers between C2- and C5-, 37 alkylated benzothiophenes between C1- and C4- and 38 alkylated Dibenzothiophenes between C1- and C4-. The relatively small number of PANHs detected within the sample may be explained by feedstock used to produce the tar. Crude petroleum has a lower relative nitrogen content to coal with <0.5% of crude petroleum compounds being present as PANHs, whereas 1-2% of coal compounds are present in the form of PANHs (Burchill et al., 1983).

Various diagnostic ratios can be used to give information about the potential source and manufacture process of coal tar contaminated samples (McGregor et al, 2012; Budzinski et al, 1997; Mauro, 2000; Yunker et al, 2012; Saber et al, 2006; McGregor et al, 2011). The ratios of phenanthrene to anthracene (Phen/Ant) and fluoranthene to pyrene (Flt/Pyr) have been used to distinguish between sources of PAH contamination (Budzinski et al. 1997; Saber et al, 2006). Phenanthrene is the most thermally stable 3-ring PAH isomer and so is much harder to break down at higher temperatures and is more likely to survive high temperature processes (525$^{o}$C to 725$^{o}$C) than anthracene (Budzinski et al, 1997). The average Phen/Ant ratio of 5.26 (4.56-5.61) is well within the range of Pyrolytic samples (<10) (Budzinski et al, 1997). Taken in isolation the Phen/Ant ratio would suggest that the sample has been pyrolytically altered however the Phen/Ant ratio should not be used in isolation and the ratio of Flt/Pyr should also be considered (Budzinski et al, 1997). The ratio of Flt/Pyr is 0.74 (0.69-0.78) and when combined with the ratio of Phen/Ant this points to the sample being petrogenic in origin. The normal operating temperature of the CWG process is between 650$^{o}$C and 700$^{o}$C (Hamper, 2006) and this may explain the low Phen/Ant ratio as the Phenanthrene will be more thermally stable at these temperatures than Anthracene. The relatively low average fluoranthene to pyrene ratio of 0.74 (0.69-0.78) also falls into the range for CWG (0.6 to 0.8) (Saber et al, 2006).

For Pyrogenic samples the anthracene/(anthracene + phenanthrene), fluoranthene/(fluoranthene + pyrene) and benzo[a]anthracene/(benzo[a]anthracene +

chrysene) are expected to be >0.1, >0.5 and >0.35 respectively (Budzinski et al, 1997; Yunker at al, 2012). The average Ant/(Ant+Phen) ratio of 0.16 (0.15-0.18) falls within the range of a Pyrogenic sample. The ratio of BaA/(BaA+Chr) is 0.55 (0.53-0.56), which again falls well within the range of a Pyrogenic rather than petrogenic sample. The Flt/(Flt+Pyr) ratio of 0.43 (0.41-0.44) falls within the petrogenic rather than pyrogenic range and also falls within the range of liquid fossil fuel combustion (0.4-0.5) (Yunker et al, 2012). This may be explained by the partial combustion of the feedstock taking place during the CWG production process. Both the Ant/(Ant+Phen) ratio and BaA/(BaA+Chr) ratio suggest that the temperature of the CWG process influences the petrogenic signature of the feedstock oil in a way that produces a tar with inferred pyrogenic characteristics. It is also possible that the use of bituminous coal as a feedstock affects these ratios.

The average Ant/(Ant+Phen) ratio of 0.16 (0.15-0.18) falls out with the expected range for coal tar and this is also the case for BaA/(BaA+Chr), with a ratio of 0.55 (0.53-0.56) and an expected ratio of 0.35. This may be explained by the Flt/(Flt+Pyr) ratio of 0.43 (0.41-0.44), which falls outside the range of solid coal combustion, but within the range of liquid fossil fuel combustion (0.4-0.5) (Yunker et al, 2012) with partial combustion of the feedstock taking place during the CWG production process.

Pristane and Phytane are two common biomarkers found in oil, and are often used to fingerprint the source of oil in contaminated samples. Powell and McKirdy. (1973) compared a series of oil and coal samples from various locations and showed ratios that correspond to different depositional environments. The Pristane/Phytane (Pri/Phy) ratio has also been proposed as an indicator of the oxicity of the oil depositional environment, based on the assumption that both Pristane and Phytane originate from the phytol side chain of chlorophyll α (Koopmans et al, 1999). The average Pri/Phy ratio of 1.88 falls within the range of both Marine oils (1.5-3.1) and Brown/Sub-Bituminous coal (1-3). As the feedstock oil used is likely to dominate the tar signature this suggests the feedstock oil used was marine in origin.

HCA analysis shows that the average of the Unknown USA Tar samples (DNAPL040) shares the highest degree of similarity with British CWG tars (Figure 4.3). Since water gas tars produced without carburetion produced insignificant levels of tar (Hamper., 2006) then the feedstock oil used in the CWG process dominates the tar residue produced. In the United Kingdom, CWG plants consumed mainly light oils for carburetion (Butterfield, 1904; Thomas, 2014b), whereas in the USA heavier or crude oils tended to be used, beginning about 1910, with the burgeoning use of the automobile (Hatheway, 2012) especially after World War I when light oils such as gasoline were in high demand (Harkins et al, 1988). This suggests that even when different feedstock oil may have been used the tars produced are still similar relative to the coal gas tars.

It is also possible that the use of bituminous coal as a solid feedstock alters the composition of the tars produced. British CWG plants almost invariably employed coke as a generator feedstock, as coke was abundant on British gasworks as a by-product of coal gas manufacture. Since non-carbureted water gas manufactured using coke only produced negligible amounts of tar, the majority of the chemical signature of British CWG tars comes from the feedstock oil used. This may not be the case when using bituminous coal due to the significant differences in compositions of bituminous coal compared to coke and so the tar produced may be influenced by the composition of the bituminous coal.

Whilst bituminous coal would have been a cheaper generator fuel than coke, the gas producing capacity of CWG when using bituminous coal was lower than coke due to uneven heating of the feedstock (Hamper, 2006). Mixing an unspecified bituminous coal with 20% coke resulted in a gas making capacity equivalent to using coke alone (Furnas, 1942), so it is possible that coke may have been added to the mix on site to increase gas production at minimal extra cost. The lack of a local source of coke would reduce the likelihood of coke being added into the feedstock mixture, especially during war time periods when coke was in high demand by the metallurgical industries. The mixing of coke into the solid feedstock could potentially affect the tar produced, if the bituminous coal does have an affect on the tar.

Figure 4.4 shows the PCA analysis of the average of the 9 Unknown USA Tar samples combined with the previously published dataset from McGregor et al. (2012). The average of the Unknown USA Tar clusters closest to the CWG/CR group, and significantly away from all of the other sample types. 81.7% of the total variance is accounted for within the first two principle components. This suggests that the PCA analysis is able to identify a CWG sample regardless of the feedstock used to produce it. This is likely down to the significantly different chemical footprint and range of compounds that are detectable within an oil based process rather than a coal based one.

It is unknown if the tar was dumped all at once or was dumped multiple times over the operational period of the landfill. The dumping into the landfill is suspected to have occurred during the 1940's until the mid-1950's. The Hasche oil reforming process was not introduced on site until 1955 and is unlikely to have produced significant amounts of tar due to the feedstock used to produced it, propane to light naphtha. This mean it is very likely that the tar consists exclusively of CWG tar rather than a mixture of oil-gas and CWG tar. It should also be noted that even if oil-gas tar was dumped into the landfill later than the CWG tar, it is unlikely that there were significant enough quantities to affect the chemical fingerprint, and so the HCA or PCA analysis.

## Conclusions

The results of this study clearly demonstrate the analytical power of GCxGC-TOFMS analysis when combined with univariate and multivariate statistics. Univariate diagnostic ratios were able to determine that the unknown blind samples were petrogenic in origin and likely produced by he CWG process. Multivariate statistics were capable of providing forensic information on the sample and confirmed that they were produced by the CWG process. The ratio of pristane to Phytane was also used to suggest that the feedstock oil used was marine in origin, possibly from the Gulf of Mexico as the samples came from Florida.

This work could be further expanded on by obtaining samples from different USA based coal gasification plants in order to assess how well the multivariate statistics work with USA coal gasification tars. The fact the analysis is capable of analysing USA CWG tars successfully suggests that they would likely analyse USA based coal gasification tars as well. The results increase the scope of the method developed in McGregor et al.,2012 clearly showing that a database developed using UK tar samples can be applied to samples from outside the UK.

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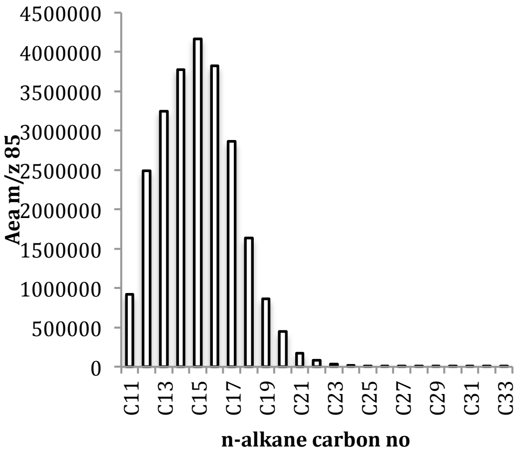
## Figures and Tables

| Sample number | Site Class | Process(es) employed | Year of Operation |
|---|---|---|---|
| 1-6 | A | Vertical retorts; potential traces of CWG, oil reforming and early horizontal retort tars | 1836 - 1971 |
| 7 | B | Horizontal retorts | 1856 - 1969 |
| 8 | B | Horizontal retorts | 1886 - 1971 |
| 9 | A/E | Horizontal (early, low temperature) and vertical retorts plus CWG plant | Ceased production by 1953 |
| 10 | B | Horizontal retorts | 1849 - 1981 |
| 11 | D | Wood preservation site - distillation of coal tar for creosote oil | Unknown |
| 12 | E | CWG plant | 1854 - unknown |
| 13 | E | CWG plant | 1885 - unknown |
| 14 and 17 | B | Horizontal retorts; potential traces of CWG and coke oven tar | |
| 15 | A | Tully gas plant; combination of vertical retorts and water gas | 1841 - 1961 |
| 16 | C | Horizontal retorts (early, low temperature) | 1854 - 1946 |
| 18 | F | Coke ovens | 1970's - present day |
| 19 | F | Coke ovens | 1930's - present day |
| 20 | A | Vertical retorts; potential traces of CWG tar | 1885 - unknown |
| 21 and 22 | C | Horizontal retorts (early, low temperature) | Ceased production by 1870 |
| 23 | A | Vertical retorts | 1915-1979 |
| 31-39 (Avg 40) | U | CWG plant with potential traces of Oil Gas and Hasche reforming gas plant | 1910 - Unknown |

Table 4.1 Sample database site history information

A = vertical retort, B = Horizontal retort, C = low temperature horizontal retort, D = creosote, E = Carburetted water gas, F = coke oven, U = unknown US coal tar samples,



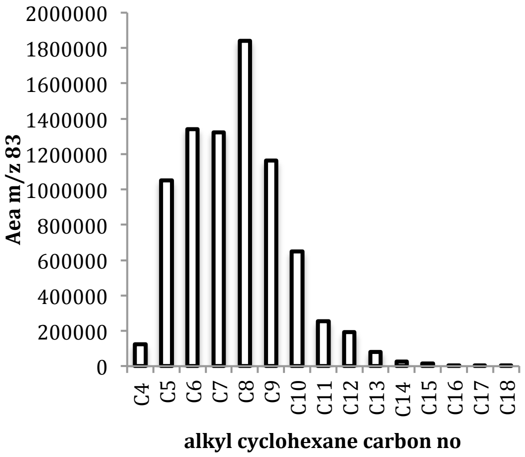


Figure 4.1 – n-alkane distribution

Figure 4.2 – Alkyl cyclohexane distribution

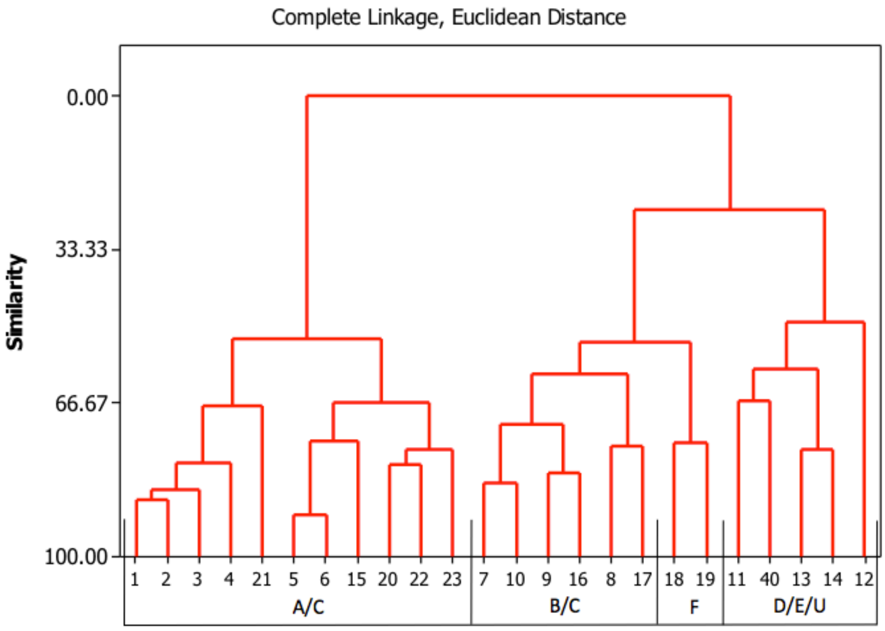


Figure 4.3 – Dendrogram of the eighth root, normalised data including unknown Tar samples using Euclidean distance and complete linkage mechanisms (A=Vertical Retort, B = Horizontal Retort, C = Low Temperature Horizontal Retort, D = Creosote, E = Carbureted Water Gas, F = Coke oven, U = Florida tar average).

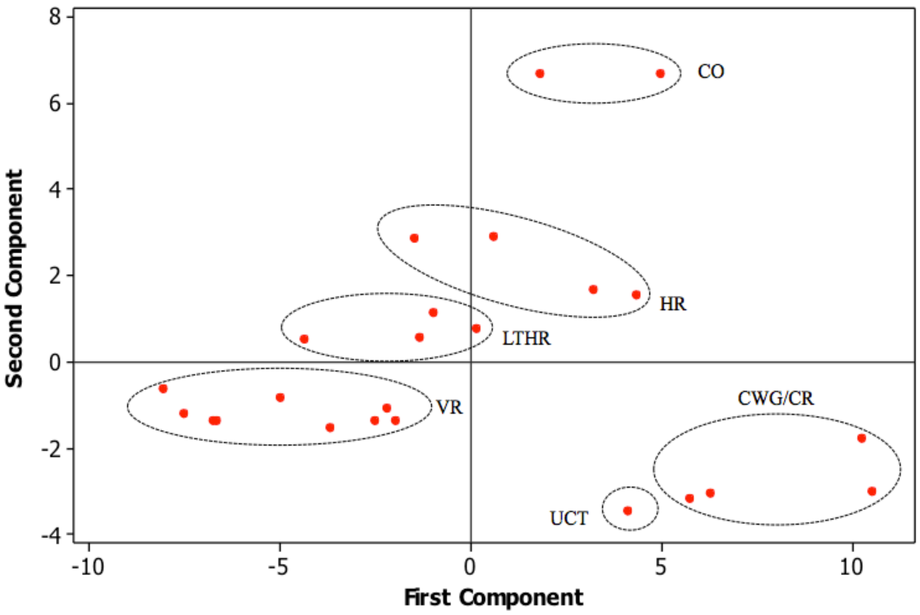


Figure 4.4 – Principle Component Analysis of Unknown Tar data set and existing British data set (CO = Coke Oven, HR = Horizontal Retort, LTHR = Low Temperature Horizontal Retort, VR = Vertical Retort, CWG = Carbureted Water Gas, CR = Creosote, UCT = Unknown Tar)

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### 4.3 Bridge – Principle Component Analysis Covariance versus Correlation

The paper presented in section 4.2 provides the principle component analysis of coal tars from varying production processes with the inclusion of samples from the USA. Principle component analysis can be performed using two different types of matrixes correlation and covariance. When the correlation matrix is used the variables are standardized, which is usually done when the variables are measured by different scales. When a covariance matrix is used the variables are not standardized.

McGregor et al., 2012 used covariance when analysing a database of 23 samples with the results shown in Figure 4.5. The PCA analysis was capable of separating the different production processes with the exception of DNAPL011, which falls within the CWG region when the sample is in fact Creosote. Creosote is a coal tar distillation product whereas CWG is an oil based gas production processes. This suggests that either the distillation process that produces the creosote affects the PCA analysis or it is also possible that the Creosote sample is contaminated with petrogenic material.

Covariance matrices are used when the variables being analysed fall within the same scale, and so likely fall within the same order of magnitude. The data is taken to the 4th root in order to reduce the impact of individual compounds on the analysis as well as reduce the impacts of concentration, however it is impossible to remove concentration from the equation completely. The range of values after the 4th root has been taken falls between a maximum of 6.161937 and a minimum of 0.02247. This range of values does not fall within the same order of magnitude and this suggests that correlation may be more appropriate for the analysis of the dataset rather than covariance.

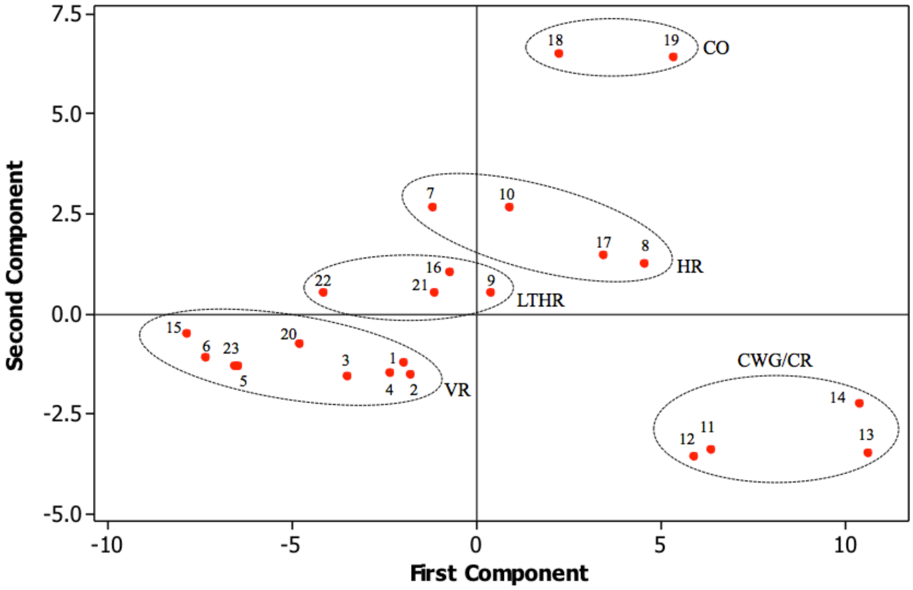

Figure 4.5 – PCA of McGregor et al., 2012 dataset using Covariance

Figure 4.6 shows the same dataset with PCA analysis performed using a correlation matrix and the main clusters are preserved. The exception being that DNAPL011 no longer clusters with the CWG tars and forms it's own cluster. These results suggest that correlation may produce better results relative to covariance, as the analysis is capable of discriminating the creosote sample from CWG tars.

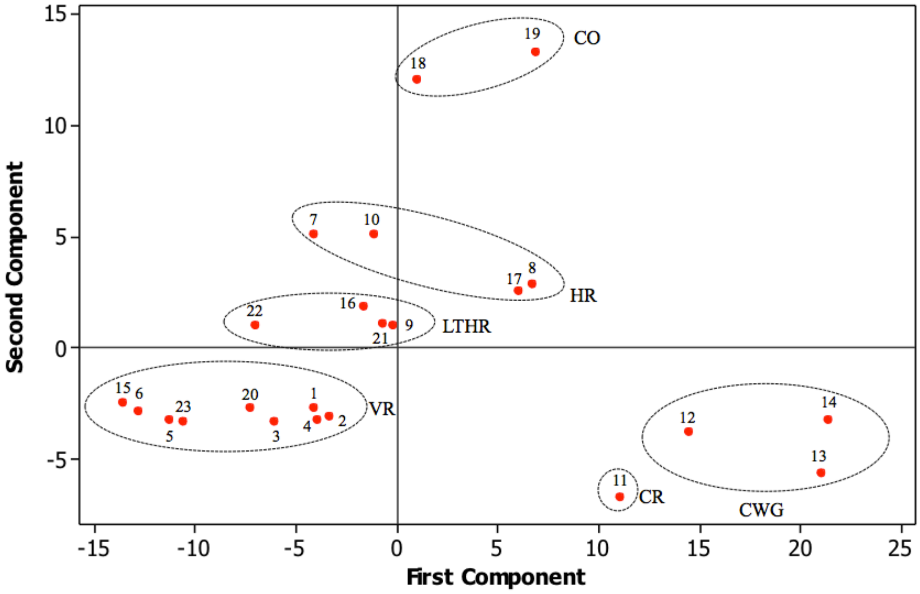

Figure 4.6 – PCA of McGregor et al., 2012 dataset using Correlation

The PCA loading plots, which show how the individual variances for each compound influence the PCA score plot, for covariance is shown in figure 4.7 and correlation is shown in figure 4.8. When comparing the two graphs the individual compounds have less influence on the PCA when correlation is used due to the standardization process used. Figure 4.8 clearly shows that several compounds have a much larger influence on the PCA including carbazole, fluoranthene, pyrene, naphthalene and dibenzofuran with phenanthrene having the largest influence. This suggests that samples that contain significant concentrations of these compounds, and others, will be influenced more heavily when covariance rather than correlation is used. This suggests that using the correlation matrix further reduces the impact of concentration from the PCA analysis, at least for those compounds that significantly influence the analysis when covariance is used. The loading plots also clearly show several important trends such as the grouping of phenol and alkyl phenols, aliphatics and toluene relative the aromatics and heterocyclic compounds. The use of correlation decreases the influence of the aromatic and heterocyclic compounds while increasing the influence of aliphatic and phenolic compounds. The presence or absence of toluene within the samples will also significantly influence where the samples fall within the PCA plot.

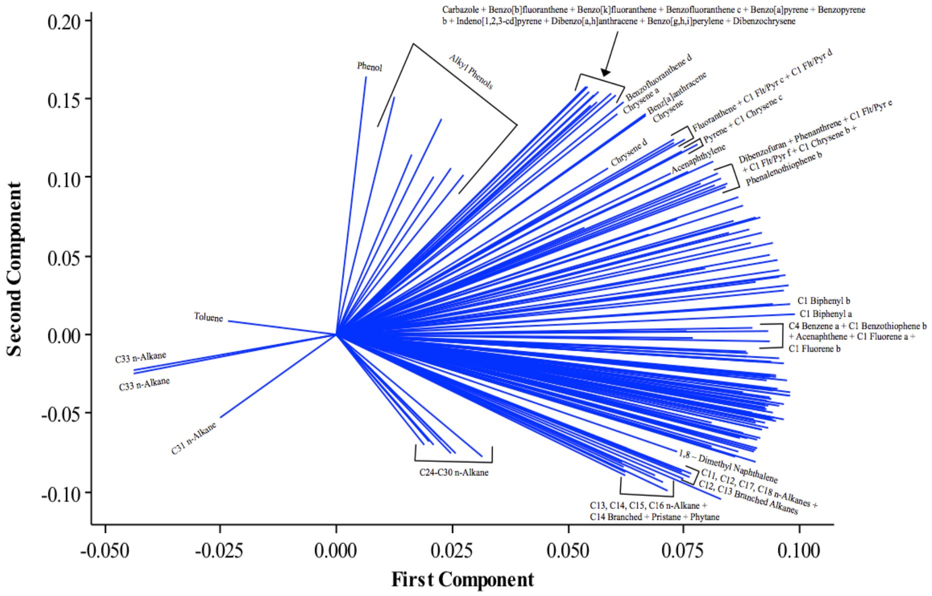

Figure 4.7 – PCA of McGregor et al., 2012 dataset loading plot correlation

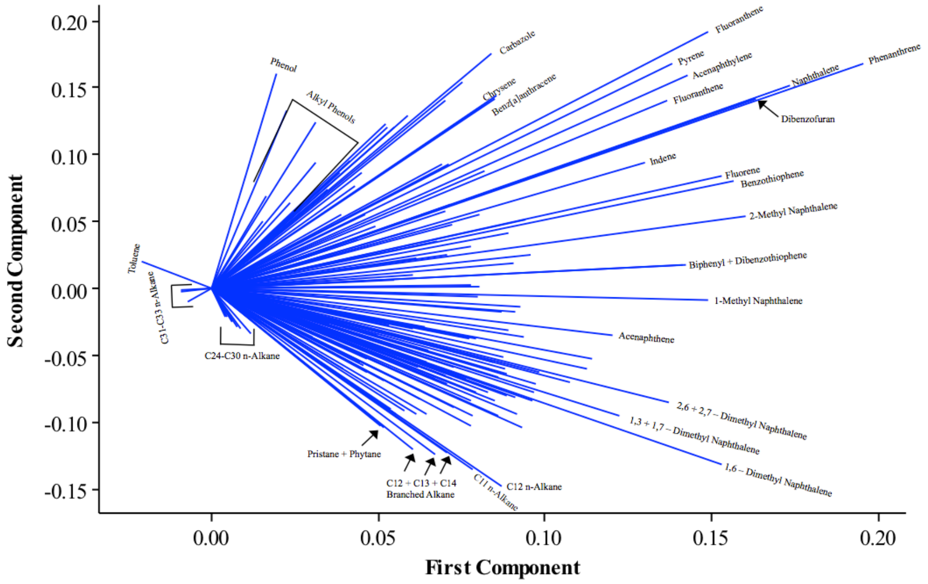

Figure 4.8 – PCA of McGregor et al., 2012 dataset loading plot Covariance

Previous work on coal tar has used pre-extraction derivatization in order to increase the number of compounds detected within a tar (Gauchotte-Lindsay et al., 2012), however pre-extraction derivatization techniques are not commonly used (Carro et al., 2013) therefore development of a new post extraction derivatization method is important, and is presented in chapter 5.

# Chapter 5
# Derivatization of Coal Tar

## 5.1 Preface

This chapter contains an original journal original journal article submitted for publication in the journal of Chemosphere in September 2016. The paper investigates the use of a post extraction derivatization method for the analysis of Creosote, a coal tar distillate, as well as in depth analysis of the range of compounds that could be detected within a single run. C. Gallacher as the main author was responsible for all the analysis and data interpretation and writing of the paper. R. Kalin and R. Lord, as project supervisors, provided support with the research as well as assistance with preparation and review of the manuscript. R. Thomas, as the industrial supervisor, provided expert knowledge in the field of coal tar and manufactured gas as well as reviewing the manuscript. C. Taylor provided expert knowledge in the field of coal tar research as well as reviewing the manuscript.

Chapter 4 presented the application of existing GCxGC and statistical methods developed using UK tars for tars produced from the USA. Previously published methods developed by Gauchotte-Lindsey et al. 2012 used pre extraction derivatization, using n-hexane as an extraction solvent, for the derivatization of hydroxylated PAHs, and other compounds containing active hydrogen. Pre extraction derivatization is not commonly used however due to difficulty in reproducibility and potential matrix effects (Carro et al. 2013). For this reason chapter 5 presents the application of a post extraction derivatization method, using dichloromethane as an extraction solvent, to a sample of Creosote, a coal tar distillate likely to contain significant concentrations of hydroxylated PAHs. Full derivatization of an unknown sample may not always occur, as the derivatization reagent must be present within excess. The use of post extraction derivatization allows for more additional derivatization reagent to be added if full derivatization does not occur. The use of dichloromethane allows for all potential derivatized compounds to be extracted, which may not always be the case with n-hexane and pre extraction derivatization. The analysis was capable of detecting 255 derivitised compounds, many of which would not have been detected without the use of derivitisation. The analysis also detected 1505 individual compounds, which is the 3rd highest total compound count of the samples presented within this thesis. The analysis was capable of identifying several compounds that may be of toxicological interest. The chapter presents the largest number of compounds detected within a Creosote published with a compound count far larger than published estimates of the number of compounds contained within Creosote. A full list of the compounds found within the sample can be found in Appendix B.

## 5.2 Qualitative and Quantitative analysis of a highly weathered derivatized Creosote by comprehensive two-dimensional gas chromatography.

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### Abstract

Creosote is a distillation product of coal tar and is widely used as wood preservative for railway sleepers, utility poles and for other applications. Creosote can have potentially negative effects on the environment and many of the components are toxic. This study presents the analysis of a Creosote sample from a former wood impregnation plant located in the UK. The sample was analysed using two dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS) and a database of compounds that could be detected was produced. The GCxGG-TOFMS was capable of detecting 1505 individual compounds, which is far more than previous estimates for the number of compounds present within Creosote. Post extraction derivatization using BTSFA with 1% TMCS was employed to increase the potential number of compounds detected with 255 derivatized compounds detected. Selected derivatized compounds were quantified with limits of detection ranging from 0.6mg/kg to 1.6mg/kg from a concentrated DNAPL. This work presents the first published full analysis of a Creosote using GCxGC-TOFMS combined with derivatization.

**Keywords:** Environmental Forensics, Creosote, GCxGC-TOFMS, Coal Tar, Derivatization

## Introduction

Creosote is viscous distillation product of coal tar, with a density slightly higher than water (Giddings *et al*. 1985), and is widely used as a wood preservative (Mateus et al. 2008). It is widely used for the treatment of wooden railway sleeper with 70% of all Creosote use in the US used on railway sleepers/crossties and 15-20% used on utility poles/cross arms (EPA, 2008). Coal tar Creosote is typically composed of approximate 85% polycyclic aromatic hydrocarbons; 10% Phenolic compounds and 5% N-, O- and S- Heterocycles (Mueller *et al*. 1989) although the overall composition may vary due to the production process, temperature and coal type used to produce the original coal tar (Johansen *et al*. 1997). Creosote can have negative effects on the environmental as for example it can inhibit plant biomass accumulation (Marwood *et al*. 2003) and many of the compounds present within Creosote are toxic, carcinogenic and mutagenic.

When Creosote DNAPL (Dense Non Aqueous Phase Liquid) is spilled into the sub surface it will penetrate the water table due to it having a higher density than water and will continue its downward migration as a separate liquid (Johansen *et al*. 1998). Within the vadose zone a portion of the volatile compounds will evaporate into the air phase, creating a gas phase contamination and infiltrating water can leach the soluble compounds present within Creosote (Johansen *et al*. 1998). Creosote within the groundwater zone will partially dissolve within the water, determined by the solubility of the individual compounds, and create a persistent long-term source of contamination. In 1978 fish in the Hersey river in Michigan USA were reported to have started tasting like "medicine" (Black. 1982) and investigation of the sediments at the bottom of the River revealed Creosote residue from a former wood preservation facility that had operated between 1902 and 1949. This demonstrated the ability of Creosote contamination to persist within the environment 20 years after plant closure and 4-5km downstream of the site (Sundström *et al*. 1986).

Polycyclic Aromatic hydrocarbons (PAHs) form an important group of compounds that have been extensively studied as they persist within the environment. PAH consist of fused aromatic rings with biochemical persistence arising from dense clouds of π-electrons on both sides of the ring structure (Wang *et al*. 2012). The toxicity of PAHs can vary greatly with the number of fused rings. For example, the 4 and 5-ring PAHs have a strong tendency to be carcinogenic and/or mutagenic, while PAH's composed of 6 or more rings have substantial mutagenicity in human cells (Yu *et al*. 1998). The US EPA lists 16 parent PAHs on the list of priority pollutants. Alkylated PAHs are also important as they can contribute substantially to the toxicity of PAH mixtures, in some cases accounting for 80% of the toxic burden (Zeigler *et al*. 2012). In order to address this issue the EPA-34 was created which includes the original 16 EPA priority PAHs with alkylated PAHs included (Arp et al. 2011). One important point of note is that due to the co-elution of the alkyl PAHs in GC the 34 PAH method actually represents several hundred individual alkylated PAH compounds (Hawthorne *et al*. 2006).

Heterocyclic compounds are also of particular interest in the context of coal tars and coal tar derived liquids, such as Creosote. A heterocyclic compound is a compound that has at least two different elements as members of its ringed structure. Of particular interest in samples of coal tar, or coal tar derived liquids, are those containing Oxygen (PAOH), Sulfur (PASH) and Nitrogen (PANH). The O, S and N heterocycles in tar are generally determined by the sulfur, oxygen and nitrogen content of the coal carbonized (McNeil. 1952) although with some temperature-dependent alteration (Gauchotte-Lindsay et al. 2012). The sulfur content within coal is present either as inorganic compounds, such as pyrite and sulfides or organic sulfur compounds, such as Poly Aromatic Sulfur hydrocarbons (PASHs). The organic sulfur content of coal is determined by the original organic matter that formed the coal deposits and takes the form of aliphatic and aromatic thiols, sulfides, disulfides and heterocylic combinations of thiophenes and dibenzothiophenes (Diez *et al*. 1994).

PANHs are highly stable relative to neutral PAH's and can persist through severe thermal conditions and so are possible compounds of toxicological interest (Yu *et al*. 1999). The toxicity of aromatic compounds greatly depends on the structure and number of fused rings. The presence of nitrogen-containing substituents, such as nitro- and amino- functional groups can enhance toxicity by up to 100-fold (Yu *et al*. 1999). This means that whilst the nitrogen content of the parent coal may be low, the possible health effects from the presence of nitrogen containing polycyclic aromatic compounds (NPAC) should not be overlooked.

Oxygen containing compounds are of special concern as they can be toxic, mutagenic and carcinogenic and are more mobile within the environment than their parent PAHs, due to their increased solubility in water. This enhanced mobility increases the potential for exposure to hydroxylated PAHs in groundwater from sites contaminated with Creosote and also increase the risks to human and environmental receptors associated with the contaminant plume. Oxygen containing compounds also form an important diagnostic component within coal tars and of particular interest are the hydroxyl- and dihydroxy- PAH's (Shi et al. 2010).

Phenolic compounds form a major group of oxygen containing compounds in coal tar and brown coal derived liquids, of which the alkyl Phenols dominate (Shi *et al*. 2010). High Phenolic content is a major characteristic of Low temperature coal tars (650ºC) and Medium temperature coal tars (800ºC) (Shi *et al*. 2012). This means that the abundance of Phenolic compounds within a tar could potentially be used to suggest the production process used or the degree of exposure that the primary tar has had to secondary degradation. This means the production process used to produce the crude coal tar from which the Creosote is distilled will affect the overall composition of the final Creosote produced.

Derivatization allows for a wider range of compounds to be detected within coal tar (Gauchotte-Lindsay *et al*. 2012). The aim of using a derivatization method for GC is to improve peak symmetry, resolution, selectivity and sensitivity of the target analytes and improve their thermal stabilities (Segura *et al*. 1998). Derivatization can increase the sensitivity of detection of a particular compound of interest by several orders of magnitude (Parkinson. 2012) and so allow for more compounds to be identified within a sample patterns that aid with structural identification.

Of particular concern when dealing with Creosote contaminated sites is the potential for groundwater contamination and contamination of other marine environments. Most environmental monitoring focuses on a small number of PAH compounds, however in the case of Creosote contaminated water bodies substantial decreases in PAH concentrations in groundwater due to remediation do not always significantly reduce the ecotoxicity (Breedveld and Sparrevik. 2000). This implies that an extended list of compounds should be considered when dealing with Creosote contaminated sites and this demonstrates a vital need for a database of compounds found within Creosote. While lists of compounds present within Creosote have been published previously such as the various lists found in Sundström *et al*. 1986, only a single paper used a GCxGC based method (Mateus *et al*. 2008), although this paper only looked at the volatile compounds emitted from wood treated with Creosote and did not analyse Creosote itself. Of the previously published lists none are as comprehensive as the database presented within this study.

## Materials and Methods

*Methods:*

All solvents used were of analytical grade purchased from Fisher Scientific (Loughborough, U.K.) and $D_{10}$-phenanthrene, $D_8$-Naphthalene, $D_{10}$-Fluorene, $D_{10}$-Fluoranthene and $D_{10}$-Pyrene were purchased from Sigma-Aldrich (Gillingham, U.K.). Quantification standards of Phenol, p-Cresol, 3,5-DimethylPhenol, 2,4,6-TrimethylPhenol, 1-Naphthol, Aniline, and 1-Hydoxypyrene were purchased from Sigma-Aldrich (Gillingham, U.K.). N,O-bis(trimethylsilyl)trifluoroacetamide

(BSTFA) with 1% trimethylchlorosilane (TMCS) was purchased from Sigma-Aldrich (Gillingham, U.K.).

Extraction was performed using an Accelerated Solvent Extraction system (ASE 350 Dionex, Camberley, UK) using 10 mL stainless steel extraction cells. Approximately 0.5g of tar was mixed with an equal amount of diatomaceous earth and Sodium Sulphate ($NaSO_4$) in a 1:1:1 ratio. Prior to extraction the samples were spiked with a recovery standard. Extraction cells were lined with 2 Dionex glass fibre filter papers and packed with 3g of silica gel 60 deactivated with 10% water. The sample mixture was then loaded into the cells and excess diatomaceous earth was added until the cell was well packed to ensure that there is no void space. Dichloromethane was used as the extracting solvent for all extractions. ASE was performed at 100$^{o}$C and 10 MPa, using one dynamic (7 min) and two static (5 min each) extractions. A flush volume of 150% and purge time of 60 s was used. The extracts were concentrated to 1 mL using a Büchi Syncore Analyst (Oldham, U.K). The extracts were then made up to exactly 10 mL using *n*-hexane. A 1 mL aliquot was then transferred to an auto sampler vial prior to analysis and spiked with $D_{10}$-Phenanthrene. All samples were derivatized using 100ul of BSTFA with 1% TMCS placed in an oven at 70$^{o}$C for 1 hour.

GCxGC TOFMS analysis was performed using a Leco Pegasus 4D (St. Joseph, Michigan) time of flight mass spectrometer, connected to an Agilent 7890A gas chromatograph equipped with a LECO thermal modulator. The TOF ion source temperature was 200 °C and the mass range 45 and 500u was scanned at a rate of 200 spectra/second. The detector voltage was set at 1700 V with an electron ionisation voltage of 70 eV.

All standards and extracts were analysed with the following primary oven temperature programme: 60°C isotherm for 2 minute, then ramp at 10°C/min to 110°C, then ramp at 3°C/min to 310 °C, and isothermal at 310°C for 15 minutes. The secondary oven and modulator temperatures were programmed at a 20 °C offset relative to the primary oven. The modulation period was 6 seconds with a 1.3 second hot pulse time and a cool time of 1.7 seconds. The injection port temperature was set to 250 °C and set to split injection with a split ratio of 50 and an injection volume of 1µl. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min.

The reversed polarity column set that was used comprised of a mid-polarity TR-50 MS supplied by Thermo Scientific (30 m × 0.25 mm i.d. × 0.25 µm film thickness) as the primary column and a non-polar Rtx-5SilMS supplied by Thames Restek (1.5 m × 0.25 mm i.d. m × 0.25 µm film thickness) as the secondary column, connected via a Thames Restek Press-tight connector.

The chromatograms from each sample were processed using Leco ChromaTOF software (Version 4.50.8.0) to search for, identify and align all peaks with a signal-to-noise ratio greater than 10.

*Sample:*

The sample was recovered using a Low Flow from a sump present on a former wood treatment facility, associated with a former tar distillery in the United Kingdom. The sample was collected within a glass bottle and stored at 4$^{o}$C prior to analysis. The sample has been previously included in the analysis by McGregor *et al*. 2011 and was shown to be highly weathered. The sample was also included in the multivariate statistics in McGregor *et al*. 2012.

*Quality Control:*

To ensure the analytical accuracy of the data produced strict quality control measures were used including: The use of reagent and procedural blanks, the use or a recovery standard containing $D_8$-Naphthalene, $D_{10}$-Fluorene, $D_{10}$-Fluoranthene and $D_{10}$-Pyrene and the use of an injection standard containing $D_{10}$-Phenanthrene. All recoveries fell within the range suggested by US EPA method 8800B of between 70% and 130% and all blanks were clean and free of contamination.

## Results and Discussion

*Composition:*

A sample previously identified as Creosote Oil, DNAPL011 (McGregor *et al*. 2011), obtained from a sump on a former wood treatment facility associated with a former tar distillery in the UK was analysed. Creosote is a distillation product of coal tar and is one of the most widely used wood preservative in the world (Mateus *et al*. 2008) and can contain up to 17% of the total composition as Phenolic compounds (Bedient *et al*. 1984). A total of 255 derivatized compounds, shown in table 5.1, were detected.

A total of 16 Phenolic compounds were also detected that could not be derivatized due to steric hinderance. Steric hinderance is the process by which compounds that contain active hydrogen may not derivatized due to the hindrance of the derivatization reaction around the hydroxyl group. For example, the derivatization of a standard of 2,4,6-Trimethyl Phenol was attempted using BSTFA, but was found not to derivatize. This is likely due to the fact that no matter where the hydroxyl group falls within the ring it will always have a methyl group on either side protecting it from derivatization. As the number of alkyl groups increases the possible number of sterically hindered isomers will likely increase as well. As well as the derivatized compounds the sample also contains 134 Aliphatic compounds, 612 PAHs/Alkyl PAHs, 217 Sulfur containing PAHs, 129 Oxygen containing PAHs, 128 Nitrogen containing PAHs and 12 Mixed Heterocycles (e.g. containing both Oxygen and Sulfur). Both cyclo-S6 and cyclo-S8 sulfur were detected giving a total of 1505 individual compounds.

| Compound | m/z | Formula | No of Isomers | Retention window (min:sec) |
|---|---|---|---|---|
| Phenol | 166 | C6H6O | 1 | 6.9, 1.505 |
| Cresols | 180 | C7H8O | 3 | 8.1, 1.725 to 8.5, 1.785 |
| C2-Phenol | 194 | C8H10O | 6 | 9.2, 1.960 to 11.1, 2.130 |
| C3-Phenol 1DB or Indanol | 206 | C9H10O | 2 | 15.0, 2.475 to 16.1, 2.454 |
| C3-Phenol | 208 | C9H12O | 11 | 10.0, 2.120 to 13.0, 2.385 |
| Napthalen-2-ol | 216 | C10H8O | 1 | 22.6, 2.530 |
| C4-Phenol 1DB or C1-Indanol | 220 | C10H12O | 11 | 15.3, 2.565 to 19.2, 2.615 |
| Hydroxybenzothiophene | 222 | C8H6OS | 1 | 23.4, 2.430 |
| C4-Phenol | 222 | C10H14O | 16 | 11.3, 2.430 to 15.1, 2.745 |
| C1-Naphthalenol | 230 | C11H10O | 3 | 24.9, 2.700 to 26.9, 2.625 |
| C5-Phenol 1DB or C2-Indanol | 234 | C11H14O | 23 | 15.7, 2.730 to 22.8, 2.740 |
| C1-Hydroxybenzothiophene | 236 | C9H8OS | 6 | 25.0, 2.560 to 27.2, 2.545 |
| C5-Phenol | 236 | C11H16O | 18 | 13.5, 2.700 to 18.1, 2.995 |
| o-Biphenyol | 242 | C12H10O | 1 | 23.4, 2.585 |
| Hydroxyacenaphthene | 242 | C12H10O | 2 | 28.8, 2.540 to 30.1, 2.605 |
| C2-Naphthalenol | 244 | C12H12O | 8 | 26.8, 2.765 to 30.9, 2.720 |
| C6-Phenol 2DB | 246 | C12H16O | 5 | 24.1, 2.800 to 28.0, 2.740 |
| C6-Phenol 1DB or C3-Indanol | 248 | C12H16O | 17 | 17.7, 2.895 to 24.5, 2.855 |
| C6-Phenol | 250 | C12H18O | 7 | 17.1, 3.035 to 20.0, 3.155 |
| Hydroxyfluorenes | 254 | C13H10O | 3 | 35.7, 2.525 to 37.3, 2.590 |
| C1-Biphenylol | 256 | C13H12O | 2 | 25.9, 2.650 to 26.5, 2.650 |
| C1-Hydroxyacenaphthene* | 256 | C13H12O | 9 | 30.7, 2.660 to 34.9, 2.650 |
| C3-Naphthalenol | 258 | C13H14O | 5 | 29.8, 2.825 to 32.0, 2.830 |
| C7-Phenol 2DB | 260 | C13H16O | 13 | 23.6, 2.955 to 29.4, 2.820 |
| C7-Phenol 1DB or C4-Indanol | 262 | C13H18O | 6 | 20.9, 2.990 to 25.3, 3.150 |
| C7-Phenol | 264 | C13H20O | 4 | 20.4, 3.220 to 23.2, 3.320 |
| Anthrol | 266 | C14H10O | 3 | 43.2, 2.490 to 44.2, 2.565 |
| C1-Hydroxyfluorene | 268 | C14H12O | 8 | 37.8, 2.605 to 40.7, 2.655 |
| C2-Biphenylol | 270 | C14H14O | 11 | 28.2, 2.685 to 31.4, 2.760 |
| C2-Hydroxyacenaphthene* | 270 | C14H14O | 11 | 34.7, 2.680 to 38.3, 2.735 |
| C8-Phenol 2DB | 274 | C14H18O | 5 | 27.0, 3.010 to 29.5, 2.985 |
| C8-Phenol 1DB or C5-Indanol | 276 | C14H20O | 2 | 25.9, 3.130 to 26.6, 3.215 |
| C8-Phenol | 278 | C14H22O | 4 | 24.3, 3.335 to 27.8, 3.440 |
| C1-Anthrol | 280 | C14H22O | 4 | 45.1, 2.550 to 47.1, 2.550 |
| C3-Biphenylol | 284 | C15H16O | 8 | 29.2, 2.790 to 33.8, 2.660 |
| C3-Hydroxyacenaphthene* | 284 | C15H16O | 7 | 37.4, 2.825 to 40.9, 2.775 |
| Hydroxy-4-ring PAH | 290 | C16H10O | 2 | 51.4, 2.445 to 51.6, 2.430 |
| C9-Phenol | 292 | C15H24O | 3 | 27.4, 3.465 to 29.6, 3.525 |
| C4-Hydroxyacenaphthene* | 298 | C16H18O | 3 | 39.8, 2.790 to 41.1, 2.760 |

Table 5.1: Total number of derivatized compounds in Creosote (DNAPL011) (DB = Double Bond) * or Hydroxydibenzofuran isomers

*Derivatization:*

The expected predominant Phenolic compounds present within coal tar Creosote are Phenol, o-Cresol, m-Cresol and p-Cresol, which should make up 50% of the total composition of pure Creosote (Mueller *et al.* 1989). However, the production process and feedstock used to produce the coal tar affects the overall composition of the distilled Creosote, for example the production of Phenols and alkyl Phenols is significantly different between vertical and horizontal retort types (McGregor *et al.* 2011). The overall concentration of select derivatized compounds is shown in table 5.2. The limits of detection for the method were calculated and ranged from 0.6mg/kg for Phenol to 1.6mg/kg for Hydroxypyrene suggesting the majority of compounds derivatized by the method would fall within this range in pure phase tar. These limits of detection would be significantly lower in environmental samples of non pure tar such as contaminated soil samples.

| Retention time (min:sec) | Compound | Conc mg/kg | LOD mg/kg | Retention time (min:sec) | Compound | Conc mg/kg | LOD mg/kg |
|---|---|---|---|---|---|---|---|
| 6.9, 1.505 | Phenol | 37.6 | 0.6 | 10.3, 2.100 | C2-Phenol | 312.7 | 0.8 |
| 8.1, 1.725 | o-Cresol | 278.2 | 0.8 | 10.6, 2.140 | C2-Phenol | 226.8 | 0.8 |
| 8.3, 1.750 | m-Cresol | 180.7 | 0.8 | 11.1, 2.130 | C2-Phenol | 164.7 | 0.8 |
| 8.5, 1.785 | p-Cresol | 112.4 | 0.8 | 22.6, 2.530 | Napthalen-2-ol | 426.1 | 0.9 |
| 9.2, 1.960 | EthylPhenol | 206.1 | 0.8 | 51.4, 2.445 | Hydroxy 4-ring PAH a | 46.5 | 1.6 |
| 9.5, 2.015 | C2-Phenol | 612.4 | 0.8 | 51.6, 2.430 | Hydroxy 4-ring PAH b | 40.2 | 1.6 |
| 9.9, 2.060 | C2-Phenol | 1957.7 | 0.8 | | | | |

Table 5.2: Concentration of selected derivatized compounds in Creosote (DNAPL011).

The relative concentrations of Phenol, o-Cresol, m-Cresol and p-Cresol found within the samples are low with only 37.6 mg/kg of Phenol and a combined concentration of 571.3 mg/kg for the 3 Cresol isomers. The most dominant Phenolic compound found in the sample was 3,5-Dimethyl Phenol, which would be expected to make up 7.5% of the predominant Phenolic compounds (Mueller at al. 1989), and is present in a concentration of 1957.7 mg/kg. Since the sample has been previously shown to be heavily weathered (McGregor *et al.* 2011) one possible explanation for the low concentrations of Phenol and Cresols is their aqueous solubility, although volatility may also play a role through volatilization into the air surrounding the sump.

p-Cresol, which is present at a concentration of 112.4 mg/kg is the most toxic of the Cresol isomers with a 5 to 10-fold concentration of either o-Cresol or m-Cresol being needed to observe the same degree of toxicity as p-Cresol (Thompson *et al*. 1994). This means that although p-Cresol has the lowest concentration of the Cresol isomers it would have the environmental highest risk associated with it. p-Cresol and Phenol also have the ability to change bacterial membrane lipid structure, increasing the degree of saturation of the lipids, as the Phenols alter the cell membrane permeability and increase their fluidity (Keweloh *et al*. 1991).

The environment effects of the Cresols do not only extend to their direct toxicity. Creosote is a complex mixture of compounds and interactions between these compounds are important when considering the overall risk associated with a contaminated site. Low concentrations of o-Cresol can increase the carcinogenicity of benz(a)pyrene, whereas high concentrations can inhibit the carcinogenic effect (Yanysheva *et al*. 1993). p-Cresol can be utilized by bacteria as a sole carbon and energy source (Yu and Loh 2002) and the presence of p-Cresol can inhibit the degradation of carbazole with incomplete degradation of carbazole at p-Cresol concentrations above 20mg/L and complete removal of carbazole can only occur when p-Cresol concentrations are below 10mg/L (Yu and Loh 2002). When concentrations of p-Cresol are higher than 120mg/L carbazole degradation is completely inhibited. This means that the concentrations of p-Cresol are important as they will affect degradation of other compounds present within the sample. p-Cresol also has the ability to inhibit the degradation of phenanthrene (Millete *et al*,.1995) and Phenol (Kar *et al*. 1997). Due to the concentrations of p-Cresol this suggests that biodegradation of carbazole is unlikely to take place within the sump itself, although it may take place within the environment around the sump.

Among the other Phenolic compounds detected the octyl (C8) and nonyl (C9) Phenols may be of particular interested from an UK/European perspective. Both octyl and nonyl Phenols are included in directive 2008/105/EC due to the fact they are potential endocrine disruptors. Octyl and Nonyl Phenols are also persistent within the environment, moderately bio accumulate and are extremely toxic to aquatic organisms. In total 4 C8 Phenols were detected (as well as 2 C8 Phenols with 1 double bond and 5 with 2 double bonds) and 3 C9 Phenols were detected within the sample. No literature could be found reporting the presence of octyl or nonyl Phenols within Creosote or coal tars. One possible reason for the lack of literature reporting octyl and nonyl Phenols within coal tar, or coal tar distillates, is that the compounds were only detected due to derivatization and derivatization techniques have not commonly been applied to coal tar. Another possible reason is that the octyl and nonyl Phenols both boil within the range of Creosote and so may be enriched during the distillation process and therefore become detectable. Octyl and nonyl Phenols may be present in other forms of coal tar, or coal tar distillate, in trace amounts and are not detected due to being present below the limits of decetion of these compounds.

*Aliphatic:*

Alkyl-cyclohexanes are compounds that are associated with being derived from petrogenic sources (Saber *et al*. 2006) and can be used for differentiation of fuel-types from petrogenic sources (Kaplan *et al*. 1997). Alkyl-cyclohexanes were detected within the Creosote sample with an alkyl range between C4 and C18. This suggests that there is a petrogenic element in the sample. One possibility is that the crude tar from which the Creosote was distilled, may have contained an element of Carburetted Water Gas (CWG) tar. The CWG was a process used at gasworks to produce a gas relatively quickly from hot coke injected with steam and then enriched with oil (Thomas, 2014). CWG tar was often mixed with coal tar to enable its sale to tar distillers. This was because CWG tar had a higher water content (due to the emulsions it would form) and contained less compounds of value to distillers making it of little or no commercial value. Mateus *et al*. 2008 published a qualitative analysis of the volatile fraction of Creosote-treated railway sleepers using GCxGC-TOFMS and detected a total of 314 compounds including alkyl-cyclohexanes. This suggests that alkyl-cyclohexanes may form a part of Creosote oil, although it could also be from petrogenic contamination of the samples. Of the 314 volatile compounds detected by Mateus *et al*. 2008 212 were detected within DNAPL011.

A wide range of other aliphatic compounds were also detected within the samples including n-alkanes from C11 to 31, Pristane and Phytane, and 36 branched alkanes between C11 and C24. A large number of alkyl-cyclopentanes and alkyl-cyclopentenes were also detected within the sample ranging from C5-Cyclopentene to C7-Cyclopentane. The overall distribution of the n-alkanes is shown in figure 1 and shows that the C12 and C13 n-alkanes dominate with a decreasing trend within increasing carbon area.

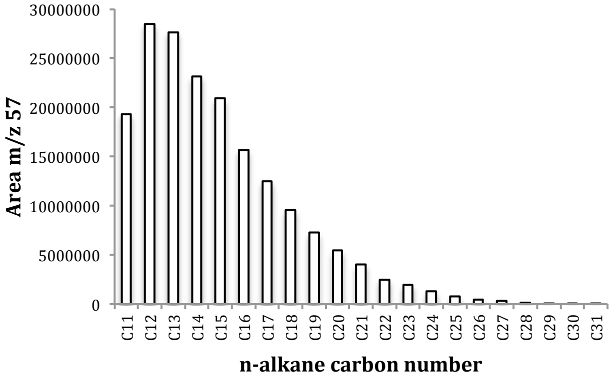

Figure 5.1 – n-alkane distribution Creosote tar sample (DNAPL011)

*PAHs:*

The single largest class of compounds present within the samples were the PAHs and alkyl PAHs. Of the EPA34 PAHs, 32 out of the 34 groups of compounds were detected within the sample. As the EPA34 list actually contains many hundreds of individual compounds a total of 168 individual compounds were detected with the majority being alkylated isomers. Only C4-Chrysene and C4-Phenanthrene, from the EPA34, were not detected. The lowest molecular weight PAH detected was Styrene ($C_8H_8$) with the highest molecular weight compound being a Dibenzopyrene isomer ($C_{24}H_{14}$). The vast majority of the PAHs detected within the sample are in the form of alkylated isomers. The concentration of the EPA16 PAHs in the sample have previously been published in McGregor *et al*. 2011 and showed that Naphthalene and Phenanthrene had the highest concentrations.

*Heterocycles:*

Of the mixed Heterocycles detected within the Creosote sample the most common were Thienobenzofurans ($C_{10}H_6OS$), 6 of which were detected, and have not previously been reported in the literature. 2,5-Dimethylbenzoxazole ($C_9H_9NO$) was also detected within the sample and has not previously been reported in coal tar or coal tar distillates. Thieno[2,3-c]pyridine ($C_7H_5NS$) has been previously reported in Anthracene oil (Burchill *et al.* 1982) and Azadibenzothiophenes ($C_{11}H_7NS$), of which 3 were detected, have been previously reported in Anthracene oil (Burchill *et al.* 1982) and solvent refined coal heavy distillate SRCII (Nishioka *et al.* 1985), although none of the mixed heterocycles have been previously reported in Creosote. Elemental Sulfur can also be found within Creosote (Sundstrom *et al.* 1986) and is found within the Creosote sample in the form of *cyclo*-hexaSulfur ($S_6$) and *cyclo*-octaSulfur ($S_8$).

PANHs form an important group of compounds of interest with DNAPL011 containing PANHs ranging from Dimethyl Pyridine ($C_7H_9N$) to 4H-Benzo[def]naphtho[2,3-b]carbazole ($C_{22}H_{13}N$). A large number of alkyl PANH isomers are present with the largest group being dimethyl carbazole with a total of 9 isomers. Of the 128 PANHs present within the sample 79 are alkylated isomers. Only a single compound containing more than 1 nitrogen was detected in the form of [1,1'-biphenyl]-4,4'-dicarbonitrile ($C_{14}H_8N_2$), which is not heterocyclic and contains two nitrile groups. The vast majority of PANHs detected within the sample are in the form of nitrogen containing heterocycles, however several compounds that have nitrogen containing functional groups were also detected. Compounds detetect that contiain functional nitrogen include 1-Naphthalenecarbonitrile and 2-Naphthalenecarbonitrile ($C_{11}H_7N$), as well as their alkylated isomers, which contain nitrogen in the form of a nitrile group.

A wide range of PASHs were detected ranging from C2-Thiophene ($C_6H_8S$) to Naptho[2,1-b]benzo[1,2-b:4,3-b']dithiophene ($C_{18}H_{10}S_2$). Naptho[2,1-b]benzo[1,2-b:4,3-b']dithiophene is one of 7 Sulfur compounds present within the sample which contains 2 Sulfur atoms within the ring as well as Thieno[2,3-b]thiophene ($C_6H_4S_2$), 3 Benzodithiophenes ($C_{10}H_6S_2$), and 2 [1]benzothieno[3,2-b][1]benzothiophene ($C_{14}H_8S_2$) isomers. C2-Thiophene is the lowest molecular weight PASH that can be detected using the GC method and so it is possible that more volatile, and lower molecular weight, PASHs are present within the sample but are undetectable. Due to the presence of Sulfur within the ring a large number of alkylated PASHs exist. Of the 217 PASHs detected 166 are in the form of alkylated isomers. C4-Benzothiophene ($C_{12}H_{14}S$) and C2-Dibenzothiophene ($C_{14}H_{12}S$) form the largest groups of isomers with 14 compounds present in each group. Of the PASHs detected alkyl-Benzothiophenes and alkyl-Dibenzothiophenes both form the largest groups with 94 compounds and 47 in each group. Only two 2-ring parent PASHs were detected within the sample, Benzo[b]thiophene and 2-Benzothiophene ($C_8H_8S$), meaning that the largest individual group of compounds is likely to be alky-Benzothiophenes as the alkyl-Dibenzothiophene group does not differentiate between the 3-ring parent PASH isomers. Of the 3-ring parent PASHs 4 were detected including Dibenzothiophene ($C_{12}H_8S$). Naphtha[1,2-b]thiophene was also detected and is the only 3-ring PASH that has been shown to be mutagenic (Jacob. 1990). A total of seven 4-ring parent PASHs were detected including phenanthro[3,4-b]thiophene ($C_{16}H_{10}S$). Phenanthro[3,4-b]thiophene is the most mutagenic PASH (Jacob. 1990) with phenanthro[4,3-b]thiophene showing a much lower mutagenicity indicating that the position of the Sulfur plays a key role in the biological effect of the compound (Jacob. 1990).

PAOHs form an important group of compounds present within coal tar and coal tar distillates and includes all heterocyclic oxygen containing compounds as well as non-heterocyclic oxygen containing compounds such as acetophenone ($C_8H_8O$), for the purposes of this study hydroxylated compounds are classified within their own group. A total of 129 PAOHs are present within the Creosote sample ranging from Benzofuran ($C_8H_6O$) to Dinapthofuran isomers ($C_{20}H_{12}O$). Of the 129 PAOHs detected 105 are in the form of Heterocycles with alkyl isomers again dominating, as well as 3 Benzobisbenzofuran isomers ($C_{18}H_{10}O_2$) containing 2 oxygen atoms within the ring. Of the remaining 24 compounds the majority are in the form of aromatic ketones such as Anthrone ($C_{14}H_{10}O$) and 4H-Cyclopenta[def]phenanthren-4-one

($C_{15}H_8O$), 1 coumarin in the form of Xanthone ($C_{14}H_{12}O$) and 2 quinones in the form of 9,10-Anthracenedione ($C_{14}H_8O_2$) and 5,12-Naphthacenedione ($C_{18}H_{10}O_2$) both of which have been previously reported in coal tar (Benhabib *et al*. 2010).

Fluorenone ($C_{13}H_8O$) has also previously been reported in coal tar (Benhabib *et al*. 2010) and could be produced during the pyrolysis process, however, it can also be produced during the metabolism of Fluorene (Grifoll et al. 1992) and Fluoranthene (Kelley et al. 1993) so it is possible it may have been produced, or a portion of it produced, during microbial degradation of the tar. Fluorenone can also be produced by the oxidation of fluorene (Korfmacher et al. 1980). Eriksson *et al*. 2000 reported increases in the concentrations of both Fluorenone and 4H-Cyclopenta[def]phenanthren-4-one during the Creosote contaminated soils. Wischmann and Steinhart. 1997 also reported increases in the concentrations of Fluorenone and 9,10-Antracenedione during the degradation of a coal tar oil, it is reportedly used as a wood-preservative so likely to be Creosote, in soil. 9,10-Antracenedione has been reported to have potential negative environmental effects as it inhibits the growth of duckweed (Mallakin *et al*. 1999) and has around 31 times higher aqueous solubility than Anthracene, although it is still has a relatively low water solubility of 1.4mg/kg $H_2O$ at 25$^oC$. The detection of these compounds suggests the possibility for bacterial activity within the sample.

*Toxicity:*

PAHs account for up to 85% of pure Creosote but only account for around 13% of the total toxicity in Creosote contaminated groundwater (Hartnik *et al*. 2007). 80% of the toxicity can be attributed to methylated benzenes, Phenolic compounds and N-heterocyclic with up to 26% of the total toxicity coming from the alkylated quinolines (Hartnik et al. 2007), which dominated the most toxic fraction analysed by Hartnik *et al*. 2007. A total of 20 alkylated quinolines were detected within our sample with 4 methyl quinolines, 8 dimethyl quinolines and 8 trimethyl quinolines, in addition to this a total of 106 other PANHs were also detected. The toxicity of dimethyl quinolines can span over two orders of magnitude and is affected by the relative position of the nitrogen within the ring as well as the relative positions of the methyl groups to the nitrogen (Birkholz *et al*. 1990). Of the other compounds detected within the most toxic fraction in Hartnik *et al.* 2007 Acridine and 2-Benzothiophene were also detected within our Creosote sample. A total of 71 alkylated benzenes were detected within the sample with 3 C3-, 10 C4-, 16 C5-, 21 C6-, 11 C7- and 10 C8-Benzenes detected several of which may contribute to the overall toxicity of the Creosote.

While in general PANH compounds are present in lower concentrations than their non-substituted PAH-analogues their higher water solubility leads to a higher bioavailability and potential toxic effects (Neuwoehner *et al.* 2009) and low molecular weight PANHs can account for up to 70% of the water-soluble fraction of Creosote (Padma *et al.* 1998). For example Quinoline has a water solubility of 60,000mg/L whereas Naphthalene has a solubility of 30mg/L. Acridine and Quinoline, both of which were detected within DNAPL011, have toxic and teratogenic effects at sufficiently low concentrations to make them potential environmental hazards (Davis *et al.* 1981). The environmental impacts of these compounds may be greater than their reported LC50 values because of sub lethal effects such as decreased growth rate that may render surviving organisms incapable of coping with environmental stress (Davis *et al.* 1981).

*Forensics:*

Since Creosote is a distillation fraction of coal tar covering the ranges 200$^{o}$C-400$^{o}$C (McNeil. 1952), the presence of compounds that boil below 200$^{o}$C, such as Styrene ($C_8H_8$), and compounds that boil well above 400$^{o}$C, such as Coronene ($C_{24}H_{12}$), suggests that the Creosote is not in the form of pure distillate and has been blended with another form of tar, most likely in the form of CWG tar. The presence of these compounds may also suggest when the CWG tar was added to the blend as if it was added before distillation Styrene and Coronene should not be distilled from the resulting tar mix.

McNeil. 1952 states that Creosote derived from vertical retort (VR) tars contain 25% tar acids (Phenolics) and 60-65% PAHs, with the majority containing one or more methyl substituent groups. McNeill. 1952 also states that in contrast coke oven (CO) and horizontal retort (HR) tars contain no more than 10% Phenols and generally 90% PAHs with a considerable proportion containing no substituent groups. It should also be noted that while HR and CO produced Creosotes do differ from those produced from VR tars the constituents of the Creosote do not vary only the relative amounts and distribution (McNeil. 1952). Coke oven tars fall loosely into two categories, those produced at low temperatures (<700°C) such as Coalite coke and those produced at higher temperatures (>700°C) (Hamper, 2006). This also applies to horizontal retort tars as early horizontal retorts operated at lower temperatures of around 600°C (Harkins *et al*. 1988) with later designs being capable of operating in excess of 1000°C (Butterfield. 1904). Low temperature coke oven tars and low temperature horizontal retort tars would both contain Phenolic compounds in greater degree than the high temperature processes of the same type (Hamper, 2006). While McNeil. 1952 does not state if the horizontal retort or coke oven tars are from a higher temperature or low temperature process it is most likely to be a high temperature process due to the compositions listed.

One of the most important differences given in McNeill. 1952 is that VR derived Creosote contains a much higher tar acid content than CO and HR tars mainly in the form of high-boiling water-insoluble compounds which are not likely to be leached out by weathering. While the paper does not directly state what these compounds would be, Woolfolk *et al*. 1950 defines these high boiling compounds as those that boil above the Xylenol (C2-Phenol) range. The presence of a large number of Phenolic compounds that boil above C2-Phenol, with 258 of the 271 Phenolic compounds (including sterically hindered phenolics) detected within the sample boiling above the C2-Phenol range, suggests that the Creosote was derived primarily from a VR tar.

The large database of compounds that the GCxGC can produce is also important from a legal forensics standpoint. Polluter pays forms the basis of environmental regulation in many European countries and the USA, for example within the European Environmental Liability Directive 2004/35/EC. In complex sites where multiple possible sources of contamination are present, increasing the potential number of unique compounds that can be identified increases the chances of establishing exactly which process the contamination has originated from. This means that the use of GCxGC greatly increases the forensic potential of a sample, with the use of the derivatization further increasing the capability of the method.

## Conclusion

The use of GCxGC-TOFMS allowed for the resolution and detection of 1505 individual compounds within a sample of Creosote and the use of derivatization allowed for a larger number of compounds to be detected than would be detected without derivatization. A large number of potential compounds of environmental interest were detected including octyl and nonyl Phenols, which have not previously been reported in coal tar, or coal tar distillates. The GCxGC analysis was able to determine that the Creosote was likely produced from a Vertical Retort tar due to the presence of high boiling Phenols, which would likely not have been detected without the use of derivatization. The GCxGC analysis was also able to detect the presence of petrogenic compounds, such as alkyl cyclohexanes, that were likely added into the tar prior to distillation. The use of GCxGC for the analysis of environmental samples increases the potential number of compounds detected within a sample without the need for any length separation methods and will likely increase with importance in the future.

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## 5.3 Potential for Carbureted Water Gas tar (CWG) contamination in non-CWG tars

The paper presented within section 5.2 provides the analysis of a Creosote sample using post extraction derivatization providing a large database of compounds. One important research question raised within the paper is the presence of CWG tars within non-CWG tar samples as many sites containing coal carbonization also operated CWG plants. Section 5.3 presents the n-alkane and alkyl cyclohexane profiles of coal tars produced by the VR, HR, LTHR and CWG processes in comparison with the Creosote tar sample derivatized in section 5.2.

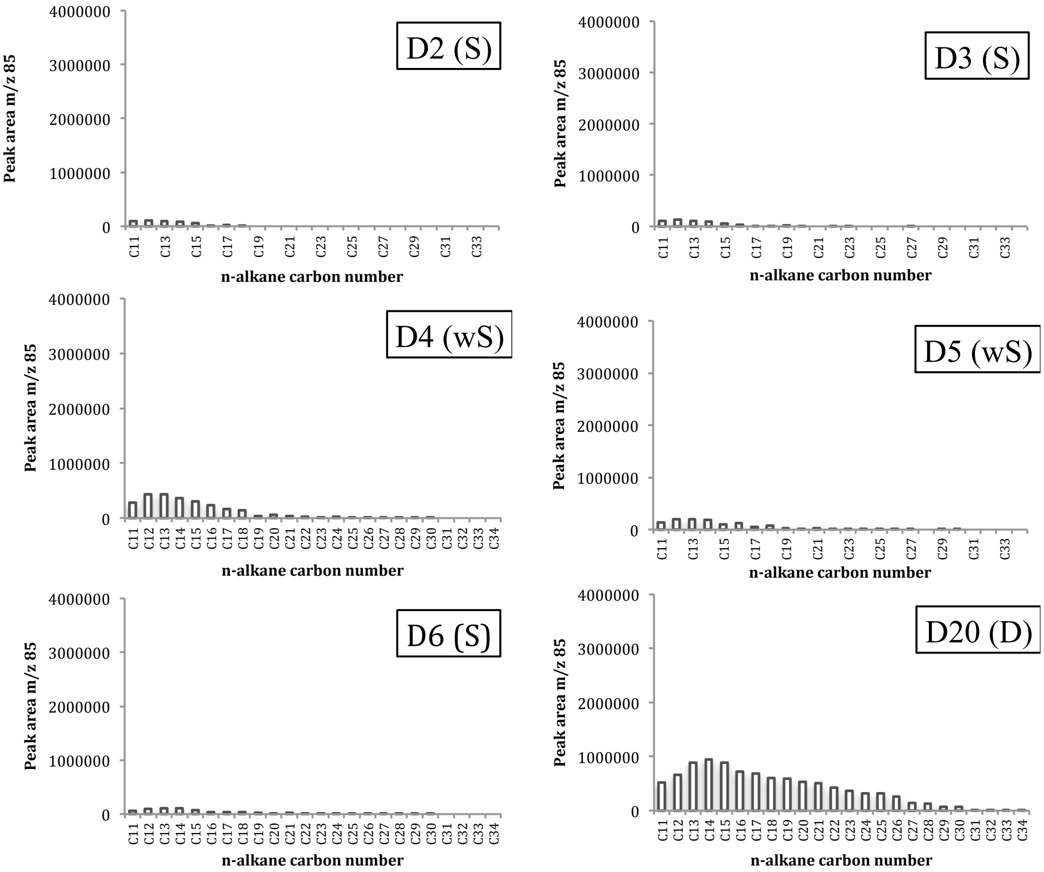

Figure 5.2 n-alkane distributions VR tars (DNAPL002, DNAPL003, DNAPL004, DNAPL005, DNAPL006 and DNAPL020). S – Soil, wS – Waterlogged Soil, D – Pure DNAPL, wD – Water and DNAPL, CWP- Contaminated Water Plume

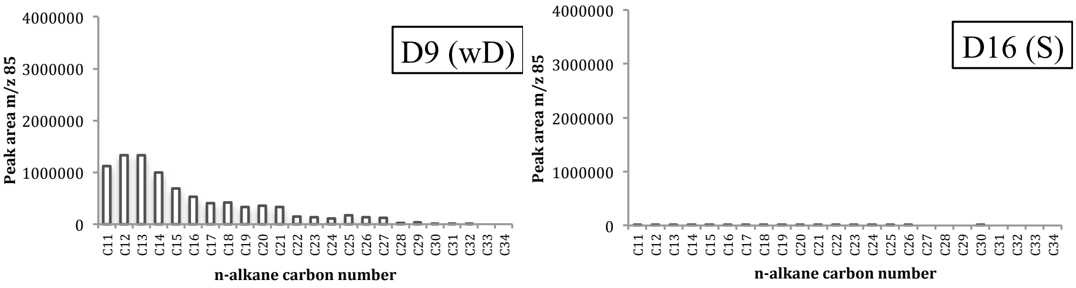

Figure 5.3 n-alkane distributions LTHR tars (DNAPL009 and DNAPL016)

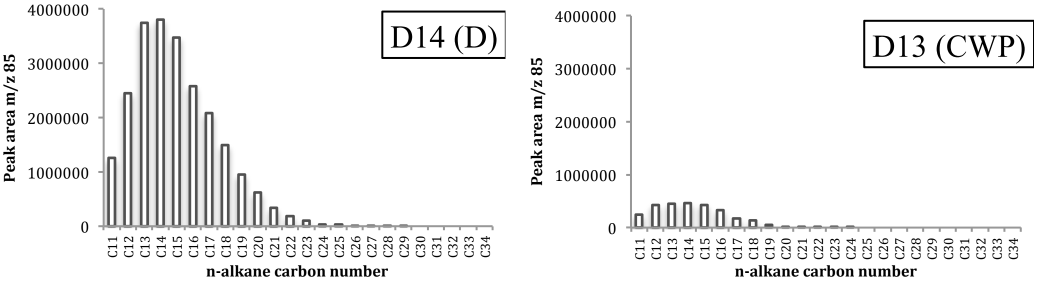

Figure 5.4 n-alkane distribution CWG tars (DNAPL013 and DNAPL014)

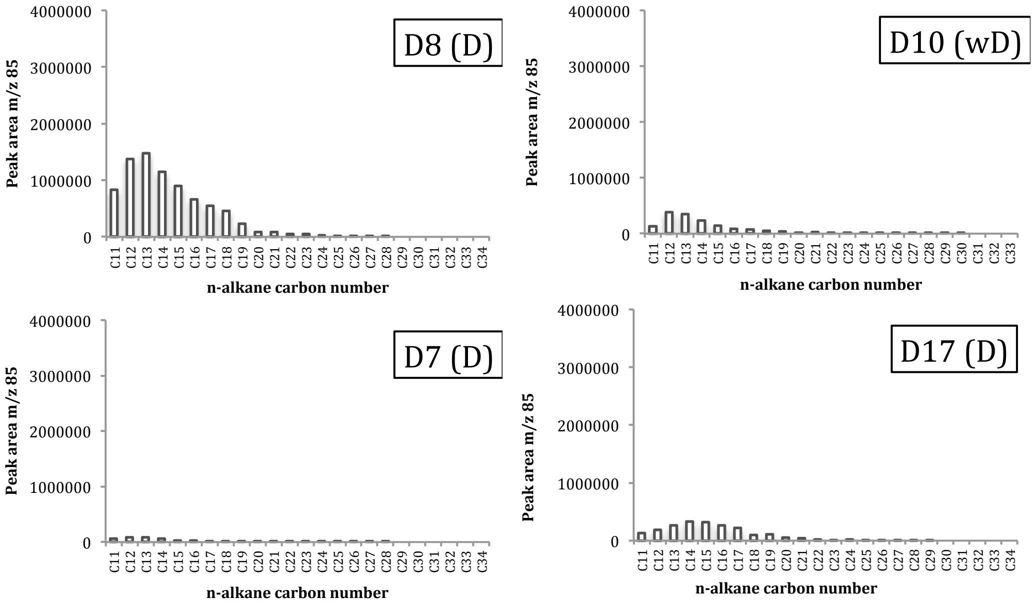

Figure 5.5 – n-alkane distribution of HR Tars DNAPL007, DNAPL008, DNAPL010 and DNAPL017. S – Soil, wS – Waterlogged Soil, D – Pure DNAPL, wD – Water and DNAPL, CWP- Contaminated Water Plume

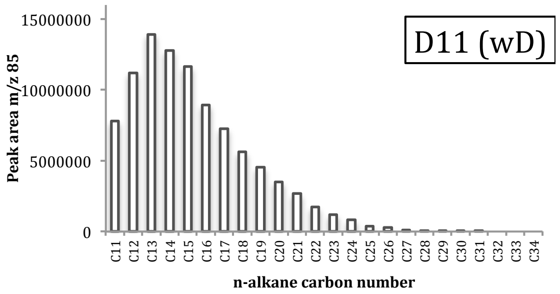

Figure 5.6 – n-alkane distribution of Creosote (Cr) (DNAPL011). wD – Water and DNAPL

The n-alkane distributions of the VR tars are shown in figure 5.2, LTHR tars in figure 5.3, CWG tars in figure 5.4, HR tars in figure 5.5 and Creosote is shown in figure 5.6. All graphs are adjusted for sample weight and recovery. Sample D14 is a CWG tar and contains significant abundances of n-alkanes and this is expected, as CWG is an oil-based process. Sample D13 is also a CWG tar but does not contain a large abundance of n-alkanes and this is likely down to weathering of the samples or the fact the sample was taken from a groundwater plume whereas D14 was taken from a tar tank and would be present in a purer form. Of the remaining samples only D8 (HR), D9 (LTHR), D11 (Cr) and D20 (VR) contain significant levels of alkanes relative to sample D14. The largest n-alkane in samples D8 and D9 is the C13 n-alkane and within sample D20 is the C14 n-alkane. Sample D14 contains 253% more C13 n-alkane than D8 and 282% more than D9 as well as containing 400% more of the C14 n-alkane than D20. The sample with the largest abundance of n-alkanes however is sample D11, which is Creosote tar, and contains significantly higher concentrations than those present within D14. For example the largest n-alkane in D11 is C13, which is present in concentrations 372% higher than those found in D14. This suggests that the Creosote tar contains significant amounts of petrogenic material and this may explain why it clusters close to the CWG tars in the PCA analysis.

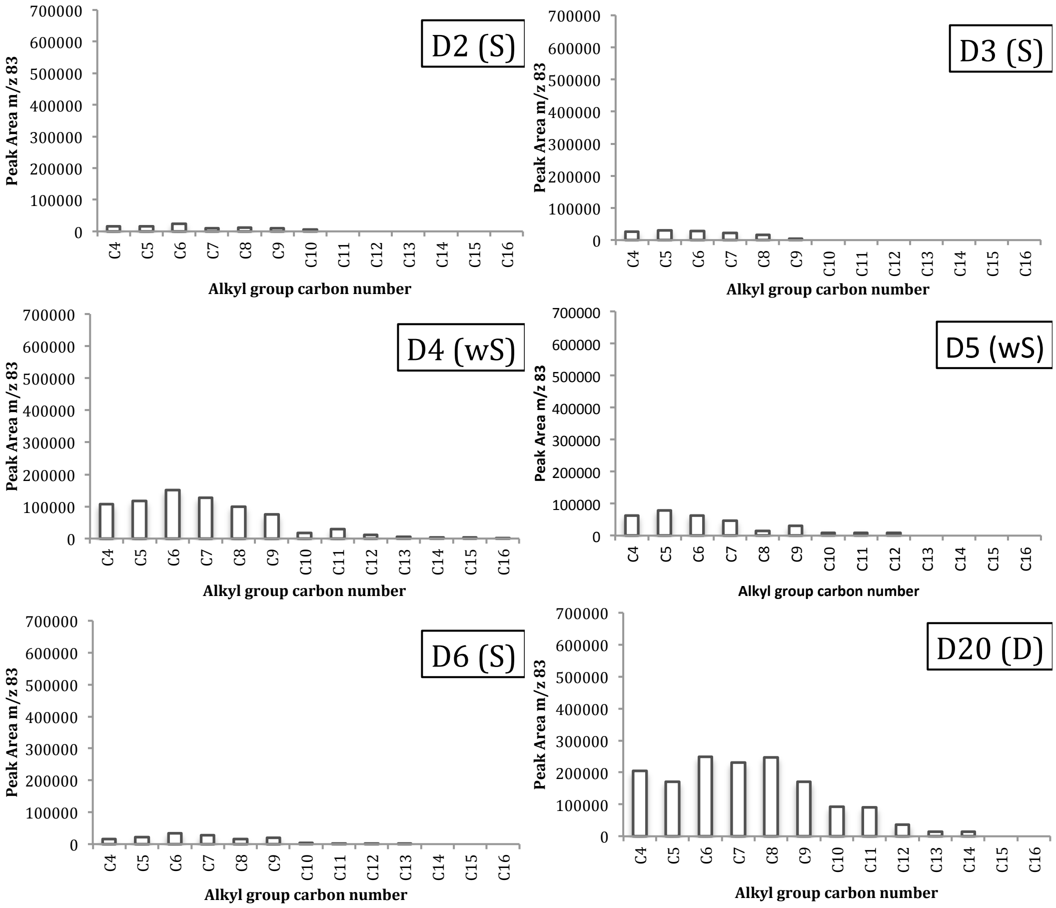

Figure 5.7 Alkyl cyclohexane distributions Vertical Retort Tars (DNAPL002, DNAPL003, DNAPL004, DNAPL005, DNAPL006 and DNAPL020). S – Soil, wS – Waterlogged Soil, D – Pure DNAPL, wD – Water and DNAPL, CWP- Contaminated Water Plume

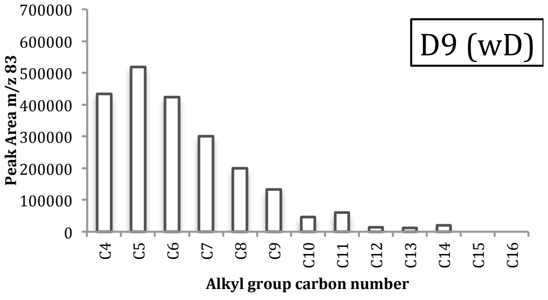

Figure 5.8 Alkyl Cyclohexane distributions Low Temperature Horizontal Retort Tars (DNAPL009). S – Soil, wS – Waterlogged Soil, D – Pure DNAPL, wD – Water and DNAPL, CWP- Contaminated Water Plume

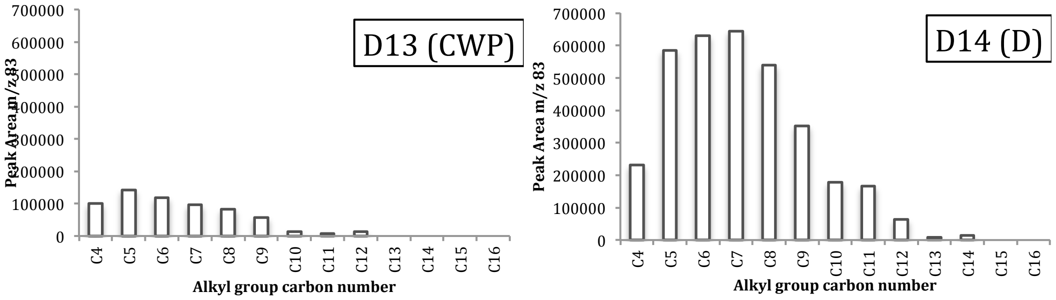

Figure 5.9 Alkyl Cyclohexane distributions Carbureted Water Gas Tars (DNAPL013, DNAPL014). S – Soil, wS – Waterlogged Soil, D – Pure DNAPL, wD – Water and DNAPL, CWP- Contaminated Water Plume

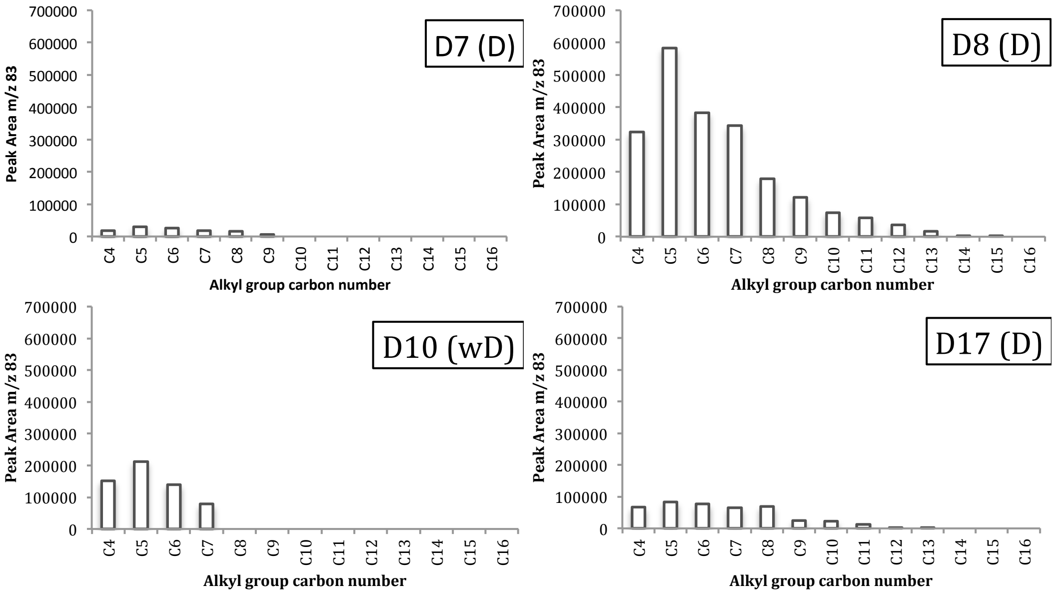

Figure 5.10 – Alkyl Cyclohexane distributions Horizontal Retort Tars DNAPL007, DNAPL008, DNAPL010 and DNAPL017. S – Soil, wS – Waterlogged Soil, D – Pure DNAPL, wD – Water and DNAPL, CWP- Contaminated Water Plume

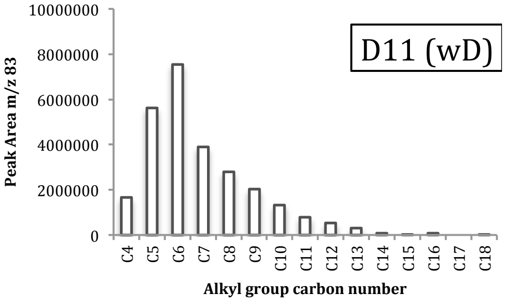

Figure 5.11 – Alkyl cyclohexane distribution Creosote (DNAPL011). S – Soil, wS – Waterlogged Soil, D – Pure DNAPL, wD – Water and DNAPL, CWP- Contaminated Water Plume

The alkyl cyclohexane distributions for the VR tars in figure 5.7, for the LTHR tars in figure 5.8, for the CWG tars in figure 5.8, for the HR tars in figure 5.9 and for Creosote in figure 5.11. All graphs are adjusted for sample weight and recovery. Largest abundances of alkyl cyclohexanes are found in sample D14 (CWG), which would be expected as alkyl cyclohexanes are petrogenic in origin and sample CWG is an oil based process. Again there are 4 other samples with significant levels of alkyl cyclohexanes. The largest peak in sample D8 and D9 is the C5 alkyl cyclohexane and in D20 is the C6 alkyl cyclohexane. Sample D14 contains 113% more C5 alkyl cyclohexane than D9 and 254% more C6 alkyl cyclohexane than D20 and sample D14 contains 100.2% more C5 alkyl cyclohexane than D8. These results suggest that the majority of the n-alkanes detected within samples D8, D9 and D20 may come from petrogenic material, such as CWG tar, that has been mixed into the coal tar. This may also apply to the remaining samples as with the exception of D16 the remaining samples all contain alkyl cyclohexanes, and so all likely have some level of petrogenic material present within them. As well as containing no alkyl cyclohexanes sample D16 also contains the lowest relative abundance of n-alkanes further suggesting that the alkanes present in the remaining samples may be pyrogenically derived. These results may also suggest that the pristane/phytane ratio of the samples may be from petrogenic material present within the samples rather than from the coal tar itself.

The Creosote tar (D11) also contains significantly concentrations of alkyl cyclohexanes. DNAPL011 contains the highest concentrations of alkyl cyclohexanes of any sample, including the CWG tars. The alkyl cyclohexane with the largest abundance in D11 is C6 and is present in concentrations 1199% higher than those present in sample D14. Sample D11 also contains 2 alkyl cyclohexanes not detected in any of the other samples in the form of the C17 and C18 alkyl cyclohexanes. This suggests that the Creosote tar contains a significant amount of petrogenic material. These results suggest that petrogenic material, likely CWG tar, was added to the coal tar that Creosote was distilled from. The distillation process may have enriched the n-alkane and alkyl cyclohexane concentrations and therefore produced Creosote with higher concentrations of n-alkanes and alkyl cyclohexanes than the original CWG tar.

As there is significant differences in the n-alkane and alkyl cyclohexane distributions of the samples spread over different production processes a database of all the compounds that can be detected within the samples is required in order to assess how other compound groups differ between the different production processes. Chapter 6 will provide an in depth comprehensive database of the compounds detected in various different samples with varying production processes.

# Chapter 6

# Comprehensive database of compounds in a wide range of coal tars

## 6.1 Preface

This chapter contains three original journal articles submitted for publication in the journal of Rapid Communications in Mass Spectrometry in September 2016. The papers contain a database of compounds detected within 16 tar samples from 5 production processes. Each paper deals with an aspect of the overall database and all three papers are to be submitted to the same journal in as an A B and C. C. Gallacher as the main author was responsible for all the analysis and data interpretation and writing of the paper. R. Kalin and R. Lord, as project supervisors, provided support with the research as well as assistance with preparation and review of the manuscript. R. Thomas, as the industrial supervisor, provided expert knowledge in the field of coal tar and manufactured gas as well as reviewing the manuscript. C. Taylor provided expert knowledge in the field of coal tar research as well as reviewing the manuscript.

Chapter 5 presented the application of post extraction derivatization to sample of Creosote, a coal tar distillate, and the detection of 255 additional compounds, many of which would not have been detected without derivatization. Chapter 5 also presents a database of compounds present with Creosote with 1505 individual compounds detected. Chapter 6 presents a database of 16 tar samples from 5 different production processes produced using GCxGC analysis combined with post extraction derivatization. The analysis produced a comprehensive database of 2373 individual compounds. The chapter also presents the analysis of a tar sample produced by an Inclined Chamber Plant including PCA and HCA analysis. This type of tar has not previously been analysed using GCxGC or multivariate statistics. A full list of all the compounds found in each sample can be found in Appendix B.

## 6.2 Comprehensive database of Manufactured Gas Plant tars – Part A Database

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### Abstract

### RATIONALE

Coal tar is a waste by-product produced by the manufactured gas industry and coke ovens. Different production processes result in the production of distinctly different tar compositions. This study presents a comprehensive database of compounds produced using two-dimensional gas chromatography combined with time-of-light mass spectrometry (GCxGC-TOFMS) analysing 16 tar samples produced by 5 distinct production processes.

### METHODS

Samples of coal tar were extracted using accelerated solvent extraction (ASE) and derivatized post extraction using BSTFA with 1% TMCS. The derivatized samples were analysed using two-dimensional gas chromatography combined with time-of-light mass spectrometry (GCxGC-TOFMS).

### RESULTS

16 tar samples from 5 different production processes, Low Temperature Horizontal Retorts, Horizontal Retorts, Vertical Retorts, Carbureted Water Gas and Coke Ovens, were analysed. 2369 unique compounds were detected with 948 Aromatic compounds, 196 aliphatic compounds, 380 sulphur containing compounds, 209 Oxygen containing compounds, 262 Nitrogen containing compounds and 15 mixed heterocycles. Derivatization allowed for the detection of 359 unique compounds, the

majority in the form of hydroxylated PAHs, many of which would not have been detected without derivatization. Of the 2369 unique compounds detected 163 compounds were found to be present within all samples.

## CONCLUSIONS

A unique comprehensive database of compounds detected within 16 tar samples from 5 different production processes was produced. This initial study indicates that different production processes produce tars with different chemical signatures and can be further expanded upon by in depth analysis of the different compound types. This database clearly demonstrates the analytical power of GCxGC-TOFMS.

**Keywords:** GCxGC-TOFMS, Coal Tar, Environmental Forensics, Derivatization

## Introduction

Manufactured gas is a process by which solid or liquid fuels, such as coal or oil, are converted into gas. These processes were used between the 1810's and 1970's for the manufacture of Gas in Britain, firstly for lighting and then later on for heating purposes[1]. Tar is a by-product of the manufactured gas process and is produced during the carbonisation of coal, or oil. Coal tars are primarily dense non-aqueous phase liquids (DNAPLs) made up of thousands of organic and inorganic compounds. Some NAPLS produced by the Carbureted Water Gas process may also be Neutral or Light NAPLS with a specific gravity close to that of water. The organic fraction is dominated by Polycyclic Aromatic Hydrocarbons[2] (PAH's) and contains many different classes of organic compounds, many present in trace quantities. Many of the organic compounds found within coal tar can be toxic, mutagenic and/or carcinogenic and have high persistence within the environment. This means that coal tar contamination forms a long-term persistent risk when it is released into the environment.

The organic compounds found at former manufactured gas plant (FMGP) sites can be divided into three classes (Pyrogenic, Petrogenic and Diagenetic) that indicate their mechanism of formation and potential sources[3]. Pyrogenic substances are produced from oxygen-depleted high temperature processes, whereas petrogenic substances originate from petroleum-based materials used on the site[3]. Diagenetic substances are produced by recent biological activity and are unlikely to contribute measurably to PAHs near a FMGP site[3].

When a coal tar DNAPL is spilled into the sub-surface it will migrate vertically through the soil and underlying geology until it reaches a highly impermeable stratum and forms a long-term source of contamination. This will often lead to the DNAPL collecting within groundwater leading to the dissolution of soluble fractions of the coal tar into the groundwater. Although the rate at which contaminant mass transfer in the flowing groundwater takes place is slow the contamination may still pose a risk to human health or the environment[4]. D'Affonseca *et al.* (2008)[4] modeled the long term degradation of coal tar contamination and found that even after 1000 years source depletion of Phenanthrene was low with 89% of the original mass still remaining. The moderately and sparingly soluble composite constituents of coal tar were also predicted to have 60% and 98% of the original mass respectively remaining. These values highlight a key contamination issue of FMGP as any residual coal tar will take an extremely long time to degrade. This can form a long-term source of environmental liability and a persistent risk to human health and the environment.

It is estimated that over 3000 FGMP sites were present within the UK[5]. The US Environmental Protection Agency have reported that due to poor handling and storage practices in the past, contamination is likely to have occurred at up to 90% of former sites[6]. In 2006 it was estimated that at least 2279 former gasworks existed which had provided a public gas supply within the British Isles[7]. This excludes privately owned gasworks and a more recent estimation of recorded public and private gasworks from 2010 estimated 3510 gasworks located within the British Isles[8].

Coal tar has been used as a crude chemical feedstock for the worldwide fine-chemical industry, such as production of dyes or creosote for wood treatment[5]. This adds environmental forensic complications, as it is possible to encounter coal-tar contamination in a broad variety of sites other than FMGPs. One of the earliest uses of coal tar was in 1824 where the by-product naphtha was used to dissolve Indian rubber into a waterproofing agent for garments. By the late 1800's, coal tar was used in the synthesis of a wide array of industrial materials and consumer products, including: dyes, perfumes, explosives and pharmaceutical[9]. Tars that were not sold to refiners may have been landfilled or disposed of in open pits[10] resulting in a potential for tar contamination at many former landfill sites. Coal tar and other FMGP by-products and wastes were also deposited on FMGP site if space was available and ground raising was required[1].

The use of GCxGC allows for the separation of Unresolved Complex Mixtures (UCM), often referred to as a big "hump" in the GC[11], which cannot be separated using traditional GC-MS analysis. Because UCMs are believed to consist of many thousands of compounds, traditional GC-MS is simply not capable of providing sufficient resolution leaving most UCM hydrocarbons unidentified. The combination of the GCxGC with the TOFMS (time-of-flight mass spectrometer) allows for the identification of compounds within the UCM that previously would be unidentifiable within the "hump" and most likely missed using GC-MS. The use of GCxGC therefore allows for the separation of coal tar without the need for a lengthy separation process.

While a large amount of research surrounding coal tar is been published the production processes used to the produce the tar are often not reported, as they are likely unknown. A comprehensive database of the compounds found in tars from various different production processes is therefore required. The following study presents a database of compounds found in 16 different tars produced by 5 distinct production process including: Horizontal Retort, Vertical Retorts, Low Temperature Horizontal Retorts, Carbureted Water Gas plants and Coke Ovens.

## Materials and Methods

### Samples:

A total of 16 tars samples, coming from 5 different tar production processes, were extracted and analysed. The different processes and sample numbers are listed below (full site information for each sample can be found in the supplementary information):

Low Temperature Horizontal Retort (LTHR): DNAPL009 (D9L) and DNAPL016 (D16L)
Vertical Retort (VR): DNAPL002-006 (D2-D6V) and DNAPL020 (D20V)
Horizontal Retort (HR): DNAPL007 (D7H), DNAPL008 (D8H), DNAPL010 (D10H) and DNAPL017 (D17H)
Carbureted Water Gas (CWG): DNAPL013 (D13C) and DNAPL014 (D14C)
Coke Oven (CO): DNAPL018 (D18CO) and DNAPL019 (D19CO)

### Methods:

All solvents used were of analytical grade purchased from Fisher Scientific (Loughborough, U.K.) and D10-phenanthrene, which was used as an injection standard, was purchased from Sigma-Aldrich (Gillingham, U.K.). D8-Naphthalene, D10-Fluorene, D10-Fluoranthene and D10-Pyrene, which were used as recovery standards, was purchased from Sigma-Aldrich (Gillingham, U.K.). BSTFA with 1% TMCS was purchased from Sigma-Aldrich (Gillingham, U.K.).

Extraction was performed using an Accelerated Solvent Extraction system (ASE 350 Dionex, Camberley, UK) using 10 mL stainless steel extraction cells. Approximately 0.5g of tar was mixed with an equal amount of diatomaceous earth ($NaSO_4$) in a 1:1 ratio. Prior to extraction the samples were spiked a recovery standard. Extraction cells were lined with 2 Dionex glass fibre filter papers and packed with 3g of silica gel 60 deactivated with 10% water. The sample mixture was then loaded into the cells and any residue was recovered with excess diatomaceous earth. Dichloromethane was used as the extracting solvent for all extractions. ASE was performed at 100°C and 10 MPa, using one dynamic (7 min) and two static (5 min each) extractions. A flush volume of 150% and purge time of 60 s was used. The extracts were concentrated to 1 mL using a Büchi Syncore Analyst (Oldham, U.K). The extracts were then made up to exactly 10 mL using *n*-hexane. A 1 mL aliquot was then transferred to an auto sampler vial prior to analysis and spiked with D10H-Phenanthrene. All samples were derivatized using 100ul of BSTFA with 1% TMCS placed in an oven at 70°C for 1 hour.

GCxGC TOFMS analysis was performed using a Leco Pegasus 4D (St. Joseph, Michigan) time of flight mass spectrometer, connected to an Agilent 7890A gas chromatograph equipped with a LECO thermal modulator. The TOF ion source temperature was 200 °C and the mass range 45 and 500u was scanned at a rate of 200 spectra/second. The detector voltage was set at 1700 V with a electron ionisation voltage of 70 eV.

All standards and extracts were analysed with the following primary oven temperature programme: 60°C isotherm for 2 minute, then ramp at 10°C/min to 110°C, then ramp at 3°C/min to 310 °C, and isothermal at 310°C for 15 minutes. The secondary oven and modulator temperatures were programmed at a 10 °C offset relative to the primary oven. The modulation period was 6 seconds with a 1.3 second hot pulse time and a cool time of 1.7 seconds. The injection port temperature was set to 250 °C and set to split injection with a split ratio of 50 and an injection volume of 1µl. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min.

The reversed polarity column set that was used comprised of a mid-polarity TR-50 MS supplied by Thermo Scientific (30 m × 0.25 mm i.d. × 0.25 µm film thickness) as the primary column and a non-polar Rtx-5SilMS supplied by Thames Restek (1.5 m × 0.25 mm i.d. m × 0.25 µm film thickness) as the secondary column, connected via a Thames Restek Press-tight connector.

The chromatograms from each sample were processed using Leco ChromaTOF software (Version 4.50.8.0) to search for, identify and align all peaks with a signal-to-noise ratio greater than 10. As it would be impractical to purchase standards of every compound present within the samples any concentration comparisons are relative comparisons of the peak area for each compound adjusted for sample weight and recovery. Only direct like for like compound comparison will be done, as the detector response will remain equivalent.

## Results and Discussion

*Database:*

A total of 5 different production processes are represented within the coal tar database including Low Temperature Horizontal Retorts, Horizontal Retorts, Vertical Retorts, Carbureted Water Gas and Coke Ovens. These 5 production processes cover a wide range of types of coal tars manufactured, although other production processes have been used. Figure 6.1 shows the overall composition of each sample as well as the total number of each compound class present within the samples. The aliphatic class includes *n*-Alkanes, *n*-Alkenes, Branched Alkanes/Alkenes and alkyl Cyclohexane/Pentanes. The PAH class includes all parent and alkyl PAHs. The derivatized class includes all hydroxylated PAHs (such as phenolics) as well as hydroxylated PASHs, which has been previously reported in coal liquids[12]. The mixed Heterocycles include heterocyclic compounds with more than one element substituted within the ring such as Oxygen-Sulphur. Thienobenzofurans are an example of a group of mixed heterocycles detected for which no literature reporting their presence within coal tar could be found. Nitrogen-Sulphur mixed heterocycles such as Azabenzothiophene were also detected, which have been previously reported in coal liquids[13] and Anthracene oil[14]. The PANH class includes all Nitrogen containing compounds present in the database, with the exception of mixed heterocycles. The PAOH class contains all Oxygen containing compounds, with the exception of hydroxylated compounds and mixed heterocycles. The PASH class contains all sulphur analogues of polycyclic aromatic hydrocarbons, with the exception of hydroxylated sulphur compounds and mixed heterocycles.

A total of 16 coal tar samples were analysed with 2369 unique compounds detected with the largest group being PAHs containing 948 compounds. The database also includes 380 PASHs, 209 PAOHs, 262 PANHs and 15 mixed Heterocycles. Finally a total of 196 aliphatic compounds were detected and 359 derivatized compounds.

Of the 2369 compounds detected 163 compounds, shown in table 1, were found to be present in all samples. The majority of these compounds were PAHs with 121 PAHs being found in all samples. A full list of the compounds found in all samples including retention times can be found in the Appendix. All 16 of the EPA 16 PAHs were detected in every samples as well as several other parent PAHs with branched PAHs dominating the list. Due the large number of possible combinations associated with branched PAHs only a select number of each was present. For example of the 23 C2-Fluorenes present in the database only 4 occurred in every sample. Of the EPA34 PAHs[15] 30 were detected within every sample with only C3-Fluorene, C3-Benzanthracene/Chrysene, C4-Benzanthracene/Chrysene and C4-Phenanthrene/Anthracene not being detected in every sample. A total of 70 individual compounds that fall within the EPA34 were detected in every sample and a total of 202 compounds detected that fall within the EPA34 that were detected in multiple samples with C3-Fluorene, C3-Benzanthracene/Chrysene, C3-Benzanthracene/Chrysene and C4-Phenanthrene/Anthracene being detected within only a single sample each. Only 2 aliphatic compounds were detected within all samples, C11 and C12 n-alkanes, while C13 to C16 n-alkanes occurred in every sample except D18CO (coke oven). A total of 22 heterocyclic compounds occur within every sample with 4 PANHs, 6 PAOHs and 11 PASHs respectively.

The presence of petrogenic substances within the samples is also possible, particularly if the site also operated a CWG plant, and alkyl cyclohexanes are often a sign of petrogenic contamination[3]. Alkyl cyclohexanes are present in all but 3 of the database samples suggesting that all but 3 have some level of petrogenic input. Both coke oven tars lack any alkyl cyclohexanes, which would be expected as the samples are fresh and should not contain a petrogenic element, as well as D16L that operated a LTHR process and did not have a CWG plant on site. Of the remaining samples, excluding the CWG tars themselves (D13C and D14C), all samples except D7H were known to have operated a CWG plant on the same site. This suggests that an amount of CWG tar is present within these samples but not in sufficient quantity to affect the multivariate statistical analysis used to determine their production processes in McGregor et al., 2012[5]. The presence of alkyl cyclohexanes within D7H may suggest that the site may have also operated a CWG plant. As the site history is limited this is a possibility, or that some other petrogenic contamination source has contaminated the sample.

*Low Temperature Horizontal Retort (LTHR):*

Horizontal retorts were the first type of retort that was widely used, initially on all sizes of gasworks. They were originally circular and made from cast iron, although this was eventually superseded by fireclay and later silica due to the low durability and poor ability to withstand high temperatures of cast iron[1]. Early low temperature horizontal retorts were heated directly by a shallow fuel bed of coke lit beneath the furnace. The direct heat radiated from the furnace to heat the retort. This design only heated the retorts to around 600°C[9] and as a result the amount of gas produced was fairly low and the decomposition of the organic compounds within the tar was limited, leading to tars more similar in nature to the parent coal[16].

The number of compounds present within sample D9L is extremely large with a total of 1568 individual compounds detected. This is the greatest number of compounds detected within any sample in the database and it also contains the greatest number of aliphatic compounds detected at 136. Sample D16L contains a relatively small number of compounds with a total of 672. Both samples were previously found to come from the LTHR process[5] and there are several possible explanations for the large discrepancy in the number of compounds detected. D16L comes from a relatively small site that ceased operations in 1946. The site was redeveloped and the tar sample was taken from the location of a former tar tank. The sample itself was present within sandy soil and so this may affect the relative amounts of organics present within the sample taken for analysis. The sample may have also undergone significant environmental weathering. D9L was taken from a tar well and comes in the form of pure DNAPL present in water. As the sample came from a tar well it is likely that losses of the water-soluble fraction of the tar to the environment are low as it is unlikely that significant flow of water took place out of the tar tank.

*Horizontal Retort (HR):*

Later horizontal retorts allowed for higher operational temperatures capable of exceeding 1000°C[17] and so greater decomposition of the organic compounds within the tar. The large surface area present within horizontal retorts allowed for a greater contact of the produced gases with the heated retort sides and so produced a greater degree of thermal cracking[18].

A total of 4 horizontal retort tars were analysed with a wide variation in the total number of compounds detected in each. D8H contained the most compounds with a total of 1517. D17H and D7H both had 1306 and 1290 compounds detected respectively and D10H contained the lowest number of compounds detected with 872. D7H was pure DNAPL taken from the base of a gasholder and is unlikely to have been exposed to the environment as a whole. D8H was taken from a former tar tank present on the site and while the sample was waterlogged it is unlikely that it has been exposed to the greater environment. D10H was taken from a tar well present on the site and some of the organic compounds present in the original tar may have leached into the water, however the tank itself was essentially sealed from the external environment. D17H was taken from a pool of tar present on the site, which was exposed to the environment for an unknown period of time but was not waterlogged. All samples are essentially crude DNAPL with a varying amount of possible water content.

*Vertical Retort (VR):*

Vertical retorts were later developed which rotated the retort by 90° and allowed for the gas making process to be run continuously. Vertical retorts generally operated a high temperature process with temperatures similar to that of horizontal retorts however because of the design of the retort they produced significantly different tars. A temperature gradient existed within a vertical retort, especially in a continuous system where coal was continuously fed by gravity. The tar fog generated can also escape vertically up through the coal without carbonizing on the hot surface of the retort reducing secondary degradation. This produces a tar uniquely separate to both LTHR and HR tars.

Of the 6 VR samples present in the data, 5 came from the same site. The number of compounds present within the samples varies greatly with D2V containing 650 compounds, D3V containing 807, D4V containing 1188, D5V containing 883 and D6V containing 833. D20V, which comes from a different site, contains a total of 1426 compounds and was in the form of pure DNAPL. D2V contains the lowest number of compounds and comes in the form of tar in a sandy soil. The low number of compounds in D2V could be down to relatively less tar present within the soil or the fact it was sampled from a different part of the site and therefore may have undergone different/more substantial weathering processes than the other samples. D2V was taken from a location that was not located near to a tar tank therefore the relative amount of tar within the sample is likely to be lower. Since D3V, D4V, D5V and D6V are from roughly the same location on the site and therefore overall compositions of the tar would be expected to be the same. D3V, D4V and D6V were all taken from within the same tar tank, which had been backfilled after closure of the gasworks, whereas D5V was taken downstream from the tar tank and was open to the environment. This suggests that D5V is more likely to have lost compounds to the environment than the other samples from the same location. It is also possible that the tar found at D5V was produced and/or deposited at a different time to D3V, D4V and D5V.

*Coke Oven tars:*

Another possible source of tar within the UK comes from coke oven tars. Coke ovens were mainly located at collieries, iron and steel works, where coke was required for the smelting process and can still be found in operation at present-day steel works. Coke ovens are the only remaining operational coal carbonizing plants in the UK[1]. The operational temperature of a coke oven determines the composition of the tar produced. Coke ovens can operate over a wide temperature range but fall into two rough classes. Low temperature coke ovens <700°C produced phenolic compounds and PANHs[19], producing tars similar to low temperature retorts. High temperature coke ovens operated in temperatures in excess of 700°C producing tars with high PAH content and the conversion of PANHs into ammonia, hydrogen cyanide, pyridine bases and nitrogen[19]. As the tar escapes from a coke oven it is forced on to the hot vertical walls and so is degraded more than in HR or VR. Metallurgical coke is produced in the 900°C to 1095°C range[20] meaning that the samples are likely produced at a high temperature.

Both coke oven samples were taken on the same day from the same location from different coke ovens. Both ovens used the same feedstock therefore any differences will be down to the different ovens used. D19CO comes from an older coke oven that has been in operation since the 1930's, whereas D18CO comes from a coke oven that has been in operation since the 1970's. The overall compositions of the samples, seen in figure 6.1, are roughly the same with a similar number of overall compounds, although the relative concentrations of the compounds can vary greatly. D18CO contains a total of 824 compounds whereas D19CO contains slightly more with 872 compounds. All of the data for the coke oven tars suggests that while both samples come from the same site, and likely use the same feedstock, they can produce tars with different overall compositions while still being distinguishable as coke oven tars in McGregor et al., 2102[5].

*Carbureted Water Gas:*

The Carbureted water gas process involved passing steam over a carbon source (usually heated coke) in order to produce gas[1]. The reaction was extremely endothermic therefore water gas was generally produced by a two-step cyclic process referred to as the run and blow cycle[9]. During the blow stage coke was heated to incandescence by a stream of air and during the run stage steam was injected into the hot coke. During the run process the fuel would gradually cool due to the endothermic nature of the reaction hence the need for a cyclic process. To improve the calorific and/or illumination value of gas produced by water gas, a spray of oil was introduced to the hot gas in the carburetor hence the name *Carbureted* water gas [10]. CWG could be made with a variety of carbon feedstock such as coke, anthracite or bituminous coal and initially was carbureted with tar light oils generated at coal gas plants. Any tars produced by the CWG process were consistent with oil gas tars, as the non-carbureted water gas process did not generate significant amounts of tar[19]. The normal operational temperature of CWG was between 650°C and 700°C[19] making it a relatively low temperature process.

Both CWG tars contain a large amount of organic compounds with 1150 detected in D13C and 1440 detected within D14C. The sample of D13C was obtained from a groundwater contamination plume and had likely spent a significant amount of time in the environment. The sample itself appears to be pure DNAPL although the water content within the sample is unknown. D14C was taken from a former gasholder that was used as a tar emulsion storage tank. This sample also appears to be pure DNAPL although the water content is again unknown. As D14C was taken from within a storage tank rather than a groundwater plume it would be expected that it has lost less of its original more water-soluble fraction, as the sample would have equilibrated with any water present within the tank. It is more likely that D13C has lost at least some of its soluble components to groundwater flow it is also likely that the sample has a higher water content than D14C.

## Conclusion

A unique comprehensive of compounds detected within 16 tars produced by 5 different production processes was produced. In total 2373 unique compounds were detected with 163 compounds detected within all samples. The 163 compounds detected within every sample are of potential forensic importance as current risk assessments relating to coal tar focus on a limited number of compounds, usually the 18 priority PAHs. Several of the 163 compounds detected within every sample may also be of potential interest from a toxicological standpoint. The results clearly demonstrated that different production processes produce distinctly different coal tars with a degree of variability within the tars produced by the same processes. This initial study clearly demonstrates the power of GCxGC-TOFMS for the forensic analysis of environmental samples and can be further expanded on by more detailed examination of the individual compound types.

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| Compound | m/z | No | Formula | Compound | m/z | No | Formula | Compound | m/z | No | Formula |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C11 n-alkane | 57 | 1 | C11H22 | Cyclopenta[def]phenanthrene | 190 | 1 | C15H10 | C1-Benzo[x]fluoranthene etc | 266 | 7 | C21H14 |
| C12 n-alkane | 57 | 1 | C12H24 | C1-Phenanthrene/Anthracene$^{\text{*EPA34}}$ | 192 | 6 | C15H12 | Indeno[1,2,3-cd]pyrene$^{\text{*EPA16 + EPA34}}$ | 276 | 1 | C22H12 |
| Styrene | 104 | 1 | C8H8 | C2-Flourene$^{\text{*EPA34}}$ | 194 | 4 | C15H14 | Dibenz(a,h)anthrance$^{\text{*EPA16 + EPA34}}$ | 278 | 1 | C22H14 |
| Indene | 116 | 1 | C9H8 | Fluoranthene$^{\text{*EPA16 + EPA34}}$ | 202 | 1 | C16H10 | m/z 278 PAH C22H14 | 278 | 2 | C22H14 |
| Indane | 118 | 1 | C9H10 | Pyrene$^{\text{*EPA16 + EPA34}}$ | 202 | 1 | C16H10 | Benzo[g,h,i]perylene$^{\text{*EPA16 + EPA34}}$ | 276 | 1 | C22H12 |
| C3-Benzene | 120 | 3 | C9H12 | Acenaphenanthrylene/Aceanthrylene | 202 | 1 | C16H10 | Dibenzochrysene | 276 | 1 | C22H12 |
| Naphthalene$^{\text{*EPA16 + EPA34}}$ | 128 | 1 | C10H8 | C2-Phenanthrene/Anthracene$^{\text{*EPA34}}$ | 206 | 5 | C16H14 | 1-Naphthalenecarbonitrile | 153 | 1 | C11H7N |
| Dihydronapthalene | 130 | 2 | C10H10 | C4-Biphenyl | 210 | 1 | C16H18 | Carbazole | 167 | 1 | C12H9N |
| Methyl Indene | 130 | 1 | C10H10 | C1-Fluoranthene/Pyrene$^{\text{*EPA34}}$ | 216 | 5 | C17H12 | Benzo[def]carbazole | 191 | 1 | C14H9N |
| C4-Benzene 1DB | 132 | 1 | C10H12 | C3-Phenanthrene/Anthracene$^{\text{*EPA34}}$ | 220 | 3 | C17H16 | Dimethyl Carbazole | 195 | 1 | C14H13N |
| Methyl Indan | 132 | 1 | C10H12 | Benzo[ghi]fluoranthene | 226 | 1 | C18H10 | Benzofuran | 118 | 1 | C8H6O |
| C4-Benzene | 134 | 1 | C10H14 | Benzo[c]Phenanthrene | 228 | 1 | C18H12 | C1-Benzofuran | 132 | 1 | C9H8O |
| C1-Naphthalene$^{\text{*EPA34}}$ | 142 | 2 | C11H10 | Benzo[a]anthracene$^{\text{*EPA16 + EPA34}}$ | 228 | 1 | C18H12 | Benzo[b]naphtho[2,3-d]furan | 218 | 1 | C16H10O |
| Acenaphthylene$^{\text{*EPA16 + EPA34}}$ | 152 | 1 | C12H8 | Chrysene$^{\text{*EPA16 + EPA34}}$ | 228 | 1 | C18H12 | Benzo[b]naphtho[2,1-d]furan | 218 | 1 | C16H10O |
| Acenaphthene$^{\text{*EPA16 + EPA34}}$ | 154 | 1 | C12H10 | Triphenylene/Napthacene | 228 | 1 | C18H12 | Benzo[b]naphtho[1,2-d]furan | 218 | 1 | C16H10O |
| Biphenyl | 154 | 1 | C12H10 | C2-Fluoranthene/Pyrene | 230 | 5 | C18H14 | 7H-Benz[de]antracen-7-one | 230 | 1 | C17H10O |
| C2-Naphthalene$^{\text{*EPA34}}$ | 156 | 8 | C12H12 | 9H-Cyclopenta[a]pyrene etc | 240 | 3 | C19H12 | C1-Benzonaphthofuran | 232 | 2 | C17H12O |
| Fluorene$^{\text{*EPA16 + EPA34}}$ | 166 | 1 | C13H10 | C1-Benzanthracenes/Chrysene$^{\text{*EPA34}}$ | 242 | 3 | C19H14 | C1-Benzothiophene | 148 | 3 | C9H8S |
| 1H-Phenalene | 166 | 1 | C13H10 | C1-Dihydro. Benz[a]anthracene | 244 | 1 | C19H16 | Phenyl Thiophene | 160 | 2 | C10H8S |
| Benz[x]indene? | 166 | 4 | C13H10 | Benzo[b]fluoranthene$^{\text{*EPA16 + EPA34}}$ | 252 | 1 | C20H12 | C3-Benzothiophene | 176 | 5 | C11H12S |
| Diphenylmethane | 167 | 1 | C13H12 | Benzo[k]fluoranthene$^{\text{*EPA16 + EPA34}}$ | 252 | 1 | C20H12 | Dibenzothiophene | 184 | 1 | C12H8S |
| C1-Biphenyl | 168 | 2 | C13H12 | Benzo[e]pyrene$^{\text{*REACH + EPA34}}$ | 252 | 1 | C20H12 | Naphtho[1,2-b]thiophene | 184 | 1 | C12H8S |
| C3-Naphthalene 1DB | 168 | 1 | C12H12 | Benzo[a]pyrene$^{\text{*EPA16 + EPA34}}$ | 252 | 1 | C20H12 | Naphtho[2,1-b]thiophene | 184 | 1 | C12H8S |
| C3-Naphthalene$^{\text{*EPA34}}$ | 170 | 4 | C13H14 | Perylene$^{\text{*EPA34}}$ | 252 | 1 | C20H12 | C1-Dibenzothiophene | 198 | 5 | C13H10S |
| Phenanthrene$^{\text{*EPA16 + EPA34}}$ | 178 | 1 | C14H10 | Binaphthalene | 254 | 2 | C20H14 | Phenanthro/Phenaleno Thiophene | 208 | 3 | C14H8S |
| Anthracene$^{\text{*EPA16 + EPA34}}$ | 178 | 1 | C14H10 | C2-Benzanthracenes/Chrysene$^{\text{*EPA34}}$ | 256 | 1 | C20H16 | Phenyl Benzothiophene | 210 | 1 | C14H10S |
| C1-Fluorene$^{\text{*EPA34}}$ | 180 | 6 | C14H12 | Cyclopenta[ghi]perylene | 264 | 1 | C21H12 | C2-Dibenzothiophene | 212 | 4 | C14H12S |
| C4-Naphthalene$^{\text{*EPA34}}$ | 184 | 5 | C14H16 | 11H-Indeno[2,1,7-cde]pyrene | 264 | 1 | C21H12 | C1-Benzonapthothiophene etc | 248 | 2 | C17H12S |

Table 6.1 – Compounds present in all database samples *A full list including retention times has been included in the appendices.

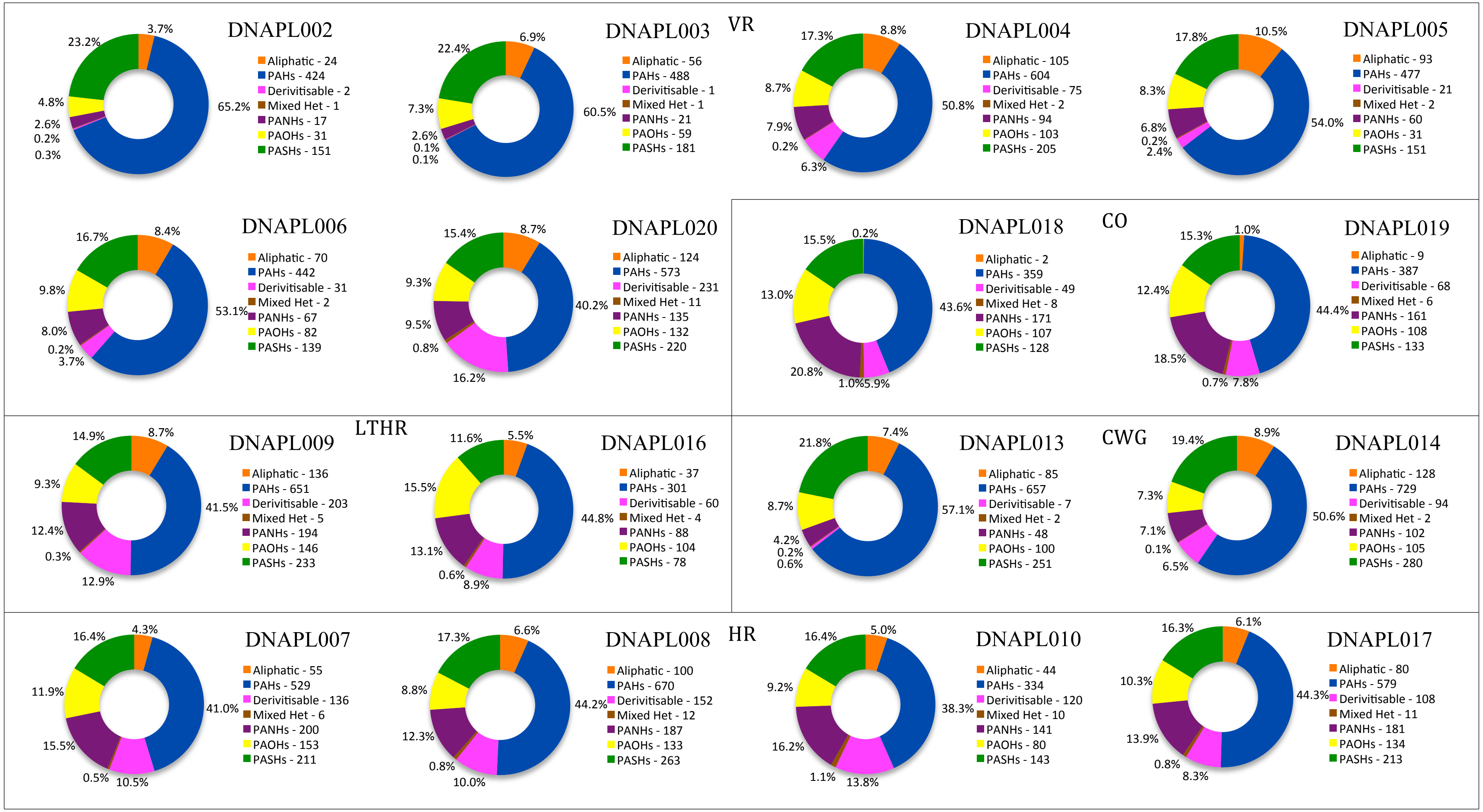

Figure 6.1 – Total number of compounds per database sample (HR = Horizontal Retort, VR = Vertical Retort, LTHR = Low Temperature Horizontal Retort, CWG = Carbureted Water Gas, CO = Coke Oven)

## 6.3 Comprehensive database of Manufactured Gas Plant tars – Part B Aliphatic and Aromatic compounds

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### Abstract

### RATIONALE

Coal tar was a by-product of the manufactured gas industry and contains a mixture of inorganic and organic compounds. As different production processes produce different tars a comprehensive database of the compounds present within coal tars from different production processes is required. This study focuses on the aliphatic and aromatic compounds present within a database produced from 16 different tars from 5 different production processes.

### METHODS

Samples of coal tar were extracted using accelerated solvent extraction (ASE) and derivatized post extraction using BSTFA with 1% TMCS. The derivatized samples were analysed using two-dimensional gas chromatography combined with time-of-light mass spectrometry (GCxGC-TOFMS).

### RESULTS

A total of 198 individual aliphatic and 951 individual aromatic compounds were detected within 16 tar samples produced by 5 different production processes. The PAH content of coal tars varies greatly depending on the production process used to produce the tars and this is clearly demonstrated within the results. The aliphatic composition of the tars provided an important piece of forensics information that

would have otherwise been missed with the detection of petrogenic compounds such as Alkyl Cyclohexanes.

**CONCLUSIONS**

The aromatic compositions of the tar samples varied greatly with the production process used as well as providing forensic information within the individual production process groups. Alkyl Cyclohexanes were detected in all samples from sites known to operate Carbureted Water Gas plants and not detected in those that did not. This important piece of forensic information suggests that many samples were contaminated with CWG tar, with the bulk of the tar coming from the main production process used on the site.

**Keywords:** GCxGC-TOFMS, Coal Tar, Environmental Forensics

## Introduction

Coal tars are primarily dense non-aqueous liquids (DNAPLs) made up of thousands of organic and inorganic compounds, with organic compounds such as Polycyclic Aromatic Hydrocarbons (PAHs) dominating the composition[1]. Coal tar can be produced from a variety of different production sources including manufactured gas and the production of coke. PAHs consist of fused aromatic rings and are persistent within the environment due to the presence of dense π-electrons on both sides of the ring structure[2]. PAHs can be toxic with the level of toxicity varying greatly with the number of fused rings and 4 and 5-ring PAHs have a strong tendency to be carcinogenic and/or mutagenic[3].

Various different manufactured gas production processes were employed over time producing tars with different chemical signatures. For example, the naphtha fraction of VR tars contain relatively more paraffin's than HR tars and significantly more than CO tars[4]. This general rule also applies to paraffin's present within the oil fraction, that boil above the Naphtha range, with VR tars typically containing 12% of its composition as paraffin's while HR and coke oven tars contain 0.9% and 0.3%

respectively[4]. The main distinction between coke coal tars and other tars type is high parent PAH content[5].

The PAH composition of coal tars can vary greatly depending on the production process used to produce the tar, as well as the feedstock used. For example, the Naphthalene content of VR tars is very low making up between 0 and 3% of the total tar[4]. This is not the case in HR or CO tars where Naphthalene is generally represent at 7% and 5% respectively of the total composition of the tar[4]. The yields of other PAHs such as anthracene and phenanthrene also follow the same general trend.

PAHs can come from either pyrolytic, petrogenic or biogenic sources. PAHs are introduced into the environment through contamination by crude oils, coal and coal tar or various refinery products. They can also occur naturally and are derived from biogenic precursors like terpenes, pigments and steroids[6].

Alkylated PAHs form an important group of compounds that are often ignored in environmental analysis due to difficulties in accurate measurement. The EPA has created a list of 16 groups of prominent C1 to C4 alkyl PAHs derivatives and combined that with the 18 parent PAH's to create the so-called 34 EPA PAHs[7]. Alkylated PAHs can serve as useful indicators for petroleum, coal tar and creosote weathering in the environment. Investigators can use alkyl PAHs to study PAH transport and migration pathways as well as the rate the pollutants degrade[8].

Alkyl PAHs have a large number of possible isomers with alkyl naphthalenes having the lowest possible number of isomers of the parent PAHs. One important point of note is that due to the co-elution of the alkyl PAHs in GC the 34 PAH method actually represents several hundred individual alkylated PAH compounds[9]. The use of GCxGC allows for the separation of alkylated PAHs with McGregor et al. 2011 reporting the separation of 12 C2 alkyl naphthalenes into 10 peaks and only 2 pairs of alkyl naphthalenes still co-eluting. The type of column setup used in the GCxGC method is important with normal phase column setups only separating 9 out of a possible 34 C3N isomers and 14 of the 112 possible C4N isomers, while reserved phase columns setups separate 14 C13N and 20 C4N peaks within the same DNAPL[10].

Alkylated PAHs have been shown to contribute substantially to the toxicity of PAH mixtures, in some cases accounting for 80% of the toxic burden[8]. In crude oil parent PAH's only make up roughly 1% of the total toxic burden with alkyl PAHs making up 99%[9]. In Benthic organisms affected by crude oil contamination only 1.4% of the TU (Toxic units available to benthic organism) is made up of the parent PAHs and the remaining 98.6% is made up by alkyl PAHs (Hawthorne et al. 2006). Historical studies, and many modern studies, focus only on the 18 (or 16) parent PAH's and this means that the risks associated with crude oil contaminated sites may be been greatly underestimated. In diesel fuel contaminated sites the parent PAHs account for 2.2% of the composition and 2.7% of the TU. In contrast the PAHs in pyrogenic FMGP samples account for 35 to 42% of the total PAH concentrations and TU (Hawthorne et al. 2006), although this will vary depending on the type of coal tar and the processes that produced it.

This study presents the in depth analysis of the aliphatic and aromatic content of 16 tar samples produced by 5 different production processes. A full database of the compounds found within the samples has been published in Gallacher et al., 2016[11].

## Materials and Methods

### Samples: See part A

A total of 16 tars samples, coming from 5 different tar production processes, were extracted and analysed. The different processes and sample numbers are listed below:

Low Temperature Horizontal Retort: DNAPL009 (D9L) and DNAPL016 (D16L)
Vertical Retort: DNAPL002-006 (D2-D6V) and DNAPL020 (D20V)
Horizontal Retort: DNAPL007 (D7H), DNAPL008 (D8H), DNAPL010 (D10H) and DNAPL017 (D17H)
Carbureted Water Gas: DNAPL013 (D13C) and DNAPL014 (D14C)
Coke Oven: DNAPL018 (D18CO) and DNAPL019 (D19CO)

**Methods:**

All solvents used were of analytical grade purchased from Fisher Scientific (Loughborough, U.K.) and D10-phenanthrene, used as an injection standard, was purchased from Sigma-Aldrich (Gillingham, U.K.). BSTFA with 1% TMCS was purchased from Sigma-Aldrich (Gillingham, U.K.). D8-Naphthalene, D10-Fluorene, D10-Fluoranthene and D10-Pyrene, was used as recovery standards, and were purchased from Sigma-Aldrich (Gillingham, U.K.).

Extraction was performed using an Accelerated Solvent Extraction system (ASE 350 Dionex, Camberley, UK) using 10 mL stainless steel extraction cells. Approximately 0.5g of tar was mixed with an equal amount of diatomaceous earth ($NaSO_4$) in a 1:1 ratio. Prior to extraction the samples were spiked a recovery standard. Extraction cells were lined with 2 Dionex glass fibre filter papers and packed with 3g of silica gel 60 deactivated with 10% water. The sample mixture was then loaded into the cells and any residue was recovered with excess diatomaceous earth. Dichloromethane was used as the extracting solvent for all extractions. ASE was performed at 100$^{o}$C and 10 MPa, using one dynamic (7 min) and two static (5 min each) extractions. A flush volume of 150% and purge time of 60 s was used. The extracts were concentrated to 1 mL using a Büchi Syncore Analyst (Oldham, U.K). The extracts were then made up to exactly 10 mL using *n*-hexane. A 1 mL aliquot was then transferred to an auto sampler vial prior to analysis and spiked with D10H-Phenanthrene. All samples were derivatized using 100ul of BSTFA with 1% TMCS placed in an oven at 70$^{o}$C for 1 hour.

GCxGC TOFMS analysis was performed using a Leco Pegasus 4D (St. Joseph, Michigan) time of flight mass spectrometer, connected to an Agilent 7890A gas chromatograph equipped with a LECO thermal modulator. The TOF ion source temperature was 200 °C and the mass range 45 and 500u was scanned at a rate of 200 spectra/second. The detector voltage was set at 1700 V with a electron ionisation voltage of 70 eV.

All standards and extracts were analysed with the following primary oven temperature programme: 60°C isotherm for 2 minute, then ramp at 10°C/min to 110°C, then ramp at 3°C/min to 310 °C, and isothermal at 310°C for 15 minutes. The secondary oven and modulator temperatures were programmed at a 10 °C offset relative to the primary oven. The modulation period was 6 seconds with a 1.3 second hot pulse time and a cool time of 1.7 seconds. The injection port temperature was set to 250 °C and set to split injection with a split ratio of 50 and an injection volume of 1µl. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min.

The reversed polarity column set that was used comprised of a mid-polarity TR-50 MS supplied by Thermo Scientific (30 m × 0.25 mm i.d. × 0.25 µm film thickness) as the primary column and a non-polar Rtx-5SilMS supplied by Thames Restek (1.5 m × 0.25 mm i.d. m × 0.25 µm film thickness) as the secondary column, connected via a Thames Restek Press-tight connector.

The chromatograms from each sample were processed using Leco ChromaTOF software (Version 4.50.8.0) to search for, identify and align all peaks with a signal-to-noise ratio greater than 10. As it would be impractical to purchase standards of every compound present within the samples any concentration comparisons are relative comparisons of the peak area for each compound adjusted for sample weight and recovery. Only direct like for like compound comparison will be done as the detector response will remain equivalent.

## Results and Discussions

### *Low Temperature Horizontal Retort (LTHR):*

Low Temperature Horizontal Retorts were the first type of retort to be widely used and produced gas from coal operating at temperatures of around 600°C[12]. This relatively low temperature led to a limited degree of decomposition of the organic compounds present within the feedstock coal and therefore the tars produced were more similar in nature to the parent coals from which it was produced.

The aliphatic compositions of the LTHR tars are significantly different with sample

D9L containing 136 aliphatic compounds, which is the most aliphatics present in any of the samples present within the database, and sample D16L containing only 37. Sample D9L contains n-alkanes between C11 and C32, whereas sample D16L contains n-alkanes between C11 and C30. There are significant differences in the relative concentrations of the n-alkanes in the LTHR samples. In both samples the maximum n-alkane is C13, however sample D9L contains 7534% more than sample D16L. Sample D9L also contains alkyl cyclohexanes between C4 and C14 but these compounds are completely absent in sample D16L. This suggests a relationship between the relative concentrations of n-alkanes and the presence of alkyl cyclohexanes within the samples. The large difference in the total number of aliphatic compounds between the samples is down to the presence of a larger number of alkenes in D9L relative to D16L (32:10); the presence of a larger number of branched alkanes in D9L relative to D16L (32:7); and the presence of 36 miscellaneous aliphatics such as alkyl cyclopentenes and alkyl cyclopentadienes within D9L that were not detected in D16L.

The total number of PAHs and Alkyl PAHs present within the LTHR tars is very different with sample D9L containing 651 individual compounds and sample D16L containing only 301. The average relative EPA16 composition of the LTHR tars is shown in figure 6.1 and shows a signature that is dominated by both Naphthalene and Phenanthrene. The main difference between the samples in terms of % composition is the relative amounts of Naphthalene and Phenanthrene with sample D9L containing 14.0% of the EPA16 PAH composition as Naphthalene, whereas D16L contains 21.8% Naphthalene. Phenanthrene makes up 13.7% of the total EPA16 composition of D9L and 15.93% of D16L. Another significant difference is present in the relative amounts of Pyrene and Fluoranthene with D9L containing 10.3% fluoranthene and 7.06% pyrene and sample D16L contains only 7.4% and 5.8% respectively. While there is variation in the relative composition of the samples in both samples Naphthalene is the largest single EPA16 compound. Sample D9L contains 201 EPA34 PAHs with sample D16L containing only 134, which is the second lowest number within the database.

The relative concentrations of the EPA16 PAHs within the LTHR tars are significantly different with sample D9L containing 535% more EPA16 PAHs overall. Sample D9L also contains significantly higher concentrations of all of the EPA16 PAHs with for example 344% more Naphthalene, 459% more Phenanthrene, 738% more Fluoranthene and 655% more Pyrene. The significantly higher concentrations of EPA16 PAHs present within D9L relative to D16L are likely down to the fact D9L is in the form of pure DNAPL in water, whereas D16L is in the form of tar saturated soil, and so likely contains less tar.

The ratio of Flt/Pyr can be used to give information about the temperature of the production process with the expected ratio of a LTHR tar being between 0.6 and 0.8 and between 1.0 and 1.4, or higher, for a higher temperature process[14]. The ratio of Flt/Pyr in D9L is 1.45 and in D16L is 1.29. Both of these values fall far outside of the range that would be expected and in fact fall into the range for higher temperature coal tars. Since the production process of the tars is known to be a low temperature process this suggests that in this case the use of the Flt/Pyr ratio gives inaccurate results that without the sample history could have led to inaccurate interpretations. It also suggests that great caution should be used when comparing value calculated on US coal tars for British coal tars. While analytical variability has been cited as a possible reason for the misinterpretation of the Flt/Pyr ratio[15] the degree of difference between the calculated values and the expected values is so large that it is unlikely to be down to analytical variability.

*Horizontal Retort (HR):*

Advances in horizontal retort technology allowed for increases in operational temperature which were capable of exceeding 1000°C[16] and resulted in a greater degree of thermal decomposition of the organic compounds found within the parent coal, and resulting tar, as well as generating a greater degree of thermal cracking[17].

The aliphatic composition of the horizontal retort tars varies widely with sample D8H containing the most aliphatic compounds of the HR tars with 100 and D10H containing the least with 44. Sample D7H contains 55 and sample D17H contains 80 with the relative concentrations of the aliphatics that the samples share varying widely. Sample D8H contains the highest relative concentrations of n-alkanes ranging between C11 and C28 with a maximum at C13. Sample D7H contains n-alkanes ranging from C11 to C28 with a maximum at C12, which is present in sample D8H at 1945% of the concentration found in D7H. Sample D10H contains n-alkanes ranging between C11 and C30 with a maximum also at C12, which is present in sample D8H at 385% of the concentration found in D10H. Finally sample D17H contains n-alkanes ranging between C11 and C29 with a maximum at C14, which is present in sample D8H at 393% of the concentration found in D17H. While the relative concentrations of n-alkanes vary widely the same general trend exists with low molecular weight n-alkanes between C11 and C18 dominating.

The alkyl cyclohexane distributions of the HR tars also vary widely. Sample D8H contains the most alkyl cyclohexanes in both concentrations and number of compounds with alkyl cyclohexanes ranging between C4 and C15 and a maximum at C5. Sample D7H contains alkyl cyclohexanes ranging between C4 and C9 with a maximum also at C5, which is present in sample D8H at 2214% of the concentration found in D7H. Sample D17H contains alkyl cyclohexanes ranging between C4 and C13 with a maximum also at C5, which is present in sample D8H at 789% the concentration found in D17H. Sample D10H contains only 4 alkyl cyclohexanes ranging between C4 and C7 with a maximum also at C5, which is present in sample D8H at 295% of the concentration present within sample D10H. This suggests that while sample D10H contains less individual alkyl cyclohexanes than sample D7H and D17H the relative concentrations of the shared compounds are higher. The results suggest that sample D8H contains significantly more petrogenic material than the other HR tars, likely from CWG tar mixed into the HR tar. The larger number of Aliphatics present within samples D8H (100) and D17H (80) relative to samples D7H (55) and D10H (44) is mainly due to the presence of a greater number of branched n-alkanes in D8H and D17H, with 28 and 24, relative to D7H and D10H, with 12 and 6. There is also a significant difference in the number of miscellaneous Aliphatics, such as alkyl cyclopentenes and alkyl cyclopentadienes, with sample

D8H containing 29 individual compounds, with D7H containing only 4, D10H containing 5 and D17H containing 11.

The average EPA16 PAH for the horizontal retort tar is shown in figure 6.1 and shows that both horizontal retorts and low temperature horizontal retorts produce similar PAH compositions, although with a greater abundance of higher molecular weight PAHs in the HR tars and more Naphthalene being present in LTHR tars. The two most abundant EPA16 PAHs in the HR tars are Phenanthrene and Naphthalene. Sample D8H contains 9.5% Naphthalene and 14.8% Phenanthrene, whereas sample D17H contains 14.2% Naphthalene and 15.8% Phenanthrene. Sample D7H contains 17.3% Naphthalene and 12.0% Phenanthrene and sample D10H contains 20.7% Naphthalene and 14.1% Phenanthrene. This means that within half of the HR tars Phenanthrene is the most abundant EPA16 PAH (D8H and D17H) and other half have Naphthalene as the most abundant EPA16 PAH (D7H and D10H). This could be down to differences in the parent coal used to produce the tar or due to degradation of the samples, as they are all environmental samples. In terms of the absolute abundances of EPA16 PAHs sample D8H contains 114% more EPA16 PAHs than D7H, 145% more than D10H and 217% more than D17H and contains higher concentrations of every EPA16 PAH with the exception of Naphthalene in D7H and D10H. Of the EPA34 PAHs sample D7H contains 188 individual compounds; sample D8H contains 191 individual compounds; sample D10H contains only 136 individual compounds; and sample D17H contains 197 individual compounds.

The total number of PAHs and Alkyl PAHs present within the HR tars varies greatly with sample D8H containing the most individual compounds with 670. Sample D17H contains the second highest with 579 and sample D7H contains 529. Sample D10H contains the lowest number of compounds with only 334 individual compounds. Sample D8H contains both the highest concentrations of EPA16 PAHs and the greatest number of PAHs and Alkyl PAHs, whereas sample D17H contains the second highest number of compounds but the lowest concentration of EPA16 PAHs overall. Several compounds appear within the HR tars that do not appear in any other tar type. These compounds include 2 C3-Benzo[x]fluoranthene isomers ($C_{23}H_{18}$) within samples D7H and D8H and 6 and 3 C4-Benzo[x]fluoranthene ($C_{24}H_{20}$) isomers in samples D7H and D8H respectively. It also includes 8 C3-Binaphthalene ($C_{23}H_{20}$) isomers in sample D7H and 11 in sample D8H. Interestingly 4 C2-Dibenzo[a,h]anthracene (C24H18) isomers are found in D7H, but not D8H, and 2 C3-Dibenzo[a,h]anthracene (C25H20) isomers are found in D8H, but not in D7H. The presence of these high molecular weight alkyl PAHs in the HR tars, that are not present in any other tars suggests, that the high production temperature enriches the higher molecular weight compounds, as the lower molecular weight compounds will degrade more readily. This means that while the high molecular weight alkyl PAHs may be present in relatively low concentrations in the parent material they are enriched as the more easily degradable compounds are destroyed.

*Vertical Retort (VR):*

The development of later Vertical Retorts rotated the retort by 90° and allowed for the continuous production of gas. Although vertical retorts operated at similar temperatures to high temperature horizontal retorts the design of vertical retorts resulted in significantly different tars being produced. As a temperature gradient existed within a vertical retort and due to fact that the tar fog generated could also escape vertically without carbonizing on the hot surface of the retort the tar produced was uniquely separate to both LTHR and HR tars.

The aliphatic composition of the vertical retort tars varies greatly, even within the 5 samples from the same site, with sample D20V containing the most individual compound with 126. Sample D2V contains only 24 aliphatics; D3V contains 56, D4V contains 105; D5V contains 93; and D6V contains 70. Sample D20V, which comes from a different site from D2-D6V, contains the highest relative concentration and the most individual n-alkanes of the VR tars ranging between C11 and C34 with a maximum at C14. Sample D2V contains the least n-alkanes ranging between C11 and C18 with a maximum at C12, which is present in sample D20V at 616% the concentration present in D2V. Sample D3V contains n-alkanes ranging between C11 and C28 with a maximum also at C12, which is present in sample D20V at

566% the concentration present in D3V. Sample D4V contains n-alkanes ranging between C11 and C30 with a maximum also at C12, which is present in D20V at 165% the concentration present in D4V. Sample D5V contains n-alkanes ranging between C11 and C30 with a maximum at C12, which is present in sample D20V at 335% the concentration present in D5V. Sample D6V contains n-alkanes ranging between C11 and C33 with a maximum at C14, which is present in sample D20V at 872% the concentration present in D6V.

In all cases as the molecular weight of the n-alkanes increases the relative difference in the concentrations found in D20V increases relative to the other VR samples. While samples D2-D6V have different relative concentrations of n-alkanes, and different total number of compounds, the trends within the samples are similar with low molecular weight n-alkanes between C11 and C17 dominating and those alkanes above C17 being present in only relatively minor levels. This is not the case in sample D20V that has significant n-alkanes between C11 and C30 following a decreasing trend from C14 and with the n-alkanes above C31 being present at only minor concentrations. This suggests that the tars from these two sites (D2-D6V and D20V) have significantly different compositions, at least in the context of aliphatics. This also extends to the alkyl cyclohexanes as while sample D4V has the widest range (C4-C16) with a maximum at C6 sample D20V contains the highest concentrations within the shared compounds (C4-C14) with a maximum also at C6, which is present at 178% of the concentration found in D4V. The alkyl cyclohexane concentrations also vary greatly within sample D2-D6V with sample D4V containing 548% more C6 than D2V; 546% more C6 than D3V; 228% more C6 than D5V; and 423% more C6 than D6V.

Sample D20V is the only sample in the database to contain C24-C29 Alkenes and the only samples with n-alkanes ranging between C11 and C34. Sample D20V is also the only sample within the database that contains n-alkanes between C11 and C34 and samples D6V and D20V are the only samples containing the C33 n-alkanes. The relatively low concentrations of n-alkanes present within sample D2-D6V and the relatively high abundances of n-alkanes present within D20V suggest that sample

D20V may be more indicative of a “normal” VR tar as VR tars are expected to contain significant alkanes as 12% of oils that boil above the naphtha range should be present as paraffins (alkanes)[4].

The average EPA16 composition of the Vertical Retort tars is shown in figure 6.2 and shows that the VR samples have extremely varied EPA16 PAH compositions, with the greatest degree of variability in the percentage of the composition that comes from Naphthalene. Samples D2V to D6V come from the same sample site whereas sample D20V came from a completely different site and has a significantly different EPA16 PAH composition. The EPA16 PAH % composition of sample D20V is also shown in figure 6.2 and shows a signature that is dominated by Phenanthrene, which makes up 31.4% of the overall EPA16 PAH composition. The EPA16 PAH % composition of samples D2-D5V, shown in figure 6.2, is similar with Naphthalene dominating, as well as large proportions of Phenanthrene and Acenaphthylene. As a general trend as the relative proportion of Naphthalene increases from sample D2 to D5V (22.2% to 30.7%), the proportions of Phenanthrene decreases (15.8% to 12.6%) and the proportions of Acenaphthylene also decreases (16.6% to 8.9%). The EPA16 PAH % composition of sample D6V is also shown in figure 6.2 and shows a very different signature to the other samples on the site (D2-D5V) and a signature that is more similar to D20V with Phenanthrene dominating.

The significant differences between sample D6V and the other samples from the same site may suggest that sample D6V is more highly degraded than the other samples and this is further suggested by the relative concentrations of the EPA16 PAHs found within the samples. Sample D6V has the lowest concentrations of EPA16 PAHs found within the VR samples with a large bias towards lower concentrations of Naphthalene and Acenaphthylene and a much smaller difference between higher molecular weight PAHs such as Benzo[a]pyrene. This suggests that sample D6V’s EPA16 PAH compositional signature has been lost due to degradation of the sample, possibly due to volatilization. Sample D20V also contains significantly higher concentrations of EPA16 PAHs relative to samples D2-D6V with 574.1% more than D2V, 548.4% more than D3V, 437.3% more than D4V, 887.8% more than D5V and 1201.8% more than D6V. As sample D20V contains much higher concentrations of EPA16 PAHs and the fact the sample is a pure DNAPL this suggests that the EPA16 PAH composition graph for sample D20V may be more indicative of a VR tar than the other samples. It should be noted however that the statistical analysis used in McGregor et al., 2012[5] is still capable of discriminating these tars as VR tars but contains does 156 compounds within the statistical analysis rather than just the EPA16, which is often solely used alone for forensic analysis.

The total number of PAHs and Alkyl PAHs present within the VR tar samples varies greatly. Sample D4V contains the most individual PAHs of the VR tars with 604 individual compounds, and the second highest concentration of EPA16 PAHs overall. Sample D20V contains the 2nd highest number of compounds with 573 and the highest concentrations of EPA16 PAHs overall. Sample D3V contains 488 compounds; D5V contains 477; D6V contains 442; and sample D2V contains 424 individual compounds overall. Of the EPA34 PAHs sample D2V contains 142; D3V contains 154; D4V contains 188; D5V contains 151; D6V contains 156; and sample D20V contains 181. The trend of the EPA34 PAHs does not exactly follow the total number of alkyl PAHs as sample D6V contains the 3rd most EPA34 PAHs but the 2nd least total PAHs overall. The PAH compositions of the VR samples also gives an important piece of forensic information as VR tars should contain less Naphthalene (0-3% of the total tar) relative to HR (7%) and CO (5%) tars. This is the case for samples D20V and D6V but not for the VR tars D2-D5V. This could suggest that the Naphthalene present within samples D2-D5V may have come from a source other than the VR tar, which is possible due to the complex history of the site. This also suggests that while the VR tars D2-D5V may contain elements from other tar types the statistical analysis developed in McGregor et al., 2012 is still able to discriminate them as being VR tars.

*Coke Oven tars (CO):*

Coke oven tars are the only form of coal tar that is still produced within the UK with the temperature of the coke oven determining the overall composition of the tar produced. Coke ovens operating at low temperatures (<700°C) produced phenolic and PANH compounds[18] whereas coke ovens operating at high temperatures (>700°C) produced tars with high PAH content.

Both CO tar samples contain a relatively small number of aliphatic compounds with D18CO containing only 2 aliphatics and D19CO containing only 9. Sample D18CO contains the C11 and C12 n-alkane whereas D19CO contains n-alkanes between C11 and C17 as well as a single n-alkene (C10) and a single branched alkane (C14). Since the samples are both of fresh coke and therefore should not contain any petrogenic contamination any aliphatics present within the sample were either produced during the breakdown of the coal within the coke oven to produce coke or were present within the original parent material. It should be noted that sample D19CO was produced from a lower temperature coke oven than D18CO and contains relatively more aliphatics, which suggests the lower temperature may result in the production of or lessen the destruction of aliphatics within the tar produced. Sample D19CO contains 213% more of the C11 n-alkane and 342% more of the C12 n-alkane relative to D18CO, however when the whole database is considered the concentrations are minor. When the database is considered as a whole, with the exception of D16L, all other samples contains n-alkane concentrations at least an order of magnitude higher than those found in D19CO. In the case of D16L the concentrations of the C11 n-alkane are 194% greater and 170% times greater for the C12 n-alkane. The low aliphatic content is expected, as only 0.3% of the oil fraction that boils above Naphtha should be present as paraffins (alkanes) within coke oven tars[4]. The low aliphatic content is likely down to the destruction of n-alkanes during the long production process of the coke, which is significantly longer than that of manufactured gas.

Both samples contain relatively the same number of PAHs and Alkyl PAHs with

D18CO containing 359 and D19CO containing 387. The difference in the total number of PAH compounds is mostly down to D19CO containing slightly more alkyl PAHs (D18CO:D19CO) such as C3-Naphthalene (5:11) and C3-Phenanthrene/Anthracene (9:13). This trend reverses for the higher molecular weight alkyl PAHs such as C1-Benzo[x]fluoranthene (14:11) and C1-Benzo[g,h,i]perylene (11:7). Both coke oven samples contain no alkylated benzenes above C4 and no alkylated Indenes or Indanes above C2. The % composition of EPA16 PAHs is shown in figure 6.1 showing that Phenanthrene is dominant. The relative compositions of the EPA16 PAHs in the samples is similar with the exception of Acenaphthylene and Phenanthrene. Sample D18CO contains only 8.0% Acenaphthylene, whereas sample D19CO contains 14.1% and sampled D18CO contains only 17.0% Phenanthrene and D19CO contains 19.9%. The coke oven tars do generally have a unique EPA16 PAH signature relative to the other tars in the database as they have the lowest relative percentage of Naphthalene. Sample D18CO also contains 124 EPA34 PAHs and sample D19CO contains 141.

The relative concentrations of EPA16 PAHs in the sample is important from a forensics standpoint as higher temperature coke ovens are associated with having higher PAH contents[18]. This can be clearly seen in the concentrations of EPA16 PAHs as sample D18CO, the higher temperature coke oven, contains 161% more EPA16 PAHs than sample D19CO. Sample D18CO also contains higher relative concentrations of all of the EPA16 PAHs with the exception of Acenaphthylene, with sample D19CO containing 109.7% more than D18CO. The remaining EPA16 PAHs are present in higher concentrations with the smallest difference in the concentrations of Acenaphthene at 119.5% and the largest being Benzo[g,h,i]Perylene at 233.0%. When the database is taken as a whole sample D18CO contains the highest total combined concentration of the EPA16 PAHs with D19CO containing the 3rd most, slightly behind D8H with 94.6% of the total present in D8H. Sample D18CO also contains the highest absolute abundances of 2/3rds of the EPA16 PAHs with the exception of Naphthalene (D7H), Acenaphthylene (D19CO), Acenaphthene (D20V), Indeno[123-c,d]pyrene (D8H), Benzo[g,h,i]Perylene (D8H) and Dibenzo[a,h]anthracene (D8H). In general this suggests that coke oven tars have a greater degree of parent PAHs relative to coal tars produced from gasification.

*Carbureted Water Gas (CWG):*

The Carbureted Water Gas process was an adaptation of the water gas process, were steam was passed over a hot carbon source (usually coke), with a spray of oil introduced to the hot gas produced in order to improve it's calorific value[19]. Since the water gas process did not generate significant amounts of tar[18] than the tar produced by the CWG process is dominated by the feedstock oil used, with a degree of temperature dependent alteration as the process operated between 650°C and 700°C[18].

The aliphatic compositions of the two CWG tars are significantly different with sample D14C containing 128 aliphatic compounds and D13C containing only 85. There is also a significant difference in the relative concentrations of the compounds that the samples share. Sample D14C contains n-alkanes between C11 and C29, whereas sample D13C contains n-alkanes between C11 and C24. The maximum n-alkane in D13C is C14 and the maximum in D14C is C15. While the concentrations are very different with D14C containing 803% more of the C14 n-alkane than D13C and 811% more of the C15 n-alkane the overall distributions of n-alkanes are similar with low molecular weight n-alkanes between C11 and C19 being dominant. Alkyl cyclohexanes are commonly associated with petrogenic contamination[14] and are present within both of the CWG samples with D14C containing between C4 and C14 and D13C containing between C4 and C12. As with the n-alkanes the relative concentrations of the compounds are significantly higher in sample D14C over D13C. For example the maximum alkyl cyclohexane in D13C is C5 but is present at 401% higher concentrations in D14C. While the relative concentrations of the compounds are very different the overall distributions of the alkyl cyclohexanes in the samples are again similar. This suggests that both CWG plants produced tars with very similar aliphatic distributions.

Both CWG tars contain a large amount of organic compounds with 1150 detected in D13C and 1440 detected within D14C. The sample of D13C was obtained from a groundwater contamination plume and had likely spent a significant amount of time in the environment. The sample itself appears to be pure DNAPL although the water content within the sample is unknown. D14C was taken from a former gasholder that was used as a tar emulsion storage tank. This sample also appears to be pure DNAPL although the water content is again unknown. As D14C was taken from within a storage tank rather than a groundwater plume it would be expected that it has lost less of its original more water-soluble fraction, as the sample would have equilibrated with any water present within the tank. It is more likely that D13C has lost at least some of its soluble components to groundwater flow it is also likely that the sample has a higher water content than D14C.

Both samples contain vastly different concentrations of the EPA16 PAHs with D14C containing 448% more EPA16 PAHs overall compared to D13C. The relative concentrations of all EPA16 PAHs are significantly higher in D14C relative to D13C with for example 294% more Naphthalene, 499% more Phenanthrene and 738% more Pyrene. This significant difference in concentrations is likely down to the nature of the samples themselves. Sample D13C was taken from a groundwater contamination plume, whereas sample D14C is in the form of pure DNAPL taken from a tar storage tank. The % composition of the CWG EPA16 PAHs is shown in figure 6.1 and shows that the two tars have similar relative amounts of two thirds of the EPA16 PAHs with the exception of Naphthalene, Acenaphthene, Phenanthrene, Fluoranthene, Pyrene and Indeno[123-c,d]pyrene. The % composition of Naphthalene in D13C is 27.7% but only 18.1% in D14C and the % composition of Acenaphthene in D13C is 4.7% and is 2.1% in D14C. The % composition of Phenanthrene in D14C is 20.4% and 18.3% in D13C; of Fluoranthene in D14C is 5.9% and 3.5% in D13C; of Pyrene in D14C is 7.1% and 4.3% in D13C; and of Indeno[123-c,d]pyrene in D14C is 4.9% and 2.8% in D13C. This means that in terms of composition D13C contains relatively more Naphthalene and Acenaphthene, whereas D4V contains relatively more Phenanthrene, Fluoranthene, Pyrene and Indeno[123-c,d]pyrene. One important thing to note is that Naphthalene is the most water soluble of the EPA16 PAHs so it is possible that the original tar that D13C came from has even higher relative amount of Naphthalene.

The total number of PAHs and Alkyl PAHs present in sample D13C is 657 and sample D14C is 729. This means that sample D14C contains the most individual PAHs of any sample in the database with sample D13C containing the 3rd most, slightly behind sample D8H that contains 671. Sample D8H contains the most alkyl PAHs of the non-CWG tars and also the highest relative concentrations, although this does not apply to every compound. All 3 samples contain Alkyl Benzenes between C3 and C8; alkyl Naphthalenes between C1 and C5; alkyl Fluorenes between C1 and C3; Alkyl Phenanthrene/Anthracenes between C1 and 4; Alkyl Fluoranthenes/Pyrenes between C1 and C3; Alkyl Chrysenes between C1 and C4; Alkyl Benzo[x]Fluoranthene isomers between C1 and C2; and C1 Dibenzo[a,h]anthracenes of which the samples share 211 individual compounds. Sample D14C also contains 37 unique compounds within the same range not detected in D13C or D8H. Sample D13C contains 36 unique compounds within the same range not detected in D14C or D8H. Sample D8H also contains 36 unique compound within the same range not found in D13C or D14C. Of the 211 compounds shared by the 3 samples both D14C and D8H contain higher relative concentrations of every individual compound relative to D13C, which is likely down to the fact the sample is contaminated groundwater rather than pure DNAPL. Sample D14C contains 130 compounds at higher relative concentrations than D8H, with D8H containing 81 compounds at higher relative concentrations to D14C. This means that overall sample D14C contains the highest relative concentrations of alkyl PAHs within the database, which is to be expected as the sample CWG process operates using oil and alkyl PAHs are more abundant in oil relative to coal[9]. Sample D14C also contains the highest number of EPA34 PAHs with 204, whereas sample D13C contains 198.

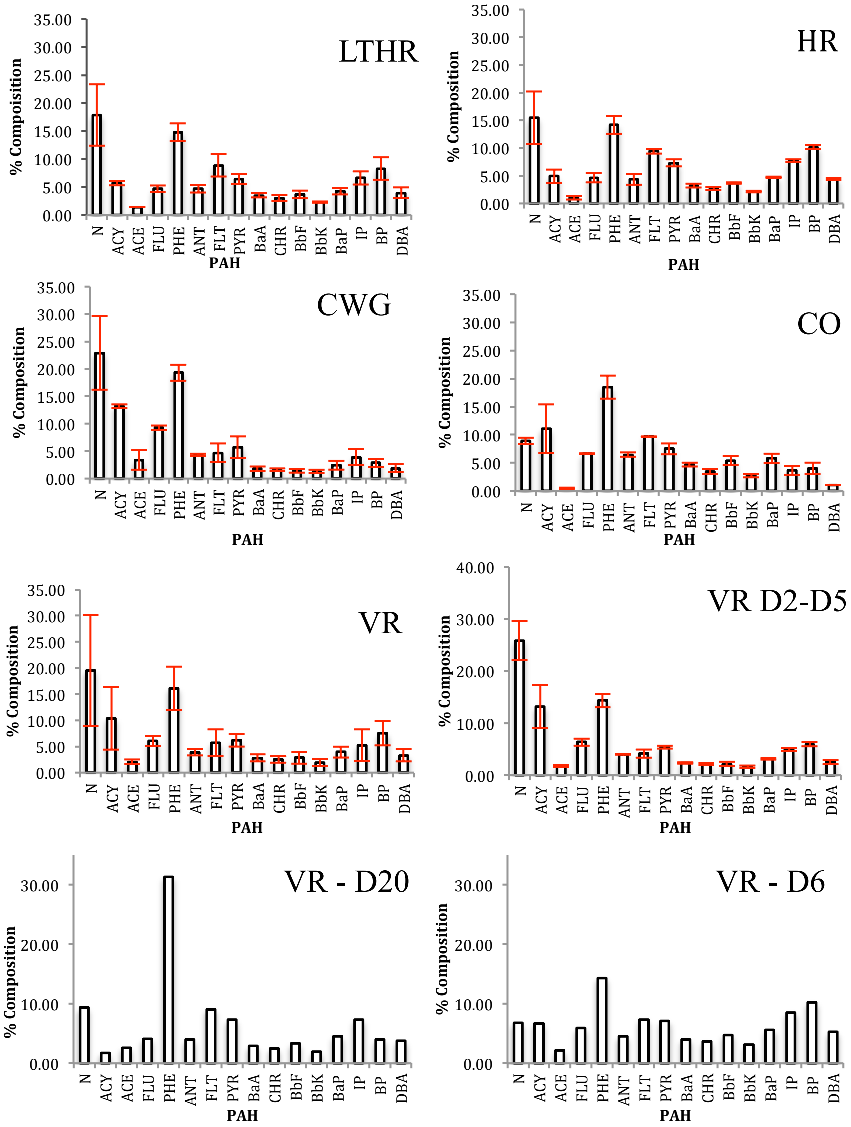

Figure 6.2 – Average EPA16 PAH compositions for Low Temperature Horizontal Retort, Horizontal Retorts, Vertical Retorts, Carburetted Water Gas and Coke Oven tars with standard deviation error bars.

## Conclusion

Different coal tar production processes produce tars with distinctly different aromatic and aliphatic compositions. The analytical method was capable of detecting 951 individual aromatic and 198 individual aliphatic compounds providing important forensic information about the samples. This is reinforced by the detection of alkyl cyclohexanes, an indicator of petrogenic material, within tars that were not produced using petroleum. Alkyl cyclohexanes were detected within all samples from sites that contained a CWG plant and not detected in those that didn't. This suggests that great care should be taken when using alkyl cyclohexanes as markers for distinguishing coal tar from petrogenic sources of contamination. It may also suggest that that the detection of alkyl cyclohexanes at former manufactured gas sites may suggest the presence of a CWG plant on site. The alkyl cyclohexane data can be combined with the PCA, and HCA, statistics in order to infer important forensic information about the sample. The average EPA PAH composition graphs are also of great forensics importance as they can be used to infer what production process produced the tar. The data is of particular importance as 5 different distinct production processes are represented, whereas most published literature contains only one process that is often not defined. Even in cases were the production process is defined it is often defined as either a CWG tar or a coal gas tar without reporting the retort type that was used. The use of GCxGC-TOFMS allows for the detection of a large number of compounds with tars that would otherwise be missed.

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## 6.4 Comprehensive database of Manufactured Gas Plant tars – Part C Heterocyclic and hydroxylated PAHs

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### Abstract

**RATIONALE**

Coal tars are a mixture of both organic and inorganic compounds and were produced as a by-product of the manufactured gas process, as well as in the production of coke. The product tar compositions varied depending on many factors such as the temperature of production and the type of retort used. For this reason a comprehensive database of the compounds found within different tar types is required. This study focuses on the heterocyclic and hydroxylated compounds present within a database produced from 16 different tars from 5 different production processes.

**METHODS**

Samples of coal tar were extracted using accelerated solvent extraction (ASE) and derivatized post extraction using BSTFA with 1% TMCS. The derivatized samples were analysed using two-dimensional gas chromatography combined with time-of-light mass spectrometry (GCxGC-TOFMS).

**RESULTS**

A total of 865 Heterocyclic compounds and 359 hydroxylated PAHs were detected within 16 tar samples produced by 5 different production process. Both the heterocyclic and hydroxylated PAH content varied greatly with the production process used with the heterocyclic compounds giving information about the feedstock used. Of the 359 hydroxylated PAHs detected the majority would not be detected without the use of derivatization.

**CONCLUSIONS**
Coal tars produced using different production processes and feedstocks produced tars with significantly different heterocyclic and hydroxylated contents. The concentrations of the individual heterocyclic compounds varied greatly even within the different production processes and provided information about the feedstock used to produce the tars. The hydroxylated PAH content of the samples provided important forensic information that would otherwise not be obtained without the use of derivatization and GCxGC-TOFMS.

**Keywords:** GCxGC-TOFMS, Coal Tar, Environmental Forensics, Derivatization

## Introduction

Coal tar is a complex mix of inorganic and organic compounds produced primarily by the former manufactured gas industry and heterocyclic compounds are a major group of compounds of interest present within coal tars. A heterocyclic compound is a compound that has at least two different elements as members of its ringed structure. Of particular interest in samples of coal tar, or coal tar contaminated soils, are those containing Oxygen, Sulphur and Nitrogen. The composition of Sulphur (PASH), Oxygen (PAOH) and Nitrogen-PAHs (PANH) in tar largely reflects those present in the parent coal[1], with some temperature-dependent alteration[2]. This makes heterocyclic compounds potential compounds of forensic interest.

Sulphur containing compounds make up an important group of compounds present within coal tars with heterocyclic Sulphur compounds dominating. The Sulphur content within coal is present either as inorganic compounds, such as pyrite and sulphides or organic Sulphur compounds, such as Poly Aromatic Sulphur Hydrocarbons (PASHs). The organic Sulphur content (OSC) of coal is determined by the original organic matter that formed the coal deposits and takes the form of aliphatic and aromatic thiols, sulphides, disulphides and heterocyclic combinations of thiophenes and dibenzothiophenes[3]. PASHs exist in an even greater variety of structures compared to PAHs due to the presence of sulphur within the ring structure, therefore the number of isomers and alkylated isomers can be extremely high making quantification and identification of individual PASHs isomers difficult[4]. The occurrence of PASHs (also known as thiaarenes) in environmental samples and fossil fuels as well as their mutagenic and carcinogenic potential has been reported.

Nitrogen is present in all fossil fuels and is associated almost exclusively with the organic portion of the crude material[5]. It usually makes up around 0.5% of crude petroleum but is found in higher concentrations (1-2%) in shale oils and coal[5]. The toxicity of nitrogen aromatic compounds greatly depends on the structure and number of fused rings. Several studies have found that nitrogen-containing substituents, such as nitro- and amino- functional groups can enhance toxicity by up to 100-fold. This means that although the nitrogen content of the parent coal may be low the possible health effects from nitrogen containing polycyclic aromatic compounds (PANH) cannot be ignored. While in general PANH compounds are present in lower concentrations than their non-substituted PAH-analogues their higher water solubility leads to a higher bioavailability and potential toxic effects within the environment[7].

The mechanisms affecting the structures of nitrogen containing compounds during pyrolysis is poorly understood. Nitrogen containing compounds are devolatilized from coals during primary pyrolysis and will be contained within the coal tar. During secondary pyrolysis nitrogen content in coal tars can also undergo secondary reactions including: conversion of tar into soot, expulsion of non-condensable gases (such as HCN) and structural rearrangements among the condensable organic products[6]. During the condensed phase benzene and naphthalene are more stable than their corresponding heterocyclic PANH's (Pyridine and quinolone), while in the vapour phase PANHs appear to be slightly more stable[8]. PANHs are highly stable relative to neutral PAH's and can persist through severe thermal conditions and so are possible compounds of toxicological interest[6].

Oxygen containing compounds are also present within coal tar in the form heterocyclic oxygen containing compounds and non-heterocyclic oxygen containing compounds such as aromatic ketones. Oxygen containing compounds can be toxic, mutagenic and carcinogenic and are more mobile within the environment than their parent PAHs due to their increases solubility in water. This makes them of special concern in ground water as they can leach out for coal tar plumes and contaminate drinking water. Benzofuran and Dibenzofuran are two important oxygen containing PAHs that are derived from coal tar and are important biomarkers for coal tar contamination.

Hydroxylated PAHs, sometimes referred to as tar acids, are another major group of oxygen containing compounds found within coal tars with the alkyl phenols dominating[9]. The tar acids composition of Vertical Retort tars varied greatly from other tars with VR tars containing 6-7 times more tar acids than Coke oven tars and 3-4 times more tar acids than Horizontal Retort tars[10]. The compounds present within the tar acid fraction are also very different with HR and CO tars containing significantly more Phenol and Cresols than VR tars, with phenol making up 25% of HR tar acids and 18% of CO tar acids[10]. VR tars acids on the other hand contain only 6% Phenol, with Cresols only making up a small proportion, with high boiling tar acids dominating[10]. A database of the heterocyclic and hydroxylated PAH content of coal tar samples from different production processes has never previously been published.

This study presents the in depth analysis of the heterocyclic and hydroxylated content of 16 tar samples produced by 5 different production processes. A full database of the compounds found within the samples has been published in Gallacher et al., 2016a[11] and an in depth analysis of the aliphatic and aromatic content can be found in Gallacher et al., 2016b[12].

**Materials and Methods**

**Samples: See part A**

A total of 16 tars samples, coming from 5 different tar production processes, were extracted and analysed. The different processes and sample numbers are listed below:

Low Temperature Horizontal Retort: DNAPL009 (D9L) and DNAPL016 (D16L)
Vertical Retort: DNAPL002-006 (D2-D6V) and DNAPL020 (D20V)
Horizontal Retort: DNAPL007 (D7H), DNAPL008 (D8H), DNAPL010 (D10H) and DNAPL017 (D17H)
Carbureted Water Gas: DNAPL013 (D13C) and DNAPL014 (D14C)
Coke Oven: DNAPL018 (D18CO) and DNAPL019 (D19CO)

**Methods:**

All solvents used were of analytical grade purchased from Fisher Scientific (Loughborough, U.K.) and D10H-phenanthrene, which was used as an injection standard, was purchased from Sigma-Aldrich (Gillingham, U.K.). BSTFA with 1% TMCS was purchased from Sigma-Aldrich (Gillingham, U.K.). D10H-phenanthrene, D8H-Naphthalene, D10H-Fluorene, D10H-Fluoranthene and D10H-Pyrene, which were used as recovery standards, were purchased from Sigma-Aldrich (Gillingham, U.K.)

Extraction was performed using an Accelerated Solvent Extraction system (ASE 350 Dionex, Camberley, UK) using 10 mL stainless steel extraction cells. Approximately 0.5g of tar was mixed with an equal amount of diatomaceous earth ($NaSO_4$) in a 1:1 ratio. Prior to extraction the samples were spiked a recovery standard. Extraction cells were lined with 2 Dionex glass fibre filter papers and packed with 3g of silica gel 60 deactivated with 10% water. The sample mixture was then loaded into the cells and any residue was recovered with excess diatomaceous earth. Dichloromethane was used as the extracting solvent for all extractions. ASE was performed at 100$^{o}$C and 10 MPa, using one dynamic (7 min) and two static (5 min each) extractions. A flush volume of 150% and purge time of 60 s was used. The extracts were concentrated to 1 mL using a Büchi Syncore Analyst (Oldham, U.K).

The extracts were then made up to exactly 10 mL using *n*-hexane. A 1 mL aliquot was then transferred to an auto sampler vial prior to analysis and spiked with D10H-Phenanthrene. All samples were derivatized using 100ul of BSTFA with 1% TMCS placed in an oven at 70$^{o}$C for 1 hour.

GCxGC TOFMS analysis was performed using a Leco Pegasus 4D (St. Joseph, Michigan) time of flight mass spectrometer, connected to an Agilent 7890A gas chromatograph equipped with a LECO thermal modulator. The TOF ion source temperature was 200 °C and the mass range 45 and 500u was scanned at a rate of 200 spectra/second. The detector voltage was set at 1700 V with a electron ionisation voltage of 70 eV.

All standards and extracts were analysed with the following primary oven temperature programme: 60°C isotherm for 2 minute, then ramp at 10°C/min to 110°C, then ramp at 3°C/min to 310 °C, and isothermal at 310°C for 15 minutes. The secondary oven and modulator temperatures were programmed at a 10 °C offset relative to the primary oven. The modulation period was 6 seconds with a 1.3 second hot pulse time and a cool time of 1.7 seconds. The injection port temperature was set to 250 °C and set to split injection with a split ratio of 50 and an injection volume of 1µl. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min.

The reversed polarity column set that was used comprised of a mid-polarity TR-50 MS supplied by Thermo Scientific (30 m × 0.25 mm i.d. × 0.25 µm film thickness) as the primary column and a non-polar Rtx-5SilMS supplied by Thames Restek (1.5 m × 0.25 mm i.d. m × 0.25 µm film thickness) as the secondary column, connected via a Thames Restek Press-tight connector.

The chromatograms from each sample were processed using Leco ChromaTOF software (Version 4.50.8.0) to search for, identify and align all peaks with a signal-to-noise ratio greater than 10. As it would be impractical to purchase standards of every compound present within the samples any concentration comparisons are relative comparisons of the peak area for each compound adjusted for sample weight and recovery. Only direct like for like compound comparison will be done as the detector response will remain equivalent.

### Results and Discussions

*Low Temperature Horizontal Retort (LTHR):*

The total number of hydroxylated PAHs present in the LTHR tar samples varies greatly with D9L containing 203 and D16L containing only 60 individual compounds. The relative concentration of the compounds varies greatly with D16L containing 196% more Phenol than D9L. D9L however contains 217% more o-Cresol, 136% more m-Cresol and 168% more p-Cresol. With increasing molecular weight the difference in relative concentrations increases greatly with D9L containing 2821% more Naphthalen-2-ol, 7388% more of the only C1-Naphthalenol found in both samples and 2509% more 4-hydroxyfluorene. Phenol is the only hydroxylated PAH present in a higher concentration in D16L compared to D9L. When the database is considered as a whole, D9L is the only sample that contains detectable Hydroxychrysene and C1-Hydroxychrysene. C2-Hydroxyflourene is also found in D9L and was only detected in sample D9L and D20V and no other samples.

The heterocylic composition of both samples varies greatly in both the number of compounds and concentrations. D9L contains a greater number of all of the heterocyclic types with 194 PANHs, 146 PAOHs and 233 PASHs. D16L contains far fewer heterocyclic compounds with only 88 PANHs, 103 PAOHs and 78 PASHs. While D16L contains less individual PANHs than D9L the relative concentrations of the majority of shared compounds are higher in D16L than D9L. For example D16L contains 436% more Benzonitrile, 254% more Quinoline, 214% more 1-Naphthalenecarbonitrile and 111% more Carbazole. This suggests that the nitrogen content of the coal used to produce sample D16L contained significantly higher nitrogen content. D9L however contains many different types of compounds that are not found in D16L such as Indole, C1-Indole and C2-Indole. D2V is the only other sample in the database that does not contain Indole or at least one Alkyl Indole compound. D9L is the only sample outside of the HR tars that contains Pyridine and Methyl Pyridine, which was not detected in any CWG, VR or CO tar samples.

While D9L does contain Pyridine it is in minor concentrations relative to the other tars that also contain it with sample D7H containing 5312% more than D9L and sample D10H containing 12650% more. The PAOH content of the LTHR tars follows the same trend as the PANHs in terms of the number of compounds with D9L containing more PAOHs, than D16L. However, unlike the PANHs, in almost all cases the relative concentrations of PAOHs detected in D9L are higher with for example 578% times more Benzofuran and 352% times more C1-Benzofuran.

The PASH composition of the samples follows the same trend as the PAOHs, with sample D9L containing both the highest relative concentrations and the largest number of individual compounds. Sample D9L contains higher concentrations of every compound that the samples share with for example, 1126% more Benzo[b]thiophene and 1170% more Dibenzothiophene. This again suggests that the coal used to produce sample D9L was significantly different to that used to produce sample D16L. Since sample D9L contains 535% more EPA 16 PAHs[12] than sample D16L this suggests the parent coal used to produce D16L contained significantly more Nitrogen than that which produced D9L. This is due to the fact sample D16L contains higher concentrations of PANHs relative to D9L, despite the fact it likely contains far less tar. The opposite is true of sulphur compounds with significantly higher concentrations found in D9L relative to D16L suggesting the coal used to produce D9L had a higher sulphur content. The difference in PAOHs present within the sample suggests that the coals likely had similar oxygen contents. While the locations of the sites are confidential it should be noted that they would not have received coal from the same coalfields and so the type of coal used may have differed.

*Horizontal Retort (HR):*

Later horizontal retorts allowed for higher operational temperatures capable of exceeding 1000°C[13] and so greater decomposition of the organic compounds within the tar. The large surface area present within horizontal retorts allowed for a greater opportunity for contact of the gases with the heated retort sides and so allow for a greater degree of thermal cracking[14].

The overall number of hydroxylated PAHs in each sample is fairly consistent with D7H containing 132, D8H containing 152, D10H containing 120 and D17H containing 108 individual compounds. The only two samples with more hydroxylated PAHs than the HR tars are D20V and D9L and of all the sample types HR tars have the most consistently high number of hydroxylated PAHs. While sample D8H contains the most individual hydroxylated PAHs it does not contain the highest relative concentrations of the hydroxylated PAHs shared by the HR tars. Sample D7H contains the 2nd most individual hydroxylated PAHs of the HR tars and generally the highest concentrations. For example sample D7H contains 599% more Phenol than D8H, 188% more than D10H and 551% more than D17H. It also contains 330% more o-Creosol than D8H, 115% more than D10H and 470% more than D17H. Sample D17H contains the least hydroxylated PAHs overall and generally contains the lowest concentrations of the shared compounds. One important point of note is that the water solubility's of the phenolic compounds decreases with increasing molecular weight therefore in samples such as D8H and D10H, which are both waterlogged DNAPL, the original tar may have contained more Phenol and Cresol, as these are the most water soluble phenolics.

High phenolic content is a major characteristic of low temperature coal tars (650°C) and medium temperature coal tars (800°C)[15]. While this is the case for the LTHR tars, which are produced at temperatures around 600°C, it also applies to the HR tars which were produced at temperatures in excess of 1000°C suggesting that high phenolic content is not entirely temperature dependent and retort type plays a role. The high amount of oxygen and water vapour available within the horizontal retort may explain the presence of abundant phenolics[16]. It should also be noted the production process used to produce the middle temperature coal tar analysed by Shi et al., 2012[15], the Lurgi process, is significantly different to any of the production processes used to produce any of the samples within the database. The high pressure used in the Lurgi process would likely affect the overall composition of the tar produced.

The heterocyclic compositions of the HR tars varies greatly with the greatest number of compounds found in D8H which contains 594 compounds including 187 PANHs, 133 PAOHs, 263 PASHs and 12 mixed Heterocycles. Sample D7H contains 570 compounds including 200 PANHs, 153 PAOHs and 211 PASHs and 6 mixed heterocycles and sample D17H contains 539 compounds including 181 PANHs, 134 PAOHs, 213 PASHs and 11 mixed heterocycles. Sample D10H contains the least number of Heterocycles, as well as the least number of compounds overall, with 374 compounds including 141 PANHs, 80 PAOHs, 143 PASHs and 10 mixed Heterocycles. As previously mentioned samples D7H, D10H and D9L are the only samples to contain pyridine and methyl pyridine. They are also the only samples that contain Aniline, Pyridine and Methyl Pyridine as while the coke oven tars (D18CO and D19CO) both contain aniline they do not contain Pyridine or Methyl Pyridine. Sample D8H also contains methyl pyridine and Aniline but lacks pyridine itself. Sample D10H contains the most Pyridine with 238% more than D7H and also contains the most aniline with 174% more aniline than D7H and 928% more aniline than D8H. The coke oven tars D18CO and D19CO also contain aniline and contain relatively more aniline than D8H but less than both D7H and D10H.

Sample D17H contains the lowest relative concentrations of the PANHs shared by the HR tars with few exceptions. Sample D7H contains both the largest number of individual PANHs as well as the highest relative concentrations of the PANHs shared by the sample, although this is not the case for every compound. For example sample D7H contains 115% more Indole than D8H and 113% more Indole than D10H and 136% more Quinoline than D8H and 130% more Quinoline than D10H. This trend is not observed for Carbazole with sample D7H containing 123% more Carbazole than D10H and D8H contains 113% more Carbazole than D7H. As a general rule sample D17H contains significantly lower concentrations of PANHs relative to the other 3 HR tars, whereas the remaining 3 HR tars have similar concentrations with a degree of variability in the concentration and number of PANHs.

The PAOH composition of the samples varies greatly and as with the PANHs sample D17H contains the lowest relative concentrations of the PAOHs that the HR tar samples share. Unlike the PANHs sample D8H contains the highest concentrations of PAOHs, but not the largest number of individual compounds. For example sample D8H contains 174% more Benzofuran than D7H and 139% more than D10H. This trend is reversed for Dibenzofuran with 125% more than D7H and 175% more than D10H. As a general trend sample D7H contains higher concentrations of PAOHs than D10H. This means the order of concentration goes from D8H to D7H to D10H and finally D17H. The concentrations of PAOHs within the HR samples follows the same concentration trend as the EPA16 PAHs[12] with sample D8H containing the highest concentrations and D17H the lowest. This is not the case for the PANHs as sample D8H contains the highest concentrations of PANHs but this is not the case for the EPA16 PAHs. This suggests that the oxygen content of the coals used to produce the HR tars were similar with the Nitrogen content varying to a greater degree.

One compound of note is 9H-Fluoren-9-one, which is present in high concentrations in sample D17H with 1052% more than D7H, 1468% more than D8H and is entirely absent in D10H. This high concentration is completely at odds with the EPA16 PAH concentrations for the HR tars and this could be down to the source of the compound. Sample D17H also contains 1560% more 9,10-Anthracenedione than D7H, 1856% more than D8H and with 9,10-Anthracenedione being completely absent from D10H. Finally sample D17H contains 4H-Cyclopenta[def]phenathren-4-one which is not detected within any of the other HR tars. These compounds are of particular interest as Fluorenone can be produced from the metabolism of Fluorene[17] and Fluoranthene[18]. Increased concentrations of Fluorenone and 4H-Cyclopenta[def]phenathren-4-one have been reported during the degradation of creosote, a coal tar distillate, contaminated soils[19] as well as increasing concentrations of Fluorenone and 9,10-Anthracendione during the degradation of coal tar oil (Steinhart, 1997). This could suggest that sample D17H may have undergone significant microbial degradation relative to the other HR tars and could provide evidence for microbial activity within tar DNAPL.

When the database is considered as a whole sample D17H contains the highest relative concentrations of 4H-Cyclopenta[def]phenathren-4-one and 9,10-Anthracenedione but not 9H-Fluoren-9-one, with D17H being the second highest. Sample D16L contains the highest concentrations of 9H-Fluoren-9-one in the database while containing the 2nd lowest concentration of EPA16 PAHs[12]. This is likely down to the nature of the sample as sample D16L is a tarry soil and so microbial breakdown of the tar is more likely to occur than in a pure DNAPL. Sample D20V contains the second highest concentrations of 4H-Cyclopenta[def]phenathren-4-one, at 51% of the concentration found in D17H, and 9,10-Anthracenedione, at 29% the concentration found in D17H. Sample D20V also contains the 3rd most 9H-Fluoren-9-one, at 35% the concentration found in D16L. Of all the samples in the database D16L, D17H and D20V contain the most 4H-Cyclopenta[def]phenathren-4-one, 9,10-Anthracenedione and 9H-Fluoren-9-one within the database. Both D17H and D20V are in the form of pure DNAPL, with D17H being taken from inside a tar tank, which suggests that bacterial metabolism may be occurring within the DNAPL.

The PASHs content of the samples varies greatly with both the largest number, 263, and highest concentrations found in sample D8H. Sample D8H also contains the second largest number of PASH compounds in the database with only D14C containing more PASHs, with 280. For example, sample D8H contains 222% more Benzo[b]thiophene than D7H, 162% more than D10H and 512% more than D17H. Sample D17H contains the smallest number of individual PASHs of the HR tars and as with the PANHs and PAOHs the lowest relative concentrations. Samples D7H and D10H contain similar numbers of PASHs with sample D10H containing 137% more Benzo[b]thiophene than D7H and 227% more Benzenethiol. This trend reverses as the molecular weight increases with sample D7H containing 109% more Dibenzothiophene than D10H; 157% more Naphtho[1,2-b]thiophene; 156% more Naphtho[2,1-b]thiophene; and 168% more Naphtho[1,2-c]thiophene/Naphtho[2,3-c]thiophene. This suggests that the original parent coal that produced D7H contains more high molecular weight PASHs, whereas D10H contained more lower molecular weight PASHs. Sample D8H may have been produced from a feedstock coal with a significantly higher Sulphur content than the other HR tars. Sample D17H may contain relatively less tar than the other samples or the Sulphur content of the feedstock coal may have been significantly lower.

*Vertical Retort Tars (VR):*

Vertical retort tars are those that were produced from vertical retorts, which were an advancement on horizontal retorts that rotated the retort by 90° allowing for the continuous generation of gas. While vertical retorts operated at high temperatures similar to horizontal retorts their unique design led to significantly different tars being produced. Vertical retort tars should contain 6-7 times as much tar acids as coke oven tars and 3-4 times as much as Horizontal retort tars[10]. While the overall phenolic content of VR tars is high the phenol content in VR tars is low making up only 6%, with small amounts of Cresol, whereas phenol accounts for 25% of the tar acid content of HR tars and 18% of the phenolic content for CO tars[10].

The total number of hydroxylated PAHs in the VR tars varies greatly with sample D2V containing 2; D3V containing 1; D4V containing 75; D5V containing 21; D6V containing 31; and D20V containing 231. Sample D20V contains the most hydroxylated PAHs within any sample within the database but is also the only sample in the database in which Phenol was not detected. It does however contain 133 alkylated phenols between C1 and C8, although it only contains the o- and p-Cresol isomers and no m- isomer. Sample D4V contains the 2nd most hydroxylated PAHs in the VR tars and contains 4399% more o-Cresol, 934% more p-Cresol, 142% more Ethyl Phenol and 253% more of a C2-Phenol isomer than sample D20V, however for every other compound the samples share the concentrations are significantly higher in sample D20V. It should also be noted that when the database is taken as a whole the concentrations of Phenol and the 3 Cresol isomers in sample D4V are small with sample D17H, the HR tar with the lowest abundance of Phenol and the 3 Cresol isomers, containing 6185% more Phenol, 2267% more o-Cresol, 1970% more m-Cresol and 7763% more p-Cresol than D4V. D20V is also the only VR sample containing C1-Anthrol (which was only found in D20V, D7H and D8H).

D20V is also the only sample in the database containing C3-Hydroxyfluorene and C3-Hydroxybenzothiophene. The wide range of the number of detivitisable compounds in D2-D6V is also interesting as all samples come for the same site and the difference in compositions may further reinforce the complex site history the samples came from.

A main characteristic of VR tars is the presence of a large abundance of high boiling, those above C2-Phenol[20], phenolic compounds[1] and this is clearly seen in D20V with the sample containing 124 phenolic compounds within this range. Of the 124 phenolic compounds present within D20V that boil above C2-Phenol 41 are unique to sample D20V. While D20V contains a large number of individual high boiling phenols it does not contain the highest concentrations of C3-Phenol or C3-Phenol 1DB. However for the alkylated phenols in the C4 range and higher the relative concentrations present with sample D20V are higher than all other samples in the database with the exception of D9L. Sample D9L shares 74 alkylated Phenols with sample D20V of which only 13 are present in higher concentrations in sample D20V. This suggests that while a large abundance of high boiling phenolic content is indicative of a VR tar[1] it also applies to LTHR tars. While the literature does state that VR tars should have a higher tar acid content than HR tars[10] this is likely referring to HR tars and not LTHR tars, as these would have been long phased out by the 1950's. When the high boiling phenolic content is compared to the HR tars higher concentrations of the majority of the high boiling phenolics are present in D20V, as the literature suggests should be the case.

The overall heterocyclic composition of the VR tars varies greatly with sample D20V containing significantly more heterocyclic compounds than the other VR tars with 498 individual heterocycles detected including 220 PASHs, 135 PANHs, 132 PAOHs and 11 mixed heterocycles. Sample D2-D6V come from the same sample site with sample D2V containing 200 individual heterocyclic compounds with 151 PASHs, 17 PANHs, 31 PAOHs and 1 mixed heterocycle. Sample D3V contains 262 individual heterocyclic compounds with 181 PASHs, 21 PANHs, 59 PAOHs and 1 mixed heterocycle. Sample D4V contains 404 individual heterocyclic compounds with 205 PASHs, 94 PANHs, 103 PAOHs and 2 mixed heterocycle. Sample D5V contains 292 individual heterocyclic compounds with 157 PASHs, 60 PANHs, 73 PAOHs and 2 mixed heterocycles. Sample D6V contains 290 individual heterocyclic compounds with 139 PASHs, 67 PANHs, 82 PAOHs and 2 mixed heterocycles.

Sample D20V contains the most PANHs within the VR tars with 135 as well as the highest relative concentrations overall. Sample D4V contains the most PANHs of the VR tars from the same site (D2-D6V) with on average concentrations an order of magnitude larger than D2V and D3V and significantly higher concentrations than D5V and D6V. Sample D20V however contains an order of magnitude larger concentrations, on average, than sample D4V. For example sample D20V contains 1055% more Carbazole than D4V; 2422% more than D5V; 2585% more than D6V; 9851% more than D2V; and 10237% more than D6V. One major exception to this trend is Indole which was only detected within VR tars D4V and D20V with sample D4V containing 731% more Indole than D20V. However, when the database is considered as a whole the concentrations of Indole in D4V are minor with similar concentrations to D9L but significantly lower concentrations than both the HR tars and CO tars. This suggests that Indole is not found within VR tars, or LTHR tars, in significant concentrations with the higher concentrations of Indole within D4V possibly coming from a source other than the VR tar, as it is only detected within 1 sample from the same site. When the database is considered as a whole the concentrations of Carbazole present within D20V are higher than LTHR tars and CWG tars but significantly lower than HR tars and CO tars. This trend applies to other PANH compounds such as 1-Napthalenecarbonitrile, Benzo[h]quinolone, Benzo[def]carbazole, Benzo[c]carbazole, Dibenzo(a,g)carbazole and Naphtho[2,3-b]carbazole.

The PAOH composition of the VR tars follows a similar trend to the PANHs with the highest concentrations and total number of compounds found in sample D20V, followed by D4V. While the concentrations, and total number, of PAOHs within sample D4V are relatively higher compared to the other samples from the same site

(D2V-D6V) they are, on average, at least an order of magnitude lower than those present within sample D20V. For example, sample D20V contains 208% more Benzofuran than D4V; 390% more than D5V; 7601% more than D6V; 8000% more than D3V; and 10116% more than D2V. It also contains 1392% more Dibenzofuran than D4V; 3110% more than D5V; 3992% more than D6V; 6383% more than D3V; and 6902% more than D2V. When the database is considered as a whole sample D20V contains relatively low concentrations of Benzofuran and C1-Benzofuran but relatively high concentrations of Dibenzofuran and Benzo[b]naphtho[2,3-d]furan, similar to those founds in the HR tars.

Acetophenone was detected within D2V but was not detected within other VR tars, and was also detected in all the HR tars and CWG tars but neither the CO tars or LTHR tars. The relative concentrations of Acetophenone are higher in sample D2V relative to D7H (140%) and D18CO (299%) but lower relative to D8H (54%), D10H (38%), D13C (79%) and D14C (34%). The concentration of Acetophenone present within sample D2V is high when the database is considered as a whole as the tar content of D2V is likely to be very low due to the nature of the sample. As Acetophenone was not detected in any of the other samples within the same site this suggests that it may come from another source other than the VR tar that makes up the bulk of the sample.

The total number of PASHs present within the VR tars is relatively high with sample D20V containing the most with 220 and sample D2V containing the least, of the VR tars, with 151 individual PASHs. Of the 220 PASHs present within VR 50 are not found in any other VR tars. Of the 170 remaining compounds 125 individual PASHs are present within sample D20V at higher concentrations than any of the other VR tars. A total of 45 PASHs are present in lower concentrations in sample D20V than in at least one of the remaining VR tars suggesting that overall D20V contains both more individual PASHs and higher relative concentrations. The majority of the compounds present in lower concentrations in D20V are alkylated PASH isomers including 3 C1-Benzothiophene isomers; 6 C2-Benzothiophene isomers; 3 C1-Dibenzothiophene isomers; and 10 C2-Dibenzothiophene isomers. Sample D6V is the only sample in the database that lacks C2-Thiophene, although it does contain many alkylated Thiophenes above C2.

The large difference in the PASH, PAOH and PANH content of samples D2V-D6V suggests the samples may have a complex history. As the samples all came from the same site they likely used the same source of feedstock coal, although the exact composition of the coal may have changed over time. As the PANH, PAOH and PASH content of coal tars is determined by their presence within the parent coal used, with a degree of temperature alteration, then the samples would be expected to have relatively similar heterocyclic compositions but this is not the case. This suggests that some of the compounds present may come from sources other than the original VR tar or could possibly point to changes in feedstock composition over time. The complex nature of samples D2V-D6V suggests that sample D20V may be more indicative of a pure VR tar with samples D2V-D6V likely contaminated with other forms of tar. This is further reinforced by the presence of a large number of high boiling Phenols present within D20V relative to the other VR tars.

*Coke Oven tars:*

Coke ovens are the only modern day source of coal tar still in operation within the UK[21]. Two distinct forms of coke oven tars exist, with low temperature coke ovens tars produced at <700°C producing phenolic compounds as well as PANHs[22]. The other form of coke oven tar comes from high temperature coke ovens, which operate in excess of 700°C and in the case of metallurgical coke between 900°C and 1095°C[23], with PANHs being converted into ammonia, hydrogen cyanide, pyridine bases and nitrogen[22].

The total number of hydroxylated PAHs within the coke oven tars are similar with sample D18CO containing 49 and sample D19CO containing 68. The larger number of individual Phenolics present with D19CO is likely down to the lower temperature used[22]. A total of 43 hydroxylated PAHs are shared between the CO tars and as expected all are present in higher relative concentrations within sample D19CO. For example sample D19CO contains 253% more Phenol; 350% more o-Cresol; 630%

more m-Cresol; 132% more p-Cresol; and 426% more Naphthalen-2-ol. The main reason for the different number of compounds in each sample is that D19CO contains more branched isomers of hydroxylated PAHs than D18CO as well as containing 1 Phenanthrol and 3 Anthrol compounds, which were not detected within D18CO. While Anthrol is present in many samples throughout the database Phenanthrol was only detected in D19CO, D7H, D8H and D9L and is entirely absent from CWG and VR tars, although sample D19CO contains the lowest concentration of Phenanthrol within the database.

Both coke oven tars contain a large number of individual heterocyclic compounds with 50% of the total individual compounds present in D18CO being present in the form of heterocycles and 47% within D19CO. As both samples were produced from the same feedstock coal any difference in the heterocyclic composition is likely down to the difference in the coke ovens themselves, although there may be variation within the feedstock coal itself.

As sample D18CO is a high temperature coke oven tar it would be expected to contain large abundances of pyridines as the above 700$^{o}$C PANHs are converted into, although not exclusively, pyridine bases[22]. While both samples have the same number of alkylated pyridines, although not the same individual compounds, the concentrations of alkylated pyridines present within D19CO are significantly higher. A total of 4 alkylated pyridines are shared by the samples with 2 C2 Pyridines, which are present in 624% and 1609% higher concentrations in D19CO, and 2 C3 Pyridines, which are present in 113% and 239% higher concentrations in D19CO. These results suggest that low temperature coke ovens produce pyridines whereas while higher temperature coke ovens may destroy them. This suggests that pyridines are among the compounds produced below 700$^{o}$C and so may not be a good marker for coke oven operational temperature.

Sample D19CO is a low temperature coke oven tar and would be expected to have higher concentrations of PANHs[22]. This is not the case for the individual number of PANHs present within each sample as D18CO contains 171 PANHs, whereas

D19CO contains only 161. In total the samples share 135 PANHs 65 of which are present in higher concentrations in D19CO relative to D18CO. A total of 69 PANHs are present in higher concentrations in D18CO relative to D19CO. The remaining shared compound, Indole, is present in essentially the same concentration. There are several concentration trends present within the shared PANHs with sample for example D18CO containing relatively more; Aniline (114%), Benzonitrile (167%), Methyl Benzonitrile (133-155%), Quinoline (118%), Carbazole (127%) and Acridine (131%). As a general trend sample D18CO contains higher concentrations of nitrile containing PANHs and parent PANHs. Sample D19CO contains relatively higher concentrations of alkylated PANHs such as C1 and C2 Indole; C1, C2 and C3 Quinoline, C1 and C2 Carbazole; and C1 and C2 Acridine. These results suggest that at higher temperatures the alkylated PANHs are lost in favour of parent PANHs and non-heterocyclic nitrogen compounds such as those containing nitrile.

The PAOHs follow the same general trends as the PANHS with D18CO dominated by parent PAOHs such as Benzofuran (163%) and Dibenzofuran (125%), as well as compounds such as phenyl benzofurans and phenyl dibenzofurans. Sample D19CO is dominated by alkylated PAOHs such as C1-Benzofuran (158%), C2 and C3 Benzofuran; C1 and C2 Dibenzofuran; and C1, C2 and C3 Benzonaphthofuran. Sample D18CO contains 107 individual PAOHs and D19CO contains 108 with 86 PAOHs shared between the samples. Of the 86-shared compounds 51 are present in higher relative concentrations in D19CO. These results suggest that higher temperature coke ovens result in tars with lower alkylated PAOH contents and higher parent PAOH content.

The number of PASHs in the two CO tars is similar with sample D18CO containing 128 and sample D19CO containing 133. In total the samples share 105 PASH compounds of which 63 are present in higher concentrations in D19CO relative to D18CO. As with the PANHs and PAOHs sample D18CO is dominated by parent PASHs such as Benzo[b]thiophene (147%), Dibenzothiophene (152%) and Phenanthro[2,1-b]thiophene (189%). Sample D18CO also contains relatively more phenyl thiophene, phenyl benzothiophene, Benzodithiophene and

Phenanthrothiophene. Sample D19CO contains relative more C2-Thiophene; C1, C2 and C3 Benzothiophene; and C1, C2 and C3-Dibenzothiophene. This suggests that the higher temperature increases the relative abundances of parent PASHs while decreasing the relative abudance of alkylated isomers. The two CO tars are also the only samples within the database that lack C3-Thiophene, or any Thiophenes in general larger than C2.

*Carbureted Water Gas (CWG):*

The Carbureted water gas process is another gas production process which used both coal, usually in the form of coke, and oil to manufacture gas. It was developed from the water gas process with the addition of oil being sprayed onto the gas produced in order to enrich its calorific value. This means that the organic compounds present within the tar produced come primarily from the oil used in the process, as the water gas process alone did not produce significant amounts of tar[22]. This results in a chemical signature that is significantly different to tars derived for coal. For example oil, generally, has a lower nitrogen content than coal with only <0.5% of the content of crude petroleum being present in the form of PANHs, whereas this number goes up to between 1% and 2% in coals[5].

D13C contains only 7 hydroxylated PAHs whereas D14C contains 94. The relative concentrations of the 7 compounds hydroxylated PAHs present in both samples varies greatly with D14C containing 18890% more Phenol, 33417% more of a C2-Phenol, 18878% more of a C3-Phenol and 1603% times more of a C4-Phenol. The relative concentration different of the heavier hydroxylated PAHs is less with 1103% more o-Biphenylol, 1100% more Hydroxyacenaphthene and 910% more 4-Hydroxyfluorene. The relatively low number, and concentrations, of hydroxylated PAHs present in D13C is likely down to the fact the sample came from a groundwater contamination plume, whereas D14C came from a tar storage tank. The size of the relative difference between the individual shared compounds suggests that the original D13C tar had a significantly different hydroxylated PAH composition to that of D14C. While sample D14C contains significantly more Phenol than sample D13C when the database is considered as a whole the concentration is small and with the exception of the VR tars all tar types contain more Phenol than the CWG tars, and the same is true for the 3 Cresol isomers.

The heterocyclic composition of the two CWG samples varies greatly with D13C containing 48 PANHs, 100 PAOHs and 251 PASHs and 2 mixed heterocycles. D14C contains 102 PANHs, 105 PAOHs and 280 PASHs and 2 mixed heterocycles. The relative compositions of the Heterocyclic compounds are interesting as it gives important forensic information about the samples. The PANH content of both samples is low with sample D14C containing significantly higher concentrations of the 32 PANHs that the CWG samples share. For example sample D14C contains 708% more Carbazole; 2086% more Acridine; and 1472% more Benzo[c]carbazole. When the database is considered a whole however the concentrations of PANHs in D14C are low with higher concentrations overall than the VR tars and LTHR tars but significantly lower concentrations than the CO and HR tars. This is in spite of the fact LTHR and VR tars are both produced from coal and therefore should have a higher nitrogen content within the tar produced.

The total number of PAOHs within both samples is similar, however the concentrations of PAOHs are vastly different with sample D14C containing higher concentrations of 57 of the 71 PAOHs the samples share. Despite the fact sample D13C likely contains significantly less tar relative to D14C, as the sample comes from groundwater, 14 PAOHs are present in higher concentrations in D13C relative to D14C. With the exemption of a single compound, a Naphthofuran isomer, the PAOHs found in higher concentrations in D13C over D14C are alkylated Benzofuran between C1 and C4. This suggests that the original tar that sample D13C came from containing significantly higher concentrations of alkylated Benzofurans, which may suggest differences in the production process or could be down to the feedstock oil used.

Both CWG tars contains a large number of PASHs with 251 in D13C and 280 in D14C. Sample D14C contains the most PASHs in the database, with only D8H (263) containing more than D13C. Of the 198 PASHs that the CWG tars share only a single compound is present in higher concentrations in D13C relative to D14C, a C3-Thiophene 1DB isomer, with all other compounds being present in higher concentrations in D14C. When the database is considered as a whole sample D14C, which is more indicative of a pure CWG tar DNAPL, contains significant concentrations of PASHs with the highest concentrations of Benzo[b]thiophene, Dibenzothiophene and C1-Benzothiophene isomers.

When the database considered as a whole significant concentrations of PASHs are present in D14C, D20V, D7H, D8H, D10H, D18CO and D19CO. Theese samples share 60 PASHs, ranging from m/z 111 to m/z 284, with D14C containing the highest relative concentrations of 37 of the 60. The samples share 23 compound with an m/z of 222 or higher of which 17 are present in higher concentrations in at least one sample relative to D14C, which suggests the CWG tar contains significantly more PASHs below m/z 222. This high PASH content may be explained by the use of oil within the process, which may have a higher organic sulphur content than many of the coals used to produce the other samples. The quality of coal or oil used to produce the manufactured gas will have a large impact in the relative amounts of PASHs presents within the samples.

## Conclusion

Coal tars that are produced using different feedstocks and production processes produced tars with significantly different heterocyclic and hydroxylated contents. In total 865 heterocyclic and 359 hydroxylated PAHs were detected. The phenolic content of coal tars varies greatly depending on the production process used to produce the tars and the phenolic content of tars can form an important piece of forensics information. The presence of absence of phenolic compounds within coal tar samples can also potentially provide information on the environmental degradation of the samples, for example if the production process is known to produce a high phenol content but a high phenol content is not detected this may suggest the phenol has been lost to the environment. This is of particular importance when assessing samples that have been exposed to water as phenol is the most water soluble of the phenolic compounds with increased molecular weight decreasing solubility. The presence of high boiling phenolics, those boiling above C2-Phenol, can also be used to suggest what retort type was used to produce a specific tar. The data produced by the two coke oven tars is of particular forensic interest as the two tars were produced by the same feedstock coal but operated at different temperatures and so clearly demonstrate the effect temperature has on the phenolic content of tars produced without the affect of different retorts, as the coke ovens don't have retorts. The results clearly showed that the lower temperature coke oven tar contained significantly more individual hydroxylated phenolics as well as higher individual concentrations. This suggests that the higher the temperature that the tar is exposed to the greater the destruction of phenolics is.

The heterocyclic content of coal tars is also important as it can provide information on the feedstock used to produce the tars. The concentrations of individual heterocylic compounds varied greatly, even within tars produced by the same production process. Again the data produced by the coke oven tars if of particular forensics interest. The information provided by these two samples can be used to suggest what affect temperature has on the tars produced. At temperatures greater than 700°C PANHs are converted into, although not exclusively, pyridine bases and so it would be expected that the higher temperature coke oven tar would contain higher concentrations of pyridines. This however is not the case and the low temperature coke oven contains significantly higher concentrations of the shared alkylated pyridines. It should be noted that pyridine itself was not detected within either coke oven tar sample and the concentration data suggest the higher temperature resulted in the destruction rather than production of pyridines. It is also expected that lower temperature coke ovens contain higher concentrations of PANHs and of the 135 PANHs shared by the two coke oven tars 65 were present in higher concentrations in the higher temperature oven with 69 present at higher concentrations in the lower temperature oven, with 1 equal compound. The results suggest that the statement that lower temperature coke oven tars contain higher concentrations of PANHs is not strictly true and a more accurate statement is that higher temperatures result in the loss of alkylated PANHs in favour of parent PANHs and non-heterocyclic nitrogen compounds such as those containing nitrile groups.

This is also the case for PAOHs and PASHs with higher temperatures resulting in the loss of alkylated PAOHs with higher parent PAOH content.

The analysis was also able to detect several compounds that might be of interest for suggesting biological activity within the tar samples. Fluoren-9-one may be of particular interest as it can be produced by the metabolism of both fluorene and fluoranthene and was found in sample D17H in concentrations far in excess of comparable tars samples. The concentrations are completely at odds with the EPA16 PAH concentrations for the HR tars. Sample D17H also contains 4H-Cyclopenta[def]phenathren-4-one, which was not detected within any of the other HR tars and has been reported during the degradation of coal tar distillate within contaminated soils. This suggests that significant biological degradation of sample D17H may have occurred and this could provide evidence for microbial activity within tar DNAPL as the sample itself is pure DNAPL taken from a tar tank. Biological activity may also have affected sample D16L as this contains the highest concentrations of Fluoren-9-one, however as the sample is tar within soil then biological degradation is not as usual as that present within sample D17H.

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## 6.5 Bridge - Woodall-Duckham Inclined Chamber Tar:

Sections 6.2, 6.3 and 6.4 present a unique comprehensive database of coal tars produced by 5 different production process. The database however does not included every production process that produced coal tar and one such process is the Woodall-Duckham Inclined Chamber Plant.

DNAPL050 (D50) is a sample of tar from a Woodall-Duckham Inclined Chamber Plant (ICP) constructed in the North West of England, UK. The site also operated a CWG plant so there is also a potential for petrogenic material to be present within the tar. The sample was analysed by GCxGC and a database of compounds present within the sample was produced as well as PCA and HCA analysis. The sample was run both derivatized and non-derivatized. The Woodall-Duckham Inclined Chamber Plant was designed to produce coke, gas and coal tar and operated in a large chamber similar to coke ovens, but operated on an incline similar to an inclined retort. The chamber was designed so that coal of any variety or size could be used and gas and residuals could be produced in larger quantities than in horizontal retorts as the chamber can be efficiently steamed at the end of the carbonizing period (Anon., 1928). The Woodall-Duckham Inclined Chamber Plant also had the advantage of being able to produce good quality coke from poorly coking coals and so increasing the field of coal supply available (Anon., 1928).

A total of 1349 compounds were detected within the derivatized run with 110 aliphatic, 541 aromatic, 119 oxygen containing aromatics, 203 sulphur containing aromatics, 170 nitrogen containing aromatics, 6 mixed heterocycles and 192 derivatized compounds. In the non-derivatized run a total of 55 hydroxylated PAHs were detected. A total of 8 hydroxylated PAHs that could not be derivatized were also detected within the derivatization run including 2,6-dimethyl phenol, 2-ethyl-6-methyl-phenol, 2,4,6-trimethyl phenol, 3 C4-phenol isomers and 2 C5-phenol isomers. These compounds could not be derivatized due to steric hindrance. Steric hindrance is the process by which compounds that contain active hydrogen may not be derivatized due to the hindrance of the derivatization reaction around the hydroxyl group. This applies to 2,4,6-trimethyl phenol due to the fact that no matter were the hydroxyl group falls within the ring it will always have a methyl group on either side protecting it from derivatization. 2,6-dimethyl phenol can also not be derivatized due to the OH group being protected by two methyl groups on either side of it. As the number of alkyl groups increases the possible number of sterically hindered isomers increases. Sample D50 is significantly different from coke oven tars with D18CO containing 824 compounds and D19CO containing 872 with the total number of compounds falling within the Horizontal Retort range (872-1517 compounds).

The PANH composition of DNAPL050 is similar to the coke oven samples, although with significant differences in the concentration of the compounds. Sample D18CO generally has higher relative abundances of PANHs relative to D19CO with D50 having higher relative abundances of PANHs relative to D18CO. For example, D50 contains 279% more benzonitrile than D18CO, 163% more indole and 116% more quinoline. Pyridine was detected within D50 and was not detected in either D18CO or D19CO and was only detected within D7H, D10H and D9L. Aniline is present in significantly higher concentrations than the coke oven samples with 2312% more than D18CO and 2624% more than D19CO. The PANH composition of D50 to the HR tars is also similar, although D50 has less individual PANHs than D7H, D8H and D17H and so only has more than D10H in terms of overall number of compounds. Sample D50 contains 137% more pyridine and 641% more aniline than D10H (which has the highest concentration of both pyridine and aniline in the HR tars). While sample D8H has the highest general concentrations of PANHs within the HR tars sample D50 has generally higher concentrations of the PANHS than D8H with for example 283% more indole, 234% more quinoline and 135% more carbazole. This data suggests that while the ICP produced fewer different types of PANHs the overall quantities of the compounds produced by the process were greater, or it could also be down to variations in the parent coal used to produce the ICP samples relative to the Coke Oven tars.

The PAOH composition of D50 is similar relative to the coke oven samples, again with the exception of relative abundance. A total of 119 PAOHs were detected in

D5V0 with 100 detected in D18CO and 105 detected in D19CO. The larger number of compounds is mainly down to the presence of 11 C4-benzofurans in D50 whereas only 1 was detected in D19CO and none were detected in D18CO. Sample D50 contains a significantly higher relative abundance of benzofuran with 911% more Benzofuran than D18CO and 1484% more than D19CO. C1-Benzofuran is also present in significantly higher concentrations with 2275% more C1-benzofuran in D5V0 relative to D18CO and 1442% more relative to D19CO. The PAOH composition of D50 relative to the HR tars shows that D50 has relatively less compounds overall, again with the exception of D10H. However, the concentrations of PAOHs found within D50 are higher relative to the HR tars. For example, D5V0 contains 172% more benzofuran than D8H, 239% than D10H, 299% than D7H and 1553% than D17H. It also contains 201% more C1-benzofuran than D8H, 362% more than D10H, 372% more than D7H and 1355% more than D17H as well as 135% more dibenzofuran than D8H, 169% more than D7H, 236% more than D10H and 342% more than D17H. This suggests that while the ICP may produce a smaller number of PAOHs it produces them in larger quantities than HR tars and this is likely down to the different production process used or possibly the composition of feedstock coal used as the ICP would likely used a wider range of coals than horizontal retorts.

The PASH composition of D50 is significantly different to the coke oven samples with 203 PASHs detected in D50 and only 128 in D18CO and 133 in D19CO respectively. The larger number of PASHs present within D50 is due to the presence of a larger number of alkylated isomers. For example, samples D18CO and D19CO only contain a single alkylated thiophene (C2-thiophene) whereas D50 contains 30 alkylated thiophenes between C2 and C5. Sample D5V0 also contains relatively higher concentrations of PASHs with for example 185% more benzo[b]thiophene than D18CO and 273% more than D19CO. This suggests that the ICP produced more sulphur compounds than coke ovens, although it is possible that differences in the parent coal used may also have an effect. The total number of PASHs present within D50 falls within the range of the Horizontal Retort tars (143-263) suggesting that the sulphur content of the tar is more similar to a HR tar than a CO tar. Sample

D50 contains relatively higher concentrations of PASHs than D7H, D10H and D17H but not D8H, although some compounds such as benzenethiol (158%) are present in higher concentrations in D50 relative to D8H the majority of compounds shared by the sample are present in higher concentrations in D8H.

The most significant difference between D50 and D18CO and D19CO is the aliphatic composition of the samples. Sample D18CO contains only 2 aliphatics whereas D19CO contains 9. Sample D50 contains 110 aliphatic compounds including alkanes, alkenes, alkyl-cyclopentanes, alkyl-cyclopentenes and alkyl-cyclohexanes. The presence of alky-cyclohexanes is important as these compounds are petrogenic in origin (Saber et al., 2006). This suggests that a degree of petrogenic material is present within the sample. n-alkenes, as well as branched alkenes, were detected between C10 and C25 with a total of 22 compounds detected. n-alkanes were detected between the range of C11 and C33, with only sample D6V and D20V containing n-alkanes up to, and beyond, C33. The n-alkane distribution if significantly different to D18CO which only contains the C11 and C12 n-alkane and D19CO containing alkanes between C11 and C17. The presence of a CWG plant on the site may suggest that an amount of CWG tar is present within the sample. Figure 6.3 shows the n-alkane distribution of sample D50 and shows low molecular weight n-alkanes dominate with a maximum at C12 and limited abundances above C19. Figure 6.4 shows the alkyl cyclohexane distribution of sample D50 with a maximum at C5.

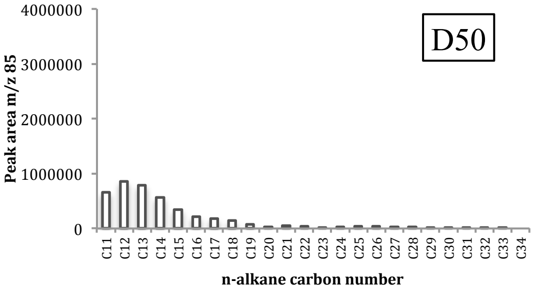

Figure 6.3 – n-alkane distribution DNAPL050

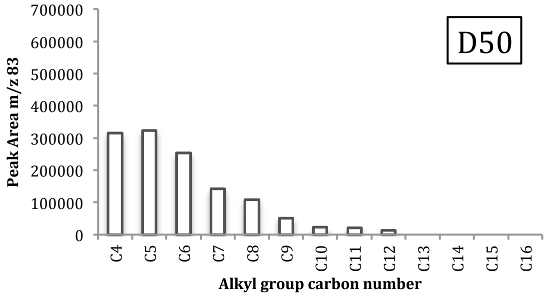

Figure 6.4 – Alkyl cyclohexane distribution DNAPL05

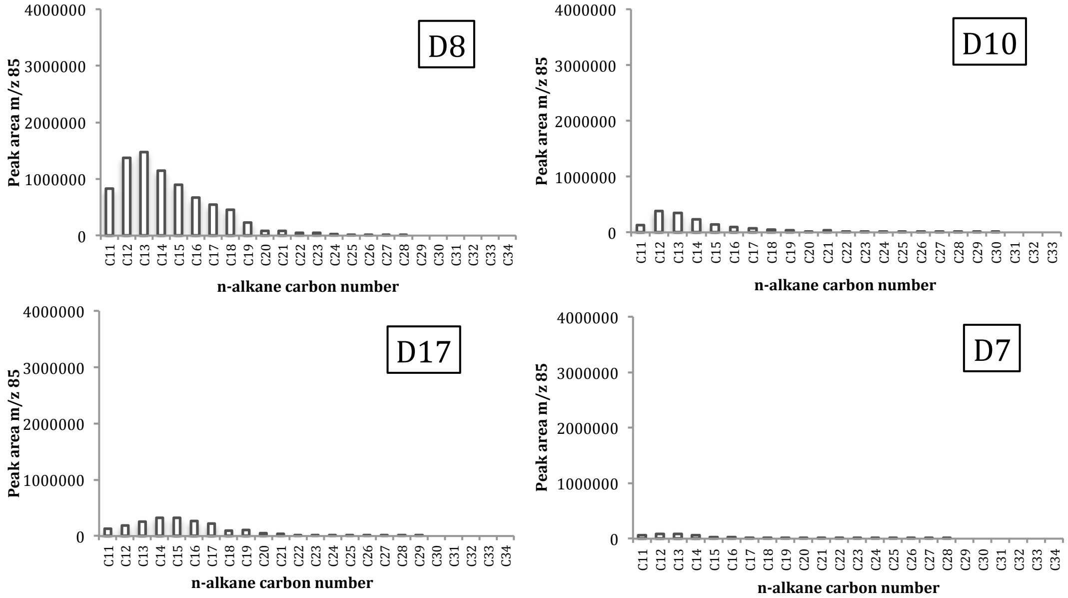

Figure 6.5 – n-alkane distribution of Horizontal Retort Tars DNAPL007, DNAPL008, DNAPL010 and DNAPL017

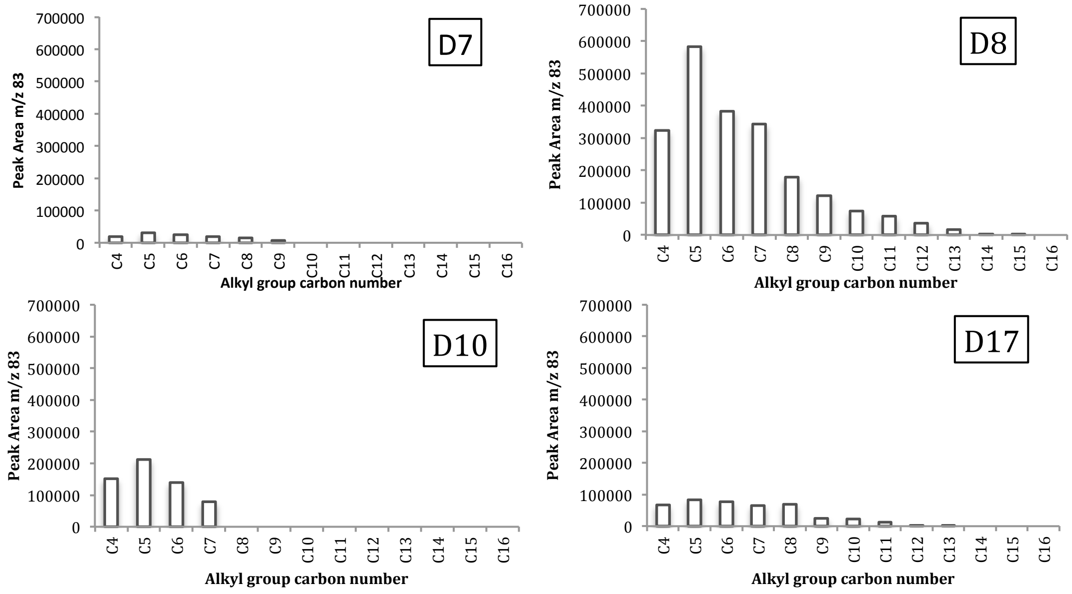

Figure 6.6 – Alkyl cyclohexane distributions Horizontal Retort Tars DNAPL007, DNAPL008, DNAPL010 and DNAPL017

The n-alkane distributions of the Horizontal Retort tar are shown in figure 6.5 and the alkyl cyclohexane distributions are shown in figure 6.6. Sample D8H shows the greatest abundance of both n-alkanes and alkyl cyclohexanes with sample D50 containing relatively more n-alkanes and alky cyclohexanes than the remaining HR tars (D7H, D10H and D17H). The presence of large amounts of alkyl cyclohexanes in both D8H and D50 suggests that they contain relatively more petrogenic material than D7H, D10H and D17H and it is possible that some of the n-alkanes present in D8H and D50 are derived from petrogenic material rather than the coal tar itself.

Another significant difference between the coke oven samples and D50 is the hydroxylated PAH composition, or derivatized compounds composition. Sample D18CO contains 49 derivatized compounds and D19CO contains 68 whereas sample D50 contains 192. D50 contains significantly more alkylated phenols than the coke oven tars in both number of individual compounds and their relative abundances. Sample D18CO contains 18 alkylated phenols ranging between C1 and C3 and sample D19CO contains 24 alkylated phenols between C1 and C4 whereas sample D50 contains 75 alkylated phenols between C1 and C6 (1DB). Sample D50 contains 191% more phenol than D19CO and 481% more than D18CO as well as significantly greater abundances of the 3 cresol isomers ranging between 291% more up to 1896% higher abundances for the 3 isomers. The increased abundance of the derivatized compounds applies to almost all compounds that the 3 samples share.

This higher phenolic content may be explained by the temperature of the inclined chamber plant as low temperature coke ovens <700°C produce phenolic compounds and PANHs (Hamper, 2006), similar to low temperature retorts. This suggests the sample came from a lower temperature process, as the relative concentrations are significantly higher than the high temperature CO tar (D18CO) and more similar to the low temperature CO tar (D19CO), although still at significantly higher concentrations overall. It is also possible that a differences in feedstock may also have an impact as both D18CO and D19CO were produced using the same feedstock, on the same site using different ovens, whereas D50 was not produced on the same site and so may have used significantly different feedstock coals as the Woodall-Duckham Inclined chamber was designed to make good coke from poorly coking coals so a wider field of coal supply was available (Anon., 1928).

Sample D50 also contains more individual derivatized compounds than any of the HR tars, with the largest amount being present in D8H with 152 compounds detected. While sample D50 contains more individual compounds than D7H it does not contain larger concentrations of the compounds shared between the samples. Sample D50 does contain relatively larger concentrations than the remaining 3 HR tars however. The only sample previously analysed that contains more individual derivatized compounds than D50 is sample D9L. The high boiling phenolic content, those that boil above C2, of D50 includes 56 alkylated phenols, 42 of which are shared with D20V and 39 with D9L. In all cases the concentrations of the higher boiling phenolics are higher in D9L relative to D50. Sample D50 contains higher concentrations of the C3-phenols (7) and C3-phenols 1DB/indanol (2) relative to D9L, however for the remaining compounds are present at higher concentrations in D9L and the overall high boiling phenolic content of D20V is similar to the HR tars, and significantly different to CO tars with a greater number of compound and higher relative concentrations.

The PAH composition of D50 is also important as high temperature coke ovens operated in temperatures in excess of 700°C producing tars with high PAH contents (Hamper, 2006). This means that if the D50 tar sample was produced at a lower temperature it would be expected to contain a lower PAH content. The total number of PAHs, and alkyl PAHs, detected within D50 is 541 whereas D18CO has only 360 and D19CO 387 with sample due to sample D50 having significantly more alkylated PAHs. The concentrations of EPA16 PAHs within the samples is important as D18CO contains 183% more EPA16 PAHs than D50 and D19CO contains 119% more. This data again suggests that the D50 sample was produced as a lower temperature as at a higher temperature more alkylated isomers have been lost and more parent PAHs produced.

The relative PAH compositions of D18CO, D19CO and D50 are shown in figure 6.7. Both D18CO and D19CO are dominated by phenanthrene making up between 17.0% and 19.92% of the total composition whereas in D50 phenanthrene only accounts for 4.96% of the total compositions. The same also applies to anthracene, which makes up 6.72% and 6.21% of the total composition of D18CO and D19CO respectively but only accounts for 1.70% of the total composition of D50. All of the other PAHs fall roughly into the same ranges with the exception of naphthalene in D50, which only makes up 15.40% relative to 9.31% (D18CO) and 8.55% (D19CO) respectively. The other exceptions are benzo[b]fluoranthene and benzo[k]fluoranthene which make up a significant portion of D50 with 10.29% and 10.85% respectively but only account for between 5.90% and 2.93% for D18CO and 4.78% and 2.5% for D19CO. It should be noted that while sample D50 contains relatively more benzo[b]fluoranthene is higher in D50 the absolute abundance is slightly higher in D18CO which contains 102% more benzo[b]fluoranthene, although D50 does have 195% more than D19CO. D50 does however contain significantly higher concentrations of benzo[k]fluoranthene with 207% more than D18CO and 393% more than D19CO. Figure 6.8 shows the relative EPA16 PAH compositions for HR tars versus D50 and while naphthalene is the most abundant compound in both the HR tars and the ICP tar sample D50 contains far less naphthalene than the HR tars, as well as far more benzo[b]fluoranthene and benzo[k]fluoranthene. Sample D50 also contains a relatively low abundance of phenanthrene and anthracene relative to both the HR and CO tars. Both figures suggest that the ICP process produces tar with a unique EPA16 PAH composition, which is different to both Coke Oven and Horizontal Retort tars.

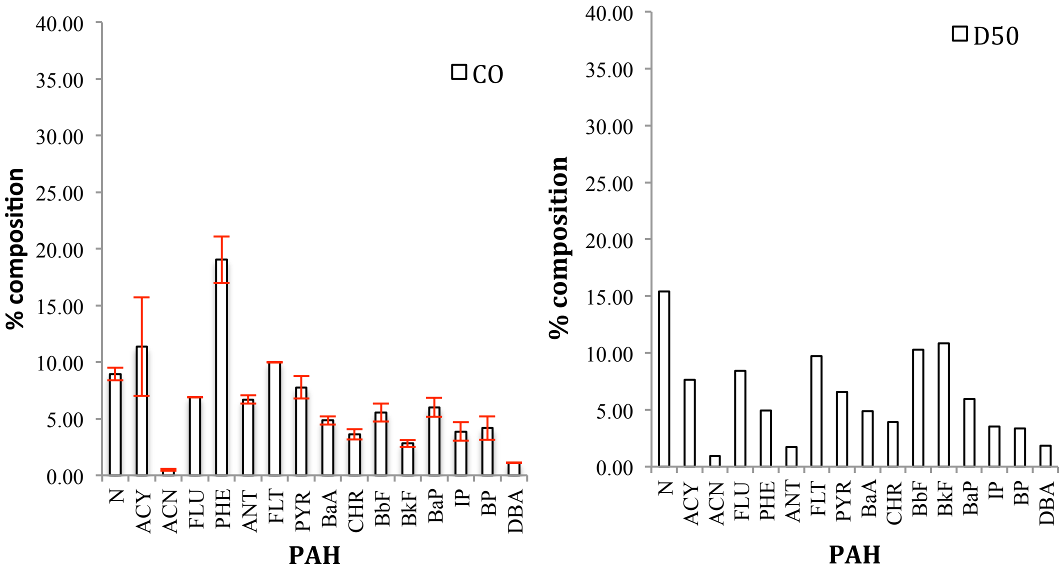

Figure 6.7 – Relative EPA 16 PAH compositions Coke Oven tars (DNAPL018 and DNAPL019) and DNAPL050

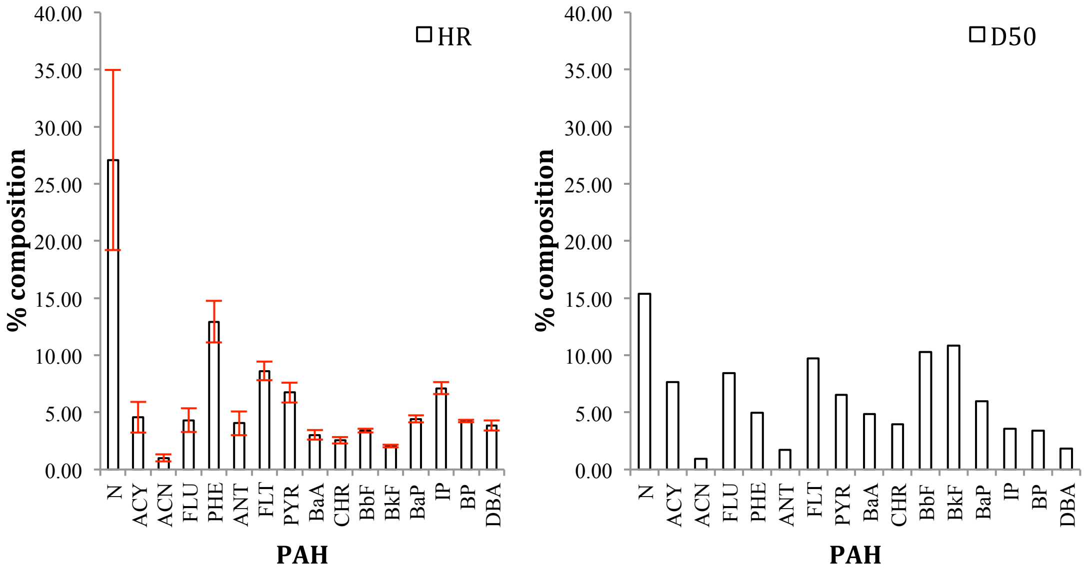

Figure 6.8 - Relative EPA 16 PAH compositions Horizontal Retort Tars (DNAPL007, DNAPL008, DNAPL010 and DNAPL017) and DNAPL050

Multivariate statistical analysis using PCA and HCA was performed on sample D50 using the dataset produced in McGregor et al., 2012. The PCA results, shown in Figure 6.9, clearly show the sample falling within the horizontal retort region and not the coke oven region. This suggests that the ICP produces tar more similar to a retort tar than a coke oven tar. This also suggests that the PCA is not capable of discriminating an ICP tar from a HR tar, although since the ICP variant would be less common in the UK than a HR the PCA will still likely give accurate results when analysing a UK based coal tar. The HCA analysis, showing in Figure 6.10, shows that the sample is most similar to samples D8H and D17H, which are both HR tars, followed by D18CO and D19CO, which are both coke oven tars. This further suggests that the tar produced by the ICP process falls in between a HR tars and a Coke oven tar, although with a greater degree of similarity to HR tars.

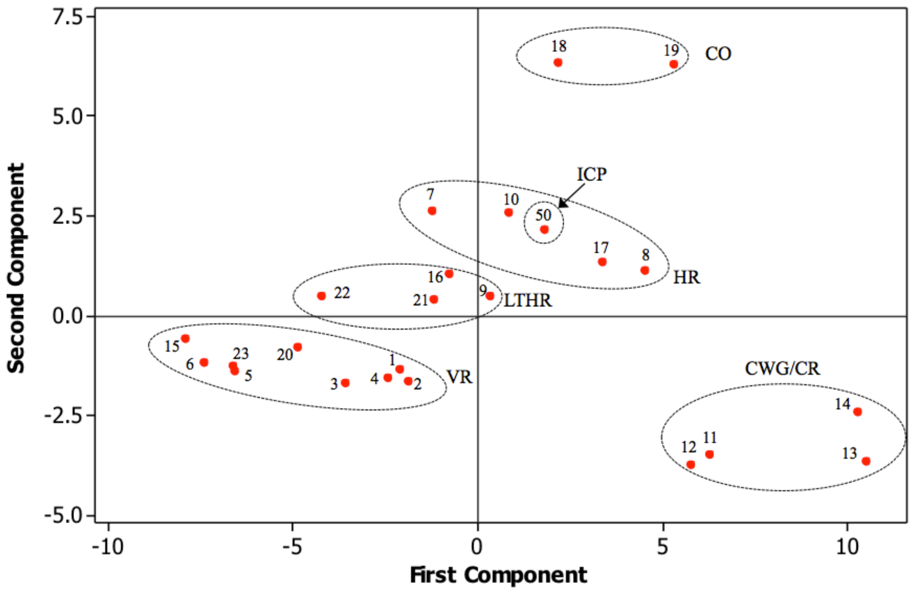

Figure 6.9 – PCA DNAPL050 using covariance matrix (CO = Coke Oven, HR = Horizontal Retort, LTHR = Low Temperature Horizontal Retort, VR = Vertical Retort, CWG = Carbureted Water Gas, CR = Creosote, ICP = Inclined Chamber Plant)

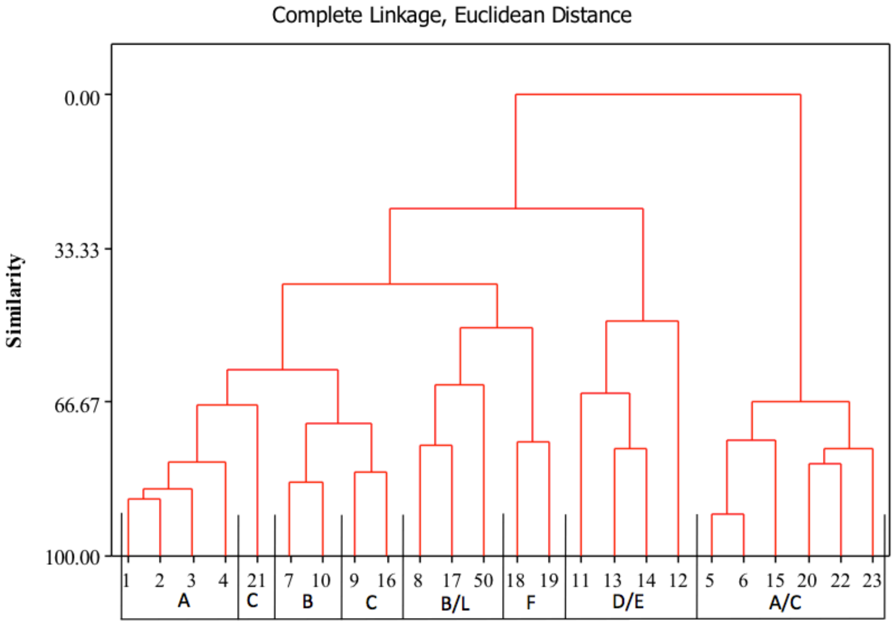

Figure 6.10 – HCA DNAPL050 using Euclidean distance and complete linkage mechanisms (A=Vertical Retort, B = Horizontal Retort, C = Low Temperature Horizontal Retort, D = Creosote, E = Carbureted Water Gas, F = Coke oven, L = Inclined Chamber Plant)

Inclined Chamber Plant tar has never previously been analysed using the statistical methods developed within McGregor et al., 2012. Another production process that has never previously been analysed using these methods is the Pintsch Gas process. Chapter 7 will provide an in depth analysis of a Pintsch gas tar, as well as statistical analysis of other new samples.

Reference:

Anon, The Book of the Woodhall Duckham Companies (2nd edition), The Woodhall Duckham Vertical Retort and Oven Construction Company (1920) Ltd, London, 1928

# Chapter 7

# Applications – Unique production process

### 7.1 Preface

This chapter contains an original journal article submitted for publication in the journal of Environmental Science & Technology in September 2016. The paper focuses on the analysis of a Pintsch Gas Tar and is unique to the scientific literature as a database of compounds present within a Pintsch Gas tar has never previously been published. C. Gallacher as the main author was responsible for all the analysis and data interpretation and writing of the paper. R. Kalin and R. Lord, as project supervisors, provided support with the research as well as assistance with preparation and review of the manuscript. R. Thomas, as the industrial supervisor, provided expert knowledge in the field of coal tar and manufactured gas as well as reviewing the manuscript. J. A. van Leeuwen provided the sample that was analysed as well as providing expert local knowledge of the site and expertise in the field of coal tar research, as well as reviewing the manuscript.

Chapter 6 presented a comprehensive database of compounds detected within coal tars with 2373 individual compounds detected within 16 tar samples from 5 different production processes. Chapter 6 also presented the analysis of a unique tar type produced by an Inclined Chamber Plant. Chapter 7 presents the analysis of a Pintsch Gas tar, a form of oil gas that has never previously been analysed. The database of compounds produced is unique to the scientific literature as a full composition Pintsch Gas tar has never previously been published, with limited literature on composition coming from the early 20th century. In total 946 individual compounds were identified within the Pintsch gas tar many of which are of potential toxicological interest. Chapter 7 also presents the PCA and HCA analysis of several tar samples that had not previously been analysed using GCxGC. A full list of the compounds found within the sample can be found in Appendix B.

## 7.2 Qualitative analysis of a Pintsch Gas Tar using comprehensive two-dimensional gas chromatography

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### Abstract

Pintsch gas was a form of manufactured oil gas used extensively in the lighting of railway coaches in the late 19th and early 20th century. It is unique to other manufactured gases due to its ability to be stored in high-pressure vessel. The process thermally degraded oil in special retorts not only producing gaseous hydrocarbons fixed in the gas phases, but also resulting in the formation of by-products such as distilled naphtha and tar. Despite Pintsch gases extensive usage, and therefore contamination with Pintsch gas tar may be expected along many railways it, has not been extensively studied. This is due to a lack of awareness of the Pintsch gas process and it's difference to other conventional gas making processes. These sites are also often located on disused sites or beneath rail infrastructure. This paper presents the analysis of a Pintsch gas tar from a former Pintsch gas production site located in the Netherlands using two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOF). An analysis of a known Pintsch gas tar using mass spectrometry has never previously been published. The data produced from the GCxGC-TOFMS was able to produce a qualitative database of compounds present within the tar with 946 individual compounds detected. This compounds ranged from aliphatic n-alkanes to heterocyclic sulphur compounds with PAHs and alkyl PAHs dominating the chemical signature.

## Introduction

Pintsch gas was a form of oil gas, which produced distilled Naphtha from petroleum or shale oil, and was used extensively in the lighting of railway coaches[1] in the late 19th and early 20th century. Pintsch gas unlike coal gas could readily be compressed under pressure and stored in small gasholders on rail carriages. As historical records of the locations of former gasworks associated with the rail industry were often not kept, estimating the number of global Pintsch gas plants is very difficult. Due to the wide use of gas lighting in railways around the world it is likely that many unknown Pintsch gas plant sites exist with between 100 and 150 estimated to have existed in the US between 1882 and 1960[2]. The overall composition of Pintsch gas varied depending on the temperature of the process and the feedstock oil used with increasing temperature resulting in higher percentages of Benzene and Toluene[1].

The process itself operated using a double retort[3] meaning that the feedstock oil was first run on to a tray at one end of a retort, the upper retort. It was then passed through to the other end of that retort into a retort of similar shape and size placed below the first retort, the lower retort[3]. The oil was introduced to the upper retort in a thin continuous stream from a micrometer cock, through a siphon pipe, falling directly onto the iron tray at the bottom of the retort in order to prevent the cold stream of oil coming into direct contact with the hot retort walls[4]. In the upper retort the oil was vaporized with the vapours passing through a neck into the lower retort, and then subjected to a high temperature of nearly 1000°C from heat radiated from the sides of the retort[3]. The temperature increased gradually as the vapours passed through the retort, and surface contact with the high temperature sides was largely avoided[3]. The use of a double retort ensured that the highest possible temperature acted upon every portion of the vaporized oil, without undue exposure to the heated surface of the retort. The temperature of the Pintsch gas process was significantly higher then the Carbureted Water Gas process (CWG), which operated at between 650°C and 700°C[5].

A furnace heated the retort itself with the flame from the furnace acting directly on all parts of the retort, so that no parts are over- or under-heated[4]. The quantity of tar produced by the process varied depending on the temperature maintained within the retorts as well as the quality of oil used[4]. When the retorts were irregularly heated a larger quantity of tar was produced[4]. There was also great variation in the tar produced by different oils with some classes yielding very light "thin" tar, which was lighter than water, while other oils produced heavy tars, which were heavier than water[4]. Within the siphons and condensers tar was deposited in amounts equal to around one-third of the volume of oil used in the process[3].

Different feedstock oils produced different tars for example Scotch Oil, most likely shale oil, produced tar that consisted mainly of higher molecular weight paraffin (alkane) and olefine (alkene) series, with about one-fifth of the volume as aromatic hydrocarbons[3]. Two distinct forms of tar were produced during the Pintsch process with the tar deposited from the process prior to collection in a gas-holder, amounting to around 5 gall. Per 1000ft of gas containing no acidic compounds, such as phenolics, or basic compounds, such as aniline or pyridine, and little or no benzene hydrocarbons[6]. It was mostly in the form of undecomposed petroleum hydrocarbons, and so likely had the same composition as the feedstock oil with some degree of temperature alteration[6].

The other form of tar produced was commonly referred to as "hydrocarbon" and was mainly free of paraffin's (alkanes) and consisted mainly of benzene and toluene, as well as dimethyl- and trimethyl-benzene, Naphthalene and hydrocarbons of the olefin (alkene) series and the "pseudo-olefine" series (e.g. amylene) and the "pseudo-acetylene" series (e.g dimethylene-ethane) as well as cyclopentadiene[6]. This tar amounts to less than 1gall. Per 1000ft. of compressed gas and was not used by tar-distillers, as it was too difficult to separate the benzene and toluene from other hydrocarbons and, within the UK, was often exported to Belgium to be used for varnish-making[6].

Only a single paper has been published analysing a possible Pintsch-oil using a GC method[7]. The sample analysed in Wanior and Ripper., 1993[7] was a mixture of waste oils taken from a former Pinstch-Oil GmbG i.L refinery site in Hanau, Germany.

The waste oil analysed was found to be chromatographically unresolved and mainly alkanes and branched alkanes were detected. NMR analysis showed very low levels of aromatics mostly in the form of BTEX. The lack of similarity to either of the tar types the Pintsch gas process produces suggests the tar is not comparable to the sample presented within this study. A complete analysis of the compounds present within a Pintsch oil gas tar using a GC, or GCxGC, has never been published with only limited literature from the early 20th century on the composition of a Pintsch-oil tar being published[1,3,6].

## Materials and Methods

### *Samples and Standards:*

A sample of tar produced by the Pintsch oil gas process was extracted using ASE. The sample was sealed and stored at 4°C prior to analysis. All solvents used were of analytical grade purchased from Fisher Scientific (Loughborough, U.K.) and $D_{10}$-Phenanthrene was purchased from Sigma-Aldrich (Gillingham, U.K.). Calibration standards were prepared using a standard mixture containing all 16 EPA PAHs purchased from Thames Restek (Saunderton Bucks, U.K.) and 4 Deuterated PAHs purchased from Sigma-Aldrich (Gillingham, U.K.).

The sample was obtained from a contaminated site in the Netherlands and was located beside the Amersfoort railway station with the contaminated site covering an area of roughly 15,000$m^2$. The tar is a dense non-aqueous phase liquid (DNAPL), which was produced at a Pinstch Gas factory that operated from 1910 to 1954. The tar was produced as a byproduct of the Pintsch gas process using gasoil (likely diesel) and was discarded on site, at first in a ditch and later within dug out lagoons. From the ditch and lagoons the tar could freely sink into the subsurface and pure phase tar accumulated at an aquitard at around 10-12 meters below ground surface (mbgs). The sample was taken from a fully filtrated monitoring well (A010F) situation near the former lagoons. 6m of tar was present within the well (6-12mbgs) at the time of sampling with the sample obtained from the bottom of the well.

*Extraction:*

Extraction was performed using an ASE 350 Accelerated Solvent Extraction system (Dionex, Camberley, UK) using 10 mL stainless steel extraction cells using the following method:

Approximately 0.5g of tar was mixed with equal amounts of sodium sulphate ($NaSO_4$) and diatomaceous earth in a 1:1:1 ratio. This removes any water present within the tar and results in a fine powder than can be quantifiably transferred into the extraction cells and ensures there is no loss of sample. The sample was spiked with a recovery standard prior to extraction.

Extraction cells were lined with 2 filter papers (to ensure unwanted particulate matter did not collect in the extract) and packed with 3g of silica gel 60 deactivated with 300µl of water. The sample mixture was then loaded into the cells and excess diatomaceous earth was added until the cell was well packed to ensure that there is no void space. Dichloromethane was used as the extracting solvent for all extractions. ASE was performed at 100$^{o}$C and 10 MPa, using one dynamic (7 min) and two static (5 min each) extractions. A flush volume of 150% and purge time of 60 s was used. The extracts were concentrated to 1 mL using a Büchi Syncore® Analyst (Oldham, U.K). The extract was then made up to exactly 10 mL using *n*-hexane. A 1 mL aliquot was then transferred to an auto sampler vial prior to analysis. Prior to analysis the extracts were spiked with $D_{10}$-Phenanthrene to be used as an internal standard.

*GCxGC-TOFMS:*

All GCxGC TOFMS analysis were performed using a Leco (St. Joseph, Michigan) time of flight mass spectrometer, model Pegasus 4D, connected to an Agilent 7890A gas chromatograph equipped with a LECO thermal modulator. The TOF ion source was fixed at 200 °C and masses between 45 and 500µ were scanned at a 200 spectra/second rate. The detector voltage was set at 1700 V and the applied electron ionisation voltage was set at 70 eV.

All standards and extracts were analysed with the primary oven temperature programmed with a hold at 75°C maintained for 1 minute, 12°C/min to 120°C, then at 3°C/min to 310 °C hold 10 minutes. The secondary oven and modulator temperatures were programmed at a 20 °C offset relative to the primary oven. The modulation period was 6 seconds with a 1.3 second hot pulse time and a cool time of 1.7 seconds. The injection port temperature was set to 250 °C and set to split injection with a split ratio of 50. One microliter of sample was injected for each run using an MPS2 twister auto-sampler (Gerstel). Helium was used as the carrier gas, with a flow rate of 1.0 mL/min.

The reversed polarity column set that was used comprised of a mid-polarity TR-50 MS supplied by Thermo Scientific (30 m x 0.25 mm i.d. x 0.25 µm film thickness) as the primary column and a non-polar Rtx-5SilMS supplied by Thames Restek (1.5 m × 0.25 mm i.d. m × 0.25 µm film thickness) as the secondary column, connected via a Thames Restek Press-tight connector.

*Data Collection and Pre-processing:*

The chromatograms from each sample were processed using Leco ChromaTOF software (Version 4.50.8.0) to search for and identify all peaks with a signal-to-noise ratio greater than 10, which is the limit of quantification. Statistical analysis was carried out using Microsoft Excel (Version 14.3.7), Minitab version 16 and Matlab R2013a. The initial pilot work did not quantify the PAHs and these will be quantified when the samples are rerun at a later date with the correct calibration mix.

Principle component analysis was carried out using 156 peaks and combined with a previously analysed data set[8] containing coal tar samples from various different production processes, e.g. Carbureted Water Gas, Coke Ovens. Prior to PCA analysis all peak areas were normalized by dividing the peak area by the sample weight and then the $D_{10}$-Phenanthrene peak area and taking the fourth root of the normalized value. 4th Root data formation is required as without data pre-processing the large range of peak intensities within the dataset results in small peaks contributing less towards the principle components regardless of their chemical importance[8]. Taking the fourth root also allows the analysis to focus on the presence/absence of contaminants rather than their concentration and so relates the data to the primary production method used instead of changes in relative concentration, which may have occurred due to environmental factors.

*Quality Control:*

To ensure the accuracy of the data produced strict quality control measures were employed including: The use of reagent and procedural blanks, including of a recovery standard (D8-Naphthalene, D10-Fluorene, D10-Fluoranthene, D10-Pyrene), an injection standard (D10-Phenanthrene) and calibration standards (EPA16 PAHs) for the GCxGC-TOFMS. The recovery of the recoveries standards fall within the range suggested by US EPA method 8800B of between 70% and 130%[8]. All blanks used were clean and free of contamination and all standard calibrations obtained were linear.

## Results and Discussion

*Overall composition:*

A total of 946 individual compounds were detected within the sample with 120 aliphatic compounds, 559 PAHs and alkyl PAHs, 49 Oxygen containing compounds (PAOH), 15 Nitrogen containing compounds (PANH) and 203 Sulphur containing compounds (PASH). The vast majority of Oxygen, Nitrogen and Sulphur containing compounds are present in the form of heterocycles. A heterocyclic compound is a compound that contains more than 1 element within the aromatic ring. Aromatic rather than aliphatic compounds heavily dominate the tar sample. The complete list of compounds detected can be found in the supplementary information.

*Aliphatic:*

A total of 120 aliphatic compounds were detected within the sample with n-alkanes ranging from C11 to C25. n-Alkenes were also detected within the sample ranging from C10 to C17. The presence of both alkanes and alkenes suggests that the tar is a mixture of both forms of tar produced by the process. This is further suggested by the presence of cyclopentadienes as both alkenes and cyclopentadienes are found within the "hydrocarbon" tar produced by the Pintsch gas process. The "hydrocarbon" tar produced however is mainly free of n-alkanes and so the presence of alkanes suggests that the first form of tar is also present. The presence of alkenes is also interesting in the context of the feedstock used as alkenes are rarely present in crude petroleum but may be present in petroleum products and are formed during the refining process[10]. This suggests that the Pintsch gas process produced alkenes similar to the refining process, although it is also possible that alkenes are present within the feedstock oil used if the feedstock oil has been refined prior to use.

Figure 7.1 shows the n-alkane distribution of the sample with figure 7.2 showing the alkyl cyclohexane distribution. Alkyl-cyclohexanes are commonly associated with being derived from petrogenic sources[11]. Kaplan et al., 1997[12] published n-alkane and alkyl cyclohexane distributions of various different petroleum products with both distributions for DNAPL043 being most similar to Diesel #1. This suggests that the original feedstock oil used to produce the Pintsch gas was a diesel oil, although it is also possible that the oil used was a blend of different distillates and this would have been driven by economic factors as well as availability[13]. It is also possible that the feedstock used during the Pintsch gas process changed over time as the site operated for several decades.

The ratio of the C17 n-alkane to pristane can be used to indicate how weathered an oil sample is with a ratio of <1.0 showing that the oil has been highly weathered[14]. The ratio of n-C17/Pristane was found to be 3.34 suggesting that the sample is not highly weathered. The n-alkane distribution of the sample also suggests that it has not undergone significant weathering due to the presence of low molecular weight n-alkanes.

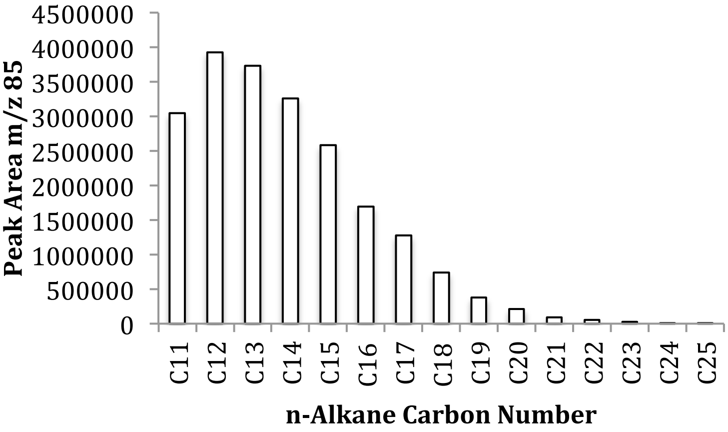

Figure 7.1 – n-alkane distribution of Pintsch Gas tar

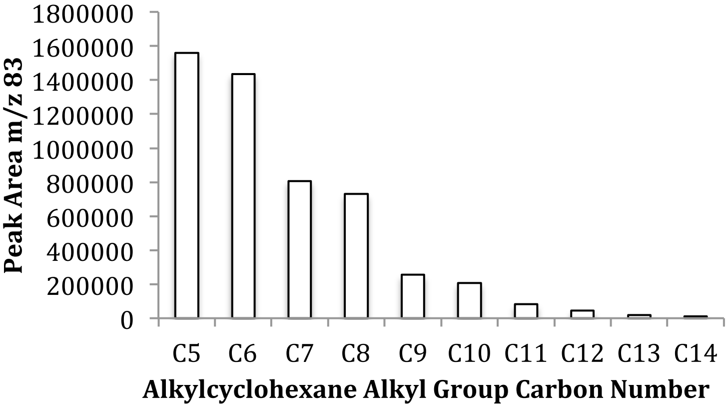

Figure 7.2 – Alkyl cyclohexane distribution of Pintsch Gas tar

*PAHs/Alkyl PAHs:*

PAHs and alkylated PAHs make up an important group of compounds found within fossil fuels and environmental samples. Two important groups of PAHs and alkylated PAHs often used for environmental forensics analysis are the EPA16 and EPA34 PAHs[15]. PAHs consist of fused aromatic rings and persist within the environment due to the dense clouds of π-electrons on both sides of the ring structure[16]. The toxicity of PAHs varies greatly with the number of rings with 4- and 5-ring PAHs tending to be carcinogenic and/or mutagenic and 6-ring PAHs tending to be substantially mutagenic[17]. Alkylated PAHs are also important as they can contribute substantially to the toxicity of PAH mixtures, and can account for up to

80% of the toxic burden[18]. In diesel fuel parent PAH's only make up around 2.7% of the total toxic burden from parent PAHs, whereas alkyl PAHs make up 97.3%[19]. This suggests that alkyl PAHs may contribute significantly to the toxic burden from Pintsch oil gas tars.

The largest group of compounds present within the sample comes in the form of PAHs with a total of 559 compounds. The lowest molecular weight PAH present within the sample is Styrene ($C_8H_8$) and the highest molecular weight PAH is the 5 Dibenzopyrene ($C_{24}H_{14}$) isomers. All of the EPA16 PAHs were detected and quantified, shown in figure 7.3, with Phenanthrene having the highest concentration present followed by Naphthalene. Of the EPA34 PAHs all 34 compound types were detected within the sample. It should be noted that EPA34 does not represent 34 compounds but rather 34 compound types, as alkylated isomers are present in many different combinations. Of the hundreds of potential EPA34 compounds that could be detected 151 were detected with the largest numbers of isomers being C4-Naphthalene and C2-Fluorene both with 18 isomers each.

Alkylated Benzenes are potential compounds of forensic interest as hardly any are present within the first type of tar produced by the process[6]. However they are present within the "hydrocarbon" tar and so the presence of alkylated benzenes again suggests the tar is a mixture of the two types. A total of 57 alkylated benzenes ranging between C3 and C7 were detected with the largest number of isomers present in the form of 17 C6-Benzene isomers. It is likely that significant concentrations of BTEX are present within the sample as Benzene and Toluene were the main components of the lighting gas produced and considerable quantities of the illuminating gas dissolved in the "hydrocarbon"[3] although these were not detected due to the GCxGC temperature program used.

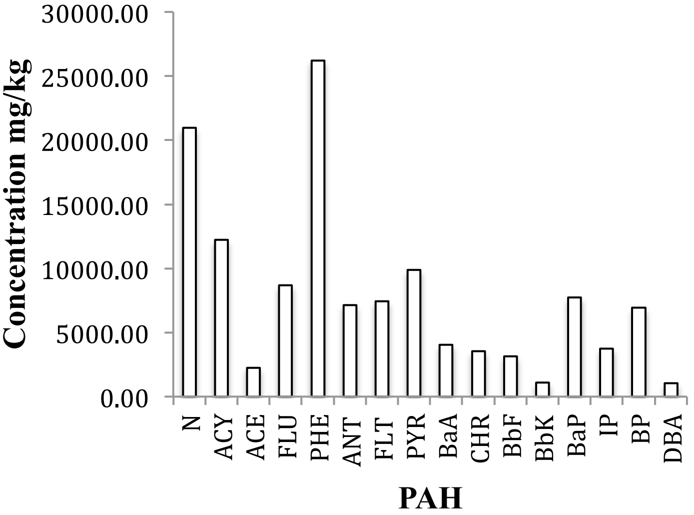

Figure 7.3 – EPA16 PAH concentrations Pintsch Gas tar

Various different diagnostic ratios can be applied to PAHs in order to provide forensic information about a sample. Diagnostic ratios for a Pintsch gas tar have never previously been published. The ratio of Phenanthrene to Anthracene (Phen/Ant) is often used to determine whether a sample is petrogenic or pyrolytic in origin. A Phen/Ant ratio of >10 indicates the samples are petrogenic in origins whereas a ratio of <10 indicates the samples are pyrogenic[11]. The ratio of Phen/Ant within the Pintsch gas sample is 3.67, which falls into the pyrolytic range. However the sample is not pyrolytic in origin and this can be explained using the ratio of Fluoranthene to Pyrene. The ratio of Fluoranthene to Pyrene is 0.75, which falls into the range of a petrogenic sample, and both ratios must be taken into account in order to give an accurate interpretation[20] and when the ratios are both taken together this points to the sample being petrogenic in origin.

The ratio of Ant/(Ant+Phen) can be used to suggest if a sample is petrogenic or pyrogenic with a ratio of <0.1 indicating the sample is petrogenic and a ratio of >0.1 pyrogenic[21]. The ratio of Ant/(Ant+Phen) is 0.21, which is within the pyrogenic range. This suggests that this ratio also cannot be accurately applied to Pintsch gas, as the high temperature of the production process likely affects the ratio. The ratio of Benzo[a]anthracene/(Benzo[a]anthracene+Chrysene) has also been used to provide forensic information about samples with a ratio of <0.2 being petrogenic and >0.35

representing combustion[22]. The ratio of BaA/(BaA+Chr) for the sample is 0.53 suggesting that the production process increases the ratio similar to the effect of combustion. This also applies to other diagnostic ratios such as Ind/(Ind+B[ghi]P) which has a ratio of 0.35 for the sample. This value falls into the range for Diesel oil of 0.12-0.71[22] as well as diesel combustion 0.18-0.69[22].

*PANH:*

A relatively small numbers of PANHs are present within the sample with only 15 compounds detected all in the form of heterocycles. This is likely down to the low nitrogen content of oil relative to coal with only <0.5% of content of crude petroleum being present as PANHs, whereas 1-2% of the content of coal is in the form of PANHs[23]. While PANHs are present in lower concentrations relative to their corresponding PAH-analogue they are more environmentally mobile due to their higher water solubilities[24]. PANHs are also highly stable relative to their corresponding PAH-analogue[25] and can persist through severe thermal conditions meaning they are likely to survive the Pintsch-gas production process.

Nitrogen containing compounds present in gas oils are present in the form of basic (e.g. pyridine) and neutral (e.g. carbazole) compounds[26]. However the tar produced by the Pintsch gas process should be free of basic compounds[6]. All of the PANH compounds present within the tar are neutral PANHs with Carbazole ($C_{12}H_9N$), which is the lowest molecular weight PANH present, and C1 and C2 Carbazole isomers dominating. Benzo[def]carbazole and Benzo[a]carbazole, Benzo[b]carbazole and Benzo[c]carbazole ($C_{16}H_{11}N$), which are the highest molecular weight PANHs detected, make up the remaining PANH compounds detected. Only 3- and 4-ring PANHs were detected within the sample.

*PAOH:*

Oxygen containing compounds can be toxic, carcinogenic and mutagenic and are more environmentally mobile than their corresponding PAH-analogues due to their increased water solubility. The oxygen containing compounds found in tar produced by coal carbonization are generally determined by the composition of the feedstock coal used[27], although with a degree of temperature alternation[28]. This also likely applies to the tars produced by the Pintsch gas process with the PAOH composition determined by parent oil used, with a degree of temperature dependent alteration.

A total of 49 PAOHs were detected within the sample ranging from Anisole ($C_7H_8O$) to 3 Benzobisbenzofuran isomers ($C_{18}H_{10}O_2$). Anisole is the only 1-ring PAOH present within the sample and the only ether detected. The largest group of PAOHs detected was those with 3 rings containing 22 compounds dominated by dibenzofuran and alkylated dibenzofuran isomers. Of the 11 2-ring PAOHs detected all are present in the form of Benzofuran and alkylated Benzofuran isomers. A total of 12 4-ring PAOHs were detected with the largest group being 7 C1-Benzonaphtofuran isomers. Only 3 5-ring PAOHs were detected in the form of benzobisbenzofuran isomers and are also the only compounds present within the sample containing 2 Oxygens. Heterocyclic PAOHs dominate with a handful of aromatic ketones making up the remainder, and a single ether compound.

*PASH:*

The occurrence of a wide range of PASHs within fossil fuels and the environmental has been widely reported as well their potential mutagenic and carcinogenic effects[29]. PASHs exist in a greater variety of structure relative to their corresponding PAH-analogues due to the presence of sulfur within the ring structure. This results in a larger number of isomers and particularly alkylated isomers, which can make it extremely difficult to quantify and identify individual PASH isomers[29]. A large number of PASHs were detected within the sample with a total of 203 PASHs ranging from Benzenethiol ($C_6H_6S$) to Benzo[4,5]triphenylono[1,12-bcd]thiophene ($C_{20}H_{10}S$).

Middle distillates, such as diesel oil, mainly contain dialiphatic sulfides, alky-substituted benzothiophenes and dibenzothiophenes isomers[30]. While no dialiphatic sulfides were detected, as they may be lost during the Pintsch gas process, alkyl benzothiophenes and alkyl dibenzothiophenes dominate the PASH composition. Of the 203 PASHs detected 40 are in the form of alkyl benzothiophenes between C1 and

C5 as well as 42 alkyl dibenzothiophenes between C1 and C4. C4-Benzothiopene makes up the largest group of individual isomers with 15 isomers detected. 2 and 3 ring PASHs make up the dominant groups of PASHs with 57 2-ring PASHs and 74 3-ring PASHs detected within the sample. Of the remaining compounds 46 4-ring PASHs, 21 1-ring PASHs, 4 5-ring PASHs and finally 1 6-ring PASH were detected. The vast majority of PASHs present within the sample are in the form of heterocycles with the exception of Benzenethiol, C1-Benzenethiol and Naphthalenethiol.

Among the 3-ring PASHs detected Naphtha[1,2-b]thiophene has been shown to be mutagenic[31]. Phenanthro[3,4-b]thiophene is the most mutagenic of the PASHs[31] and was detected within the sample. The position of the sulphur within the ring structure directly influences the potential mutagenic effect as phenanthro[4,3-b]thiophene, an isomer of Phenanthro[3,4-b]thiophene, that was not detected within the sample, has a significantly lower mutagenic effect than Phenanthro[3,4-b]thiophene[31]. Benzo[2,3]phenanthro[4,5-bcd]thiophene was also detected and has been shown to be an extremely powerful mutagen and is an even stronger mutagen than it's corresponding PAH analogue benzo[a]pyrene[31].

*Biomarkers:*

Biomarkers that are commonly detected within crude oil include terpenes, such as hopanes, and Steranes[32]. No hopanes or Steranes were detected and this may be down to the feedstock used to produce the Pintsch gas. During the refining process high molecular weight biomarkers, such as hopanes, are removed from the crude oil[32] thus further suggesting that diesel oil was used to produce the Pintsch gas. It is also possible that the Pintsch gas production process itself removes hopanes and Steranes due to the high temperature of the process. Alkenes are also rarely present within crude oil but may be present in petroleum products, having been formed during the refining process[10]. The alkenes detected within the sample may have been present in the original feedstock diesel oil used to produce the tar or may have also been produced during the Pintsch gas production process itself.

*Multivariate statistics:*

Multivariate statistical analysis of the samples was carried out using the method published in McGregor et al., 2012[8]. The data for DNAPL043 was added to the existing British dataset and HCA and PCA analysis was performed. The HCA analysis, shown in figure 7.4, clearly shows that the Pintsch gas sample is most similar to the CWG tars found within the British database. This would be expected, as the CWG process is also an oil-based process and so would produce similar compositions of tars. PCA analysis, shown in figure 7.5, shows the Pintsch gas sample clustering with the CWG samples with 81.5% of the total variance explained within the first 2 PC's.

These results suggest that while the multivariate statistical analysis is capable of distinguishing the coal gas and coke oven tar samples from oil based tar samples it is not capable of discriminating between Pintsch gas and CWG samples. The CWG process and Pintsch gas process likely produce tars of similar compositions as the composition of CWG tars is dominated by the feedstock oil used and Pintsch oil gas solely uses oil. The results also suggest that the different temperatures of the processes do not significantly affect the statistical analysis as the CWG process generally operated between 650°C and 700°C, whereas the Pintsch gas process operated at temperatures of nearly 1000°C.

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## Figures

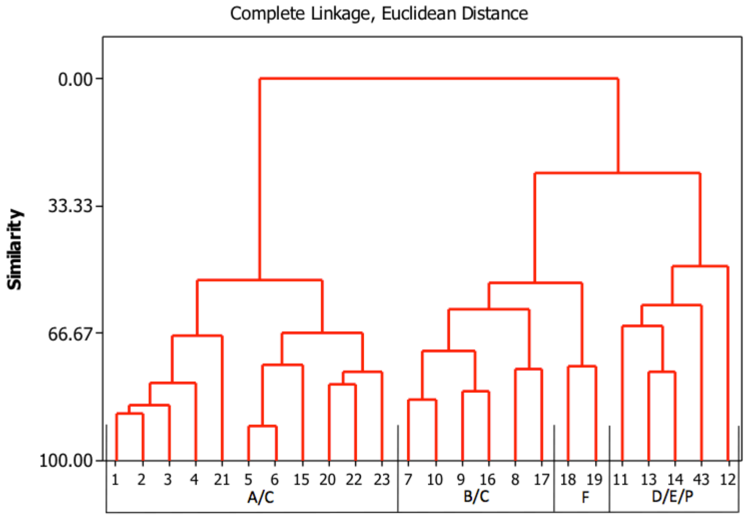

Figure 7.4 – Dendrogram of the eighth root, normalised data including Pintsch Tar samples using Euclidean distance and complete linkage mechanisms (A=Vertical Retort, B = Horizontal Retort, C = Low Temperature Horizontal Retort, D = Creosote, E = Carbureted Water Gas, F = Coke oven, P = Pintsch Tar).

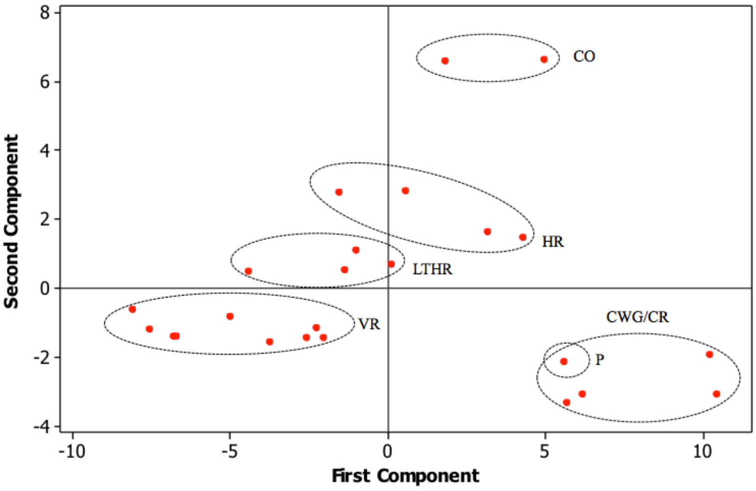

Figure 7.5 – Principle Component Analysis of existing British data set with Pintsch Tar added  (CO = Coke Oven, HR = Horizontal Retort, LTHR = Low Temperature Horizontal Retort, VR = Vertical Retort, CWG = Carbureted Water Gas, CR = Creosote, P = Pintsch Tar)

### 7.3 Bridge – Additional tar sample statistics

Section 7.2 provides an in depth comprehensive analysis of a Pintsch Oil gas tar, a unique tar type that has never previously been analysed using GCxGC. Both chapters 6 and 7 provide information on tar samples that have never previously been analysed. Several other samples were received over the course of the PhD and multivariate statistical analysis was performed, although not a full database of compounds. The results are presented below.

DNAPL047 was obtained from a former manufactured gas plant operating in Scotland, UK. The sample was analysed using GCxGC-TOFMS and PCA and HCA analysis using the database developed by McGregor et al., 2012 was performed. PCA analysis, shown in figure 7.6, shows the sample clearly falling into the horizontal retort region with HCA analysis, shown in figure 7.7, showing the sample is most similar to sample D21 (LTHR), followed by the two coke oven tars (D18 and D18) and then Horizontal retort and Vertical retort tars. While these results suggest that the sample is from a Horizontal retort the site ceased operation in 1901 and so a Low Temperature Horizontal Retort may be more likely.

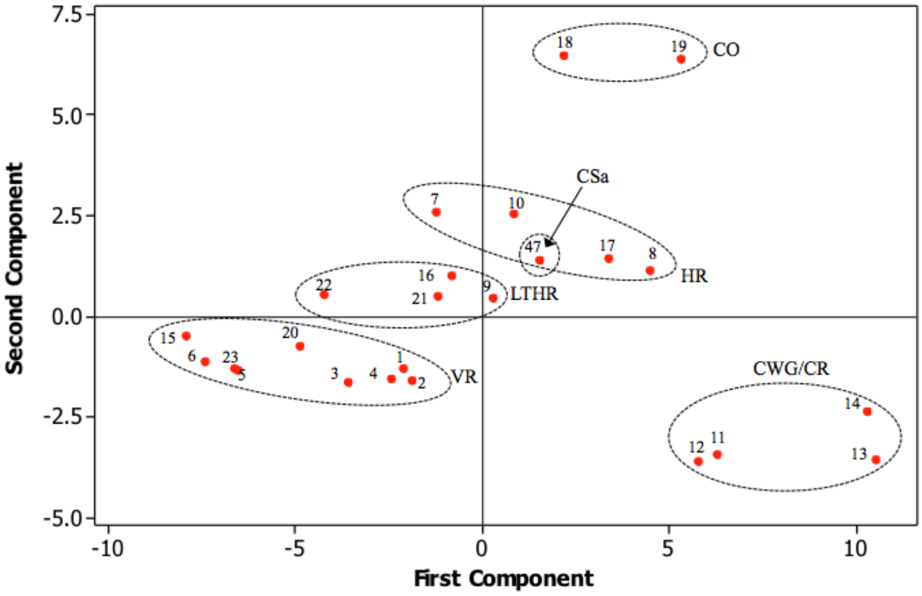

Figure 7.6 – PCA DNAPL047 using covariance matrix (CO = Coke Oven, HR = Horizontal Retort, LTHR = Low Temperature Horizontal Retort, VR = Vertical Retort, CWG = Carbureted Water Gas, CR = Creosote, CSa = Central Scotland Tar a)

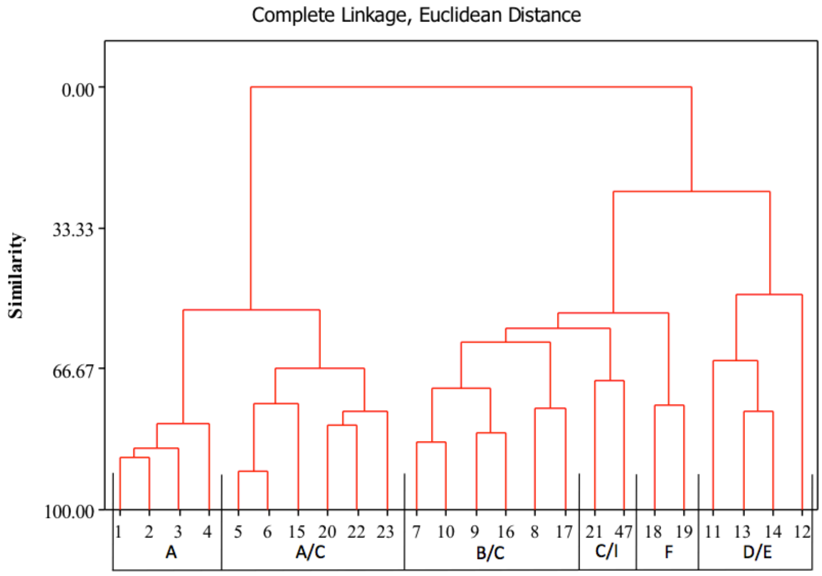

Figure 7.7 – HCA DNAPL047 using Euclidean distance and complete linkage mechanisms (A=Vertical Retort, B = Horizontal Retort, C = Low Temperature Horizontal Retort, D = Creosote, E = Carbureted Water Gas, F = Coke oven, I = Central Scotland Tar a)

DNAPL048 was obtained from the site of a former manufactured gas plant in Arnhem, Holland. The sample was analysed using GCxGC-TOFMS and PCA and HCA analysis using the database developed by McGregor et al., 2012 was performed. PCA analysis, shown in figure 7.8, clearly shows the sample falling outside of the production process clusters and into a cluster of it's own. This suggests that the sample may be from a production process that has never previously been analysed. HCA analysis, shown in figure 7.9, shows the sample is most similar to samples D8 (HR) and D17 (HR) followed by several other HR and LTHR samples (D7, D9, D10 and D16). This suggests that the process used may have been similar to, but not the same as, a horizontal retort process.

The sample site has a complex history with a mixture of horizontal retorts, vertical retorts and chamber ovens, which were neither vertical or horizontal but somewhere in between. In 1923 the site contained 16 half generator ovens with 8 horizontal retorts 3m in length and 6 full generator chamber ovens with 6 vertical retorts of 5m in length. In 1924 8 of the horizontal retorts were removed with the remaining 8 horizontal retorts removed in 1928. In 1932 the site was expanded with all old ovens replaced with 4 chamber ovens which were neither vertical nor horizontal but somewhere in between. The PCA analysis suggests that the sample tar was neither a HR or VR tar and therefore likely came from the 4 chamber ovens added in 1932. It is also possible that the sample represents a mixture of several different tar types although as the other tar types that would have been produced on the site are VR and HR tars then if this was the case the PCA results would be expected to fall between the HR and VR regions rather than the HR and CO regions. This may further suggest that the tar came from the chamber ovens as the process was somewhere between a horizontal retort and a coke oven. This is the first example of a chamber oven tar analysed using this multivariate statistical method.

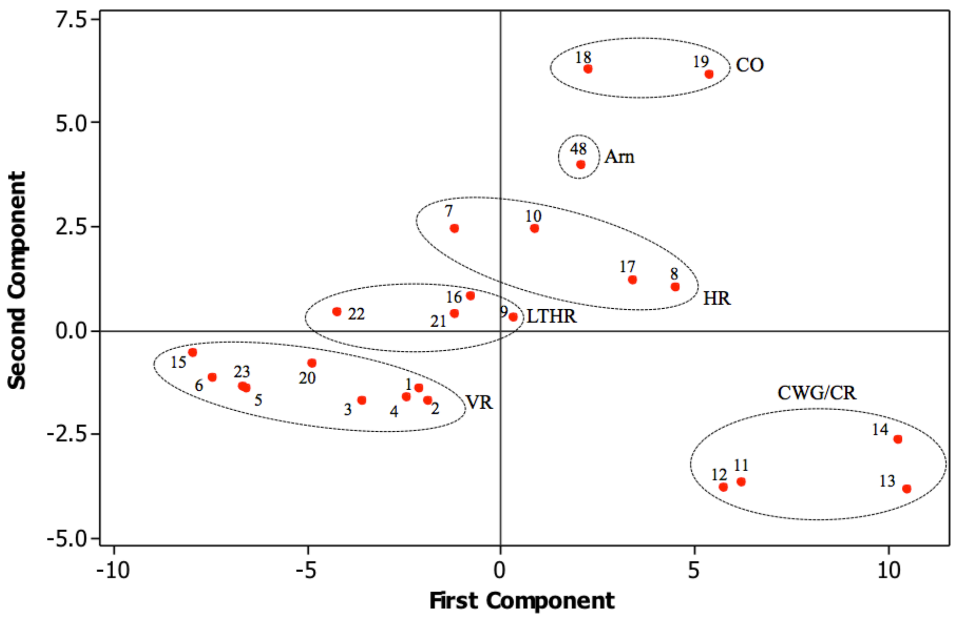

Figure 7.8 – PCA DNAPL048 using covariance matrix (CO = Coke Oven, HR = Horizontal Retort, LTHR = Low Temperature Horizontal Retort, VR = Vertical Retort, CWG = Carbureted Water Gas, CR = Creosote, Arn = Arnhem Tar)

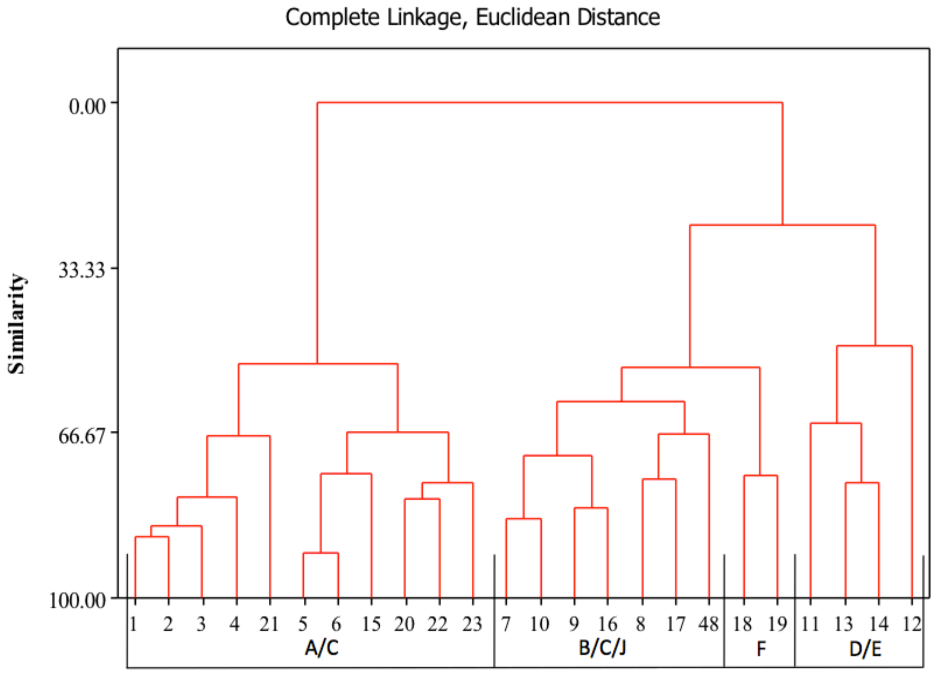

Figure 7.9 – HCA DNAPL048 using Euclidean distance and complete linkage mechanisms (A=Vertical Retort, B = Horizontal Retort, C = Low Temperature Horizontal Retort, D = Creosote, E = Carbureted Water Gas, F = Coke oven, J = Arnhem Tar)

DNAPL49 was also obtained from a former manufactured gas plant that operated in Scotland, UK. The PCA analysis of the sample is shown in figure 7.10 and clearly shows the sample falling with the LTHR region. The HCA analysis is shown in figure 7.11 and shows the sample is most similar to the Coke oven tars followed by horizontal and low temperature horizontal retorts. This suggests that the HCA is unable to provide correct information about the process that produced the tar, as the site was a manufactured gas site and not a coke oven site. The PCA analysis suggests that the sample was produced by a LTHR, although a higher temperature HR cannot be excluded due to how close the other HR region the sample falls on the PCA.

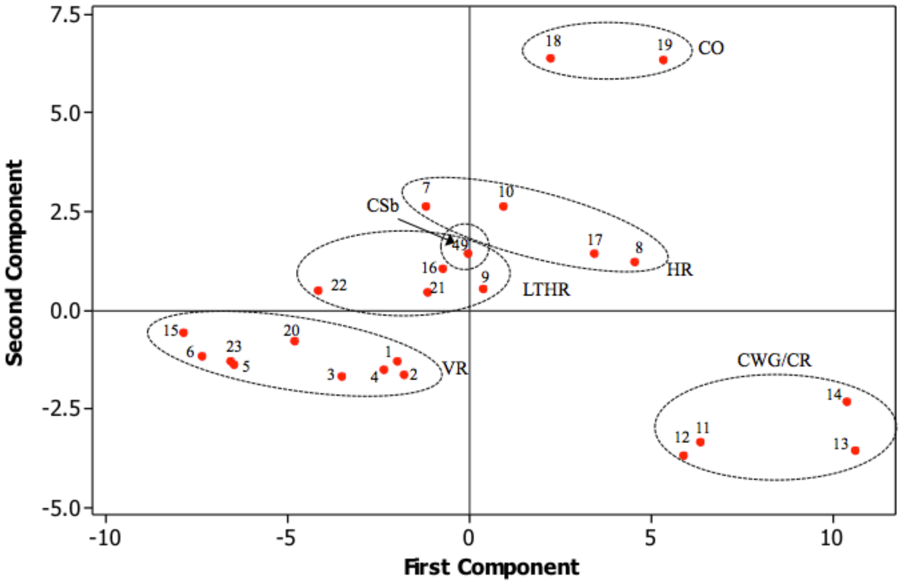

Figure 7.10 – PCA DNAPL049 using covariance matrix (CO = Coke Oven, HR = Horizontal Retort, LTHR = Low Temperature Horizontal Retort, VR = Vertical Retort, CWG = Carbureted Water Gas, CR = Creosote, CSb = Central Scotland Tar b)

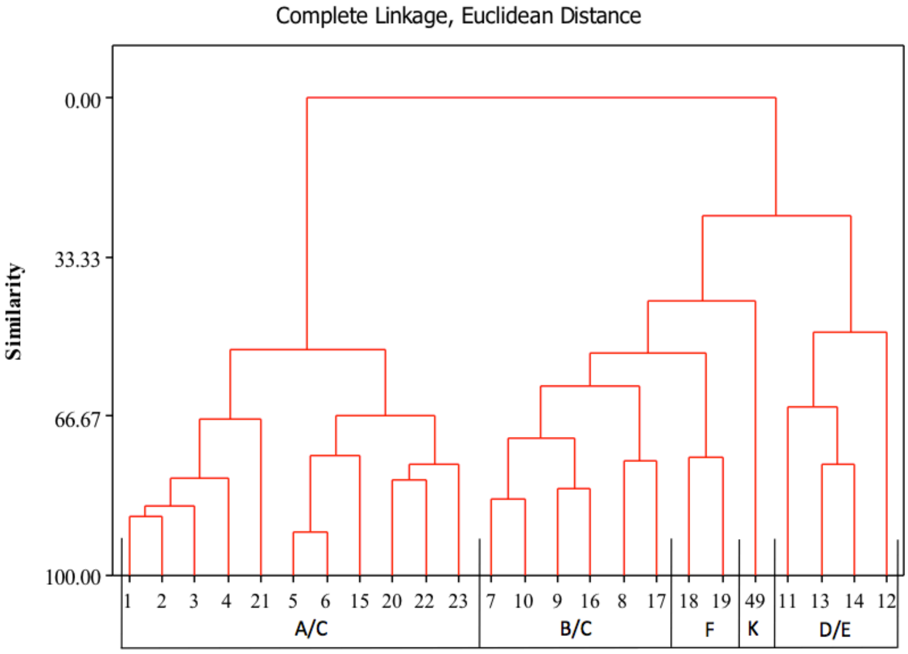

Figure 7.11 – HCA DNAPL049 using Euclidean distance and complete linkage mechanisms (A=Vertical Retort, B = Horizontal Retort, C = Low Temperature Horizontal Retort, D = Creosote, E = Carbureted Water Gas, F = Coke oven, K = Central Scotland Tar b)

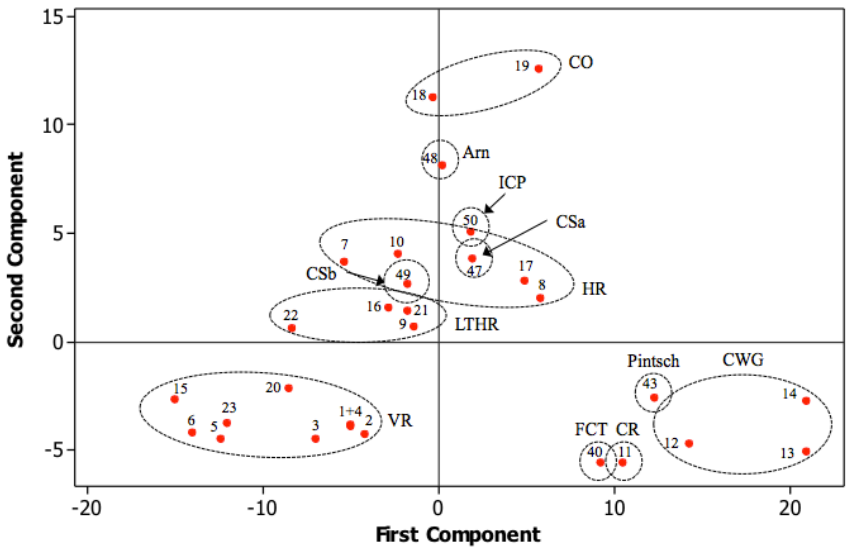

Figure 7.12 – PCA full data set using covariance matrix (CO = Coke Oven, HR = Horizontal Retort, LTHR = Low Temperature Horizontal Retort, VR = Vertical Retort, CWG = Carbureted Water Gas, CR = Creosote, FCT = Florida Coal Tar, Pintsch = Pintsch Gas Tar, LTCO = Low Temperature Coke Oven Tar, CSa = Central Scotland Tar a, CSb = Central Scotland Tar b, Arn = Arnhem Tar)

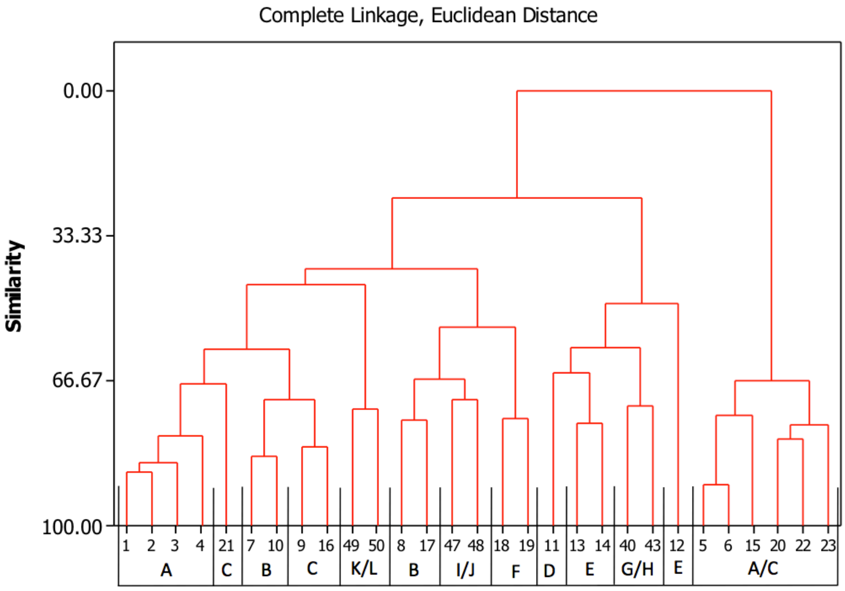

Figure 7.13 – HCA full data set using Euclidean distance and complete linkage mechanisms (A=Vertical Retort, B = Horizontal Retort, C = Low Temperature Horizontal Retort, D = Creosote, E = Carbureted Water Gas, F = Coke oven, G = Florida Coal Tar, H = Pintsch Gas Tar, I = Central Scotland Tar a, J = Arnhem Tar, K = Central Scotland Tar b, L = Low Temperature Coke Oven Tar).

The PCA analysis of the full database of samples, including all new samples, is shown in figure 7.12 with the individual sample interpretations largely unaffected. The exception to this trend is sample D49 that falls within the LTHR region when the PCA analysis is performed without the other new samples (D40, D43, D47, D48 and D50) excluded. However, the inclusion of the other new tar samples moves D49 into the HR tar region suggesting that the sample may be derived from a HR process rather than a LTHR process. In both cases the sample falls near to the edge of the production process regions, which may suggest the result is borderline between the LTHR and HR regions. It is possible that sample D49 is in fact a mixture of both LTHR and HR tar and therefore plots close to each of these regions. The HCA analysis of the full database of samples, including all new samples, is shown in figure 7.13.

# Chapter 8

# Conclusions

## 8.1 Research Aims and Objectives

The following research aims and objectives were outlined in Chapter 1:

1. To apply existing coal tar GCxGC analysis methods, including multivariate statistical analysis, to samples produced by production processes that have not been previously analysed.
2. The apply existing coal tar GCxGC analysis methods developed using British based coal tars, including multivariate statistical analysis, to tar samples produced from outside of the UK.
3. The development of a post extraction derivatization method to increase the number of compounds, particularly hydroxylated PAHs, which can be detected within coal tar.
4. The development of a database of compounds present within coal tars and the evaluation of the differences produced by different production processes.
5. The expansion of the existing coal tar database for the multivariate statistical analysis of coal tar and the assessment of the influence of additional samples on data interpretation.

Aim and objective no. 1 was achieved within the work presented in chapter 1 with the samples from Florida USA, as well as in chapter 6 with the Woodall-Duckham Inclined Chamber Plant tar and chapter 7 with the Pintsch Oil Gas tar. Both the Florida and Pintsch gas samples fell within the regions that would be expected with both tar types being oil-based tars falling close to the CWG region in the PCA analysis. The Inclined Chamber Plant tar fell within the HR tar region on the PCA analysis suggested that the PCA analysis is not capable of distinguishing an ICP tar from a HR tar.

Aim and Objective no. 2 was achieved within the work presented in chapter 1, with the Florida samples from the USA, and chapter 7, with the Pintsch Gas tar from the Netherlands. Chapter 7 also presents the PCA and HCA analysis of samples from Arnhem, the Netherlands. In all cases the statistical analysis developed using British coal tars could be applied to samples produced from outside of the UK.

Aim and Objective no. 3 was achieved within the work presented in chapter 5 with post extracted derivatization applied to a sample of Creosote, with 255 derivatized hydroxylated PAHs detected. The vast majority of the derivatized compounds detected within the creosote sample analysed in chapter 5 would not be detectable without derivatization. Post extraction derivatization was also applied to the samples presented within chapter 6, with a database of 16 tars produced from 5 different production processes as well as a single Inclined Chamber Plant tar.

Aim and Objective no. 4 was achieved within the work presented in chapter 6 with a database of 16 tar samples produced from 5 different production processes. The total number of detectable compounds is also presented in chapter 4, Creosote, and Chapter 7, Pintsch Gas tar. The database of compounds presented in chapter 6 contains 2373 unique compounds detected within at least 1 of the tar samples. The database of compounds presented in chapter number 7 is unique, as the overall composition of a Pintsch Gas tar has never previously been published.

Aim and Objective no. 5 was achieved within the work presented within chapter 7 with all new samples added to the existing British database for PCA and HCA analysis. With the addition of 6 new samples including the Arnhem tar, Inclined Chamber Plant tar, Perth tar, Falkirk Tar, Pintsch Gas tar and the average of the Florida tar samples the PCA analysis remains intact and capable of discriminating between different tar types.

This thesis presents the refinement of existing methods for analysis of coal tar using GCxGC, as well as the development of new methods, and expands the scope of using

GCxGC for the analysis of coal tar. The database of compounds produced is unique to the scientific literature, as the samples cover a wide range of production processes from a wide range of locations. The analysis of a Pintsch Gas tar is of particular note, as a full analysis of a Pintsch gas tar has never been published with the vast majority of the literature coming form the early 20th century. The work presented within this thesis fulfills all of the aims and objectives put forward for the project.

## 8.2 Future Work

The comprehensive database of compounds detected within tars produced by varying production processes is unique and could be further expanded upon by the addition of samples from other production processes. The data presented within this thesis also presents the compounds detected within Inclined Chamber Plants and by the Pintsch Gas processes but addition production processes such as X could be included to further expand the database and increase it's novelty. The database could be further expanded by the inclusion of tars produced in countries other than the UK as the feedstock coals used to produce the tars may vary greatly depending on the country of production.

The work presented in chapter 4 on the application of the existing statistical methods to a US based tar could be further expanded on by the addition of additional samples from the US. The tar analysed in chapter 4 came from the CWG process and the analysis of US coal gasification tars would further validate the method for the analysis of non-UK tars. Additional CWG tars from the US would also be important to analyse in order to assess how the different potential feedstock oils used affected the overall tar composition and the interpretation of the PCA results.

The derivatization method presented in chapter 5 could be further expanded upon by the use of additional derivatization techniques as well as the assessment of additional silylation reagents. BSTFA with 1% TMCS was used to derivatize all samples, however other silylation reagents are available such as MTBSFTA and MSTFA.

These could be assessed to see which reagent produces the best results for analysing coal tar. Alkylation could also be an important derivatization reaction that could be applied to coal tars in an effect to detect fatty acids. Alkylation using BF3 methanol produces converts fatty acids into fatty acids methyl esters and produces a permanent derivatized product. This can be used in tandem with silylation, with alkylation being used first, in order to increase the potential number of compounds that could be detected.

Column chromatography is commonly used for the analysis of coal tars using GC-MS as this allows for different chemical classes to be separated and analysed using GC-MS without the need for GCxGC separation. However this could be applied to samples that are to be analysed using GCxGC to increase the potential number of compounds that can be detected. Currently the potential number of compounds that can be detected are limited by the concentration of the largest peak within the sample, usually Naphthalene or Phenanthrene in the case of coal tars. The current method for the analysis of coal tar uses 1ul of sample taken from 10ml with a split ratio of 50. This means that 1/500000th of the original concentration of the compounds reaches the detector and in some cases is still close to the point of detector saturation, and so potentially damaging it. If a column separation method could be developed that separates the PAHs from other compound types, such as heterocycles and hydroxylated PAHs, the PAH fraction could be run under the same conditions but the other fraction/s could be run at a lower dilution factor and therefore increase the potential number of compounds detected.

Another possible column chromatography application method would be the use of amide impregnated silica gel to extract acidic compounds, with an aim of analysing fatty acids, from the coal tar samples and so increasing the potential scope of the analysis method.

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# Appendices

A comprehensive database of compounds detected within the tars, and presented in chapter 6, is shown below in Appendix A.

Appendix B is in the form of a digital excel file containing the compounds database information for all samples as well as the statistical values used for all multivariate statistical analysis.

# Appendix A

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C10-Alkene | C10H20 | 55 | 5.1, 1.820 |
| C10-Alkene | C10H20 | 55 | 5.3, 1.735 |
| C10-Alkene | C10H20 | 55 | 5.5, 1.845 |
| C10-Alkene | C10H20 | 55 | 5.7, 1.790 |
| C11-Alkene | C11H22 | 55 | 6.3, 1.865 |
| C11-Alkene | C11H22 | 55 | 6.6, 1.830 |
| C11-Alkene | C11H22 | 55 | 7.1, 1.890 |
| C12-Alkene | C12H24 | 55 | 7.9, 2.105 |
| C12-Alkene | C12H24 | 55 | 8.2, 2.050 |
| C12-Alkene | C12H24 | 55 | 8.5, 2.080 |
| C13-Alkene | C13H26 | 55 | 9.0, 2.305 |
| C13-Alkene | C13H26 | 55 | 9.8, 2.495 |
| C13-Alkene | C13H26 | 55 | 10.2, 2.540 |
| C13-Alkene | C13H26 | 55 | 10.5, 2.570 |
| C14-Alkene | C14H28 | 55 | 11.5, 3.095 |
| C14-Alkene | C14H28 | 55 | 12.2, 2.985 |
| C14-Alkene | C14H28 | 55 | 12.7, 2.995 |
| C15-Alkene | C15H30 | 55 | 15.0, 3.405 |
| C15-Alkene | C15H30 | 55 | 15.5, 3.400 |
| C15-Alkene | C15H30 | 55 | 15.9, 3.420 |
| C16-Alkene | C16H32 | 55 | 18.1, 3.715 |
| C16-Alkene | C16H32 | 55 | 18.7, 3.670 |
| C16-Alkene | C16H32 | 55 | 19.1, 3.835 |
| C17-Alkene | C17H34 | 55 | 21.4, 3.980 |
| C17-Alkene | C17H34 | 55 | 21.7, 4.025 |
| C17-Alkene | C17H34 | 55 | 21.9, 3.885 |
| C17-Alkene | C17H34 | 55 | 22.4, 3.860 |
| C18-Alkene | C18H36 | 55 | 24.7, 4.035 |
| C18-Alkene | C18H36 | 55 | 25.2, 4.000 |
| C18-Alkene | C18H36 | 55 | 25.7, 3.945 |
| C19-Alkene | C19H38 | 55 | 27.9, 4.120 |
| C19-Alkene | C19H38 | 55 | 28.5, 4.055 |
| C20-Alkene | C20H40 | 55 | 31.1, 4.175 |
| C20-Alkene | C20H40 | 55 | 31.6, 4.095 |
| C21-Alkene | C21H42 | 55 | 34.2, 4.200 |
| C21-Alkene | C21H42 | 55 | 34.7, 4.125 |
| C22-Alkene | C22H44 | 55 | 37.1, 4.250 |
| C22-Alkene | C22H44 | 55 | 37.6, 4.155 |
| C23-Alkene | C23H46 | 55 | 40.0, 4.255 |
| C23-Alkene | C23H46 | 55 | 42.0, 4.345 |
| C24-Alkene | C24H48 | 55 | 42.7, 4.295 |
| C25-Alkene | C25H50 | 55 | 45.4, 4.290 |
| C26-Alkene | C26H52 | 55 | 48.0, 4.245 |
| C27-Alkene | C27H54 | 55 | 50.4, 4.305 |
| C28-Alkene | C28H56 | 55 | 52.8, 4.335 |
| C29-Alkene | C29H58 | 55 | 55.1, 4.345 |
| C11 n-alkane | C11H24 | 57 | 6.2, 1.920 |
| C12 n-alkane | C12H26 | 57 | 7.8, 2.150 |
| C13 n-alkane | C13H28 | 57 | 9.6, 2.710 |
| C14 n-alkane | C14H30 | 57 | 11.9, 3.260 |
| C15 n-alkane | C15H32 | 57 | 14.7, 3.730 |

Appendix 1 – Aliphatic database

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C16 n-alkane | C16H34 | 57 | 17.7, 4.085 |
| C17 n-alkane | C17H36 | 57 | 21.0, 4.265 |
| C18 n-alkane | C18H38 | 57 | 24.3, 4.385 |
| C19 n-alkane | C19H40 | 57 | 27.5, 4.470 |
| C20 n-alkane | C20H42 | 57 | 30.7, 4.500 |
| C21 n-alkane | C21H44 | 57 | 33.8, 4.525 |
| C22 n-alkane | C22H46 | 57 | 36.7, 4.520 |
| C23 n-alkane | C23H48 | 57 | 39.5, 4.525 |
| C24 n-alkane | C24H50 | 57 | 42.3, 4.550 |
| C25 n-alkane | C25H52 | 57 | 44.9, 4.535 |
| C26 n-alkane | C26H54 | 57 | 47.5, 4.560 |
| C27 n-alkane | C27H56 | 57 | 50.0, 4.610 |
| C28 n-alkane | C28H58 | 57 | 52.3, 4.545 |
| C29 n-alkane | C29H60 | 57 | 54.6, 4.535 |
| C30 n-alkane | C30H62 | 57 | 56.8, 4.565 |
| C31 n-alkane | C31H64 | 57 | 59.1, 4.550 |
| C32 n-alkane | C32H66 | 57 | 61.2, 4.575 |
| C33 n-alkane | C33H68 | 57 | 63.1, 4.565 |
| C34 n-alkane | C34H70 | 57 | 65.2, 4.550 |
| C11 Branched Alkane | C11H24 | 57 | 5.2, 1.950 |
| C11 Branched Alkane | C11H24 | 57 | 5.6, 1.970 |
| C12 Branched Alkane | C12H26 | 57 | 6.5, 2.005 |
| C12 Branched Alkane | C12H26 | 57 | 6.9, 2.010 |
| C11 Branched Alkane | C11H24 | 57 | 7.1, 2.000 |
| C12 Branched Alkane | C12H26 | 57 | 7.2, 2.050 |
| C13 Branched Alkane | C13H28 | 57 | 7.8, 2.265 |
| C13 Branched Alkane | C13H28 | 57 | 8.2, 2.445 |
| C13 Branched Alkane | C13H28 | 57 | 8.3, 2.395 |
| C13 Branched Alkane | C13H28 | 57 | 8.6, 2.475 |
| C14 Branched Alkane | C14H30 | 57 | 8.7, 2.630 |
| C14 Branched Alkane | C14H30 | 57 | 9.8, 2.850 |
| C14 Branched Alkane | C14H30 | 57 | 10.6, 3.045 |
| C14 Branched Alkane | C14H30 | 57 | 10.9, 3.250 |
| C14 Branched Alkane | C14H30 | 57 | 11.1, 3.140 |
| C14 Branched alkane | C14H30 | 57 | 11.7, 3.375 |
| C15 Branched Alkane | C15H32 | 57 | 13.0, 3.750 |
| C15 Branched alkane | C15H32 | 57 | 13.3, 3.580 |
| C15 Branched Alkane | C15H32 | 57 | 13.4, 3.665 |
| C15 branched alkane | C15H32 | 57 | 13.7, 3.555 |
| C15 Branched Alkane | C15H32 | 57 | 15.6, 4.180 |
| C16 Branched alkane | C16H34 | 57 | 15.8, 4.015 |
| C16 Branched Alkane | C16H34 | 57 | 16.2, 4.105 |
| C16 Branched Alkane | C16H34 | 57 | 16.3, 4.090 |
| C16 Branched Alkane | C16H34 | 57 | 16.7, 4.040 |
| C16 Branched alkane | C16H34 | 57 | 17.0, 4.205 |
| C16 Branched alkane | C16H34 | 57 | 17.7, 4.260 |
| C16 Branched Alkane | C16H34 | 57 | 18.6, 4.465 |
| C17 Branched Alkane | C17H36 | 57 | 18.9, 4.295 |
| C17 Branched Alkane | C17H36 | 57 | 19.5, 4.350 |
| C17 Branched Alkane | C17H36 | 57 | 19.9, 4.300 |
| C17 Branched Alkane | C17H36 | 57 | 21.7, 4.620 |
| C18 Branched Alkane | C18H38 | 57 | 22.8, 4.490 |

Appendix 1 – Aliphatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C18 Branched Alkane | C18H38 | 57 | 23.2, 4.620 |
| C18 Branched Alkane | C18H38 | 57 | 24.7, 4.730 |
| C19 Branched Alkane Dimethyl | C19H40 | 57 | 26.0, 4.535 |
| Heptadecane, 2,6,10,14-tetramethyl- | C21H44 | 57 | 26.3, 4.870 |
| C19 branched alkane | C19H40 | 57 | 26.4, 4.785 |
| C19 Branched Alkane | C19H40 | 57 | 27.2, 4.745 |
| C19 Branched Alkane | C19H40 | 57 | 28.6, 4.625 |
| C20 Branched Alkane | C20H42 | 57 | 28.9, 4.610 |
| C20 branched alkane | C20H42 | 57 | 29.3, 4.810 |
| C20 Branched Alkane | C20H42 | 57 | 29.6, 4.515 |
| C20 Branched Alkane | C20H42 | 57 | 31.7, 4.645 |
| C21 Branched Alkane | C21H44 | 57 | 34.7, 4.615 |
| C21 branched alkane | C21H44 | 57 | 35.4, 4.855 |
| C21 branched alkane | C21H44 | 57 | 35.8, 4.820 |
| C22 Branched Alkane | C22H46 | 57 | 37.6, 4.630 |
| C22 branched alkane | C22H46 | 57 | 38.3, 4.840 |
| Pristane | C19H40 | 57 | 20.2, 4.665 |
| Phytane | C20H42 | 57 | 23.7, 4.745 |
| C4-Cyclohexane | C10H20 | 55 | 5.8, 1.720 |
| C5-Cyclohexane | C11H22 | 55 | 7.4, 1.845 |
| C6-Cyclohexane | C12H24 | 55 | 9.2, 2.320 |
| C7-Cyclohexane | C13H26 | 55 | 11.5, 2.810 |
| C8-Cyclohexane | C14H28 | 55 | 14.4, 3.230 |
| C9-Cyclohexane | C15H30 | 55 | 17.5, 3.580 |
| C10-Cyclohexane | C16H32 | 55 | 20.9, 3.755 |
| C11-Cyclohexane | C17H34 | 55 | 24.3, 3.925 |
| C12-Cyclohexane | C18H36 | 55 | 27.8, 3.975 |
| C13-Cyclohexane | C19H38 | 55 | 31.1, 4.020 |
| C14-Cyclohexane | C20H40 | 55 | 34.3, 4.075 |
| C15-Cyclohexane | C21H42 | 55 | 37.4, 4.085 |
| C16-Cyclohexane | C22H44 | 55 | 40.4, 4.095 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 5.2, 1.365 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 5.4, 1.660 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 5.6, 1.640 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 5.9, 1.605 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 6.3, 1.600 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 6.4, 1.605 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 6.7, 1.595 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 6.8, 1.595 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 7.1, 1.580 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 7.3, 1.620 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 7.7, 1.675 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 7.8, 1.690 |
| C5-Cylcopentadiene isomer | C10H16 | 136 | 7.9, 1.700 |
| C5-Cyclopentene isomer | C10H18 | 138 | 5.3, 1.680 |
| C5-Cyclopentene isomer | C10H18 | 138 | 5.7, 1.685 |
| C5-Cyclopentene isomer | C10H18 | 138 | 5.9, 1.690 |
| C5-Cyclopentene isomer | C10H18 | 138 | 6.2, 1.670 |
| C5-Cyclopentene isomer | C10H18 | 138 | 6.4, 1.665 |
| C5-Cyclopentene isomer | C10H18 | 138 | 7.2, 1.650 |
| C5-Cyclopentene isomer | C10H18 | 138 | 7.7, 1.740 |
| 1,1'-Bicyclopentyl | C10H18 | 138 | 6.7, 1.675 |
| C6-Cylcopentadiene isomer | C11H18 | 150 | 6.4, 1.685 |

Appendix 1 – Aliphatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C6-Cylcopentadiene isomer | C11H18 | 150 | 6.7, 1.695 |
| C6-Cylcopentadiene isomer | C11H18 | 150 | 6.9. 1.700 |
| C6-Cylcopentadiene isomer | C11H18 | 150 | 7.2, 1.685 |
| C6-Cylcopentadiene isomer | C11H18 | 150 | 7.4, 1.730 |
| C6-Cylcopentadiene isomer | C11H18 | 150 | 7.7, 1.775 |
| C6-Cylcopentadiene isomer | C11H18 | 150 | 8.1, 1.855 |
| C6-Cylcopentadiene isomer | C11H18 | 150 | 8.4, 1.885 |
| C6-Cylcopentadiene isomer | C11H18 | 150 | 8.7, 1.915 |
| C6-Cylcopentadiene isomer | C11H18 | 150 | 8.8, 1.925 |
| C6-Cylcopentadiene isomer | C11H18 | 150 | 9.1, 1.970 |
| C6-Cyclopentene isomer | C11H20 | 152 | 6.5, 1.790 |
| C6-Cyclopentene isomer | C11H20 | 152 | 6.8, 1.740 |
| C6-Cyclopentene isomer | C11H20 | 152 | 7.1, 1.735 |
| C6-Cyclopentene isomer | C11H20 | 152 | 7.3, 1.795 |
| C6-Cyclopentene isomer | C11H20 | 152 | 7.4, 1.805 |
| C6-Cyclopentene isomer | C11H20 | 152 | 7.8, 1.865 |
| C6-Cyclopentene isomer | C11H20 | 152 | 8.2, 1.915 |
| C6-Cyclopentene isomer | C11H20 | 152 | 9.1, 2.060 |
| C11H22 | ??? | 154 | 6.4, 1.850 |
| C11H22 | ??? | 154 | 7.3, 1.875 |
| C7-Cylcopentadiene isomer | C12H20 | 164 | 8.5, 2.010 |
| C7-Cylcopentadiene isomer | C12H20 | 164 | 8.9, 2.075 |
| 164, 149 | C12H20 | 164 | 7.6, 1.835 |
| 164, 149 | C12H20 | 164 | 10.0, 2.140 |
| 164, 149 | C12H20 | 164 | 10.9, 2.215 |
| 164, 149 | C12H20 | 164 | 11.1, 2.240 |
| 164, 135 | C12H20 | 164 | 11.4, 2.290 |
| C7-Cyclopentene isomer | C12H22 | 166 | 6.8, 1.875 |
| C7-Cyclopentene isomer | C12H22 | 166 | 7.2, 1.850 |
| C7-Cyclopentene isomer | C12H22 | 166 | 7.8, 1.735 |
| C7-Cyclopentene isomer | C12H22 | 166 | 8.0, 2.055 |
| C7-Cyclopentene isomer | C12H22 | 166 | 8.1, 2.065 |
| C7-Cyclopentene isomer | C12H22 | 166 | 8.4, 2.105 |
| C7-Cyclopentene isomer | C12H22 | 166 | 8.9, 2.170 |
| C7-Cyclopentene isomer | C12H22 | 166 | 9.2, 2.205 |
| C7-Cyclopentene isomer | C12H22 | 166 | 9.5, 2.270 |
| C7-Cyclopentene isomer | C12H22 | 166 | 9.9, 2.305 |
| C7-Cyclopentene isomer | C12H22 | 166 | 10.2, 2.315 |
| 1,1'-Bicyclohexyl | C12H22 | 166 | 11.8, 2.525 |

Appendix 1 – Aliphatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Toluene | C7H8 | 91 | 5.2, 1.030 |
| Styrene | C8H8 | 104 | 5.2, 1.320 |
| Ethylbenzene | C8H10 | 106 | 5.2, 1.235 |
| Indene | C9H8 | 116 | 8.3, 1.430 |
| Methyl Styrene | C9H10 | 118 | 6.6, 1.360 |
| Benzene, 2-propenyl- | C9H10 | 118 | 6.8, 1.345 |
| Benzene, cyclopropyl- | C9H10 | 118 | 7.4, 1.390 |
| Indane | C9H10 | 118 | 7.7, 1.425 |
| Benzene, 1-ethyl-2-methyl- | C9H12 | 120 | 5.2, 1.420 |
| C3-Benzene | C9H12 | 120 | 5.7, 1.430 |
| C3-Benzene | C9H12 | 120 | 5.9, 1.400 |
| C3-Benzene | C9H12 | 120 | 6.3, 1.420 |
| C3-Benzene | C9H12 | 120 | 6.5, 1.395 |
| C3-Benzene | C9H12 | 120 | 7.1, 1.390 |
| Naphthalene | C10H8 | 128 | 12.3, 1.735 |
| 1,2-dihydronapthalene | C10H10 | 130 | 10.3, 1.705 |
| 1,4-dihydronapthalene | C10H10 | 130 | 10.6, 1.705 |
| Methyl Indene | C10H10 | 130 | 11.1, 1.745 |
| C4-Benzene 1DB | C10H12 | 132 | 6.7, 1.430 |
| C4-Benzene 1DB | C10H12 | 132 | 7.0, 1.420 |
| C4-Benzene 1DB | C10H12 | 132 | 7.4, 1.460 |
| C4-Benzene 1DB | C10H12 | 132 | 7.6, 1.480 |
| C4-Benzene 1DB | C10H12 | 132 | 8.0, 1.560 |
| C4-Benzene 1DB | C10H12 | 132 | 8.2, 1.570 |
| C4-Benzene 1DB | C10H12 | 132 | 8.4, 1.580 |
| C4-Benzene 1DB | C10H12 | 132 | 8.6, 1.655 |
| C4-Benzene 1DB | C10H12 | 132 | 9.2, 1.670 |
| C4-Benzene 1DB | C10H12 | 132 | 9.6, 1.720 |
| Methyl Indane | C10H12 | 132 | 9.9, 1.740 |
| 1,2,3,4-tetrahydro-Napthalene | C10H12 | 132 | 10.6, 1.745 |
| C4-Benzene | C10H14 | 134 | 6.4, 1.495 |
| C4-Benzene | C10H14 | 134 | 6.5, 1.480 |
| C4-Benzene | C10H14 | 134 | 6.7, 1.440 |
| C4-Benzene | C10H14 | 134 | 7.2, 1.460 |
| C4-Benzene | C10H14 | 134 | 7.4, 1.480 |
| C4-Benzene | C10H14 | 134 | 7.6, 1.510 |
| C4-Benzene | C10H14 | 134 | 7.8, 1.540 |
| C4-Benzene | C10H14 | 134 | 8.0, 1.560 |
| C4-Benzene | C10H14 | 134 | 8.2, 1.575 |
| C4-Benzene | C10H14 | 134 | 8.5, 1.665 |
| C4-Benzene | C10H14 | 134 | 8.7, 1.670 |
| C4-Benzene | C10H14 | 134 | 9.6, 1.755 |
| 1H-Indene, 1-ethylidene- | C11H10 | 141 | 14.0, 1.950 |
| 1H-Indene, 1-ethylidene- | C11H10 | 141 | 14.4, 1.940 |
| 1H-Indene, 1-ethylidene- | C11H10 | 141 | 14.7, 1.955 |
| 1H-Indene, 1-ethylidene- | C11H10 | 141 | 14.9, 1.945 |
| 2-Methyl Naphthalene | C11H10 | 142 | 15.2, 2.030 |
| 1-Methyl Naphthalene | C11H10 | 142 | 16.2, 1.960 |
| Dimethyl Indene | C11H12 | 144 | 10.2, 1.755 |
| Dimethyl Indene | C11H12 | 144 | 10.7, 1.790 |
| Benzene, 1-cyclopenten-1-yl- | C11H12 | 144 | 11.0, 1.820 |
| Ethenyl Dihydro Indene | C11H12 | 144 | 11.2, 1.865 |
| Ethenyl Dihydro Indene | C11H12 | 144 | 11.4, 1.885 |

Appendix 2 – Aromatic database

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Ethenyl Dihydro Indene | C11H12 | 144 | 11.6, 1.895 |
| Dimethyl Indene | C11H12 | 144 | 12.0, 1.920 |
| Dimethyl Indene | C11H12 | 144 | 12.1, 1.865 |
| Dimethyl Indene | C11H12 | 144 | 12.7, 1.960 |
| Dimethyl Indene | C11H12 | 144 | 12.8, 1.920 |
| Dimethyl Indene | C11H12 | 144 | 13.0, 1.965 |
| Dimethyl Indene | C11H12 | 144 | 13.4, 1.955 |
| Methyl Dihydro Naphthalene | C11H12 | 144 | 13.6, 2.050 |
| Dimethyl Indene | C11H12 | 144 | 13.9, 2.000 |
| 2-Ethyl-1-H-Indene | C11H12 | 144 | 14.1, 1.980 |
| Dimethyl Indene | C11H12 | 144 | 14.3, 2.015 |
| Dimethyl Indene | C11H12 | 144 | 14.8, 1.990 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 8.1, 1.640 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 8.4, 1.645 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 8.6, 1.660 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 8.9, 1.705 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 9.1, 1.740 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 9.3, 1.750 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 9.7, 1.810 |
| C5-Benzene 1DB | C11H14 | 146 | 10.0, 1.825 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 10.2, 1.875 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 10.4, 1.875 |
| C5-Benzene 1DB | C11H14 | 146 | 10.6, 1.885 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 10.7, 1.885 |
| C5-Benzene 1DB | C11H14 | 146 | 11.1, 1.915 |
| C5-Benzene 1DB | C11H14 | 146 | 11.3, 1.935 |
| C5-Benzene 1DB | C11H14 | 146 | 11.4, 1.965 |
| C5-Benzene 1DB | C11H14 | 146 | 11.9, 1.965 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 12.2, 2.060 |
| C5-Benzene 1DB | C11H14 | 146 | 12.4, 2.020 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 12.7, 2.050 |
| Dihydro, dimethyl Indene | C11H14 | 146 | 12.9, 2.050 |
| Naphthalene, 1,2,3,4-tetrahydro-5-methyl- | C11H14 | 146 | 13.1, 2.045 |
| Naphthalene, 1,2,3,4-tetrahydro-6-methyl- | C11H14 | 146 | 13.4, 2.085 |
| C5-Benzene | C11H16 | 148 | 7.6, 1.605 |
| C5-Benzene | C11H16 | 148 | 7.8, 1.650 |
| C5-Benzene | C11H16 | 148 | 7.9, 1.635 |
| C5-Benzene | C11H16 | 148 | 8.0, 1.630 |
| Benzene, pentamethyl- | C11H16 | 148 | 8.2, 1.660 |
| C5-Benzene | C11H16 | 148 | 8.9, 1.770 |
| C5-Benzene | C11H16 | 148 | 9.0, 1.790 |
| C5-Benzene | C11H16 | 148 | 9.1, 1.810 |
| C5-Benzene | C11H16 | 148 | 9.3, 1.825 |
| C5-Benzene | C11H16 | 148 | 9.4, 1.835 |
| C5-Benzene | C11H16 | 148 | 9.6, 1.850 |
| C5-Benzene | C11H16 | 148 | 10.0, 1.875 |
| C5-Benzene | C11H16 | 148 | 10.2, 1.915 |
| C5-Benzene | C11H16 | 148 | 10.6, 1.935 |
| C5-Benzene | C11H16 | 148 | 11.0, 1.950 |
| C5-Benzene | C11H16 | 148 | 11.5, 1.995 |
| Acenaphthylene | C12H8 | 152 | 22.2, 2.015 |
| Acenaphthene | C12H10 | 154 | 23.0, 2.100 |
| Biphenyl | C12H10 | 154 | 18.5, 2.035 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Naphthalene, 2-ethenyl- | C12H10 | 154 | 19.7, 2.095 |
| C12H12 | C12H12 | 156 | 15.7, 2.100 |
| C12H12 | C12H12 | 156 | 17.0, 2.145 |
| C12H12 | C12H12 | 156 | 17.3, 2.165 |
| C12H12 | C12H12 | 156 | 17.5, 2.195 |
| C12H12 | C12H12 | 156 | 17.7, 2.165 |
| C12H12 | C12H12 | 156 | 18.0, 2.185 |
| Naphthalene, 2-ethyl- | C12H12 | 156 | 18.2, 2.175 |
| 2,6 and 2,7 Dimethyl Naphthalene | C12H12 | 156 | 18.5, 2.225 |
| Naphthalene, 1-ethyl- | C12H12 | 156 | 18.7, 2.130 |
| 1,6 and 1,7 and 1,3 Dimethyl Naphthalene | C12H12 | 156 | 19.2, 2.195 |
| 2,3 Dimethyl Naphthalene | C12H12 | 156 | 19.4, 2.210 |
| 1,4 Dimethyl Naphthalene | C12H12 | 156 | 20.0, 2.220 |
| 1,5 Dimethyl Naphthalene | C12H12 | 156 | 20.3, 2.175 |
| 1,2 Dimethyl Naphthalene | C12H12 | 156 | 20.5, 2.170 |
| 1,8 Dimethyl Naphthalene | C12H12 | 156 | 21.0, 2.175 |
| C3-Indene isomer | C12H14 | 158 | 13.2, 2.070 |
| C3-Indene isomer | C12H14 | 158 | 13.4, 2.095 |
| C3-Indene isomer | C12H14 | 158 | 13.6, 2.080 |
| C3-Indene isomer | C12H14 | 158 | 13.8, 2.100 |
| C3-Indene isomer | C12H14 | 158 | 14.1, 2.130 |
| C3-Indene isomer | C12H14 | 158 | 14.3, 2.090 |
| C3-Indene isomer | C12H14 | 158 | 14.8, 2.125 |
| C3-Indene isomer | C12H14 | 158 | 15.1, 2.120 |
| C3-Indene isomer | C12H14 | 158 | 15.4, 2.150 |
| C3-Indene isomer | C12H14 | 158 | 15.8, 2.165 |
| C3-Indene isomer | C12H14 | 158 | 15.9, 2.265 |
| C3-Indene isomer | C12H14 | 158 | 16.1, 2.245 |
| C3-Indene isomer | C12H14 | 158 | 16.5, 2.225 |
| C3-Indene isomer | C12H14 | 158 | 16.7, 2.235 |
| C3-Indene isomer | C12H14 | 158 | 16.9, 2.245 |
| C3-Indene isomer | C12H14 | 158 | 17.6, 2.245 |
| C3-Indene isomer | C12H14 | 158 | 18.0, 2.245 |
| C3-Indene isomer | C12H14 | 158 | 18.5, 2.240 |
| C3-Indene isomer | C12H14 | 158 | 18.7, 2.260 |
| C3-Indene isomer | C12H14 | 158 | 18.9, 2.250 |
| C3-Indene isomer | C12H14 | 158 | 19.1, 2.255 |
| C3-Dihydro indene | C12H16 | 160 | 9.1, 1.800 |
| C3-Dihydro indene | C12H16 | 160 | 9.9, 1.910 |
| C3-Dihydro indene | C12H16 | 160 | 10.1, 1.925 |
| C3-Dihydro indene | C12H16 | 160 | 10.4, 1.920 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 10.7, 1.985 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 10.9, 2.020 |
| C3-Dihydro indene | C12H16 | 160 | 11.2, 1.975 |
| C3-Dihydro indene | C12H16 | 160 | 11.5, 2.030 |
| C3-Indane | C12H16 | 160 | 11.7, 2.065 |
| Benzene, cyclohexyl- | C12H16 | 160 | 11.8, 2.045 |
| C3-Indane | C12H16 | 160 | 11.9, 2.025 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 12.0, 2.130 |
| C3-Indane | C12H16 | 160 | 12.1, 2.045 |
| C3-Indane | C12H16 | 160 | 12.4, 2.110 |
| C3-Indane | C12H16 | 160 | 12.6, 2.095 |
| C3-Indane | C12H16 | 160 | 12.8, 2.150 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 13.1, 2.170 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 13.2, 2.140 |
| Ethyl Tetrahydro Naphthalene | C12H16 | 160 | 13.5, 2.155 |
| C3-Indane | C12H16 | 160 | 13.6, 2.220 |
| C3-Dihydro indene | C12H16 | 160 | 13.8, 2.190 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 14.1, 2.330 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 14.2, 2.205 |
| Benzene, cyclohexyl- | C12H16 | 160 | 14.3, 2.235 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 14.4, 2.205 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 14.7, 2.180 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 14.9, 2.200 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 15.1, 2.220 |
| C3-Indane | C12H16 | 160 | 16.7, 2.320 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 17.1, 2.275 |
| C2-Tetrahydro Naphthalene | C12H16 | 160 | 17.6, 2.360 |
| C6-Benzene | C12H18 | 162 | 9.3, 1.880 |
| C6-Benzene | C12H18 | 162 | 9.4, 1.885 |
| C6-Benzene | C12H18 | 162 | 9.5, 1.920 |
| C6-Benzene | C12H18 | 162 | 9.6, 1.925 |
| C6-Benzene | C12H18 | 162 | 9.8, 1.970 |
| C6-Benzene | C12H18 | 162 | 10.0, 1.985 |
| C6-Benzene | C12H18 | 162 | 10.4, 2.040 |
| C6-Benzene | C12H18 | 162 | 10.6, 2.025 |
| C6-Benzene | C12H18 | 162 | 10.8, 2.065 |
| C6-Benzene | C12H18 | 162 | 11.0, 2.080 |
| C6-Benzene | C12H18 | 162 | 11.2, 2.110 |
| C6-Benzene | C12H18 | 162 | 11.4, 2.135 |
| C6-Benzene | C12H18 | 162 | 11.6, 2.155 |
| C6-Benzene | C12H18 | 162 | 12.0, 2.180 |
| C6-Benzene | C12H18 | 162 | 12.2, 2.200 |
| C6-Benzene | C12H18 | 162 | 12.4, 2.135 |
| C6-Benzene | C12H18 | 162 | 12.6, 2.210 |
| C6-Benzene | C12H18 | 162 | 12.8, 2.210 |
| C6-Benzene | C12H18 | 162 | 13.7, 2.195 |
| C6-Benzene | C12H18 | 162 | 14.5, 2.275 |
| C6-Benzene | C12H18 | 162 | 15.1, 2.295 |
| Fluorene | C13H10 | 166 | 26.6, 2.170 |
| 1H-Phenalene | C13H10 | 166 | 25.8, 2.170 |
| Benz[x]indene? | C13H10 | 166 | 27.0, 2.130 |
| Benz[x]indene? | C13H10 | 166 | 27.8, 2.130 |
| Benz[x]indene? | C13H10 | 166 | 28.4, 2.125 |
| Benz[x]indene? | C13H10 | 166 | 28.6, 2.140 |
| Diphenylmethane | C13H12 | 167 | 20.5, 2.055 |
| C1-Biphenyl | C13H12 | 168 | 18.5, 2.135 |
| C1-Biphenyl | C13H12 | 168 | 19.3, 2.165 |
| C1-Biphenyl | C13H12 | 168 | 21.5, 2.200 |
| C1-Biphenyl | C13H12 | 168 | 21.6, 2.225 |
| C1-Biphenyl | C13H12 | 168 | 21.9, 2.175 |
| C1-Biphenyl | C13H12 | 168 | 22.3, 2.180 |
| C3-Naphthalene 1DB | C13H12 | 168 | 23.1, 2.215 |
| C3-Naphthalene 1DB | C13H12 | 168 | 23.3, 2.200 |
| C3-Naphthalene 1DB | C13H12 | 168 | 23.8, 2.385 |
| C1-Biphenyl | C13H12 | 168 | 24.3, 2.230 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C1-Biphenyl | C13H12 | 168 | 24.7, 2.225 |
| C3-Naphthalene 1DB | C13H12 | 168 | 25.2, 2.230 |
| C3-Naphthalene 1DB | C13H12 | 168 | 25.5, 2.235 |
| C3-Naphthalene 1DB | C13H12 | 168 | 25.7, 2.260 |
| C3-Naphthalene 1DB | C13H12 | 168 | 26.6, 2.225 |
| C1-Biphenyl | C13H12 | 168 | 27.0, 2.210 |
| C3-Naphthalene 1DB | C13H12 | 168 | 27.2, 2.205 |
| C3-Naphthalene | C13H14 | 170 | 20.0, 2.270 |
| C3-Naphthalene | C13H14 | 170 | 21.3, 2.295 |
| C3-Naphthalene | C13H14 | 170 | 21.7, 2.335 |
| C3-Naphthalene | C13H14 | 170 | 21.9, 2.275 |
| C3-Naphthalene | C13H14 | 170 | 22.1, 2.295 |
| C3-Naphthalene | C13H14 | 170 | 22.5, 2.275 |
| C3-Naphthalene | C13H14 | 170 | 22.6, 2.325 |
| C3-Naphthalene | C13H14 | 170 | 22.8, 2.340 |
| C3-Naphthalene | C13H14 | 170 | 23.0, 2.305 |
| C3-Naphthalene | C13H14 | 170 | 23.3, 2.250 |
| C3-Naphthalene | C13H14 | 170 | 23.6, 2.340 |
| C3-Naphthalene | C13H14 | 170 | 24.3, 2.320 |
| C3-Naphthalene | C13H14 | 170 | 24.5, 2.315 |
| C3-Naphthalene | C13H14 | 170 | 25.3, 2.275 |
| C3-Naphthalene | C13H14 | 170 | 25.6, 2.290 |
| C3-Naphthalene | C13H14 | 170 | 26.4, 2.275 |
| C4-Indene | C13H16 | 172 | 14.8, 2.245 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 15.5, 2.270 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 15.7, 2.270 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 16.1, 2.320 |
| C4-Indene | C13H16 | 172 | 16.4, 2.350 |
| C4-Indene | C13H16 | 172 | 16.6, 2.305 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 16.9, 2.290 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 17.1, 2.330 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 17.8, 2.325 |
| C4-Indene | C13H16 | 172 | 18.0, 2.325 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 18.2, 2.395 |
| C4-Indene | C13H16 | 172 | 18.3, 2.350 |
| C4-Indene | C13H16 | 172 | 18.7, 2.355 |
| C4-Indene | C13H16 | 172 | 18.9, 2.360 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 19.0, 2.350 |
| C4-Indene | C13H16 | 172 | 19.3, 2.405 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 19.7, 2.460 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 19.9, 2.395 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 20.2, 2.335 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 20.8, 2.470 |
| C3-Dihydro Naphthalene | C13H16 | 172 | 21.1, 2.435 |
| C4-Dihydro Indene | C13H18 | 174 | 12.4, 2.225 |
| C4-Dihydro Indene | C13H18 | 174 | 13.0, 2.215 |
| C4-Dihydro Indene | C13H18 | 174 | 13.3, 2.250 |
| C4-Dihydro Indene | C13H18 | 174 | 13.6, 2.265 |
| C4-Dihydro Indene | C13H18 | 174 | 13.7, 2.300 |
| C4-Dihydro Indene | C13H18 | 174 | 13.9, 2.315 |
| C4-Indane | C13H18 | 174 | 14.1, 2.260 |
| C4-Dihydro Indene | C13H18 | 174 | 14.4, 2.295 |
| C4-Indane | C13H18 | 174 | 14.8, 2.310 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C3-Tetrahydro Naphthalene | C13H18 | 174 | 14.9, 2.345 |
| C3-Tetrahydro Naphthalene | C13H18 | 174 | 15.3, 2.340 |
| C3-Tetrahydro Naphthalene | C13H18 | 174 | 15.4, 2.385 |
| C3-Tetrahydro Naphthalene | C13H18 | 174 | 15.6, 2.375 |
| C4-Indane | C13H18 | 174 | 15.8, 2.345 |
| C4-Indane | C13H18 | 174 | 16.0, 2.290 |
| C4-Indane | C13H18 | 174 | 16.3, 2.545 |
| C4-Indane | C13H18 | 174 | 16.9, 2.395 |
| C3-Tetrahydro Naphthalene | C13H18 | 174 | 17.0, 2.470 |
| C4-Indane | C13H18 | 174 | 17.3, 2.450 |
| C4-Indane | C13H18 | 174 | 17.5, 2.455 |
| C3-Tetrahydro Naphthalene | C13H18 | 174 | 17.7, 2.455 |
| C3-Tetrahydro Naphthalene | C13H18 | 174 | 18.4, 2.450 |
| C3-Tetrahydro Naphthalene | C13H18 | 174 | 18.6, 2.455 |
| C4-Indane | C13H18 | 174 | 19.2, 2.450 |
| C7-Benzene | C13H20 | 176 | 11.4, 2.175 |
| C7-Benzene | C13H20 | 176 | 12.1, 2.285 |
| C7-Benzene | C13H20 | 176 | 12.6, 2.335 |
| C7-Benzene | C13H20 | 176 | 13.0, 2.370 |
| C7-Benzene | C13H20 | 176 | 13.3, 2.380 |
| C7-Benzene | C13H20 | 176 | 13.5, 2.395 |
| C7-Benzene | C13H20 | 176 | 13.8, 2.440 |
| C7-Benzene | C13H20 | 176 | 14.0, 2.410 |
| C7-Benzene | C13H20 | 176 | 14.1, 2.490 |
| C7-Benzene | C13H20 | 176 | 14.4, 2.465 |
| C7-Benzene | C13H20 | 176 | 14.8, 2.460 |
| C7-Benzene | C13H20 | 176 | 15.6, 2.505 |
| Phenanthrene | C14H10 | 178 | 34.9, 2.135 |
| Anthracene | C14H10 | 178 | 35.1, 2.150 |
| C1-Fluorene | C14H12 | 180 | 26.8, 2.225 |
| C1-Fluorene | C14H12 | 180 | 27.7, 2.265 |
| 1,1'-Biphenyl, 4-ethenyl- | C14H12 | 180 | 27.8, 2.205 |
| C1-Fluorene | C14H12 | 180 | 29.2, 2.210 |
| C1-Fluorene | C14H12 | 180 | 29.4, 2.285 |
| C1-Fluorene | C14H12 | 180 | 30.1, 2.275 |
| C1-Fluorene | C14H12 | 180 | 30.3, 2.270 |
| C1-Fluorene | C14H12 | 180 | 30.6, 2.260 |
| C1-Fluorene | C14H12 | 180 | 31.3, 2.230 |
| C1-Fluorene | C14H12 | 180 | 31.7, 2.250 |
| C1-Fluorene | C14H12 | 180 | 31.9, 2.240 |
| C1-Fluorene | C14H12 | 180 | 32.1, 2.235 |
| C1-Fluorene | C14H12 | 180 | 32.4, 2.235 |
| C1-Fluorene | C14H12 | 180 | 32.8, 2.195 |
| C1-Fluorene | C14H12 | 180 | 33.1, 2.200 |
| C1-Fluorene | C14H12 | 180 | 33.3, 2.215 |
| C1-Fluorene | C14H12 | 180 | 33.5, 2.195 |
| C1-Fluorene | C14H12 | 180 | 33.8, 2.190 |
| C1-Fluorene | C14H12 | 180 | 34.0, 2.185 |
| Phenanthrene, 9,10-dihydro- | C14H12 | 180 | 30.1, 2.185 |
| Anthracene, 9,10-dihydro- | C14H12 | 180 | 30.8, 2.180 |
| C2-Biphenyl | C14H14 | 182 | 18.6, 2.215 |
| C2-Biphenyl | C14H14 | 182 | 19.3, 2.240 |
| C2-Biphenyl | C14H14 | 182 | 20.5, 2.215 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C2-Biphenyl | C14H14 | 182 | 21.6, 2.220 |
| C2-Biphenyl | C14H14 | 182 | 21.8, 2.260 |
| C2-Biphenyl | C14H14 | 182 | 22.0, 2.275 |
| C2-Biphenyl | C14H14 | 182 | 22.2, 2.235 |
| C2-Biphenyl | C14H14 | 182 | 23.1, 2.230 |
| C2-Biphenyl | C14H14 | 182 | 23.7, 2.135 |
| C2-Biphenyl | C14H14 | 182 | 23.9, 2.310 |
| C2-Biphenyl | C14H14 | 182 | 24.9, 2.255 |
| C2-Biphenyl | C14H14 | 182 | 25.2, 2.280 |
| C2-Biphenyl | C14H14 | 182 | 25.4, 2.275 |
| C2-Biphenyl | C14H14 | 182 | 25.8, 2.285 |
| C2-Biphenyl | C14H14 | 182 | 26.1, 2.305 |
| C2-Biphenyl | C14H14 | 182 | 26.7, 2.320 |
| C2-Biphenyl | C14H14 | 182 | 27.1, 2.260 |
| C2-Biphenyl | C14H14 | 182 | 28.1, 2.365 |
| C2-Biphenyl | C14H14 | 182 | 29.1, 2.465 |
| C2-Biphenyl | C14H14 | 182 | 29.5, 2.310 |
| C2-Biphenyl | C14H14 | 182 | 29.8, 2.285 |
| C2-Biphenyl | C14H14 | 182 | 30.0, 2.335 |
| C2-Biphenyl | C14H14 | 182 | 30.5, 2.315 |
| C2-Biphenyl | C14H14 | 182 | 31.2, 2.330 |
| C2-Biphenyl | C14H14 | 182 | 31.6, 2.300 |
| C2-Biphenyl | C14H14 | 182 | 32.0, 2.325 |
| C2-Biphenyl | C14H14 | 182 | 32.3, 2.300 |
| C4-Naphthalene | C14H16 | 184 | 22.8, 2.400 |
| C4-Naphthalene | C14H16 | 184 | 23.4, 2.440 |
| C4-Naphthalene | C14H16 | 184 | 24.0, 2.370 |
| C4-Naphthalene | C14H16 | 184 | 24.3, 2.415 |
| C4-Naphthalene | C14H16 | 184 | 24.7, 2.460 |
| C4-Naphthalene | C14H16 | 184 | 25.0, 2.415 |
| C4-Naphthalene | C14H16 | 184 | 25.2, 2.460 |
| C4-Naphthalene | C14H16 | 184 | 25.4, 2.405 |
| C4-Naphthalene | C14H16 | 184 | 25.7, 2.420 |
| C4-Naphthalene | C14H16 | 184 | 25.9, 2.425 |
| C4-Naphthalene | C14H16 | 184 | 26.1, 2.355 |
| C4-Naphthalene | C14H16 | 184 | 26.4, 2.415 |
| C4-Naphthalene | C14H16 | 184 | 26.8, 2.435 |
| C4-Naphthalene | C14H16 | 184 | 27.1, 2.405 |
| C4-Naphthalene | C14H16 | 184 | 27.6, 2.450 |
| C4-Naphthalene | C14H16 | 184 | 28.2, 2.455 |
| C4-Naphthalene | C14H16 | 184 | 28.4, 2.420 |
| C4-Naphthalene | C14H16 | 184 | 28.7, 2.405 |
| C4-Naphthalene | C14H16 | 184 | 29.3, 2.410 |
| C4-Naphthalene | C14H16 | 184 | 29.5, 2.405 |
| C4-Naphthalene | C14H16 | 184 | 29.7, 2.415 |
| C4-Naphthalene | C14H16 | 184 | 30.6, 2.375 |
| C4-Indene isomer | C14H18 | 186 | 15.3, 2.415 |
| C4-Indene isomer | C14H18 | 186 | 17.7, 2.415 |
| C4-Indene isomer | C14H18 | 186 | 17.9, 2.485 |
| C4-Indene isomer | C14H18 | 186 | 18.6, 2.450 |
| C4-Indene isomer | C14H18 | 186 | 18.8, 2.460 |
| C4-Indene isomer | C14H18 | 186 | 19.2, 2.435 |
| C4-Indene isomer | C14H18 | 186 | 19.7, 2.555 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C4-Indene isomer | C14H18 | 186 | 20.0, 2.530 |
| C4-Indene isomer | C14H18 | 186 | 20.4, 2.535 |
| C4-Indene isomer | C14H18 | 186 | 20.6, 2.500 |
| C4-Indene isomer | C14H18 | 186 | 20.8, 2.550 |
| C4-Indene isomer | C14H18 | 186 | 21.6, 2.495 |
| C4-Indene isomer | C14H18 | 186 | 21.9, 2.470 |
| C4-Indene isomer | C14H18 | 186 | 22.0, 2.450 |
| C4-Indene isomer | C14H18 | 186 | 22.9, 2.485 |
| C4-Indene isomer | C14H18 | 186 | 23.5, 2.520 |
| C4-Indene isomer | C14H18 | 186 | 24.0, 2.495 |
| C4-Indene isomer | C14H18 | 186 | 25.1, 2.490 |
| C4-Indene isomer | C14H18 | 186 | 25.5, 2.470 |
| C4-Indane isomer | C14H20 | 188 | 14.5, 2.460 |
| C4-Indane isomer | C14H20 | 188 | 15.5, 2.510 |
| C4-Indane isomer | C14H20 | 188 | 16.4, 2.520 |
| C4-Indane isomer | C14H20 | 188 | 16.7, 2.510 |
| C4-Indane isomer | C14H20 | 188 | 17.0, 2.545 |
| C4-Indane isomer | C14H20 | 188 | 17.2, 2.535 |
| C4-Indane isomer | C14H20 | 188 | 17.7, 2.550 |
| C4-Indane isomer | C14H20 | 188 | 18.1, 2.560 |
| C4-Indane isomer | C14H20 | 188 | 18.6, 2.585 |
| C4-Indane isomer | C14H20 | 188 | 18.7, 2.540 |
| C4-Indane isomer | C14H20 | 188 | 19.3, 2.570 |
| C4-Indane isomer | C14H20 | 188 | 19.6, 2.575 |
| C4-Indane isomer | C14H20 | 188 | 19.9, 2.520 |
| C4-Indane isomer | C14H20 | 188 | 20.1, 2.580 |
| C4-Indane isomer | C14H20 | 188 | 20.4, 2.610 |
| C4-Indane isomer | C14H20 | 188 | 21.0, 2.690 |
| C4-Indane isomer | C14H20 | 188 | 22.0, 2.580 |
| 1,4,5,6-Tetramethyl 1,2,3,4-tetrahydronapthalene | C14H20 | 188 | 21.2, 2.480 |
| 4H-Cyclopenta[def]phenanthrene | C15H10 | 190 | 39.4, 2.190 |
| Cyclopropa[b]anthracene or Benz[fg]acenaphthylene | C15H10 | 190 | 40.5, 2.155 |
| Cyclopropa[b]anthracene or Benz[fg]acenaphthylene | C15H10 | 190 | 41.6, 2.140 |
| C8-Benzene | C14H22 | 190 | 14.3, 2.540 |
| C8-Benzene | C14H22 | 190 | 14.7, 2.595 |
| C8-Benzene | C14H22 | 190 | 14.8, 2.620 |
| C8-Benzene | C14H22 | 190 | 15.2, 2.615 |
| C8-Benzene | C14H22 | 190 | 15.5, 2.640 |
| C8-Benzene | C14H22 | 190 | 16.4, 2.670 |
| C8-Benzene | C14H22 | 190 | 16.9, 2.730 |
| C8-Benzene | C14H22 | 190 | 17.2, 2.760 |
| C8-Benzene | C14H22 | 190 | 17.3, 2.725 |
| C8-Benzene | C14H22 | 190 | 17.5, 2.725 |
| C8-Benzene | C14H22 | 190 | 17.9, 2.675 |
| Phenyl Indene | C15H12 | 192 | 31.8, 2.260 |
| Phenyl Indene | C15H12 | 192 | 32.6, 2.135 |
| Phenyl Indene | C15H12 | 192 | 33.6, 2.135 |
| Phenyl Indene | C15H12 | 192 | 34.3, 2.315 |
| Phenyl Indene | C15H12 | 192 | 35.2, 2.280 |
| Phenyl Indene | C15H12 | 192 | 35.9, 2.350 |
| Phenyl Indene | C15H12 | 192 | 36.9, 2.185 |
| Phenyl Indene | C15H12 | 192 | 37.3, 2.170 |
| Phenyl Indene | C15H12 | 192 | 37.5, 2.250 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C1-Phenanthrene | C15H12 | 192 | 38.1, 2.215 |
| C1-Phenanthrene | C15H12 | 192 | 38.3, 2.220 |
| C1-Phenanthrene | C15H12 | 192 | 38.5, 2.235 |
| C1-Anthracene | C15H12 | 192 | 39.0, 2.220 |
| C1-Anthracene | C15H12 | 192 | 39.2, 2.180 |
| C1-Anthracene | C15H12 | 192 | 39.4, 2.190 |
| C15H12 | C15H12 | 192 | 40.8, 2.170 |
| C2-Flourene | C15H14 | 194 | 29.0, 2.335 |
| C2-Flourene | C15H14 | 194 | 30.2, 2.320 |
| C2-Flourene | C15H14 | 194 | 31.1, 2.285 |
| C2-Flourene | C15H14 | 194 | 31.5, 2.265 |
| C2-Flourene | C15H14 | 194 | 32.3, 2.280 |
| C2-Flourene | C15H14 | 194 | 32.6, 2.330 |
| C2-Flourene | C15H14 | 194 | 33.1, 2.340 |
| C2-Flourene | C15H14 | 194 | 33.5, 2.370 |
| C2-Flourene | C15H14 | 194 | 33.7, 2.395 |
| C2-Flourene | C15H14 | 194 | 33.8, 2.355 |
| C2-Flourene | C15H14 | 194 | 34.1, 2.355 |
| C2-Flourene | C15H14 | 194 | 34.4, 2.330 |
| C2-Flourene | C15H14 | 194 | 34.7, 2.320 |
| C2-Flourene | C15H14 | 194 | 35.0, 2.340 |
| C2-Flourene | C15H14 | 194 | 35.2, 2.310 |
| C2-Flourene | C15H14 | 194 | 35.4, 2.355 |
| C2-Flourene | C15H14 | 194 | 35.7, 2.330 |
| C2-Flourene | C15H14 | 194 | 36.2, 2.300 |
| C2-Flourene | C15H14 | 194 | 36.7, 2.295 |
| C2-Flourene | C15H14 | 194 | 37.0, 2.335 |
| C2-Flourene | C15H14 | 194 | 37.2, 2.270 |
| C2-Fluorene | C15H14 | 194 | 38.0, 2.240 |
| C2-Flourene | C15H14 | 194 | 38.2, 2.285 |
| C3-Biphenyl | C15H16 | 196 | 25.0, 2.305 |
| C3-Biphenyl | C15H16 | 196 | 25.2, 2.340 |
| C3-Biphenyl | C15H16 | 196 | 26.3, 2.325 |
| C3-Biphenyl | C15H16 | 196 | 26.8, 2.220 |
| C3-Biphenyl | C15H16 | 196 | 27.7, 2.390 |
| C3-Biphenyl | C15H16 | 196 | 28.0, 2.340 |
| C3-Biphenyl | C15H16 | 196 | 28.3, 2.345 |
| C3-Biphenyl | C15H16 | 196 | 28.7, 2.350 |
| C3-Biphenyl | C15H16 | 196 | 29.0, 2.385 |
| C3-Biphenyl | C15H16 | 196 | 30.5, 2.340 |
| C3-Biphenyl | C15H16 | 196 | 30.9, 2.395 |
| C3-Biphenyl | C15H16 | 196 | 32.0, 2.365 |
| C5-Naphthalene | C15H18 | 198 | 26.6, 2.570 |
| C5-Naphthalene | C15H18 | 198 | 27.1, 2.520 |
| C5-Naphthalene | C15H18 | 198 | 27.3, 2.540 |
| C5-Naphthalene | C15H18 | 198 | 27.5, 2.545 |
| C5-Naphthalene | C15H18 | 198 | 28.0, 2.500 |
| C5-Naphthalene | C15H18 | 198 | 28.4, 2.535 |
| C5-Naphthalene | C15H18 | 198 | 28.8, 2.480 |
| C5-Naphthalene | C15H18 | 198 | 28.9, 2.570 |
| C5-Naphthalene | C15H18 | 198 | 29.1, 2.500 |
| C5-Naphthalene | C15H18 | 198 | 29.3, 2.525 |
| C5-Naphthalene | C15H18 | 198 | 29.6, 2.535 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C5-Naphthalene | C15H18 | 198 | 29.8, 2.555 |
| C5-Naphthalene | C15H18 | 198 | 30.3, 2.535 |
| C5-Naphthalene | C15H18 | 198 | 30.5, 2.535 |
| C5-Naphthalene | C15H18 | 198 | 30.7, 2.500 |
| C5-Naphthalene | C15H18 | 198 | 31.1, 2.520 |
| C5-Naphthalene | C15H18 | 198 | 33.4, 2.495 |
| C5-Naphthalene | C15H18 | 198 | 35.3, 2.475 |
| Fluoranthene | C16H10 | 202 | 44.5, 2.165 |
| Pyrene | C16H10 | 202 | 46.7, 2.135 |
| Acenaphenanthrylene/aceanthrylene | C16H10 | 202 | 45.5, 2.130 |
| Acenaphenanthrylene/aceanthrylene | C16H10 | 202 | 46.2, 2.120 |
| Anthracene, 9-ethenyl- | C16H12 | 204 | 37.2, 2.110 |
| Phenyl Naphthalene | C16H12 | 204 | 41.0, 2.155 |
| Phenyl Naphthalene | C16H12 | 204 | 42.6, 2.240 |
| Acephenanthrylene, 4,5-dihydro- | C16H12 | 204 | 42.7, 2.265 |
| Phenyl Naphthalene | C16H12 | 204 | 42.8, 2.235 |
| Phenyl Naphthalene | C16H12 | 204 | 43.2, 2.200 |
| Naphthalene, 1,8-di-1-propynl- | C16H12 | 204 | 43.3, 2.250 |
| Phenyl Naphthalene | C16H12 | 204 | 43.4, 2.215 |
| Phenyl Naphthalene | C16H12 | 204 | 43.6, 2.315 |
| Pyrene, 4,5-dihydro- | C16H12 | 204 | 46.2, 2.155 |
| Phenyl Naphthalene | C16H12 | 204 | 46.3, 2.165 |
| Phenyl Naphthalene | C16H12 | 204 | 46.6, 2.170 |
| C2-Phenanthrene | C16H14 | 206 | 34.8, 2.345 |
| C2-Phenanthrene | C16H14 | 206 | 35.7, 2.185 |
| C2-Phenanthrene | C16H14 | 206 | 36.2, 2.175 |
| C2-Phenanthrene | C16H14 | 206 | 38.8, 2.320 |
| C2-Phenanthrene | C16H14 | 206 | 39.9, 2.270 |
| C2-Phenanthrene | C16H14 | 206 | 40.2, 2.260 |
| C2-Phenanthrene | C16H14 | 206 | 40.6, 2.280 |
| C2-Phenanthrene | C16H14 | 206 | 41.1, 2.290 |
| C2-Phenanthrene | C16H14 | 206 | 41.4, 2.290 |
| C2-Phenanthrene | C16H14 | 206 | 41.6, 2.290 |
| C2-Anthracene | C16H14 | 206 | 42.2, 2.265 |
| C2-Anthracene | C16H14 | 206 | 42.4, 2.280 |
| C2-Anthracene | C16H14 | 206 | 42.7, 2.270 |
| C2-Anthracene | C16H14 | 206 | 42.9, 2.265 |
| C2-Anthracene | C16H14 | 206 | 43.2, 2.235 |
| C2-Anthracene | C16H14 | 206 | 43.5, 2.350 |
| C2-Anthracene | C16H14 | 206 | 43.8, 2.230 |
| Ethyl Anthracene | C16H14 | 206 | 44.3, 2.230 |
| C3-Fluorene | C16H16 | 208 | 29.0, 2.310 |
| C3-Fluorene | C16H16 | 208 | 29.6, 2.325 |
| C3-Fluorene | C16H16 | 208 | 31.5, 2.245 |
| C3-Fluorene | C16H16 | 208 | 32.5, 2.275 |
| C3-Fluorene | C16H16 | 208 | 33.2, 2.380 |
| C3-Fluorene | C16H16 | 208 | 33.6, 2.395 |
| C3-Fluorene | C16H16 | 208 | 34.1, 2.395 |
| C3-Fluorene | C16H16 | 208 | 33.9, 2.280 |
| C3-Fluorene | C16H16 | 208 | 35.6, 2.330 |
| C3-Fluorene | C16H16 | 208 | 35.8, 2.340 |
| C3-Fluorene | C16H16 | 208 | 36.1, 2.415 |
| C3-Fluorene | C16H16 | 208 | 36.5, 2.425 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C2-Dihydro Anthracene | C16H16 | 208 | 37.0, 2.465 |
| C3-Fluorene | C16H16 | 208 | 37.1, 2.430 |
| C3-Fluorene | C16H16 | 208 | 37.4, 2.405 |
| C2-Dihydro Anthracene | C16H16 | 208 | 37.7, 2.430 |
| C3-Fluorene | C16H16 | 208 | 37.8, 2.400 |
| C2-Dihydro Anthracene | C16H16 | 208 | 37.9, 2.405 |
| C2-Dihydro Anthracene | C16H16 | 208 | 38.4, 2.390 |
| C2-Dihydro Anthracene | C16H16 | 208 | 38.7, 2.390 |
| C3-Fluorene | C16H16 | 208 | 39.0, 2.400 |
| C2-Dihydro Anthracene | C16H16 | 208 | 39.3, 2.385 |
| C3-Fluorene | C16H16 | 208 | 39.6, 2.295 |
| C3-Fluorene | C16H16 | 208 | 40.1, 2.355 |
| C4-Biphenyl | C16H18 | 210 | 28.3, 2.345 |
| C4-Biphenyl | C16H18 | 210 | 29.3, 2.295 |
| C4-Biphenyl | C16H18 | 210 | 29.9, 2.270 |
| C4-Biphenyl | C16H18 | 210 | 31.5, 2.400 |
| C4-Biphenyl | C16H18 | 210 | 31.8, 2.435 |
| C4-Biphenyl | C16H18 | 210 | 33.1, 2.475 |
| C4-Biphenyl | C16H18 | 210 | 33.7, 2.460 |
| C4-Biphenyl | C16H18 | 210 | 34.4, 2.430 |
| C4-Biphenyl | C16H18 | 210 | 34.9, 2.400 |
| C4-Biphenyl | C16H18 | 210 | 35.0, 2.445 |
| C4-Biphenyl | C16H18 | 210 | 35.3, 2.460 |
| C4-Biphenyl | C16H18 | 210 | 35.5, 2.465 |
| C4-Biphenyl | C16H18 | 210 | 35.9, 2.435 |
| C4-Biphenyl | C16H18 | 210 | 36.7, 2.415 |
| C4-Biphenyl | C16H18 | 210 | 37.2, 2.440 |
| C4-Biphenyl | C16H18 | 210 | 38.8, 2.480 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 47.5, 2.230 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 47.6, 2.245 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 48.7, 2.195 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 48.9, 2.180 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 49.2, 2.180 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 49.4, 2.185 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 49.7, 2.180 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 50.6, 2.170 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 50.9, 2.165 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 51.2, 2.135 |
| C1-Fluoranthene/Pyrene | C17H12 | 216 | 51.8, 2.165 |
| 218, 203 C17H14 | C17H14 | 218 | 37.8, 2.215 |
| Anthracene, 9-(2-propenyl)- | C17H14 | 218 | 40.1, 2.165 |
| 218, 203 C17H14 | C17H14 | 218 | 40.2, 2.185 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 40.3, 2.215 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 40.6, 2.225 |
| Anthracene, 9-(1-propenyl)- | C17H14 | 218 | 40.7, 2.185 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 41.4, 2.180 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 42.2, 2.060 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 42.5, 2.120 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 44.0, 2.215 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 44.2, 2.215 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 44.4, 2.220 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 44.8, 2.175 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 45.1, 2.185 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Phenyl Methyl Naphthalene | C17H14 | 218 | 46.4, 2.280 |
| Phenyl Methyl Naphthalene | C17H14 | 218 | 49.0, 2.235 |
| 4H-Benz[de]anthracene, 5,6-dihydro | C17H14 | 218 | 49.5, 2.245 |
| 4H-Benz[de]anthracene, 5,6-dihydro | C17H14 | 218 | 50.0, 2.190 |
| 4H-Benz[de]anthracene, 5,6-dihydro | C17H14 | 218 | 50.3, 2.225 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 43.5, 2.345 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 43.8, 2.345 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 44.2, 2.320 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 44.3, 2.360 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 44.5, 2.345 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 44.7, 2.380 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 45.0, 2.340 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 45.2, 2.345 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 45.5, 2.315 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 45.7, 2.365 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 45.8, 2.325 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 46.0, 2.320 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 46.4, 2.315 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 46.7, 2.340 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 46.9, 2.350 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 47.1, 2.325 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 47.4, 2.390 |
| C3-Phenanthrene/Anthracene | C17H16 | 220 | 48.4, 2.290 |
| 9(10H)-Pheanthrenone, 1-diazo- | C14H8N2O | 220 | 53.0, 2.025 |
| C5-Biphenyl | C17H20 | 224 | 37.7, 2.490 |
| C5-Biphenyl | C17H20 | 224 | 35.9, 2.470 |
| C5-Biphenyl | C17H20 | 224 | 36.4, 2.530 |
| C5-Biphenyl | C17H20 | 224 | 36.5, 2.500 |
| C5-Biphenyl | C17H20 | 224 | 37.0, 2.530 |
| C5-Biphenyl | C17H20 | 224 | 37.2, 2.510 |
| C5-Biphenyl | C17H20 | 224 | 38.0, 2.470 |
| C5-Biphenyl | C17H20 | 224 | 38.3, 2.500 |
| C5-Biphenyl | C17H20 | 224 | 38.5, 2.490 |
| C5-Biphenyl | C17H20 | 224 | 39.2, 2.640 |
| C5-Biphenyl | C17H20 | 224 | 39.4, 2.595 |
| Benzo[ghi]fluoranthene | C18H10 | 226 | 54.8, 2.150 |
| C18H12 | C18H12 | 228 | 48.4, 2.180 |
| C18H12 | C18H12 | 228 | 49.5, 2.205 |
| C18H12 | C18H12 | 228 | 50.3, 2.235 |
| C18H12 | C18H12 | 228 | 51.0, 2.190 |
| C18H12 | C18H12 | 228 | 53.8, 2.275 |
| Benzo[c]Phenanthrene | C18H12 | 228 | 55.0, 2.100 |
| Benzo[a]anthracene | C18H12 | 228 | 56.4, 2.140 |
| Chrysene | C18H12 | 228 | 57.0, 2.115 |
| Tiphenylene/Napthacene | C18H12 | 228 | 57.4, 2.150 |
| 230, 215, 152 C18H14 | C18H14 | 230 | 45.6, 2.115 |
| m-Terphenyl | C18H14 | 230 | 46.4, 2.145 |
| p-Terphenyl | C18H14 | 230 | 47.7, 2.160 |
| 230, 204 | C18H14 | 230 | 48.2, 2.190 |
| Naphthacene, 5,12-dihydro- | C18H14 | 230 | 49.5, 2.150 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 49.4, 2.210 |
| 5,6-Dihydrochrysene | C18H14 | 230 | 50.4, 2.325 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 50.5, 2.305 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 50.9, 2.380 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 51.2, 2.295 |
| o-Terphenyl | C18H14 | 230 | 51.5, 2.160 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 51.6, 2.260 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 51.9, 2.240 |
| Naphthacene, 5,12-dihydro- | C18H14 | 230 | 52.0, 2.175 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 52.2, 2.250 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 52.5, 2.235 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 52.7, 2.335 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 53.1, 2.235 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 53.3, 2.250 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 53.6, 2.225 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 54.2, 2.225 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 54.5, 2.220 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 54.7, 2.215 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 55.1, 2.210 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 55.4, 2.225 |
| C2-Fluoranthene/Pyrene | C18H14 | 230 | 55.8, 2.225 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 42.3, 2.170 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 42.7, 2.210 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 43.0, 2.180 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 43.8, 2.175 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 44.6, 2.080 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 44.8, 2.195 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 45.1, 2.130 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 45.6, 2.195 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 46.0, 2.105 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 46.4, 2.275 |
| Dimethyl, Phenyl Naphthalene | C18H16 | 232 | 47.0, 2.270 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 46.7, 2.375 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 47.0, 2.465 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 47.2, 2.430 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 47.4, 2.440 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 47.9, 2.420 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 48.1, 2.410 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 48.4, 2.405 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 49.0, 2.420 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 49.3, 2.420 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 49.6, 2.380 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 50.0, 2.405 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 50.4, 2.310 |
| C4-Phenanthrene/Anthracene | C18H18 | 234 | 50.9, 2.325 |
| 9H-Cyclopenta[a]pyrene isomer | C19H12 | 240 | 57.5, 2.240 |
| 9H-Cyclopenta[a]pyrene isomer | C19H12 | 240 | 58.3, 2.250 |
| 9H-Cyclopenta[a]pyrene isomer | C19H12 | 240 | 58.5, 2.275 |
| 9H-Cyclopenta[a]pyrene isomer | C19H12 | 240 | 59.2, 2.265 |
| 9H-Cyclopenta[a]pyrene isomer | C19H12 | 240 | 59.6, 2.200 |
| 9H-Cyclopenta[a]pyrene isomer | C19H12 | 240 | 60.4, 2.250 |
| 9H-Cyclopenta[a]pyrene isomer | C19H12 | 240 | 60.7, 2.240 |
| 9H-Cyclopenta[a]pyrene isomer | C19H12 | 240 | 61.0, 2.225 |
| 9H-Cyclopenta[a]pyrene isomer | C19H12 | 240 | 62.3, 2.220 |
| 9H-Cyclopenta[a]pyrene isomer | C19H12 | 240 | 62.9, 2.195 |
| Phenyl Fluorene | C19H14 | 242 | 49.0, 2.125 |

Appendix 2 – Aromatic Database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C1-Chrysene | C19H14 | 242 | 50.9, 2.145 |
| Phenyl Fluorene | C19H14 | 242 | 51.6, 2.165 |
| Phenyl Fluorene | C19H14 | 242 | 52.0, 2.170 |
| C1-Chrysene | C19H14 | 242 | 53.1, 2.080 |
| C1-Chrysene | C19H14 | 242 | 53.5, 2.180 |
| C1-Chrysene | C19H14 | 242 | 54.2, 2.205 |
| C1-Chrysene | C19H14 | 242 | 54.9, 2.200 |
| C1-Chrysene | C19H14 | 242 | 55.4, 2.230 |
| C1-Chrysene | C19H14 | 242 | 56.5, 2.185 |
| C1-Chrysene | C19H14 | 242 | 57.6, 2.200 |
| C1-Chrysene | C19H14 | 242 | 58.4, 2.150 |
| C1-Chrysene | C19H14 | 242 | 58.7, 2.215 |
| C1-Chrysene | C19H14 | 242 | 59.1, 2.210 |
| C1-Chrysene | C19H14 | 242 | 59.2, 2.215 |
| C1-Chrysene | C19H14 | 242 | 59.4, 2.185 |
| C1-Chrysene | C19H14 | 242 | 59.7, 2.180 |
| C1-Chrysene | C19H14 | 242 | 59.9, 2.235 |
| C1-Chrysene | C19H14 | 242 | 60.2, 2.175 |
| C1-Chrysene | C19H14 | 242 | 60.5, 2.195 |
| C1-Chrysene | C19H14 | 242 | 60.9, 2.180 |
| C1-Chrysene | C19H14 | 242 | 61.2, 2.165 |
| 8,9-Dihydro-7H-cyclopenta[a]pyrene | C19H14 | 242 | 60.8, 2.205 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 54.4, 2.365 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 54.6, 2.310 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 55.0, 2.305 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 55.2, 2.290 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 55.4, 2.305 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 55.5, 2.280 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 55.6, 2.320 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 55.7, 2.280 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 55.9, 2.300 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 56.1, 2.295 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 56.6, 2.265 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 56.8, 2.330 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 57.1, 2.265 |
| Dihydro, Methyl Benz[a]anthracene | C19H16 | 244 | 57.3, 2.265 |
| Benzo[b]fluoranthene | C20H12 | 252 | 64.7, 2.165 |
| Benzo[k]fluoranthene | C20H12 | 252 | 64.9, 2.165 |
| Benzo[x]fluoranthene | C20H12 | 252 | 65.1, 2.135 |
| Benzo[x]fluoranthene | C20H12 | 252 | 65.6, 2.155 |
| Benzo[x]fluoranthene | C20H12 | 252 | 65.8, 2.210 |
| Benzo[e]pyrene | C20H12 | 252 | 67.2, 2.125 |
| Benzo[a]pyrene | C20H12 | 252 | 67.5, 2.130 |
| Perylene | C20H12 | 252 | 68.4, 2.105 |
| Binaphthalene | C20H14 | 254 | 57.5, 2.075 |
| Binaphthalene | C20H14 | 254 | 57.7, 2.145 |
| Binaphthalene | C20H14 | 254 | 60.5, 2.135 |
| Binaphthalene | C20H14 | 254 | 61.1, 2.125 |
| Binaphthalene | C20H14 | 254 | 61.4, 2.140 |
| Binaphthalene | C20H14 | 254 | 61.7, 2.155 |
| Binaphthalene | C20H14 | 254 | 63.0, 2.230 |
| Phenyl Phenanthrene | C20H14 | 254 | 61.8, 2.215 |
| Phenyl Phenanthrene | C20H14 | 254 | 62.1, 2.205 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Dihydro Benzo(a)Pyrene | C20H14 | 254 | 62.8, 2.295 |
| Dihydro Benzo(a)Pyrene | C20H14 | 254 | 63.0, 2.320 |
| Dihydro Benzo(a)Pyrene | C20H14 | 254 | 63.3, 2.295 |
| Phenyl Anthracene | C20H14 | 254 | 66.4, 2.185 |
| Phenyl Anthracene | C20H14 | 254 | 68.3, 2.110 |
| C2-Chrysene | C20H16 | 256 | 56.8, 2.315 |
| C2-Chrysene | C20H16 | 256 | 58.9, 2.235 |
| C2-Chrysene | C20H16 | 256 | 59.3, 2.210 |
| C2-Chrysene | C20H16 | 256 | 59.4, 2.220 |
| C2-Chrysene | C20H16 | 256 | 59.8, 2.205 |
| C2-Chrysene | C20H16 | 256 | 60.0, 2.210 |
| C2-Chrysene | C20H16 | 256 | 60.3, 2.235 |
| C2-Chrysene | C20H16 | 256 | 60.5, 2.265 |
| C2-Chrysene | C20H16 | 256 | 61.1, 2.245 |
| C2-Chrysene | C20H16 | 256 | 61.3, 2.265 |
| C2-Chrysene | C20H16 | 256 | 61.5, 2.245 |
| C2-Chrysene | C20H16 | 256 | 61.8, 2.265 |
| C2-Chrysene | C20H16 | 256 | 61.9, 2.275 |
| C2-Chrysene | C20H16 | 256 | 62.0, 2.260 |
| C2-Chrysene | C20H16 | 256 | 62.1, 2.335 |
| C2-Chrysene | C20H16 | 256 | 62.3, 2.235 |
| C2-Chrysene | C20H16 | 256 | 62.5, 2.260 |
| C2-Chrysene | C20H16 | 256 | 62.7, 2.250 |
| C2-Chrysene | C20H16 | 256 | 62.9, 2.240 |
| C2-Chrysene | C20H16 | 256 | 63.2, 2.225 |
| C2-Chrysene | C20H16 | 256 | 63.5, 2.225 |
| C2-Chrysene | C20H16 | 256 | 64.1, 2.225 |
| C2-Chrysene | C20H16 | 256 | 64.6, 2.295 |
| 4H-Benzo[def]cyclopenta[mno]chrysene | C21H12 | 264 | 69.5, 2.250 |
| 11H-Cyclopenta[ghi]perylene | C21H12 | 264 | 70.6, 2.190 |
| 11H-Indeno[2,1,7-cde]pyrene | C21H12 | 264 | 71.4, 2.190 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 66.7, 2.230 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 67.0, 2.260 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 67.1, 2.230 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 67.3, 2.250 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 67.5, 2.215 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 67.9, 2.205 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 68.2, 2.240 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 68.4, 2.190 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 68.6, 2.190 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 68.8, 2.185 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 69.1, 2.195 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 69.3, 2.200 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 69.6, 2.220 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 69.8, 2.215 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 70.0, 2.220 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 70.2, 2.175 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 70.4, 2.190 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 70.5, 2.205 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 70.9, 2.205 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 71.7, 2.165 |
| C1-Benzo[x]fluoranthene isomer | C21H14 | 266 | 72.1, 2.240 |
| C1-Binaphthalene | C21H16 | 268 | 62.5, 2.220 |

Appendix 2 – Aromatic database

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C1-Binaphthalene | C21H16 | 268 | 62.7, 2.280 |
| C1-Binaphthalene | C21H16 | 268 | 63.0, 2.205 |
| C1-Binaphthalene | C21H16 | 268 | 63.5, 2.150 |
| C1-Binaphthalene | C21H16 | 268 | 63.7, 2.190 |
| C1-Binaphthalene | C21H16 | 268 | 64.0, 2.200 |
| C1-Binaphthalene | C21H16 | 268 | 64.2, 2.210 |
| C1-Binaphthalene | C21H16 | 268 | 65.3, 2.230 |
| C1-Binaphthalene | C21H16 | 268 | 66.2, 2.235 |
| C1-Binaphthalene | C21H16 | 268 | 66.3, 2.195 |
| C1-Binaphthalene | C21H16 | 268 | 66.7, 2.160 |
| C1-Binaphthalene | C21H16 | 268 | 66.9, 2.220 |
| C1-Binaphthalene | C21H16 | 268 | 67.2, 2.200 |
| C1-Binaphthalene | C21H16 | 268 | 67.8, 2.195 |
| C3-Chrysene | C21H18 | 270 | 60.3, 2.410 |
| C3-Chrysene | C21H18 | 270 | 61.2, 2.360 |
| C3-Chrysene | C21H18 | 270 | 61.6, 2.280 |
| C3-Chrysene | C21H18 | 270 | 62.2, 2.275 |
| C3-Chrysene | C21H18 | 270 | 62.6, 2.250 |
| C3-Chrysene | C21H18 | 270 | 62.7, 2.275 |
| C3-Chrysene | C21H18 | 270 | 63.1, 2.265 |
| C3-Chrysene | C21H18 | 270 | 63.9, 2.325 |
| C3-Chrysene | C21H18 | 270 | 64.5, 2.315 |
| C3-Chrysene | C21H18 | 270 | 65.3, 2.295 |
| C3-Chrysene | C21H18 | 270 | 64.8, 2.305 |
| m/z 276 PAH C22H12 | C22H12 | 276 | 73.1, 2.275 |
| m/z 276 PAH C22H12 | C22H12 | 276 | 73.8, 2.205 |
| m/z 276 PAH C22H12 | C22H12 | 276 | 74.0, 2.250 |
| Indeno[1,2,3-cd]pyrene | C22H12 | 276 | 74.5, 2.275 |
| m/z 276 PAH C22H12 | C22H12 | 276 | 75.9, 2.455 |
| Benzo[g,h,i]perylene | C22H12 | 276 | 76.8, 2.460 |
| m/z 276 PAH C22H12 | C22H12 | 276 | 77.1, 2.230 |
| m/z 276 PAH C22H12 | C22H12 | 276 | 77.5, 2.545 |
| Dibenzochrysene | C22H12 | 276 | 77.8, 2.565 |
| Phenyl Pyrene | C22H14 | 278 | 64.1, 2.185 |
| Phenyl Pyrene | C22H14 | 278 | 64.5, 2.140 |
| Phenyl Pyrene | C22H14 | 278 | 66.6, 2.155 |
| Phenyl Pyrene | C22H14 | 278 | 67.4, 2.095 |
| Phenyl Pyrene | C22H14 | 278 | 67.8, 2.120 |
| Phenyl Pyrene | C22H14 | 278 | 68.1, 2.180 |
| Phenyl Pyrene | C22H14 | 278 | 69.1, 2.160 |
| Phenyl Pyrene | C22H14 | 278 | 69.6, 2.125 |
| Phenyl Pyrene | C22H14 | 278 | 70.6, 2.140 |
| Phenyl Pyrene | C22H14 | 278 | 72.5, 2.230 |
| m/z 278 PAH C22H14 | C22H14 | 278 | 73.3, 2.135 |
| m/z 278 PAH C22H14 | C22H14 | 278 | 73.7, 2.190 |
| m/z 278 PAH C22H14 | C22H14 | 278 | 74.4, 2.250 |
| Dibenzo[a,h]anthracene | C22H14 | 278 | 74.7, 2.285 |
| m/z 278 PAH C22H14 | C22H14 | 278 | 75.4, 2.340 |
| m/z 278 PAH C22H14 | C22H14 | 278 | 75.5, 2.335 |
| m/z 278 PAH C22H14 | C22H14 | 278 | 75.9, 2.365 |
| m/z 278 PAH C22H14 | C22H14 | 278 | 77.2, 2.540 |
| m/z 278 PAH C22H14 | C22H14 | 278 | 78.3, 2.640 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 69.0, 2.300 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 69.4, 2.280 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 70.0, 2.270 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 70.3, 2.280 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 70.8, 2.250 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 71.0, 2.230 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 71.2, 2.225 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 71.3, 2.245 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 71.9, 2.235 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 72.0, 2.250 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 72.3, 2.240 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 72.4, 2.240 |
| C2-Benzo[x]fluoranthene | C22H16 | 280 | 72.7, 2.235 |
| C2-Binaphthalene | C22H18 | 282 | 66.6, 2.370 |
| C2-Binaphthalene | C22H18 | 282 | 67.3, 2.280 |
| C2-Binaphthalene | C22H18 | 282 | 67.9, 2.270 |
| C2-Binaphthalene | C22H18 | 282 | 68.1, 2.285 |
| C2-Binaphthalene | C22H18 | 282 | 68.3, 2.265 |
| C2-Binaphthalene | C22H18 | 282 | 68.4, 2.275 |
| C2-Binaphthalene | C22H18 | 282 | 68.6, 2.290 |
| C2-Binaphthalene | C22H18 | 282 | 68.7, 2.280 |
| C2-Binaphthalene | C22H18 | 282 | 69.0, 2.270 |
| C2-Binaphthalene | C22H18 | 282 | 69.3, 2.335 |
| C4-Chrysene | C22H20 | 284 | 64.0, 2.355 |
| C4-Chrysene | C22H20 | 284 | 64.6, 2.335 |
| C4-Chrysene | C22H20 | 284 | 64.9, 2.330 |
| C4-Chrysene | C22H20 | 284 | 65.3, 2.320 |
| C4-Chrysene | C22H20 | 284 | 65.4, 2.315 |
| C4-Chrysene | C22H20 | 284 | 66.0, 2.330 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 75.5, 2.465 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 75.8, 2.450 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 76.4, 2.495 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 76.7, 2.525 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 76.8, 2.575 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 77.0, 2.590 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 77.7, 2.655 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 79.0, 2.780 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 79.4, 2.760 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 79.6, 2.835 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 80.2, 2.870 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 80.9, 2.935 |
| C1-Benzo[g,h,i]perylene isomer | C23H14 | 290 | 81.1, 2.970 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 72.4, 2.260 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 72.6, 2.215 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 73.0, 2.265 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 73.3, 2.240 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 73.7, 2.250 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 74.1, 2.275 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 74.9, 2.380 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 75.5, 2.425 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 76.1, 2.505 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 76.5, 2.505 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 76.8, 2.545 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 77.0, 2.580 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 77.3, 2.615 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 78.2, 2.700 |
| C1-Dibenzo[a,h]anthracene isomer | C23H16 | 292 | 78.7, 2.715 |
| C3-Benzo[x]fluoranthene | C23H18 | 292 | 69.4, 2.145 |
| C3-Benzo[x]fluoranthene | C23H18 | 292 | 70.3, 2.215 |
| C3-Benzo[x]fluoranthene | C23H18 | 292 | 70.8, 2.220 |
| C3-Benzo[x]fluoranthene | C23H18 | 292 | 73.5, 2.320 |
| C3-Binaphthalene | C23H20 | 296 | 68.7, 2.365 |
| C3-Binaphthalene | C23H20 | 296 | 68.9, 2.365 |
| C3-Binaphthalene | C23H20 | 296 | 69.6, 2.355 |
| C3-Binaphthalene | C23H20 | 296 | 70.6, 2.335 |
| C3-Binaphthalene | C23H20 | 296 | 70.8, 2.335 |
| C3-Binaphthalene | C23H20 | 296 | 71.1, 2.325 |
| C3-Binaphthalene | C23H20 | 296 | 71.4, 2.340 |
| C3-Binaphthalene | C23H20 | 296 | 71.6, 2.335 |
| Coronene | C24H12 | 300 | 87.7, 3.645 |
| Corenene | C24H12 | 300 | 88.1, 3.525 |
| Coronene | C24H12 | 300 | 88.4, 3.690 |
| Coronene | C24H12 | 300 | 90.8, 3.400 |
| Dibenzopyrene | C24H14 | 302 | 83.8, 3.305 |
| Dibenzopyrene | C24H14 | 302 | 84.2, 3.270 |
| Dibenzopyrene | C24H14 | 302 | 85.1, 3.410 |
| Dibenzopyrene | C24H14 | 302 | 85.5, 3.390 |
| Dibenzopyrene | C24H14 | 302 | 85.6, 3.390 |
| Dibenzopyrene | C24H14 | 302 | 85.9, 3.510 |
| Dibenzopyrene | C24H14 | 302 | 86.1, 3.490 |
| Dibenzopyrene | C24H14 | 302 | 86.3, 3.575 |
| Dibenzopyrene | C24H14 | 302 | 86.7, 3.525 |
| Dibenzopyrene | C24H14 | 302 | 87.4, 3.515 |
| Dibenzopyrene | C24H14 | 302 | 87.9, 3.625 |
| Dibenzopyrene | C24H14 | 302 | 90.2, 3.185 |
| Dibenzopyrene | C24H14 | 302 | 91.1, 3.235 |
| Dibenzopyrene | C24H14 | 302 | 91.7, 3.345 |
| Dibenzopyrene | C24H14 | 302 | 92.1, 3.345 |
| Dibenzopyrene | C24H14 | 302 | 92.3, 3.315 |
| C2-Dibenzo[a,h]anthracene isomer | C24H18 | 306 | 75.8, 2.535 |
| C2-Dibenzo[a,h]anthracene isomer | C24H18 | 306 | 76.3, 2.585 |
| C2-Dibenzo[a,h]anthracene isomer | C24H18 | 306 | 77.3, 2.685 |
| C2-Dibenzo[a,h]anthracene isomer | C24H18 | 306 | 77.9, 2.710 |
| C4-Benzo[x]fluoranthene | C24H20 | 308 | 72.6, 2.300 |
| C4-Benzo[x]fluoranthene | C24H20 | 308 | 73.1, 2.305 |
| C4-Benzo[x]fluoranthene | C24H20 | 308 | 73.6, 2.265 |
| C4-Benzo[x]fluoranthene | C24H20 | 308 | 74.2, 2.315 |
| C4-Benzo[x]fluoranthene | C24H20 | 308 | 74.6, 2.345 |
| C4-Benzo[x]fluoranthene | C24H20 | 308 | 75.0, 2.390 |
| C4-Benzo[x]fluoranthene | C24H20 | 308 | 76.9, 2.000 |
| C3-Dibenzo[a,h]anthracene isomer | C25H20 | 320 | 80.9, 3.105 |
| C3-Dibenzo[a,h]anthracene isomer | C25H20 | 320 | 81.2, 3.175 |

Appendix 2 – Aromatic database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Phenol | C6H6O | 166 | 6.9, 1.505 |
| o-Cresol | C7H8O | 180 | 8.1, 1.725 |
| m-Cresol | C7H8O | 180 | 8.3, 1.750 |
| p-Cresol | C7H8O | 180 | 8.5, 1.785 |
| Ethenylphenol | C8H8O | 192 | 11.1, 2.095 |
| Ethylphenol | C8H10O | 194 | 9.2, 1.960 |
| C2-Phenol | C8H10O | 194 | 9.5, 2.015 |
| C2-Phenol | C8H10O | 194 | 9.9, 2.060 |
| C2-Phenol | C8H10O | 194 | 10.3, 2.100 |
| C2-Phenol | C8H10O | 194 | 10.4, 2.090 |
| C2-Phenol | C8H10O | 194 | 10.6, 2.140 |
| C2-Phenol | C8H10O | 194 | 11.1, 2.130 |
| C3-Phenol 2DB | C9H80 | 204 | 14.3, 2.300 |
| C3-Phenol 2DB | C9H80 | 204 | 15.6, 2.415 |
| C3-Phenol 2DB | C9H80 | 204 | 16.3, 2.380 |
| C3-Phenol 2DB | C9H80 | 204 | 15.6, 2.410 |
| C3-Phenol 2DB | C9H80 | 204 | 17.0, 2.450 |
| C3-Phenol 2DB | C9H80 | 204 | 17.1, 2.415 |
| C3 Phenol 2DB | C9H80 | 204 | 17.3, 2.485 |
| C3-Phenol 1DB | C9H10O | 206 | 12.6, 2.370 |
| C3-Phenol 1DB | C9H10O | 206 | 13.2, 2.360 |
| C3-Phenol 1DB | C9H10O | 206 | 15.0, 2.475 |
| C3-Phenol 1DB | C9H10O | 206 | 15.6, 2.325 |
| C3-Phenol 1DB | C9H10O | 206 | 16.1, 2.454 |
| C3-Phenol 1DB | C9H10O | 206 | 16.2, 2.480 |
| C3-Phenol | C9H12O | 208 | 10.0, 2.120 |
| C3-Phenol | C9H12O | 208 | 10.7, 2.265 |
| C3-Phenol | C9H12O | 208 | 10.8, 2.250 |
| C3-Phenol | C9H12O | 208 | 10.9, 2.295 |
| C3-Phenol | C9H12O | 208 | 11.2, 2.290 |
| C3-Phenol | C9H12O | 208 | 11.5, 2.290 |
| C3-Phenol | C9H12O | 208 | 11.8, 2.345 |
| C3-Phenol | C9H12O | 208 | 11.9, 2.360 |
| C3-Phenol | C9H12O | 208 | 12.3, 2.425 |
| C3-Phenol | C9H12O | 208 | 12.4, 2.420 |
| C3-Phenol | C9H12O | 208 | 12.6, 2.430 |
| C3-Phenol | C9H12O | 208 | 12.8, 2.370 |
| C3-Phenol | C9H12O | 208 | 13.0, 2.385 |
| C3-Phenol | C9H12O | 208 | 14.1, 2.505 |
| C3-Phenol | C9H12O | 208 | 14.3, 2.445 |
| Naphthalen-1-ol | C10H8O | 216 | 21.8, 2.500 |
| Naphthalen-2-ol | C10H8O | 216 | 22.6, 2.530 |
| C4-Phenol 2DB | C10H10O | 218 | 16.3, 2.610 |
| C4-Phenol 2DB | C10H10O | 218 | 18.5, 2.915 |
| C4-Phenol 2DB | C10H10O | 218 | 18.8, 2.620 |
| C4-Phenol 2DB | C10H10O | 218 | 19.0, 2.595 |
| C4-Phenol 2DB | C10H10O | 218 | 19.3, 2.575 |
| C4-Phenol 2DB | C10H10O | 218 | 19.7, 2.545 |
| C4-Phenol 2DB | C10H10O | 218 | 19.9, 2.565 |
| C4-Phenol 2DB | C10H10O | 218 | 20.6, 2.635 |
| C4-Phenol 1DB | C10H12O | 220 | 15.3, 2.565 |
| C4-Phenol 1DB | C10H12O | 220 | 15.6, 2.590 |
| C4-Phenol 1DB | C10H12O | 220 | 15.8, 2.620 |

Appendix 3 – Derivatized database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C4-Phenol 1DB | C10H12O | 220 | 15.9, 2.700 |
| C4-Phenol 1DB | C10H12O | 220 | 16.6, 2.605 |
| C4-Phenol 1DB | C10H12O | 220 | 16.7, 2.650 |
| C4-Phenol 1DB | C10H12O | 220 | 16.9, 2.620 |
| C4-Phenol 1DB | C10H12O | 220 | 17.3, 2.650 |
| C4-Phenol 1DB | C10H12O | 220 | 18.0, 2.690 |
| C4-Phenol 1DB | C10H12O | 220 | 18.2, 2.705 |
| C4-Phenol 1DB | C10H12O | 220 | 18.4, 2.670 |
| C4-Phenol 1DB | C10H12O | 220 | 19.0, 2.685 |
| C4-Phenol 1DB | C10H12O | 220 | 19.2, 2.615 |
| Hydroxybenzothiophene | C8H6OS | 222 | 22.1, 2.410 |
| Hydroxybenzothiophene | C8H6OS | 222 | 22.5, 2.430 |
| Hydroxybenzothiophene | C8H6OS | 222 | 23.1, 2.650 |
| Hydroxybenzothiophene | C8H6OS | 222 | 23.4, 2.430 |
| Hydroxybenzothiophene | C8H6OS | 222 | 23.8, 2.420 |
| C4-Phenol | C10H14O | 222 | 11.3, 2.430 |
| C4-Phenol | C10H14O | 222 | 11.6, 2.410 |
| C4-Phenol | C10H14O | 222 | 11.9, 2.440 |
| C4-Phenol | C10H14O | 222 | 12.0, 2.510 |
| C4-Phenol | C10H14O | 222 | 12.4, 2.535 |
| C4-Phenol | C10H14O | 222 | 12.6, 2.535 |
| C4-Phenol | C10H14O | 222 | 12.7, 2.495 |
| C4-Phenol | C10H14O | 222 | 12.8, 2.555 |
| C4-Phenol | C10H14O | 222 | 13.0, 2.555 |
| C4-Phenol | C10H14O | 222 | 13.2, 2.555 |
| C4-Phenol | C10H14O | 222 | 13.3, 2.515 |
| C4-Phenol | C10H14O | 222 | 13.4, 2.615 |
| C4-Phenol | C10H14O | 222 | 13.7, 2.525 |
| C4-Phenol | C10H14O | 222 | 13.8, 2.585 |
| C4-Phenol | C10H14O | 222 | 14.0, 2.670 |
| C4-Phenol | C10H14O | 222 | 14.3, 2.645 |
| C4-Phenol | C10H14O | 222 | 14.4, 2.635 |
| C4-Phenol | C10H14O | 222 | 14.9, 2.630 |
| C4-Phenol | C10H14O | 222 | 15.1, 2.745 |
| C4-Phenol | C10H14O | 222 | 15.4, 2.625 |
| C4-Phenol | C10H14O | 222 | 15.8, 2.785 |
| C1-Naphthalenol | C11H10O | 230 | 24.2, 2.650 |
| C1-Naphthalenol | C11H10O | 230 | 24.9, 2.700 |
| C1-Naphthalenol | C11H10O | 230 | 25.2, 2.655 |
| C1-Naphthalenol | C11H10O | 230 | 26.0, 2.665 |
| C1-Naphthalenol | C11H10O | 230 | 26.4, 2.585 |
| C1-Naphthalenol | C11H10O | 230 | 26.5, 2.660 |
| C1-Naphthalenol | C11H10O | 230 | 26.9, 2.625 |
| C1-Naphthalenol | C11H10O | 230 | 28.3, 2.795 |
| C5-Phenol 2DB | C11H12O | 232 | 19.9, 2.725 |
| C5-Phenol 2DB | C11H12O | 232 | 21.2, 2.745 |
| C5-Phenol 2DB | C11H12O | 232 | 21.5, 2.790 |
| C5-Phenol 2DB | C11H12O | 232 | 22.5, 2.775 |
| C5-Phenol 2DB | C11H12O | 232 | 22.8, 2.690 |
| C5-Phenol 2DB | C11H12O | 232 | 23.5, 2.750 |
| C5-Phenol 2DB | C11H12O | 232 | 23.8, 2.735 |
| C5-Phenol 1DB | C11H14O | 234 | 15.7, 2.730 |
| C5-Phenol 1DB | C11H14O | 234 | 16.6, 2.765 |

Appendix 3 – Derivatized database compounds

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 16.8, 2.770 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 17.0, 2.750 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 17.3, 2.765 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 17.5, 2.795 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 17.8, 2.785 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 18.0, 2.770 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 18.2, 2.825 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 18.5, 2.780 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 18.8, 2.805 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 19.0, 2.795 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 19.1, 2.760 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 19.5, 2.760 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 19.6, 2.730 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 19.7, 2.805 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 19.8, 2.780 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 19.9, 2.775 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 20.2, 2.825 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 20.7, 2.890 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 20.8, 2.775 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 21.3, 2.720 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 21.7, 2.835 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 22.3, 2.830 |
| C5-Phenol 1DB | $C_{11}H_{14}O$ | 234 | 22.8, 2.740 |
| C1-Hydroxybenzothiophene | $C_9H_8OS$ | 236 | 25.0, 2.560 |
| C1-Hydroxybenzothiophene | $C_9H_8OS$ | 236 | 25.8, 2.615 |
| C1-Hydroxybenzothiophene | $C_9H_8OS$ | 236 | 26.0, 2.500 |
| C1-Hydroxybenzothiophene | $C_9H_8OS$ | 236 | 26.3, 2.615 |
| C1-Hydroxybenzothiophene | $C_9H_8OS$ | 236 | 26.7, 2.555 |
| C1-Hydroxybenzothiophene | $C_9H_8OS$ | 236 | 26.8, 2.515 |
| C1-Hydroxybenzothiophene | $C_9H_8OS$ | 236 | 27.2, 2.545 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 13.5, 2.700 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 13.7, 2.685 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 14.1, 2.735 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 14.4, 2.785 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 14.5, 2.685 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 14.8, 2.815 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 14.9, 2.820 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 15.3, 2.860 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 15.4, 2.835 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 15.6, 2.860 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 15.8, 2.800 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 15.9, 2.765 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 16.1, 2.840 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 16.3, 2.880 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 16.7, 2.865 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 16.9, 2.955 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 17.2, 2.900 |
| C5-Phenol | $C_{11}H_{16}O$ | 236 | 18.1, 2.995 |
| o-Biphenyol | $C_{12}H_{10}O$ | 242 | 23.4, 2.585 |
| Hydroxyacenaphthene | $C_{12}H_{10}O$ | 242 | 28.8, 2.540 |
| Hydroxyacenaphthene | $C_{12}H_{10}O$ | 242 | 30.1, 2.605 |
| C2-Naphthalenol | $C_{12}H_{12}O$ | 244 | 26.6, 2.735 |
| C2-Naphthalenol | $C_{12}H_{12}O$ | 244 | 26.8, 2.765 |

Appendix 3 – Derivatized database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C2-Naphthalenol | C12H12O | 244 | 27.4, 2.770 |
| C2-Naphthalenol | C12H12O | 244 | 27.8, 2.380 |
| C2-Naphthalenol | C12H12O | 244 | 28.0, 2.785 |
| C2-Naphthalenol | C12H12O | 244 | 28.3, 2.655 |
| C2-Naphthalenol | C12H12O | 244 | 28.9, 2.760 |
| C2-Naphthalenol | C12H12O | 244 | 29.2, 2.760 |
| C2-Naphthalenol | C12H12O | 244 | 29.6, 2.765 |
| C2-Naphthalenol | C12H12O | 244 | 30.0, 2.285 |
| C2-Naphthalenol | C12H12O | 244 | 30.2, 2.700 |
| C2-Naphthalenol | C12H12O | 244 | 30.9, 2.720 |
| C6-Phenol 2DB | C12H16O | 246 | 24.1, 2.800 |
| C6-Phenol 2DB | C12H16O | 246 | 24.9, 2.815 |
| C6-Phenol 2DB | C12H16O | 246 | 25.9, 2.755 |
| C6-Phenol 2DB | C12H16O | 246 | 26.1, 2.800 |
| C6-Phenol 2DB | C12H16O | 246 | 28.0, 2.740 |
| C6-Phenol 1DB | C12H16O | 248 | 17.7, 2.895 |
| C6-Phenol 1DB | C12H16O | 248 | 18.6, 2.935 |
| C6-Phenol 1DB | C12H16O | 248 | 19.1, 2.970 |
| C6-Phenol 1DB | C12H16O | 248 | 19.6, 3.020 |
| C6-Phenol 1DB | C12H16O | 248 | 20.1, 2.940 |
| C6-Phenol 1DB | C12H16O | 248 | 20.3, 2.895 |
| C6-Phenol 1DB | C12H16O | 248 | 21.6, 2.830 |
| C6-Phenol 1DB | C12H16O | 248 | 21.8, 2.975 |
| C6-Phenol 1DB | C12H16O | 248 | 22.0, 2.930 |
| C6-Phenol 1DB | C12H16O | 248 | 22.3, 2.915 |
| C6-Phenol 1DB | C12H16O | 248 | 22.6, 2.890 |
| C6-Phenol 1DB | C12H16O | 248 | 22.7, 2.950 |
| C6-Phenol 1DB | C12H16O | 248 | 23.1, 2.950 |
| C6-Phenol 1DB | C12H16O | 248 | 23.6, 2.865 |
| C6-Phenol 1DB | C12H16O | 248 | 23.7, 2.910 |
| C6-Phenol 1DB | C12H16O | 248 | 24.3, 2.955 |
| C6-Phenol 1DB | C12H16O | 248 | 24.5, 2.855 |
| C6-Phenol | C12H18O | 250 | 17.1, 3.035 |
| C6-Phenol | C12H18O | 250 | 17.4, 3.070 |
| C6-Phenol | C12H18O | 250 | 17.6, 3.020 |
| C6-Phenol | C12H18O | 250 | 18.1, 3.040 |
| C6-Phenol | C12H18O | 250 | 18.3, 3.105 |
| C6-Phenol | C12H18O | 250 | 18.6, 2.955 |
| C6-phenol | C12H18O | 250 | 18.8, 3.160 |
| C6-Phenol | C12H18O | 250 | 19.0, 2.925 |
| C6-Phenol | C12H18O | 250 | 19.6, 2.900 |
| C6-Phenol | C12H18O | 250 | 20.0, 3.155 |
| C6-Phenol | C12H18O | 250 | 20.4, 2.995 |
| C6-Phenol | C12H18O | 250 | 21.3, 3.195 |
| C2-Hydroxybenzothiophene | C9H8OS | 250 | 28.6, 2.755 |
| C2-Hydroxybenzothiophene | C9H8OS | 250 | 28.9, 2.600 |
| C2-Hydroxybenzothiophene | C9H8OS | 250 | 29.5, 2.660 |
| C2-Hydroxybenzothiophene | C9H8OS | 250 | 30.0, 2.550 |
| 4-Hydroxyfluorene | C13H10O | 254 | 35.7, 2.525 |
| Hydroxyfluorene | C13H10O | 254 | 36.7, 2.575 |
| 2-Hydroxyfluroene | C13H10O | 254 | 37.3, 2.590 |
| C1-Biphenylol | C13H12O | 256 | 25.9, 2.650 |
| C1-Biphenylol | C13H12O | 256 | 26.5, 2.650 |

Appendix 3 – Derivatized database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C1-Hydroxyacenaphthene/hydroxydibenzofuran | C13H12O | 256 | 30.7, 2.660 |
| C1-Hydroxyacenaphthene/hydroxydibenzofuran | C13H12O | 256 | 31.3, 2.580 |
| C1-Hydroxyacenaphthene/hydroxydibenzofuran | C13H12O | 256 | 31.9, 2.585 |
| C1-Hydroxyacenaphthene/hydroxydibenzofuran | C13H12O | 256 | 32.3, 2.715 |
| C1-Hydroxyacenaphthene/hydroxydibenzofuran | C13H12O | 256 | 32.8, 2.515 |
| C1-Hydroxyacenaphthene/hydroxydibenzofuran | C13H12O | 256 | 33.3, 2.660 |
| C1-Hydroxyacenaphthene/hydroxydibenzofuran | C13H12O | 256 | 33.4, 2.635 |
| C1-Hydroxyacenaphthene/hydroxydibenzofuran | C13H12O | 256 | 33.6, 2.680 |
| C1-Hydroxyacenaphthene/hydroxydibenzofuran | C13H12O | 256 | 34.2, 2.675 |
| C1-Hydroxyacenaphthene/hydroxydibenzofuran | C13H12O | 256 | 34.9, 2.650 |
| C3-Naphthalenol | C13H14O | 258 | 29.8, 2.825 |
| C3-Naphthalenol | C13H14O | 258 | 30.1, 2.855 |
| C3-Naphthalenol | C13H14O | 258 | 30.3, 2.730 |
| C3-Naphthalenol | C13H14O | 258 | 31.0, 2.910 |
| C3-Naphthalenol | C13H14O | 258 | 31.8, 2.830 |
| C3-Naphthalenol | C13H14O | 258 | 32.0, 2.830 |
| C3-Naphthalenol | C13H14O | 258 | 33.3, 2.710 |
| C3-Naphthalenol | C13H14O | 258 | 33.7, 2.695 |
| C7-Phenol 2DB | C13H16O | 260 | 23.6, 2.955 |
| C7-Phenol 2DB | C13H16O | 260 | 25.4, 2.930 |
| C7-Phenol 2DB | C13H16O | 260 | 26.2, 2.905 |
| C7-Phenol 2DB | C13H16O | 260 | 26.8, 2.910 |
| C7-Phenol 2DB | C13H16O | 260 | 27.1, 2.855 |
| C7-Phenol 2DB | C13H16O | 260 | 27.3, 2.895 |
| C7-Phenol 2DB | C13H16O | 260 | 27.6, 2.885 |
| C7-Phenol 2DB | C13H16O | 260 | 28.0, 2.915 |
| C7-Phenol 2DB | C13H16O | 260 | 28.1, 2.870 |
| C7-Phenol 2DB | C13H16O | 260 | 28.6, 2.830 |
| C7-Phenol 2DB | C13H16O | 260 | 28.8, 2.910 |
| C7-Phenol 2DB | C13H16O | 260 | 29.2, 2.890 |
| C7-Phenol 2DB | C13H16O | 260 | 29.4, 2.820 |
| C7-Phenol 1DB | C13H18O | 262 | 20.9, 2.990 |
| C7-Phenol 1DB | C13H18O | 262 | 22.6, 3.045 |
| C7-Phenol 1DB | C13H18O | 262 | 23.8, 3.085 |
| C7-Phenol 1DB | C13H18O | 262 | 24.3, 3.035 |
| C7-Phenol 1DB | C13H18O | 262 | 24.5, 3.020 |
| C7-Phenol 1DB | C13H18O | 262 | 25.3, 3.150 |
| C7-Phenol | C13H20O | 264 | 20.0, 3.260 |
| C7-Phenol | C13H20O | 264 | 20.4, 3.220 |
| C7-Phenol | C13H20O | 264 | 21.1, 3.220 |
| C7-Phenol | C13H20O | 264 | 21.7, 3.290 |
| C7-Phenol | C13H20O | 264 | 22.6, 3.180 |
| C7-Phenol | C13H20O | 264 | 23.2, 3.320 |
| C3-Hydroxybenzothiophene | C10H10OS | 264 | 31.3, 2.710 |
| C3-Hydroxybenzothiophene | C10H10OS | 264 | 32.3, 2.600 |
| C3-Hydroxybenzothiophene | C10H10OS | 264 | 32.9, 2.665 |
| Phenanthrol | C14H10O | 266 | 41.2, 2.490 |
| Anthrol | C14H10O | 266 | 43.2, 2.490 |
| Anthrol | C14H10O | 266 | 43.4, 2.505 |
| Anthrol | C14H10O | 266 | 44.2, 2.565 |
| C1-Hydroxyfluorene | C14H12O | 268 | 37.8, 2.605 |
| C1-Hydroxyfluorene | C14H12O | 268 | 38.4, 2.700 |
| C1-Hydroxyfluorene | C14H12O | 268 | 38.8, 2.575 |

Appendix 3 – Derivatized database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C1-Hydroxyfluorene | C14H12O | 268 | 39.0, 2.555 |
| C1-Hydroxyfluorene | C14H12O | 268 | 39.2, 2.745 |
| C1-Hydroxyfluorene | C14H12O | 268 | 39.4, 2.620 |
| C1-Hydroxyfluorene | C14H12O | 268 | 39.5, 2.605 |
| C1-Hydroxyfluorene | C14H12O | 268 | 39.7, 2.655 |
| C1-Hydroxyfluorene | C14H12O | 268 | 40.2, 2.665 |
| C1-Hydroxyfluorene | C14H12O | 268 | 40.4, 2.670 |
| C1-Hydroxyfluorene | C14H12O | 268 | 40.7, 2.655 |
| C2-Biphenylol | C14H14O | 270 | 28.2, 2.685 |
| C2-Biphenylol | C14H14O | 270 | 28.5, 2.735 |
| C2-Biphenylol | C14H14O | 270 | 28.7, 2.715 |
| C2-Biphenylol | C14H14O | 270 | 28.9, 2.690 |
| C2-Biphenylol | C14H14O | 270 | 29.0, 2.695 |
| C2-Biphenylol | C14H14O | 270 | 29.5, 2.670 |
| C2-Biphenylol | C14H14O | 270 | 30.1, 2.660 |
| C2-Biphenylol | C14H14O | 270 | 30.4, 2.675 |
| C2-Biphenylol | C14H14O | 270 | 30.7, 2.600 |
| C2-Biphenylol | C14H14O | 270 | 31.1, 2.660 |
| C2-Biphenylol | C14H14O | 270 | 31.4, 2.760 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 33.7, 2.790 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 34.3, 2.635 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 34.7, 2.680 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 35.1, 2.650 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 35.3, 2.630 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 35.5, 2.745 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 35.8, 2.745 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 36.1, 2.615 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 36.2, 2.720 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 36.5, 2.640 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 37.3, 2.750 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 37.9, 2.705 |
| C2-Hydroxyacenaphthene/C1-hydroxydibenzofuran | C14H14O | 270 | 38.3, 2.735 |
| Hydroxy(dibenzo/naphtho)thiophene | C12H8OS | 272 | 41.6, 2.500 |
| Hydroxy(dibenzo/naphtho)thiophene | C12H8OS | 272 | 42.7, 2.520 |
| Hydroxy(dibenzo/naphtho)thiophene | C12H8OS | 272 | 43.2, 2.550 |
| C8-Phenol 2DB | C14H18O | 274 | 26.3, 2.970 |
| C8-Phenol 2DB | C14H18O | 274 | 27.0, 3.010 |
| C8-Phenol 2DB | C14H18O | 274 | 28.0, 2.990 |
| C8-Phenol 2DB | C14H18O | 274 | 28.2, 3.050 |
| C8-Phenol 2DB | C14H18O | 274 | 28.7, 2.940 |
| C8-Phenol 2DB | C14H18O | 274 | 29.3, 2.905 |
| C8-Phenol 2DB | C14H18O | 274 | 29.5, 2.985 |
| C1-Anthrol | C15H12O | 280 | 44.6, 2.215 |
| C1-Anthrol | C15H12O | 280 | 45.1, 2.550 |
| C1-Anthrol | C15H12O | 280 | 45.5, 2.555 |
| C1-Anthrol | C15H12O | 280 | 46.1, 2.600 |
| C1-Anthrol | C15H12O | 280 | 47.1, 2.550 |
| C2-Hydroxyfluorene | C15H14O | 282 | 39.3, 2.700 |
| C2-Hydroxyfluorene | C15H14O | 282 | 39.6, 2.720 |
| C2-Hydroxyfluorene | C15H14O | 282 | 39.9, 2.675 |
| C2-Hydroxyfluorene | C15H14O | 282 | 41.1, 2.685 |
| C2-Hydroxyfluorene | C15H14O | 282 | 41.2, 2.675 |
| C2-Hydroxyfluorene | C15H14O | 282 | 41.8, 2.770 |

Appendix 3 – Derivatized database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C2-Hydroxyfluorene | C15H14O | 282 | 42.3, 2.655 |
| C2-Hydroxyfluorene | C15H14O | 282 | 42.5, 2.725 |
| C2-Hydroxyfluorene | C15H14O | 282 | 42.7, 2.690 |
| C2-Hydroxyfluorene | C15H14O | 282 | 43.4, 2.760 |
| C2-Hydroxyfluorene | C15H14O | 282 | 44.1, 2.705 |
| C3-Biphenylol | C15H16O | 284 | 29.2, 2.790 |
| C3-Biphenylol | C15H16O | 284 | 30.7, 2.780 |
| C3-Biphenylol | C15H16O | 284 | 31.1, 2.730 |
| C3-Biphenylol | C15H16O | 284 | 31.3, 2.760 |
| C3-Biphenylol | C15H16O | 284 | 31.6, 2.750 |
| C3-Biphenylol | C15H16O | 284 | 32.7, 2.705 |
| C3-Biphenylol | C15H16O | 284 | 33.0, 2.685 |
| C3-Biphenylol | C15H16O | 284 | 33.8, 2.660 |
| C3-Hydroxyacenaphthene/C2-hydroxydibenzofuran | C15H16O | 284 | 37.4, 2.825 |
| C3-Hydroxyacenaphthene/C2-hydroxydibenzofuran | C15H16O | 284 | 37.9, 2.630 |
| C3-Hydroxyacenaphthene/C2-hydroxydibenzofuran | C15H16O | 284 | 38.0, 2.770 |
| C3-Hydroxyacenaphthene/C2-hydroxydibenzofuran | C15H16O | 284 | 38.3, 2.785 |
| C3-Hydroxyacenaphthene/C2-hydroxydibenzofuran | C15H16O | 284 | 38.5, 2.715 |
| C3-Hydroxyacenaphthene/C2-hydroxydibenzofuran | C15H16O | 284 | 39.7, 2.715 |
| C3-Hydroxyacenaphthene/C2-hydroxydibenzofuran | C15H16O | 284 | 40.0, 2.750 |
| C3-Hydroxyacenaphthene/C2-hydroxydibenzofuran | C15H16O | 284 | 40.2, 2.780 |
| C3-Hydroxyacenaphthene/C2-hydroxydibenzofuran | C15H16O | 284 | 40.9, 2.775 |
| Hydroxy-4-ring PAH | C16H10O | 290 | 49.3, 2.600 |
| Hydroxy-4-ring PAH | C16H10O | 290 | 51.4, 2.445 |
| Hydroxy-4-ring PAH | C16H10O | 290 | 51.6, 2.430 |
| Hydroxy-4-ring PAH | C16H10O | 290 | 52.4, 2.495 |
| Hydroxy-4-ring PAH | C16H10O | 290 | 53.8, 2.465 |
| C3-Hydroxyfluorene | C16H16O | 296 | 43.3, 2.630 |
| C3-Hydroxyfluorene | C16H16O | 296 | 44.4, 2.655 |
| C4-Hydroxyacenaphthene/C3-hydroxydibenzofuran | C16H18O | 298 | 39.8, 2.790 |
| C4-Hydroxyacenaphthene/C3-hydroxydibenzofuran | C16H18O | 298 | 40.6, 2.795 |
| C4-Hydroxyacenaphthene/C3-hydroxydibenzofuran | C16H18O | 298 | 41.1, 2.760 |
| C4-Hydroxyacenaphthene/C3-hydroxydibenzofuran | C16H18O | 298 | 41.5, 2.660 |
| C1-hydroxy-4-ring PAH | C17H20O | 304 | 53.0, 2.530 |
| C1-Hydroxy-4-ring PAH | C17H20O | 304 | 54.1, 2.570 |
| C1-Hydroxy-4-ring PAH | C17H20O | 304 | 55.1, 2.520 |
| HydroxyChrysene | C18H12O | 318 | 56.8, 2.555 |
| HydroxyChrysene | C18H12O | 318 | 57.7, 2.485 |
| HydroxyChrysene | C18H12O | 318 | 58.2, 2.580 |
| HydroxyChrysene | C18H12O | 318 | 59.9, 2.580 |
| C1-Hydroxychrysene | C19H14O | 332 | 61.5, 2.625 |

Appendix 3 – Derivatized database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Azabenzothiophene | C7H5NS | 135 | 16.6, 1.695 |
| Thienobenzofurans | C10H6OS | 174 | 25.5, 2.115 |
| Thienobenzofurans | C10H6OS | 174 | 26.0, 2.120 |
| Thienobenzofurans | C10H6OS | 174 | 26.3, 2.055 |
| Thienobenzofurans | C10H6OS | 174 | 26.6, 1.945 |
| Thienobenzofurans | C10H6OS | 174 | 27.3, 2.120 |
| Thienobenzofurans | C10H6OS | 174 | 27.7, 2.040 |
| Thienobenzofurans | C10H6OS | 174 | 28.3, 2.035 |
| Azadibenzothiophen or azanaphthothiophene | C11H7NS | 185 | 35.7, 2.100 |
| Azadibenzothiophen or azanaphthothiophene | C11H7NS | 185 | 37.0, 2.065 |
| Azadibenzothiophen or azanaphthothiophene | C11H7NS | 185 | 37.4, 2.085 |
| Azadibenzothiophen or azanaphthothiophene | C11H7NS | 185 | 38.3, 2.025 |
| 2H-Naphtho[1,8-bc]thiophen-2-one | C11H6OS | 186 | 38.0, 1.975 |
| 3-Cyano-4,6-diphenylpyridine-2(1H)-thione | C18H12N2S | 288 | 81.1, 3.070 |

Appendix 4 - Mixed Heterocycle database

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Pyridine | C5H5N | 79 | 6.0, 1.010 |
| Methyl Pyridine | C6H7N | 93 | 5.4, 1.100 |
| Methyl Pyridine | C6H7N | 93 | 7.2, 1.070 |
| Methyl Pyridine | C6H7N | 93 | 7.4, 1.070 |
| Methyl Pyridine | C6H7N | 93 | 7.8, 1.070 |
| Aniline | C6H5NH2 | 93 | 7.9, 1.255 |
| Benzonitrile | C7H5N | 103 | 8.1, 1.275 |
| Pyridine, 4-ethenyl- | C7H7N | 105 | 5.2, 1.415 |
| p-Aminotoluene | C7H9N | 106 | 10.0, 1.450 |
| Dimethyl Pyridine | C7H9N | 107 | 6.0, 1.170 |
| Dimethyl Pyridine | C7H9N | 107 | 6.3, 1.145 |
| Dimethyl Pyridine | C7H9N | 107 | 6.6, 1.135 |
| Dimethyl Pyridine | C7H9N | 107 | 6.7, 1.110 |
| Dimethyl Pyridine | C7H9N | 107 | 6.9, 1.090 |
| Dimethyl Pyridine | C7H9N | 107 | 7.2, 1.170 |
| Dimethyl Pyridine | C7H9N | 107 | 7.5, 1.185 |
| Dimethyl Pyridine | C7H9N | 107 | 7.7, 1.170 |
| Dimethyl Pyridine | C7H9N | 107 | 8.0, 1.180 |
| Dimethyl Pyridine | C7H9N | 107 | 8.2, 1.150 |
| Dimethyl Pyridine | C7H9N | 107 | 8.4, 1.170 |
| Methyl Benzonitrile | C8H7N | 117 | 9.6, 1.445 |
| Methyl Benzonitrile | C8H7N | 117 | 9.9, 1.455 |
| Methyl Benzonitrile | C8H7N | 117 | 10.2, 1.435 |
| Methyl Benzonitrile | C8H7N | 117 | 10.5, 1.470 |
| Benzyl Nitrile | C8H7N | 117 | 13.0, 1.500 |
| Indole | C8H7N | 117 | 17.6, 1.700 |
| C3 Pyridine | C8H11N | 121 | 6.8, 1.260 |
| C3 Pyridine | C8H11N | 121 | 6.9, 1.265 |
| C3 Pyridine | C8H11N | 121 | 7.1, 1.245 |
| C3 Pyridine | C8H11N | 121 | 7.6, 1.275 |
| C3 Pyridine | C8H11N | 121 | 7.8, 1.315 |
| C3 Pyridine | C8H11N | 121 | 8.1, 1.345 |
| C3 Pyridine | C8H11N | 121 | 8.8, 1.260 |
| Trimethyl Pyrazine | C7H10N2 | 121 | 9.0, 1.475 |
| Trimethyl Pyrazine | C7H10N2 | 121 | 9.7, 1.585 |
| Benzenamine, 2,5-dimethyl- | C8H11N | 121 | 11.9, 1.645 |

Appendix 5 – PANH database

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| 1,4-Benzenediamine, 2-methyl- | C7H10N2 | 122 | 9.6, 1.530 |
| Quinoline | C9H7N | 129 | 15.0, 1.740 |
| Isoquinoline | C9H7N | 129 | 16.4, 1.750 |
| C1-Indole | C9H9N | 130 | 20.0, 1.785 |
| C1-Indole | C9H9N | 130 | 20.5, 1.840 |
| C1-Indole | C9H9N | 130 | 20.7, 1.835 |
| C1-Indole | C9H9N | 130 | 21.0, 1.825 |
| Methyl Quinoline | C10H9N | 143 | 16.8, 1.875 |
| Methyl Quinoline | C10H9N | 143 | 17.0, 1.915 |
| Methyl Quinoline | C10H9N | 143 | 17.2, 1.870 |
| Methyl Quinoline | C10H9N | 143 | 17.7, 1.925 |
| Methyl Quinoline | C10H9N | 143 | 18.4, 1.920 |
| Methyl Quinoline | C10H9N | 143 | 18.7, 1.925 |
| Methyl Quinoline | C10H9N | 143 | 18.9, 1.935 |
| Methyl Quinoline | C10H9N | 143 | 19.1, 1.995 |
| Methyl Quinoline | C10H9N | 143 | 19.7, 1.930 |
| Methyl Quinoline | C10H9N | 143 | 20.0, 1.920 |
| x-Naphthalenamine | C10H9N | 143 | 27.5, 1.880 |
| x-Naphthalenamine | C10H9N | 143 | 28.2, 1.880 |
| C2-Indole | C10H11N | 144 | 22.4, 1.955 |
| C2-Indole | C10H11N | 144 | 22.9, 1.940 |
| C2-Indole | C10H11N | 144 | 23.2, 1.920 |
| C2-Indole | C10H11N | 144 | 23.5, 2.000 |
| C2-Indole | C10H11N | 144 | 23.7, 1.965 |
| C2-Indole | C10H11N | 144 | 24.1, 1.935 |
| Methyl Cinnoline | C9H8N2 | 144 | 13.2, 1.885 |
| Methyl Cinnoline | C9H8N2 | 144 | 15.3, 1.895 |
| Indolizine, 2,3-dimethyl- | C10H11N | 145 | 23.1, 1.915 |
| 2H-Isoindole, 4,7-dimethyl- | C10H11N | 145 | 23.9, 1.975 |
| 1-Naphthalenecarbonitrile | C11H7N | 153 | 25.0, 1.905 |
| 2-Naphthalenecarbonitrile | C11H7N | 153 | 26.1, 1.945 |
| Pyridine, 4-phenyl- | C11H9N | 155 | 18.5, 2.050 |
| Pyridine, 2-phenyl- | C11H9N | 155 | 22.7, 1.970 |
| Dimethyl Quinoline | C11H11N | 157 | 18.1, 2.060 |
| Dimethyl Quinoline | C11H11N | 157 | 19.3, 2.030 |
| Dimethyl Quinoline | C11H11N | 157 | 19.6, 2.040 |
| Dimethyl Quinoline | C11H11N | 157 | 20.3, 2.070 |
| Dimethyl Quinoline | C11H11N | 157 | 20.7, 2.105 |
| Dimethyl Quinoline | C11H11N | 157 | 21.4, 2.025 |
| Dimethyl Quinoline | C11H11N | 157 | 21.7, 2.055 |
| Dimethyl Quinoline | C11H11N | 157 | 23.4, 2.075 |
| Dimethyl Quinoline | C11H11N | 157 | 23.4, 2.155 |
| Dimethyl Quinoline | C11H11N | 157 | 23.5, 2.095 |
| Dimethyl Quinoline | C11H11N | 157 | 23.7, 2.085 |
| C3-Indole | C11H13N | 158 | 24.2, 1.995 |
| C3-Indole | C11H13N | 158 | 25.6, 2.060 |
| C3-Indole | C11H13N | 158 | 26.0, 2.070 |
| C3-Indole | C11H13N | 158 | 26.8, 2.050 |
| C3-Indole | C11H13N | 158 | 26.9, 2.050 |
| C1-Naphthalenecarbonitrile | C12H9N | 167 | 27.7, 2.055 |
| C1-Naphthalenecarbonitrile | C12H9N | 167 | 28.1, 2.075 |
| C1-Naphthalenecarbonitrile | C12H9N | 167 | 28.6, 2.035 |
| C1-Naphthalenecarbonitrile | C12H9N | 167 | 30.0, 2.005 |

Appendix 5 – PANH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C1-Naphthalenecarbonitrile | $C_{12}H_9N$ | 167 | 30.3, 1.990 |
| Azafluorene | $C_{12}H_9N$ | 167 | 33.7, 1.950 |
| Carbazole | $C_{12}H_9N$ | 167 | 38.6, 1.910 |
| Indenepyridine | $C_{12}H_9N$ | 167 | 39.5, 1.870 |
| Indenepyridine | $C_{12}H_9N$ | 167 | 41.8, 1.870 |
| Indenepyridine | $C_{12}H_9N$ | 167 | 42.1, 1.905 |
| 3-Methyl-5-phenylpyridine | $C_{12}H_{11}N$ | 169 | 24.2, 2.035 |
| Pyridine, 2-(phenylmethyl)- | $C_{12}H_{11}N$ | 169 | 24.5, 2.010 |
| Trimethyl Quinoline | $C_{12}H_{13}N$ | 171 | 21.5, 2.215 |
| Trimethyl Quinoline | $C_{12}H_{13}N$ | 171 | 22.4, 2.205 |
| Trimethyl Quinoline | $C_{12}H_{13}N$ | 171 | 22.7, 2.210 |
| Trimethyl Quinoline | $C_{12}H_{13}N$ | 171 | 22.8, 2.205 |
| Trimethyl Quinoline | $C_{12}H_{13}N$ | 171 | 23.0, 2.235 |
| $C_{12}H_{13}N$ ??? Or $C_{11}H_{12}N_2$ ??? | ??? | 171 | 26.9, 2.120 |
| $C_{12}H_{13}N$ ??? Or $C_{11}H_{12}N_2$ ??? | ??? | 171 | 27.1, 2.105 |
| $C_{12}H_{13}N$ ??? Or $C_{11}H_{12}N_2$ ??? | ??? | 171 | 27.4, 2.075 |
| $C_{12}H_{13}N$ ??? Or $C_{11}H_{12}N_2$ ??? | ??? | 171 | 27.7, 2.080 |
| $C_{12}H_{13}N$ ??? Or $C_{11}H_{12}N_2$ ??? | ??? | 171 | 28.1, 2.170 |
| $C_{12}H_{13}N$ ??? Or $C_{11}H_{12}N_2$ ??? | ??? | 171 | 28.5, 2.070 |
| $C_{12}H_{13}N$ ??? Or $C_{11}H_{12}N_2$ ??? | ??? | 171 | 28.8, 2.185 |
| $C_{12}H_{13}N$ ??? Or $C_{11}H_{12}N_2$ ??? | ??? | 171 | 29.1, 2.065 |
| $C_{12}H_{13}N$ ??? Or $C_{11}H_{12}N_2$ ??? | ??? | 171 | 29.4, 2.080 |
| $C_{12}H_{13}N$ ??? Or $C_{11}H_{12}N_2$ ??? | ??? | 171 | 32.6, 2.070 |
| Phenylbenzonitrile | $C_{13}H_9N$ | 179 | 30.6, 1.960 |
| Benzo[h]quinoline | $C_{13}H_9N$ | 179 | 36.0, 2.035 |
| Acridine | $C_{13}H_9N$ | 179 | 36.4, 2.035 |
| Benzo[g]quinoline or Benzo[f]isoquinoline | $C_{13}H_9N$ | 179 | 36.9, 2.020 |
| NPAC $C_{13}H_9N$ | $C_{13}H_9N$ | 179 | 37.2, 1.900 |
| Phenanthridine | $C_{13}H_9N$ | 179 | 37.3, 2.065 |
| Benzo[f]quinoline | $C_{13}H_9N$ | 179 | 37.5, 2.040 |
| NPAC $C_{13}H_9N$ | $C_{13}H_9N$ | 179 | 38.2, 2.045 |
| NPAC $C_{13}H_9N$ | $C_{13}H_9N$ | 179 | 38.5, 2.055 |
| NPAC $C_{13}H_9N$ | $C_{13}H_9N$ | 179 | 39.0, 2.055 |
| Pyridine, 2(2-phenylethenyl)- | $C_{13}H_{11}N$ | 180 | 45.4, 1.940 |
| C1 Naphthaleneacetonitrile | $C_{13}H_{11}N$ | 181 | 31.8, 2.205 |
| C1 Naphthaleneacetonitrile | $C_{13}H_{11}N$ | 181 | 32.3, 2.230 |
| Methyl Carbazole | $C_{13}H_{11}N$ | 181 | 40.1, 2.005 |
| Methyl Carbazole | $C_{13}H_{11}N$ | 181 | 41.6, 2.000 |
| Methyl Carbazole | $C_{13}H_{11}N$ | 181 | 42.4, 1.960 |
| Methyl Carbazole | $C_{13}H_{11}N$ | 181 | 42.7, 1.940 |
| Methyl Carbazole | $C_{13}H_{11}N$ | 181 | 43.5, 2.025 |
| Methyl Carbazole | $C_{13}H_{11}N$ | 181 | 43.9, 1.895 |
| Methyl Carbazole | $C_{13}H_{11}N$ | 181 | 44.4, 1.910 |
| Methyl Carbazole | $C_{13}H_{11}N$ | 181 | 44.8, 1.910 |
| 9H-fluorene-9-carbonitrile | $C_{14}H_9N$ | 191 | 31.8, 2.140 |
| NPAC | $C_{14}H_9N$ | 191 | 44.4, 2.030 |
| Benzo[def]carbazole | $C_{14}H_9N$ | 191 | 50.9, 1.905 |
| Methyl Acridine | $C_{14}H_{11}N$ | 193 | 37.1, 2.170 |
| Methyl Acridine | $C_{14}H_{11}N$ | 193 | 37.2, 2.125 |
| Methyl Acridine | $C_{14}H_{11}N$ | 193 | 39.1, 2.115 |
| Methyl Acridine | $C_{14}H_{11}N$ | 193 | 39.5, 2.120 |
| Methyl Acridine | $C_{14}H_{11}N$ | 193 | 39.8, 2.140 |
| Methyl Acridine | $C_{14}H_{11}N$ | 193 | 40.4, 2.130 |

Appendix 5 – PANH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Methyl Acridine | $C_{14}H_{11}N$ | 193 | 40.8, 2.120 |
| Methyl Acridine | $C_{14}H_{11}N$ | 193 | 42.5, 2.075 |
| Phenyl Indole | $C_{14}H_{11}N$ | 193 | 44.1, 1.590 |
| Phenyl Indole | $C_{14}H_{11}N$ | 193 | 45.0, 2.020 |
| Phenyl Indole | $C_{14}H_{11}N$ | 193 | 45.6, 1.865 |
| Phenyl Indole | $C_{14}H_{11}N$ | 193 | 47.3, 1.415 |
| Phenyl Indole | $C_{14}H_{11}N$ | 193 | 47.6, 1.865 |
| Dimethyl Carbazole | $C_{14}H_{13}N$ | 195 | 43.0, 2.105 |
| Dimethyl Carbazole | $C_{14}H_{13}N$ | 195 | 43.8, 2.070 |
| Dimethyl Carbazole | $C_{14}H_{13}N$ | 195 | 44.0, 2.060 |
| Dimethyl Carbazole | $C_{14}H_{13}N$ | 195 | 44.2, 2.055 |
| Dimethyl Carbazole | $C_{14}H_{13}N$ | 195 | 44.3, 2.065 |
| Dimethyl Carbazole | $C_{14}H_{13}N$ | 195 | 44.4, 2.095 |
| Dimethyl Carbazole | $C_{14}H_{13}N$ | 195 | 44.6, 2.080 |
| Dimethyl Carbazole | $C_{14}H_{13}N$ | 195 | 45.0, 2.055 |
| Dimethyl Carbazole | $C_{14}H_{13}N$ | 195 | 45.3, 2.055 |
| Dimethyl Carbazole | $C_{14}H_{13}N$ | 195 | 45.4, 2.145 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 45.9, 2.065 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 46.2, 2.025 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 46.6, 2.125 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 46.8, 2.140 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 47.1, 2.020 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 47.8, 2.030 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 48.3, 2.100 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 48.5, 2.090 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 48.8, 2.060 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 49.0, 2.040 |
| Azapyrene isomer | $C_{15}H_9N$ | 203 | 50.1, 2.065 |
| [1,1'-biphenyl]-4,4'-dicarbonitrile | $C_{14}H_8N_2$ | 204 | 42.2, 2.050 |
| [1,1'-biphenyl]-4,4'-dicarbonitrile | $C_{14}H_8N_2$ | 204 | 43.0, 2.060 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 45.1, 2.070 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 47.6, 1.440 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 48.3, 2.045 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 51.3, 2.000 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 52.4, 2.010 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 52.6, 2.015 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 53.5, 2.015 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 53.9, 1.990 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 54.0, 2.010 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 54.2, 1.985 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 54.7, 1.945 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 55.0, 1.960 |
| Phenyl Isoquinoline | $C_{15}H_{11}N$ | 204 | 55.4, 1.935 |
| Dimethyl Acridine | $C_{15}H_{13}N$ | 207 | 40.6, 2.195 |
| Dimethyl Acridine | $C_{15}H_{13}N$ | 207 | 41.7, 2.195 |
| C1-Azapyrene isomer | $C_{16}H_{11}N$ | 217 | 48.1, 2.195 |
| C1-Azapyrene isomer | $C_{16}H_{11}N$ | 217 | 50.0, 2.170 |
| C1-Azapyrene isomer | $C_{16}H_{11}N$ | 217 | 50.2, 2.155 |
| 1-Aminopyrene | $C_{16}H_{11}N$ | 217 | 50.7, 2.090 |
| Benzo[c]carbazole | $C_{16}H_{11}N$ | 217 | 57.9, 2.010 |
| Benzo[a]carbazole | $C_{16}H_{11}N$ | 217 | 59.9, 1.985 |
| Benzo[b]carbazole | $C_{16}H_{11}N$ | 217 | 60.7, 1.930 |
| Benzo[c]acridine | $C_{17}H_{11}N$ | 229 | 55.3, 2.100 |

Appendix 5 – PANH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Benzo[a]acridine | C17H11N | 229 | 56.8, 2.170 |
| Naphtho(2,3-h)quinoline | C17H11N | 229 | 57.3, 2.070 |
| 4-Azachrysene | C17H11N | 229 | 57.8, 2.065 |
| Naphtho(2,1-f)quinoline | C17H11N | 229 | 58.6, 2.095 |
| 2-Azachrysene | C17H11N | 229 | 59.2, 2.075 |
| Benzo(a)phenazine | C16H10N2 | 230 | 53.2, 2.205 |
| Diphenyl Pyridine/C2-Azapyrene isomer | C17H13N | 231 | 58.1, 2.125 |
| Diphenyl Pyridine/C2-Azapyrene isomer | C17H13N | 231 | 59.3, 2.165 |
| Diphenyl Pyridine/C2-Azapyrene isomer | C17H13N | 231 | 60.3, 2.065 |
| Diphenyl Pyridine/C2-Azapyrene isomer | C17H13N | 231 | 60.6, 2.065 |
| Diphenyl Pyridine/C2-Azapyrene isomer | C17H13N | 231 | 61.2, 2.060 |
| Diphenyl Pyridine/C2-Azapyrene isomer | C17H13N | 231 | 61.6, 2.020 |
| Diphenyl Pyridine/C2-Azapyrene isomer | C17H13N | 231 | 62.2, 2.050 |
| Diphenyl Pyridine/C2-Azapyrene isomer | C17H13N | 231 | 62.5, 2.000 |
| Diphenyl Pyridine/C2-Azapyrene isomer | C17H13N | 231 | 62.7, 2.010 |
| Diphenyl Pyridine/C2-Azapyrene isomer | C17H13N | 231 | 63.0, 1.995 |
| Dibenzo(b,def)carbazole isomer | C18H11N | 241 | 62.4, 2.180 |
| Dibenzo(b,def)carbazole isomer | C18H11N | 241 | 62.6, 2.145 |
| Dibenzo(b,def)carbazole isomer | C18H11N | 241 | 62.8, 2.135 |
| Dibenzo(b,def)carbazole isomer | C18H11N | 241 | 63.7, 2.120 |
| Dibenzo(b,def)carbazole isomer | C18H11N | 241 | 68.7, 2.015 |
| Dibenzo(b,def)carbazole isomer | C18H11N | 241 | 69.6, 2.030 |
| Dibenzo(b,def)carbazole isomer | C18H11N | 241 | 70.4, 2.000 |
| Dibenzo(b,def)carbazole isomer | C18H11N | 241 | 70.8, 2.005 |
| Dibenzo(b,def)carbazole isomer | C18H11N | 241 | 71.0, 1.990 |
| Dibenzo(b,def)carbazole | C18H11N | 241 | 57.9, 2.265 |
| Phenyl Carbazole | C18H13N | 243 | 59.8, 1.800 |
| Methyl Benz[x]acridine | C18H13N | 243 | 64.5, 2.000 |
| Methyl Benz[x]acridine | C18H13N | 243 | 67.1, 2.050 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 63.3, 2.110 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 63.4, 2.190 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 63.6, 2.095 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 63.8, 2.110 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 63.9, 2.100 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 64.1, 2.075 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 64.6, 2.100 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 64.8, 2.085 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 65.2, 2.075 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 65.7, 2.055 |
| Methyl Diphenyl Pyridine/C3-Azapyrene isomer | C18H15N | 245 | 66.1, 2.050 |
| Benz(a)anthracene-x-carbonitrile | C19H11N | 253 | 64.0, 2.145 |
| Benz(a)anthracene-x-carbonitrile | C19H11N | 253 | 67.8, 2.095 |
| Benz(a)anthracene-x-carbonitrile | C19H11N | 253 | 68.0, 2.105 |
| Benz(a)anthracene-x-carbonitrile | C19H11N | 253 | 68.4, 2.105 |
| Benz(a)anthracene-x-carbonitrile | C19H11N | 253 | 68.7, 2.095 |
| Benz(a)anthracene-x-carbonitrile | C19H11N | 253 | 68.9, 2.120 |
| Benz(a)anthracene-x-carbonitrile | C19H11N | 253 | 69.2, 2.115 |
| Phenyl Acridine | C19H13N | 255 | 70.5, 2.050 |
| Phenyl Acridine | C19H13N | 255 | 71.3, 2.025 |
| Phenyl Acridine | C19H13N | 255 | 71.8, 2.040 |
| Dimethyl Benz[x]acridine | C19H15N | 257 | 69.2, 2.025 |
| Dimethyl Benz[x]acridine | C19H15N | 257 | 70.2, 2.025 |
| C20H13N | C20H13N | 267 | 72.7, 2.215 |

Appendix 5 – PANH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Dibenzo(a,g)carbazole | C20H13N | 267 | 76.9, 2.360 |
| C20H13N | C20H13N | 267 | 77.6, 2.400 |
| Naphtho[2,3-b]carbazole | C20H13N | 267 | 78.6, 2.475 |
| 13H-Dibenzo[a,i]carbazole | C20H13N | 267 | 79.2, 2.550 |
| C20H13N | C20H13N | 267 | 79.5, 2.555 |
| C20H13N | C20H13N | 267 | 80.3, 2.570 |
| Dibenz(x,x)Acridine | C21H13N | 279 | 72.0, 2.185 |
| Dibenz(x,x)Acridine | C21H13N | 279 | 73.1, 2.175 |
| Dibenz(x,x)Acridine | C21H13N | 279 | 73.3, 2.175 |
| Dibenz(x,x)Acridine | C21H13N | 279 | 73.7, 2.205 |
| Dibenz(x,x)Acridine | C21H13N | 279 | 74.0, 2.180 |
| Dibenz(x,x)Acridine | C21H13N | 279 | 74.9, 2.275 |
| 4H-Benzo[def]naphtho[2,3-b]carbazole | C22H13N | 291 | 80.7, 2.965 |
| C21H14N2 | C21H14N2 | 294 | 80.0, 2.270 |

Appendix 5 – PANH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Benzene, methoxy- | C7H8O | 108 | 6.0, 1.265 |
| Benzofuran | C8H6O | 118 | 7.5, 1.315 |
| Benzofuran, 2,3-dihydro- | C8H8O | 120 | 9.6, 1.485 |
| Acetophenone | C8H8O | 120 | 10.2, 1.425 |
| 1,2-Naphthaelenedione | C10H6O2 | 130 | 13.6, 1.685 |
| C1-Benzofuran | C9H8O | 132 | 9.4, 1.585 |
| C1-Benzofuran | C9H8O | 132 | 9.6, 1.600 |
| 1H-Inden-1-one, 2,3-dihydro- | C9H8O | 132 | 16.9, 1.755 |
| 1H-Inden-1-one, 2,3-dihydro- | C9H8O | 132 | 17.7, 1.745 |
| Benzofuran, 2-ethenyl- | C10H8O | 144 | 13.2, 1.850 |
| C2-Benzofuran | C10H10O | 146 | 11.0, 1.915 |
| C2-Benzofuran | C10H10O | 146 | 11.2, 1.755 |
| C2-Benzofuran | C10H10O | 146 | 11.6, 1.825 |
| C2-Benzofuran | C10H10O | 146 | 11.8, 1.835 |
| C2-Benzofuran | C10H10O | 146 | 12.0, 1.865 |
| C2-Benzofuran | C10H10O | 146 | 12.3, 1.910 |
| C2-Benzofuran | C10H10O | 146 | 12.5, 1.875 |
| C2-Benzofuran | C10H10O | 146 | 12.8, 1.910 |
| C2-Benzofuran | C10H10O | 146 | 13.3, 1.910 |
| 1-Naphthalenecarboxaldehyde | C11H8O | 156 | 19.2, 2.040 |
| C3-Benzofuran | C11H12O | 160 | 13.7, 2.030 |
| C3-Benzofuran | C11H12O | 160 | 13.9, 1.995 |
| C3-Benzofuran | C11H12O | 160 | 14.1, 2.040 |
| C3-Benzofuran | C11H12O | 160 | 14.3, 2.045 |
| C3-Benzofuran | C11H12O | 160 | 14.6, 2.085 |
| C3-Benzofuran | C11H12O | 160 | 14.9, 2.090 |
| C3-Benzofuran | C11H12O | 160 | 15.2, 2.140 |
| C3-Benzofuran | C11H12O | 160 | 15.7, 2.190 |
| C3-Benzofuran | C11H12O | 160 | 16.1, 2.155 |
| C3-Benzofuran | C11H12O | 160 | 16.8, 2.140 |
| Ethanone, 1(2,3,4-trimethylphenyl)- | C11H14O | 162 | 9.7, 1.920 |
| Ethanone, 1(2,3,4-trimethylphenyl)- | C11H14O | 162 | 10.3, 1.955 |
| Ethanone, 1(2,3,4-trimethylphenyl)- | C11H14O | 162 | 10.7, 1.785 |
| Ethanone, 1(2,3,4-trimethylphenyl)- | C11H14O | 162 | 11.7, 1.870 |
| Ethanone, 1(2,3,4-trimethylphenyl)- | C11H14O | 162 | 12.4, 1.930 |
| Dibenzofuran | C12H8O | 168 | 24.0, 2.140 |

Appendix 6 – PAOH database

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Naphtho[2,1-b]furan | C12H8O | 168 | 25.2, 2.090 |
| Naphtho[2,1-b]furan | C12H8O | 168 | 25.8, 2.080 |
| Naphtho[2,1-b]furan | C12H8O | 168 | 26.9, 2.080 |
| 1(2H)-Acenaphthylenone | C12H8O | 168 | 31.7, 1.945 |
| Diphenyl Ether | C12H10O | 170 | 19.4, 2.040 |
| 2-ethyl-3-methylene-indan-1-one | C12H12O | 172 | 19.3, 2.395 |
| C4-Benzofuran | C12H14O | 174 | 16.2, 2.210 |
| C4-Benzofuran | C12H14O | 174 | 16.7, 2.240 |
| C4-Benzofuran | C12H14O | 174 | 17.0, 2.235 |
| C4-Benzofuran | C12H14O | 174 | 17.2, 2.255 |
| C4-Benzofuran | C12H14O | 174 | 17.4, 2.280 |
| C4-Benzofuran | C12H14O | 174 | 17.7, 2.290 |
| C4-Benzofuran | C12H14O | 174 | 18.0, 2.300 |
| C4-Benzofuran | C12H14O | 174 | 18.8, 2.320 |
| C4-Benzofuran | C12H14O | 174 | 19.0, 2.340 |
| C4-Benzofuran | C12H14O | 174 | 19.3, 2.380 |
| C4-Benzofuran | C12H14O | 174 | 19.8, 2.375 |
| 9H-Fluoren-9-one | C13H8O | 180 | 33.7, 2.080 |
| 1H-Phenalen-1-one | C13H8O | 180 | 36.9, 2.035 |
| C1-Dibenzofuran | C13H10O | 182 | 27.3, 2.240 |
| C1-Dibenzofuran | C13H10O | 182 | 27.8, 2.270 |
| C1-Dibenzofuran | C13H10O | 182 | 28.4, 2.265 |
| C1-Dibenzofuran | C13H10O | 182 | 28.5, 2.220 |
| C1-Dibenzofuran | C13H10O | 182 | 28.9, 2.320 |
| C1-Dibenzofuran | C13H10O | 182 | 29.3, 2.170 |
| C1-Dibenzofuran | C13H10O | 182 | 29.7, 2.295 |
| C1-Dibenzofuran | C13H10O | 182 | 30.4, 2.230 |
| C1-Dibenzofuran | C13H10O | 182 | 30.9, 2.290 |
| C1-Dibenzofuran | C13H10O | 182 | 31.3, 2.275 |
| C3-Dihydro Inden-1-one | C13H16O | 188 | 19.4, 2.375 |
| C3-Dihydro Inden-1-one | C13H16O | 188 | 19.9, 2.410 |
| C3-Dihydro Inden-1-one | C13H16O | 188 | 20.1, 2.405 |
| C3-Dihydro Inden-1-one | C13H16O | 188 | 20.3, 2.380 |
| C3-Dihydro Inden-1-one | C13H16O | 188 | 20.8, 2.435 |
| C3-Dihydro Inden-1-one | C13H16O | 188 | 22.4, 2.120 |
| Phenyl-Benzofuran | C14H10O | 194 | 32.0, 2.145 |
| Phenyl-Benzofuran | C14H10O | 194 | 32.3, 2.250 |
| Phenyl-Benzofuran | C14H10O | 194 | 32.6, 2.295 |
| Phenyl-Benzofuran | C14H10O | 194 | 33.1, 2.080 |
| Phenyl-Benzofuran | C14H10O | 194 | 34.1, 2.210 |
| Anthrone | C14H10O | 194 | 35.9, 2.190 |
| C2-Dibenzofuran | C14H12O | 196 | 29.7, 2.360 |
| C2-Dibenzofuran | C14H12O | 196 | 30.8, 2.355 |
| C2-Dibenzofuran | C14H12O | 196 | 31.0, 2.350 |
| C2-Dibenzofuran | C14H12O | 196 | 31.4, 2.400 |
| C2-Dibenzofuran | C14H12O | 196 | 31.5, 2.355 |
| C2-Dibenzofuran | C14H12O | 196 | 31.7, 2.315 |
| C2-Dibenzofuran | C14H12O | 196 | 31.9, 2.325 |
| C2-Dibenzofuran | C14H12O | 196 | 32.1, 2.340 |
| C2-Dibenzofuran | C14H12O | 196 | 32.4, 2.325 |
| C2-Dibenzofuran | C14H12O | 196 | 32.9, 2.455 |
| 9-Methoxyfluorene | C14H12O | 196 | 33.7, 2.330 |
| Xanthone | C14H12O | 196 | 38.4, 2.040 |

Appendix 6 – PAOH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Cyclopenta(def)phenanthrenone | C15H8O | 204 | 44.7, 2.085 |
|  | C15H10O | 206 | 40.0, 2.260 |
|  | C15H10O | 206 | 40.4, 2.230 |
|  | C15H10O | 206 | 40.6, 2.205 |
|  | C15H10O | 206 | 40.9, 2.155 |
| C15H12O | C15H12O | 208 | 36.3, 2.095 |
| 9,10-Anthracenedione | C14H8O2 | 208 | 42.5, 2.030 |
| Phenyl Chromene | C15H12O | 208 | 39.7, 2.210 |
| Phenyl Chromene | C15H12O | 208 | 39.8, 2.265 |
| Dimethyl Xanthene | C15H14O | 210 | 31.9, 2.430 |
| Dimethyl Xanthene | C15H14O | 210 | 33.0, 2.435 |
| Dimethyl Xanthene | C15H14O | 210 | 33.4, 2.425 |
| Dimethyl Xanthene | C15H14O | 210 | 33.6, 2.435 |
| Dimethyl Xanthene | C15H14O | 210 | 33.9, 2.455 |
| Dimethyl Xanthene | C15H14O | 210 | 34.1, 2.465 |
| Dimethyl Xanthene | C15H14O | 210 | 34.4, 2.465 |
| Dimethyl Xanthene | C15H14O | 210 | 34.7, 2.420 |
| Dimethyl Xanthene | C15H14O | 210 | 36.2, 2.380 |
| Dimethyl Xanthene | C15H14O | 210 | 36.5, 2.455 |
| Dimethyl Xanthene | C15H14O | 210 | 37.0, 2.365 |
| Benzo[b]naphtho[2,3-d]furan | C16H10O | 218 | 45.7, 2.215 |
| Benzo[b]naphtho[2,1-d]furan | C16H10O | 218 | 46.6, 2.170 |
| Benzo[b]naphtho[1,2-d]furan | C16H10O | 218 | 47.0, 2.205 |
| Benzo[k,l]xanthene | C16H10O | 218 | 48.0, 2.160 |
| C16H10O | C16H10O | 218 | 48.2, 2.125 |
| C16H10O | C16H10O | 218 | 49.3, 2.195 |
| 10-Methylanthracene-9-carboxaldehyde | C16H12O | 220 | 43.7, 2.375 |
| 11H-Benzo[a]fluoren-11-one | C17H10O | 230 | 53.8, 2.120 |
| 1-Pyrene-carboxaldehyde | C17H10O | 230 | 54.9, 2.180 |
| 11H-Benzo[b]fluoren-11-one | C17H10O | 230 | 55.7, 2.115 |
| 7H-Benz[de]antracen-7-one | C17H10O | 230 | 59.0, 2.030 |
| C1-Benzonaphthofuran | C17H12O | 232 | 47.1, 2.280 |
| C1-Benzonaphthofuran | C17H12O | 232 | 47.5, 2.385 |
| C1-Benzonaphthofuran | C17H12O | 232 | 47.6, 2.360 |
| C1-Benzonaphthofuran | C17H12O | 232 | 47.7, 2.295 |
| C1-Benzonaphthofuran | C17H12O | 232 | 48.5, 2.290 |
| C1-Benzonaphthofuran | C17H12O | 232 | 48.9, 2.275 |
| C1-Benzonaphthofuran | C17H12O | 232 | 49.2, 2.240 |
| C1-Benzonaphthofuran | C17H12O | 232 | 49.4, 2.235 |
| C1-Benzonaphthofuran | C17H12O | 232 | 49.6, 2.250 |
| C1-Benzonaphthofuran | C17H12O | 232 | 49.8, 2.255 |
| C1-Benzonaphthofuran | C17H12O | 232 | 50.1, 2.270 |
| C1-Benzonaphthofuran | C17H12O | 232 | 50.2, 2.285 |
| C1-Benzonaphthofuran | C17H12O | 232 | 50.4, 2.265 |
| C1-Benzonaphthofuran | C17H12O | 232 | 50.8, 2.250 |
| C1-Benzonaphthofuran | C17H12O | 232 | 51.1, 2.255 |
| C2-Benzonaphthofuran | C18H14O | 246 | 51.9, 2.355 |
| ??? | C18H10O | 242 | 58.0, 2.200 |
| ??? | C18H10O | 242 | 58.3, 2.190 |
| ??? | C18H10O | 242 | 59.1, 2.235 |
| ??? | C18H10O | 242 | 59.7, 2.160 |
| Naptho[2,1,8,7-klmn]xanthene | C18H10O | 242 | 63.5, 2.085 |
| Phenyldibenzofuran | C18H12O | 244 | 51.4, 2.110 |

Appendix 6 – PAOH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Phenyldibenzofuran | C18H12O | 244 | 51.8, 2.235 |
| Phenyldibenzofuran | C18H12O | 244 | 51.9, 2.205 |
| Phenyldibenzofuran | C18H12O | 244 | 52.3, 2.230 |
| Phenyldibenzofuran | C18H12O | 244 | 52.4, 2.205 |
| C2-Benzonaphthofuran | C18H14O | 246 | 50.7, 2.325 |
| C2-Benzonaphthofuran | C18H14O | 246 | 50.9, 2.300 |
| C2-Benzonaphthofuran | C18H14O | 246 | 51.1, 2.315 |
| C2-Benzonaphthofuran | C18H14O | 246 | 51.3, 2.365 |
| C2-Benzonaphthofuran | C18H14O | 246 | 51.4, 2.325 |
| C2-Benzonaphthofuran | C18H14O | 246 | 52.0, 2.320 |
| C2-Benzonaphthofuran | C18H14O | 246 | 52.2, 2.315 |
| C2-Benzonaphthofuran | C18H14O | 246 | 52.4, 2.360 |
| C2-Benzonaphthofuran | C18H14O | 246 | 52.6, 2.310 |
| C2-Benzonaphthofuran | C18H14O | 246 | 52.8, 2.355 |
| C2-Benzonaphthofuran | C18H14O | 246 | 53.0, 2.350 |
| C2-Benzonaphthofuran | C18H14O | 246 | 53.3, 2.325 |
| C2-Benzonaphthofuran | C18H14O | 246 | 53.4, 2.335 |
| C2-Benzonaphthofuran | C18H14O | 246 | 53.7, 2.335 |
| C2-Benzonaphthofuran | C18H14O | 246 | 54.0, 2.335 |
| C2-Benzonaphthofuran | C18H14O | 246 | 54.5, 2.300 |
| 5,12- Napthacenedione | C18H10O2 | 258 | 63.2, 2.075 |
|  | C19H14O | 258 | 53.7, 2.175 |
|  | C19H14O | 258 | 54.0, 2.345 |
|  | C19H14O | 258 | 54.7, 2.370 |
|  | C19H14O | 258 | 54.9, 2.355 |
| Benzo[1,2-b:4,5-b']bisbenzofuran isomer | C18H10O2 | 258 | 56.0, 2.255 |
| Benzo[1,2-b:4,5-b']bisbenzofuran isomer | C18H10O2 | 258 | 57.1, 2.260 |
| Benzo[1,2-b:4,5-b']bisbenzofuran isomer | C18H10O2 | 258 | 57.8, 2.240 |
| Benzo[1,2-b:4,5-b']bisbenzofuran isomer | C18H10O2 | 258 | 58.2, 2.205 |
| 5,12- Napthacenedione | C18H10O2 | 258 | 63.2, 2.075 |
| C3-Benzonaphthofuran | C19H16O | 260 | 53.6, 2.385 |
| C3-Benzonaphthofuran | C19H16O | 260 | 54.2, 2.390 |
| C3-Benzonaphthofuran | C19H16O | 260 | 54.4, 2.400 |
| C3-Benzonaphthofuran | C19H16O | 260 | 54.6, 2.390 |
| C3-Benzonaphthofuran | C19H16O | 260 | 54.8, 2.400 |
| C3-Benzonaphthofuran | C19H16O | 260 | 55.0, 2.390 |
| C3-Benzonaphthofuran | C19H16O | 260 | 55.2, 2.400 |
| C3-Benzonaphthofuran | C19H16O | 260 | 55.3, 2.380 |
| C3-Benzonaphthofuran | C19H16O | 260 | 55.5, 2.395 |
| C3-Benzonaphthofuran | C19H16O | 260 | 55.8, 2.340 |
| C3-Benzonaphthofuran | C19H16O | 260 | 56.0, 2.390 |
| C3-Benzonaphthofuran | C19H16O | 260 | 56.2, 2.395 |
| C3-Benzonaphthofuran | C19H16O | 260 | 56.7, 2.350 |
| C3-Benzonaphthofuran | C19H16O | 260 | 57.3, 2.340 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 64.1, 2.235 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 64.8, 2.220 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 64.9, 2.195 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 65.6, 2.205 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 65.9, 2.200 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 66.1, 2.220 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 66.7, 2.170 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 64.1, 2.250 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 64.8, 2.230 |

Appendix 6 – PAOH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 65.8, 2.210 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 66.2, 2.220 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 66.3, 2.225 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 66.6, 2.205 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 67.2, 2.210 |
| Dinaptho[1,2-b:1',2'-d]furan isomer | C20H12O | 268 | 67.6, 2.205 |
| Naphthalene, 1-(2-naphthalenyoxy)- | C20H14O | 270 | 65.2, 2.345 |
| 2,3,6,7-Dibenzofluorene | C21H12O | 280 | 73.1, 2.225 |
| 2,3,6,7-Dibenzofluorene | C21H12O | 280 | 73.3, 2.240 |
| 2,3,6,7-Dibenzofluorene | C21H12O | 280 | 73.7, 2.230 |
| 1H-Inden-1-one, 2,3-diphenyl | C21H14O | 282 | 67.4, 2.230 |
| 1H-Inden-1-one, 2,3-diphenyl | C21H14O | 282 | 67.7, 2.305 |
| 1H-Inden-1-one, 2,3-diphenyl | C21H14O | 282 | 68.7, 2.290 |
| 1H-Inden-1-one, 2,3-diphenyl | C21H14O | 282 | 69.1, 2.230 |

Appendix 6 – PAOH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Benzenethiol | C6H6S | 110 | 5.7, 1.270 |
| C2-Thiophene | C6H8S | 111 | 4.8, 1.215 |
| C2-Thiophene | C6H8S | 111 | 5.1, 1.305 |
| C2-Thiophene | C6H8S | 111 | 5.4, 1.300 |
| C3-Thiophene 1DB | C7H8S | 124 | 7.2, 1.355 |
| C3-Thiophene 1DB | C7H8S | 124 | 7.4, 1.350 |
| C3-Thiophene 1DB | C7H8S | 124 | 7.7, 1.395 |
| C3-Thiophene 1DB | C7H8S | 124 | 8.6, 1.475 |
| Benzenethiol, 4-methyl | C7H8S | 124 | 9.1, 1.505 |
| C3-Thiophene | C7H10S | 126 | 6.0, 1.380 |
| C3-Thiophene | C7H10S | 126 | 6.3, 1.385 |
| C3-Thiophene | C7H10S | 126 | 6.4, 1.370 |
| C3-Thiophene | C7H10S | 126 | 7.1, 1.360 |
| Benzo[b]thiophene | C8H6S | 134 | 13.0, 1.705 |
| Cyclopent[c]thapyran | C8H6S | 134 | 13.4, 1.705 |
| 2-Benzothiophene | C8H6S | 134 | 13.9, 1.725 |
| Benzo[b]thiophene, 2,3-dihydro- | C8H8S | 136 | 15.3, 1.795 |
| Benzo[c]thiophene, 1,3-dihydro- | C8H8S | 136 | 16.0, 1.850 |
| C4-Thiophene 1DB | C8H10S | 138 | 8.7, 1.565 |
| C4-Thiophene 1DB | C8H10S | 138 | 8.9, 1.585 |
| C4-Thiophene 1DB | C8H10S | 138 | 9.1, 1.610 |
| C4-Thiophene 1DB | C8H10S | 138 | 9.5, 1.635 |
| C4-Thiophene 1DB | C8H10S | 138 | 9.9, 1.700 |
| C4-Thiophene 1DB | C8H10S | 138 | 10.7, 1.740 |
| C4-Thiophene 1DB | C8H10S | 138 | 10.9, 1.740 |
| C4-Thiophene 1DB | C8H10S | 138 | 11.1, 1.550 |
| 3,4-Dimethylthiophenol | C8H10S | 138 | 9.7, 1.675 |
| Benzenemethanethiol, 4-methyl- | C8H10S | 138 | 10.3, 1.635 |
| C4-Thiophene | C8H12S | 140 | 6.8, 1.440 |
| C4-Thiophene | C8H12S | 140 | 7.4, 1.480 |
| C4-Thiophene | C8H12S | 140 | 7.6, 1.505 |
| C4-Thiophene | C8H12S | 140 | 7.9, 1.530 |
| C4-Thiophene | C8H12S | 140 | 8.1, 1.545 |
| C4-Thiophene | C8H12S | 140 | 8.5, 1.575 |
| C4-Thiophene | C8H12S | 140 | 8.7, 1.610 |
| C4-Thiophene | C8H12S | 140 | 8.9, 1.650 |

Appendix 7 – PASH database

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Thieno[3,2-b]thiophene | C6H4S2 | 140 | 13.8, 1.720 |
| Thieno[2,3-b]thiophene | C6H4S2 | 140 | 14.0, 1.690 |
| C1-Benzothiophene | C9H8S | 148 | 15.6, 1.910 |
| C1-Benzothiophene | C9H8S | 148 | 16.1, 1.925 |
| C1-Benzothiophene | C9H8S | 148 | 16.5, 1.920 |
| C5-Thiophene | C9H14S | 154 | 8.2, 1.645 |
| C5-Thiophene | C9H14S | 154 | 8.3, 1.640 |
| C5-Thiophene | C9H14S | 154 | 8.6, 1.670 |
| C5-Thiophene | C9H14S | 154 | 8.8, 1.690 |
| C5-Thiophene | C9H14S | 154 | 9.0, 1.730 |
| C5-Thiophene | C9H14S | 154 | 9.1, 1.755 |
| C5-Thiophene | C9H14S | 154 | 9.3, 1.740 |
| C5-Thiophene | C9H14S | 154 | 9.5, 1.790 |
| C5-Thiophene | C9H14S | 154 | 9.6, 1.795 |
| C5-Thiophene | C9H14S | 154 | 9.9, 1.800 |
| C5-Thiophene | C9H14S | 154 | 10.1, 1.830 |
| C5-Thiophene | C9H14S | 154 | 10.3, 1.840 |
| C5-Thiophene | C9H14S | 154 | 10.5, 1.910 |
| C5-Thiophene | C9H14S | 154 | 10.6, 1.880 |
| 2-Phenyl Thiophene | C10H8S | 160 | 20.1, 1.990 |
| 3-Phenyl Thiophene | C10H8S | 160 | 20.7, 1.995 |
| Naphthalenethiol | C10H8S | 160 | 21.1, 2.005 |
| Naphthalenethiol | C10H8S | 160 | 21.4, 2.030 |
| C2-Benzothiophene | C10H10S | 162 | 18.3, 2.145 |
| C2-Benzothiophene | C10H10S | 162 | 18.8, 2.200 |
| C2-Benzothiophene | C10H10S | 162 | 19.0, 2.150 |
| C2-Benzothiophene | C10H10S | 162 | 19.2, 2.110 |
| C2-Benzothiophene | C10H10S | 162 | 19.4, 2.140 |
| C2-Benzothiophene | C10H10S | 162 | 19.8, 2.125 |
| C2-Benzothiophene | C10H10S | 162 | 20.1, 2.130 |
| C2-Benzothiophene | C10H10S | 162 | 20.3, 2.120 |
| C2-Benzothiophene | C10H10S | 162 | 21.0, 2.140 |
| C2-Benzothiophene | C10H10S | 162 | 21.4, 2.110 |
| C2-Benzothiophene | C10H10S | 162 | 22.1, 2.100 |
| C6-Thiophene | C10H16S | 168 | 11.1, 2.015 |
| C6-Thiophene | C10H16S | 168 | 11.3, 2.070 |
| C6-Thiophene | C10H16S | 168 | 11.6, 2.105 |
| C6-Thiophene | C10H16S | 168 | 11.9, 2.125 |
| Benzyl Thiophene | C11H10S | 174 | 21.2, 2155 |
| Benzyl Thiophene | C11H10S | 174 | 21.8, 2.070 |
| Phenylmethyl Thiophene | C11H10S | 174 | 23.1, 2.220 |
| Phenylmethyl Thiophene | C11H10S | 174 | 23.3, 2.180 |
| Phenylmethyl Thiophene | C11H10S | 174 | 23.6, 2.190 |
| Phenylmethyl Thiophene | C11H10S | 174 | 24.1, 2.185 |
| Phenylmethyl Thiophene | C11H10S | 174 | 24.4, 2.205 |
| Phenylmethyl Thiophene | C11H10S | 174 | 24.6, 2.160 |
| Phenylmethyl Thiophene | C11H10S | 174 | 24.8, 2.155 |
| Phenylmethyl Thiophene | C11H10S | 174 | 24.9, 2.180 |
| Phenylmethyl Thiophene | C11H10S | 174 | 25.3, 2.180 |
| Phenylmethyl Thiophene | C11H10S | 174 | 27.3, 2.080 |
| Phenylmethyl Thiophene | C11H10S | 174 | 27.7, 2.045 |
| C3-Benzothiophene | C11H12S | 176 | 21.3, 2.245 |
| C3-Benzothiophene | C11H12S | 176 | 21.6, 2.255 |

Appendix 7 – PASH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C3-Benzothiophene | C11H12S | 176 | 21.7, 2.310 |
| C3-Benzothiophene | C11H12S | 176 | 21.9, 2.230 |
| C3-Benzothiophene | C11H12S | 176 | 22.1, 2.230 |
| C3-Benzothiophene | C11H12S | 176 | 22.2, 2.290 |
| C3-Benzothiophene | C11H12S | 176 | 22.5, 2.260 |
| C3-Benzothiophene | C11H12S | 176 | 22.6, 2.280 |
| C3-Benzothiophene | C11H12S | 176 | 22.8, 2.280 |
| C3-Benzothiophene | C11H12S | 176 | 22.9, 2.290 |
| C3-Benzothiophene | C11H12S | 176 | 23.3, 2.165 |
| C3-Benzothiophene | C11H12S | 176 | 23.5, 2.150 |
| C3-Benzothiophene | C11H12S | 176 | 23.7, 2.250 |
| C3-Benzothiophene | C11H12S | 176 | 24.2, 2.145 |
| C3-Benzothiophene | C11H12S | 176 | 24.5, 2.275 |
| C3-Benzothiophene | C11H12S | 176 | 24.7, 2.125 |
| C3-Benzothiophene | C11H12S | 176 | 25.1, 2.260 |
| C3-Benzothiophene | C11H12S | 176 | 25.6, 2.230 |
| C3-Benzothiophene | C11H12S | 176 | 26.0, 2.220 |
| Dibenzothiophene | C12H8S | 184 | 33.9, 2.120 |
| Naphtho[1,2-b]thiophene | C12H8S | 184 | 34.2, 2.085 |
| Naphtho[2,1-b]thiophene | C12H8S | 184 | 35.5, 2.055 |
| Naphtho[1,2-c] or [2,3-c]thiophene | C12H8S | 184 | 36.6, 2.055 |
| Naphtho[2,3-b]thiophene | C12H8S | 184 | 38.1, 2.035 |
| Methyl-Naphtho[1,8-bc]thiophene | C12H10S | 186 | 30.4, 2.230 |
| Methyl-Naphtho[1,8-bc]thiophene | C12H10S | 186 | 31.2, 2.190 |
| Methyl-Naphtho[1,8-bc]thiophene | C12H10S | 186 | 31.4, 2.165 |
| Methyl-Naphtho[1,8-bc]thiophene | C12H10S | 186 | 31.6, 2.310 |
| Methyl-Naphtho[1,8-bc]thiophene | C12H10S | 186 | 32.0, 2.165 |
| Methyl-Naphtho[1,8-bc]thiophene | C12H10S | 186 | 32.2, 2.165 |
| Diphenyl Sulfide | C12H10S | 186 | 36.7, 2.115 |
| Methyl-Naphtho[1,8-bc]thiophene | C12H10S | 186 | 35.6, 2.090 |
| Methyl-Naphtho[1,8-bc]thiophene | C12H10S | 186 | 36.8, 2.085 |
| Methyl-Naphtho[1,8-bc]thiophene | C12H10S | 186 | 37.7, 2.170 |
| C4-Benzothiophene | C12H14S | 190 | 23.2, 2.365 |
| C4-Benzothiophene | C12H14S | 190 | 23.9, 2.290 |
| C4-Benzothiophene | C12H14S | 190 | 24.5, 2.375 |
| C4-Benzothiophene | C12H14S | 190 | 24.6, 2.320 |
| C4-Benzothiophene | C12H14S | 190 | 24.9, 2.335 |
| C4-Benzothiophene | C12H14S | 190 | 25.1, 2.305 |
| C4-Benzothiophene | C12H14S | 190 | 25.3, 2.345 |
| C4-Benzothiophene | C12H14S | 190 | 25.5, 2.330 |
| C4-Benzothiophene | C12H14S | 190 | 25.6, 2.335 |
| C4-Benzothiophene | C12H14S | 190 | 26.0, 2.325 |
| C4-Benzothiophene | C12H14S | 190 | 26.2, 2.405 |
| C4-Benzothiophene | C12H14S | 190 | 26.6, 2.350 |
| C4-Benzothiophene | C12H14S | 190 | 26.8, 2.345 |
| C4-Benzothiophene | C12H14S | 190 | 27.1, 2.365 |
| C4-Benzothiophene | C12H14S | 190 | 28.0, 2.365 |
| C4-Benzothiophene | C12H14S | 190 | 28.5, 2.390 |
| C4-Benzothiophene | C12H14S | 190 | 28.9, 2.320 |
| C4-Benzothiophene | C12H14S | 190 | 29.3, 2.345 |
| Benzodithiophene | C10H6S2 | 190 | 34.0, 2.070 |
| Benzodithiophene | C10H6S2 | 190 | 34.1, 2.070 |
| Benzodithiophene | C10H6S2 | 190 | 34.5, 2.060 |

Appendix 7 – PASH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Benzodithiophene | C10H6S2 | 190 | 35.0, 2.030 |
| Benzodithiophene | C10H6S2 | 190 | 36.3, 2.000 |
| Benzodithiophene | C10H6S2 | 190 | 36.8, 2.030 |
| Benzodithiophene | C10H6S2 | 190 | 37.3, 2.030 |
| Benzodithiophene | C10H6S2 | 190 | 37.6, 1.925 |
| Cyclic Sulphur S6 | S6 | 192 | 27.8, 1.860 |
| C1-Dibenzothiophene | C13H10S | 198 | 36.7, 2.205 |
| C1-Dibenzothiophene | C13H10S | 198 | 37.3, 2.215 |
| C1-Dibenzothiophene | C13H10S | 198 | 37.6, 2.180 |
| C1-Dibenzothiophene | C13H10S | 198 | 38.1, 2.175 |
| C1-Dibenzothiophene | C13H10S | 198 | 38.3, 2.185 |
| C1-Dibenzothiophene | C13H10S | 198 | 38.4, 2.155 |
| C1-Dibenzothiophene | C13H10S | 198 | 38.7, 2.145 |
| C1-Dibenzothiophene | C13H10S | 198 | 39.3, 2.180 |
| C1-Dibenzothiophene | C13H10S | 198 | 39.8, 2.150 |
| C1-Dibenzothiophene | C13H10S | 198 | 40.0, 2.125 |
| C1-Dibenzothiophene | C13H10S | 198 | 40.3, 2.105 |
| C1-Dibenzothiophene | C13H10S | 198 | 40.6, 2.120 |
| C5-Benzothiophene | C13H16S | 204 | 26.5, 2.440 |
| C5-Benzothiophene | C13H16S | 204 | 27.2, 2.430 |
| C5-Benzothiophene | C13H16S | 204 | 27.5, 2.425 |
| C5-Benzothiophene | C13H16S | 204 | 27.8, 2.425 |
| C5-Benzothiophene | C13H16S | 204 | 28.1, 2.485 |
| C5-Benzothiophene | C13H16S | 204 | 28.9, 2.455 |
| C5-Benzothiophene | C13H16S | 204 | 29.0, 2.465 |
| C5-Benzothiophene | C13H16S | 204 | 29.5, 2.560 |
| Methyl Benzodithiophene | C11H8S2 | 204 | 38.0, 2.235 |
| Methyl Benzodithiophene | C11H8S2 | 204 | 38.5, 2.180 |
| Methyl Benzodithiophene | C11H8S2 | 204 | 39.2, 2.195 |
| Phenanthro/Phenaleno Thiophene | C14H8S | 208 | 44.7, 2.110 |
| Phenanthro/Phenaleno Thiophene | C14H8S | 208 | 45.0, 2.090 |
| Phenanthro/Phenaleno Thiophene | C14H8S | 208 | 45.8, 2.095 |
| Phenanthro/Phenaleno Thiophene | C14H8S | 208 | 46.3, 2.105 |
| Phenanthro/Phenaleno Thiophene | C14H8S | 208 | 47.2, 2.090 |
| Phenanthro/Phenaleno Thiophene | C14H8S | 208 | 47.8, 2.060 |
| Phenyl Benzothiophene | C14H10S | 210 | 39.0, 2.070 |
| Phenyl Benzothiophene | C14H10S | 210 | 39.2, 2.060 |
| Phenyl Benzothiophene | C14H10S | 210 | 41.6, 2.175 |
| Phenyl Benzothiophene | C14H10S | 210 | 41.9, 2.210 |
| Phenyl Benzothiophene | C14H10S | 210 | 42.1, 2.170 |
| Phenyl Benzothiophene | C14H10S | 210 | 42.4, 2.235 |
| Phenyl Benzothiophene | C14H10S | 210 | 43.2, 2.120 |
| C2-Dibenzothiophene | C14H12S | 212 | 39.5, 2.280 |
| C2-Dibenzothiophene | C14H12S | 212 | 39.8, 2.295 |
| C2-Dibenzothiophene | C14H12S | 212 | 40.0, 2.295 |
| C2-Dibenzothiophene | C14H12S | 212 | 40.2, 2.285 |
| C2-Dibenzothiophene | C14H12S | 212 | 40.4, 2.385 |
| C2-Dibenzothiophene | C14H12S | 212 | 40.6, 2.410 |
| C2-Dibenzothiophene | C14H12S | 212 | 40.8, 2.380 |
| C2-Dibenzothiophene | C14H12S | 212 | 41.0, 2.375 |
| C2-Dibenzothiophene | C14H12S | 212 | 41.1, 2.375 |
| C2-Dibenzothiophene | C14H12S | 212 | 41.3, 2.245 |
| C2-Dibenzothiophene | C14H12S | 212 | 41.4, 2.275 |

Appendix 7 – PASH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| Benzodithiophene | $C_{10}H_6S_2$ | 190 | 35.0, 2.030 |
| Benzodithiophene | $C_{10}H_6S_2$ | 190 | 36.3, 2.000 |
| Benzodithiophene | $C_{10}H_6S_2$ | 190 | 36.8, 2.030 |
| Benzodithiophene | $C_{10}H_6S_2$ | 190 | 37.3, 2.030 |
| Benzodithiophene | $C_{10}H_6S_2$ | 190 | 37.6, 1.925 |
| Cyclic Sulphur S6 | $S_6$ | 192 | 27.8, 1.860 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 36.7, 2.205 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 37.3, 2.215 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 37.6, 2.180 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 38.1, 2.175 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 38.3, 2.185 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 38.4, 2.155 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 38.7, 2.145 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 39.3, 2.180 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 39.8, 2.150 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 40.0, 2.125 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 40.3, 2.105 |
| C1-Dibenzothiophene | $C_{13}H_{10}S$ | 198 | 40.6, 2.120 |
| C5-Benzothiophene | $C_{13}H_{16}S$ | 204 | 26.5, 2.440 |
| C5-Benzothiophene | $C_{13}H_{16}S$ | 204 | 27.2, 2.430 |
| C5-Benzothiophene | $C_{13}H_{16}S$ | 204 | 27.5, 2.425 |
| C5-Benzothiophene | $C_{13}H_{16}S$ | 204 | 27.8, 2.425 |
| C5-Benzothiophene | $C_{13}H_{16}S$ | 204 | 28.1, 2.485 |
| C5-Benzothiophene | $C_{13}H_{16}S$ | 204 | 28.9, 2.455 |
| C5-Benzothiophene | $C_{13}H_{16}S$ | 204 | 29.0, 2.465 |
| C5-Benzothiophene | $C_{13}H_{16}S$ | 204 | 29.5, 2.560 |
| Methyl Benzodithiophene | $C_{11}H_8S_2$ | 204 | 38.0, 2.235 |
| Methyl Benzodithiophene | $C_{11}H_8S_2$ | 204 | 38.5, 2.180 |
| Methyl Benzodithiophene | $C_{11}H_8S_2$ | 204 | 39.2, 2.195 |
| Phenanthro/Phenaleno Thiophene | $C_{14}H_8S$ | 208 | 44.7, 2.110 |
| Phenanthro/Phenaleno Thiophene | $C_{14}H_8S$ | 208 | 45.0, 2.090 |
| Phenanthro/Phenaleno Thiophene | $C_{14}H_8S$ | 208 | 45.8, 2.095 |
| Phenanthro/Phenaleno Thiophene | $C_{14}H_8S$ | 208 | 46.3, 2.105 |
| Phenanthro/Phenaleno Thiophene | $C_{14}H_8S$ | 208 | 47.2, 2.090 |
| Phenanthro/Phenaleno Thiophene | $C_{14}H_8S$ | 208 | 47.8, 2.060 |
| Phenyl Benzothiophene | $C_{14}H_{10}S$ | 210 | 39.0, 2.070 |
| Phenyl Benzothiophene | $C_{14}H_{10}S$ | 210 | 39.2, 2.060 |
| Phenyl Benzothiophene | $C_{14}H_{10}S$ | 210 | 41.6, 2.175 |
| Phenyl Benzothiophene | $C_{14}H_{10}S$ | 210 | 41.9, 2.210 |
| Phenyl Benzothiophene | $C_{14}H_{10}S$ | 210 | 42.1, 2.170 |
| Phenyl Benzothiophene | $C_{14}H_{10}S$ | 210 | 42.4, 2.235 |
| Phenyl Benzothiophene | $C_{14}H_{10}S$ | 210 | 43.2, 2.120 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 39.5, 2.280 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 39.8, 2.295 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 40.0, 2.295 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 40.2, 2.285 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 40.4, 2.385 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 40.6, 2.410 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 40.8, 2.380 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 41.0, 2.375 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 41.1, 2.375 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 41.3, 2.245 |
| C2-Dibenzothiophene | $C_{14}H_{12}S$ | 212 | 41.4, 2.275 |

Appendix 7 – PASH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C3-Dibenzothiophene | C15H14S | 226 | 45.6, 2.325 |
| C3-Dibenzothiophene | C15H14S | 226 | 45.9, 2.310 |
| C3-Dibenzothiophene | C15H14S | 226 | 46.1, 2.310 |
| Benzo[b]naphtho[2,1-d]thiophene | C16H10S | 234 | 53.0, 2.190 |
| Benzo[b]naphtho[1,2-d]thiophene | C16H10S | 234 | 53.6, 2.170 |
| Benzo[b]naphtho[2,3-d]thiophene | C16H10S | 234 | 54.4, 2.140 |
| Anthra(1,2-b)thiophene | C16H10S | 234 | 55.4, 2.115 |
| Phenanthro[4,3-b]thiophene | C16H10S | 234 | 55.8, 2.150 |
| Phenanthro[1,2-b]thiophene | C16H10S | 234 | 55.9, 2.145 |
| Phenanthro[3,4-b]thiophene | C16H10S | 234 | 56.2, 2.080 |
| Anthra(2,1-b)thiophene | C16H10S | 234 | 56.3, 2.100 |
| Phenanthro[2,1-b]thiophene | C16H10S | 234 | 56.4, 2.075 |
| Phenanthro[3,2-b]thiophene | C16H10S | 234 | 57.0, 2.095 |
| Phenanthro[2,3-b]thiophene | C16H10S | 234 | 57.7, 2.160 |
| Anthra(2,3-b)thiophene | C16H10S | 234 | 57.9, 2.145 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 46.4, 2.075 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 48.7, 2.190 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 49.2, 2.260 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 50.0, 2.280 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 50.3, 2.290 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 50.6, 2.345 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 51.3, 2.360 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 51.9, 2.365 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 52.1, 2.320 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 52.6, 2.295 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 53.0, 2.325 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 53.2, 2.225 |
| C2-Phenanthro/Phenaleno Thiophene | C16H12S | 236 | 54.3, 2.140 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 46.3, 2.270 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 46.6, 2.370 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 46.7, 2.310 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 46.8, 2.335 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 47.1, 2.370 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 47.3, 2.290 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 47.5, 2.345 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 47.6, 2.345 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 47.9, 2.295 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 48.3, 2.275 |
| C2-Phenyl Benzothiophene | C16H14S | 238 | 48.7, 2.245 |
| C4-Dibenzothiophene | C16H16S | 240 | 44.3, 2.380 |
| C4-Dibenzothiophene | C16H16S | 240 | 44.8, 2.400 |
| C4-Dibenzothiophene | C16H16S | 240 | 45.4, 2.405 |
| C4-Dibenzothiophene | C16H16S | 240 | 45.9, 2.385 |
| C4-Dibenzothiophene | C16H16S | 240 | 46.1, 2.410 |
| C4-Dibenzothiophene | C16H16S | 240 | 46.4, 2.440 |
| C4-Dibenzothiophene | C16H16S | 240 | 46.7, 2.400 |
| C4-Dibenzothiophene | C16H16S | 240 | 47.3, 2.375 |
| C4-Dibenzothiophene | C16H16S | 240 | 48.3, 2.360 |
| C4-Dibenzothiophene | C16H16S | 240 | 48.5, 2.370 |
| C4-Dibenzothiophene | C16H16S | 240 | 48.9, 2.370 |
| C4-Dibenzothiophene | C16H16S | 240 | 49.5, 2.360 |
| [1]benzothieno[3,2-b][1]benzothiophene isomer | C14H8S2 | 240 | 52.4, 2.245 |
| [1]benzothieno[3,2-b][1]benzothiophene isomer | C14H8S2 | 240 | 54.6, 2.170 |

Appendix 7 – PASH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| [1]benzothieno[3,2-b][1]benzothiophene isomer | C14H8S2 | 240 | 55.1, 2.105 |
| [1]benzothieno[3,2-b][1]benzothiophene isomer | C14H8S2 | 240 | 56.5, 2.065 |
| [1]benzothieno[3,2-b][1]benzothiophene isomer | C14H8S2 | 240 | 57.0, 2.070 |
| [1]benzothieno[3,2-b][1]benzothiophene isomer | C14H8S3 | 240 | 57.1, 2.140 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 56.5, 2.230 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 56.6, 2.210 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 56.9, 2.240 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 57.2, 2.200 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 57.4, 2.205 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 57.8, 2.195 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 58.1, 2.205 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 58.3, 2.190 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 58.4, 2.175 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 58.6, 2.185 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 58.8, 2.170 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 59.1, 2.165 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 59.2, 2.155 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 59.8, 2.165 |
| Cyclic Octaatomic sulphur | S8 | 256 | 47.5, 1.940 |
| Benzo[2,3]phenanthro[4,5-bcd]thiophene | C18H10S | 258 | 63.4, 2.245 |
| Benzo[1,2]phenaleno[3,4-bc]thiophene | C18H10S | 258 | 64.4, 2.155 |
| Pyreno[4,5-b]thiophene | C18H10S | 258 | 64.5, 2.140 |
| Triphenyleno[4,5-bcd]thiophene | C18H10S | 258 | 65.3, 2.150 |
| Chryseno[4,5]thiophene | C18H10S | 258 | 65.9, 2.120 |
| Pyreno[1,2-b]thiophene | C18H10S | 258 | 66.6, 2.120 |
| Pyreno[2,1-b]thiophene | C18H10S | 258 | 67.0, 2.115 |
| Benzo[4,5]phenyleno[1,9]thiophene | C18H10S | 258 | 67.4, 2.120 |
| Benzo[4,5]phenyleno[9,1]thiophene | C18H10S | 258 | 68.5, 2.105 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 54.3, 2.360 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 55.3, 2.050 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 57.9, 2.100 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 59.3, 2.100 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 60.0, 2.175 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 60.6, 2.155 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 60.8, 2.225 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 61.8, 2.145 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 59.0, 2.375 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 59.2, 2.285 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 59.4, 2.275 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 59.7, 2.265 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 60.0, 2.245 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 60.3, 2.250 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 60.5, 2.250 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 60.7, 2.260 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 61.0, 2.225 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 61.2, 2.260 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 61.8, 2.260 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 56.5, 2.310 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 56.8, 2.350 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 56.9, 2.340 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 57.2, 2.340 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 57.5, 2.320 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 57.7, 2.345 |

Appendix 7 – PASH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| [1]benzothieno[3,2-b][1]benzothiophene isomer | C14H8S2 | 240 | 55.1, 2.105 |
| [1]benzothieno[3,2-b][1]benzothiophene isomer | C14H8S2 | 240 | 56.5, 2.065 |
| [1]benzothieno[3,2-b][1]benzothiophene isomer | C14H8S2 | 240 | 57.0, 2.070 |
| [1]benzothieno[3,2-b][1]benzothiophene isomer | C14H8S3 | 240 | 57.1, 2.140 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 56.5, 2.230 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 56.6, 2.210 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 56.9, 2.240 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 57.2, 2.200 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 57.4, 2.205 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 57.8, 2.195 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 58.1, 2.205 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 58.3, 2.190 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 58.4, 2.175 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 58.6, 2.185 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 58.8, 2.170 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 59.1, 2.165 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 59.2, 2.155 |
| C1-Benzonapthothiophene isomer | C17H12S | 248 | 59.8, 2.165 |
| Cyclic Octaatomic sulphur | S8 | 256 | 47.5, 1.940 |
| Benzo[2,3]phenanthro[4,5-bcd]thiophene | C18H10S | 258 | 63.4, 2.245 |
| Benzo[1,2]phenaleno[3,4-bc]thiophene | C18H10S | 258 | 64.4, 2.155 |
| Pyreno[4,5-b]thiophene | C18H10S | 258 | 64.5, 2.140 |
| Triphenyleno[4,5-bcd]thiophene | C18H10S | 258 | 65.3, 2.150 |
| Chryseno[4,5]thiophene | C18H10S | 258 | 65.9, 2.120 |
| Pyreno[1,2-b]thiophene | C18H10S | 258 | 66.6, 2.120 |
| Pyreno[2,1-b]thiophene | C18H10S | 258 | 67.0, 2.115 |
| Benzo[4,5]phenyleno[1,9]thiophene | C18H10S | 258 | 67.4, 2.120 |
| Benzo[4,5]phenyleno[9,1]thiophene | C18H10S | 258 | 68.5, 2.105 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 54.3, 2.360 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 55.3, 2.050 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 57.9, 2.100 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 59.3, 2.100 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 60.0, 2.175 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 60.6, 2.155 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 60.8, 2.225 |
| Phenyl Dibenzothiophene | C18H12S | 260 | 61.8, 2.145 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 59.0, 2.375 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 59.2, 2.285 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 59.4, 2.275 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 59.7, 2.265 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 60.0, 2.245 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 60.3, 2.250 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 60.5, 2.250 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 60.7, 2.260 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 61.0, 2.225 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 61.2, 2.260 |
| C2-Benzonapthothiophene isomer | C18H14S | 262 | 61.8, 2.260 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 56.5, 2.310 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 56.8, 2.350 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 56.9, 2.340 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 57.2, 2.340 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 57.5, 2.320 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 57.7, 2.345 |

Appendix 7 – PASH database continued

| Compound | Formula | m/z | Retention time |
|---|---|---|---|
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 58.2, 2.325 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 58.6, 2.310 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 58.9, 2.290 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 59.2, 2.300 |
| C1-Pyreno[1,2-b]thiophene isomer | C18H12S | 272 | 59.8, 2.345 |
| C1-Phenyl Dibenzothiophene | C19H14S | 274 | 63.1, 2.230 |
| C1-Phenyl Dibenzothiophene | C19H14S | 274 | 64.0, 2.215 |
| C1-Phenyl Dibenzothiophene | C19H14S | 274 | 65.4, 2.180 |
| Benzo[2,3]fluorantheno[1,12-bcd]thiophene | C20H10S | 282 | 76.2, 2.415 |
| Perylo[1,12-bcd]thiophene | C20H10S | 282 | 76.9, 2.470 |
| Benzo[4,5]triphenyleno[1,12-bcd]thiophene | C20H10S | 282 | 77.3, 2.525 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 76.0, 2.450 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 76.3, 2.475 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 77.0, 2.530 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 77.3, 2.595 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 68.7, 2.200 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 72.0, 2.205 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 73.0, 2.170 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 73.2, 2.195 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 73.4, 2.185 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 73.5, 2.250 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 73.7, 2.180 |
| Benzophenanthrothiophene isomer | C20H12S | 284 | 74.4, 2.215 |
| C18H10S2 | C18H10S2 | 290 | 72.3, 2.255 |
| Naptho[2,1-b]benzo[1,2-b:4,3-b']dithiophene | C18H10S2 | 290 | 78.9, 2.790 |
| C18H10S2 | C18H10S2 | 290 | 79.7, 2.830 |

Appendix 7 – PASH database continued