

# Coal Tar Forensics

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# WHAT IS COAL TAR?

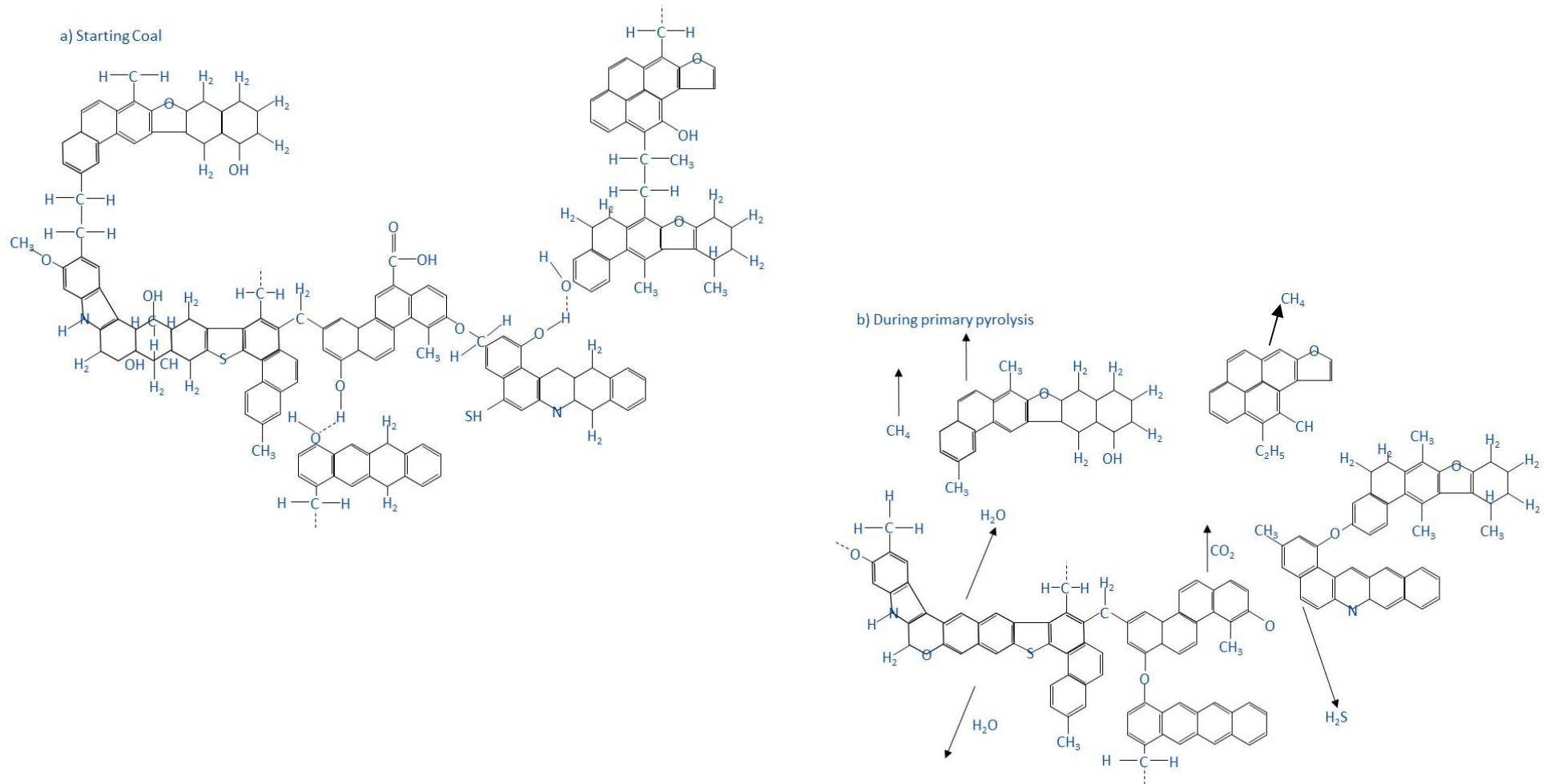
- A by-product of gas manufacturing & coke making
- Complex mixture of organic and inorganic compounds, some toxic or carcinogenic.
- > 3,000 former gasworks in the UK, >10,000 in Europe.
- Coal tar, DNAPLs – immobile and persistent source of pollution – gradual dissolution of soluble components.
- Carburetted Water Gas tar, LNAPLs/NNAPLs – mobile, can form large product plumes.





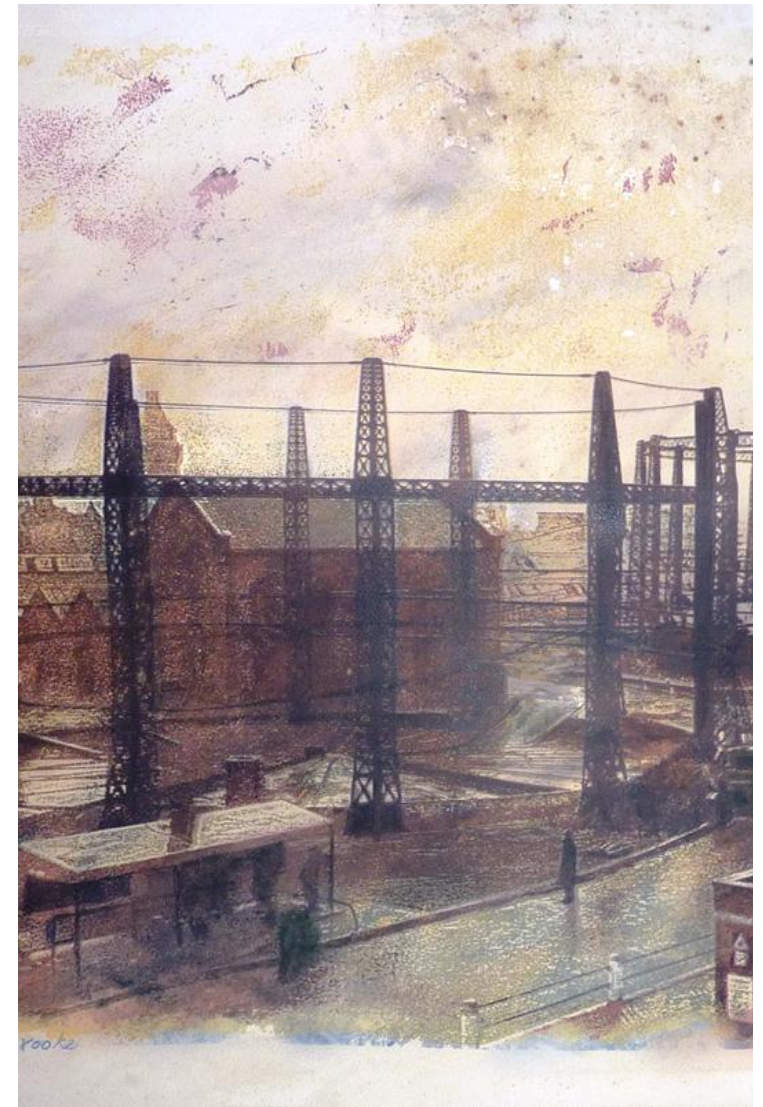
# HOW DOES COAL TAR FORM?

- Hypothetical model for Pittsburgh seam coal (Solomon and others, 1991).

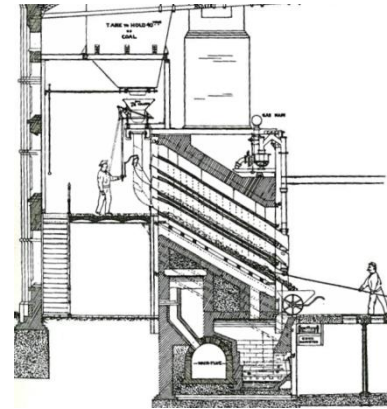


# COMPOSITION OF TYPICAL LONDON COAL TAR

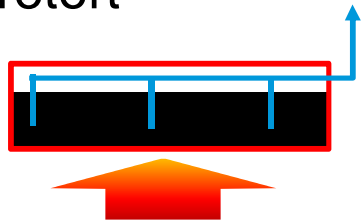
	Per cent. by weight.	Remarks.
Specific gravity at 15.5 deg. C. = 1.192.		
Aqueous ammoniacal liquor .....	3.53	
Light oils (distilling over below 170 C.).....	1.99	Lighter than water. Include benzol, which is used for the manufacture of aniline.
Middle oils (distilling over between 170 and 270 C.) .....	18.46	Include naphthalene and carbolic acid.
Anthracene oils (distilling over above 270 C.) .....	12.20	From which alizarin is manufactured.
Pitch (medium) .....	59.20	Used for paving, roofing, varnishes, patent fuel, &c
Loss on distillation .....	4.62	
	<hr/> 100.00	



# EVOLUTION OF GAS MANUFACTURE 19<sup>TH</sup> C.

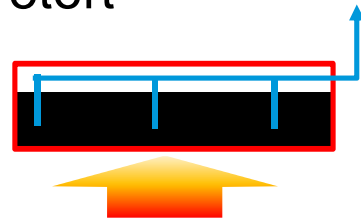


- Low temp. horizontal retort



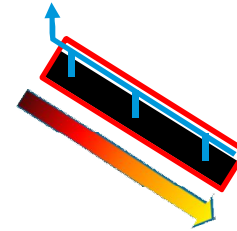
- Hand operated
- Gas coals
- Radiant heated
- Low temps
- **Tars rich in phenols and paraffins.**

- High temp. horizontal retort



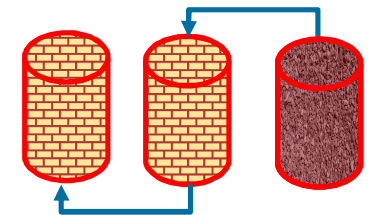
- Mechanised
- Gas coals
- Producer heated
- High temps
- **Tars rich in benzene & naphthalene.**

- Inclined retort



- Mechanised
- Gas coals
- Producer heated
- **Differential heating affects tar composition.**

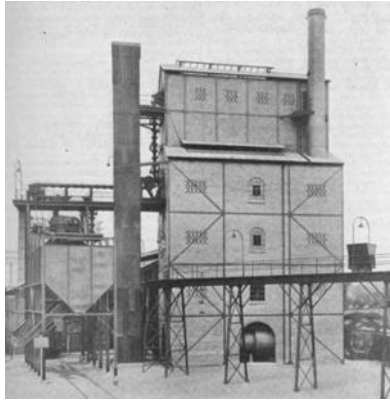
- Water Gas



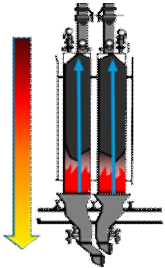
- Mechanised
- Coke - self heated
- Enriched with oil
- **Oil based tars with coke signature.**



# EVOLUTION OF GAS MANUFACTURE 20<sup>TH</sup> C.



• Vertical retort



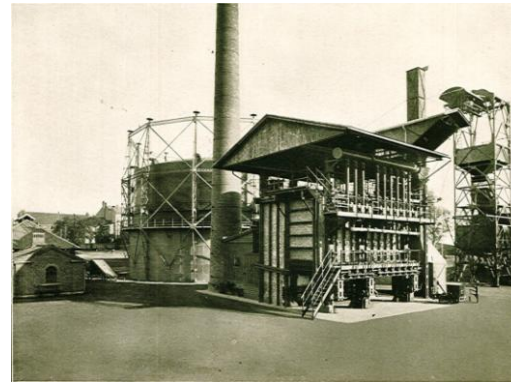
- Gas coals
- Producer heated
- Differential heating
- **Tars varying composition.**



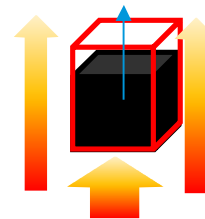
• Coke Oven



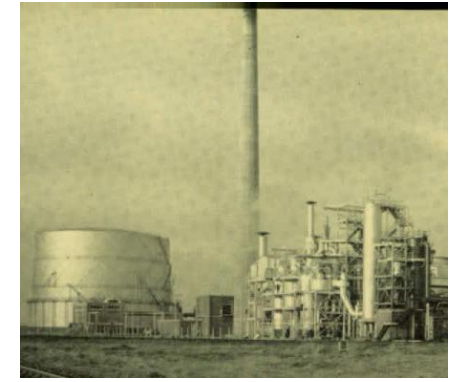
- Coking coals
- Producer heated
- High temps
- **Tars very rich in benzene & naphthalene.**



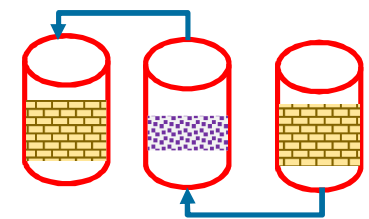
• Chamber Ovens



- Coking coals
- Producer heated
- High temps
- **Tars rich in benzene & naphthalene.**



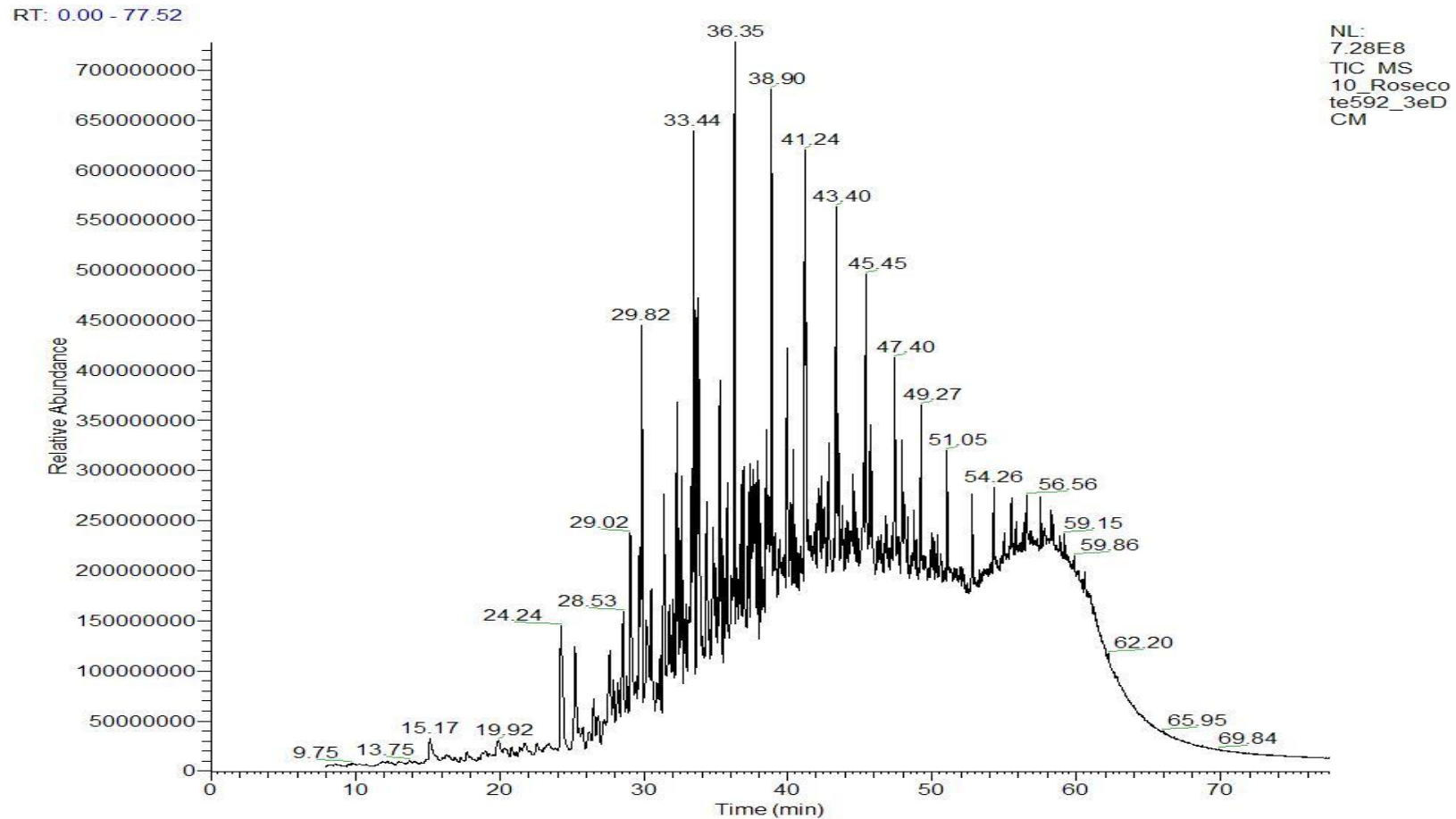
• Oil Gas



- Oil heated
- Tars entirely oil based
- **Tar dependent on feedstock oil composition.**

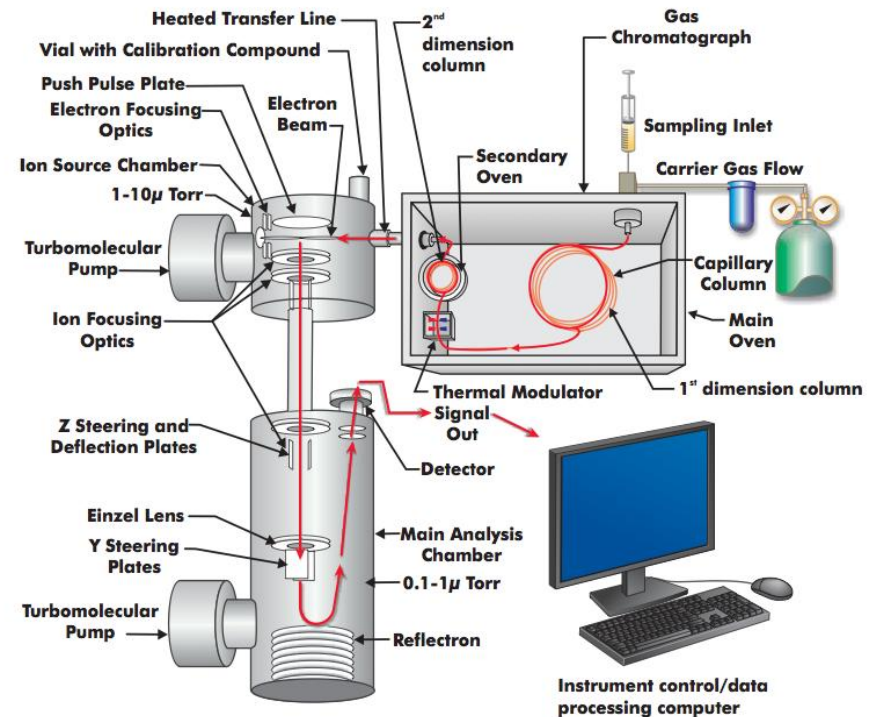
# TRADITIONAL ANALYSIS OF COAL TAR

- Struggles with the complex nature of coal tar.



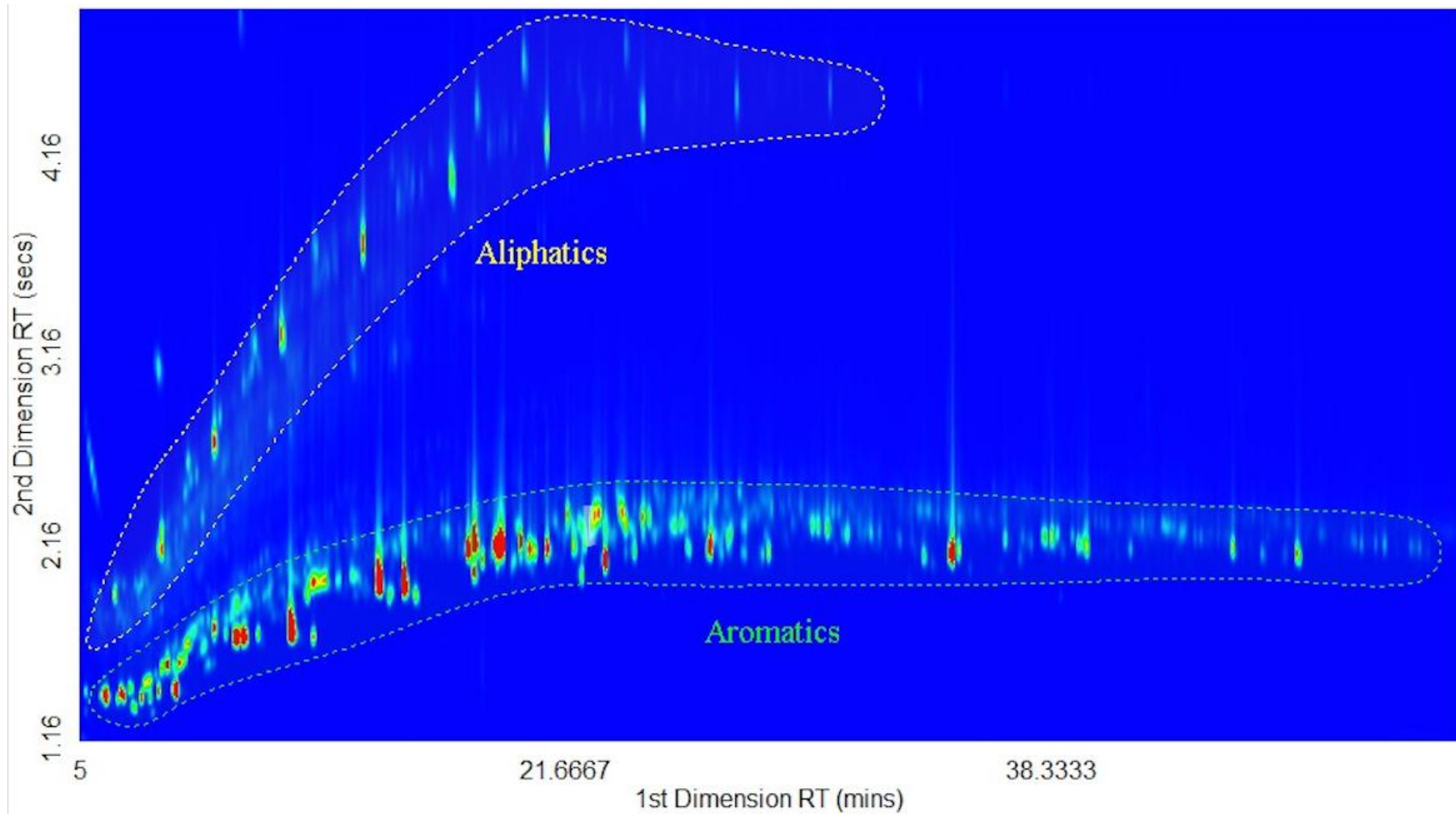
# GCxGC ANALYSIS

- GCxGC involves the use of two columns of different polarity to separate organic compounds across horizontal and vertical dimensions.
- Traditional GC only separates across horizontal dimensions.
- GCxGC allows for the separation of complex organic mixtures that cannot be resolved by traditional GC analysis



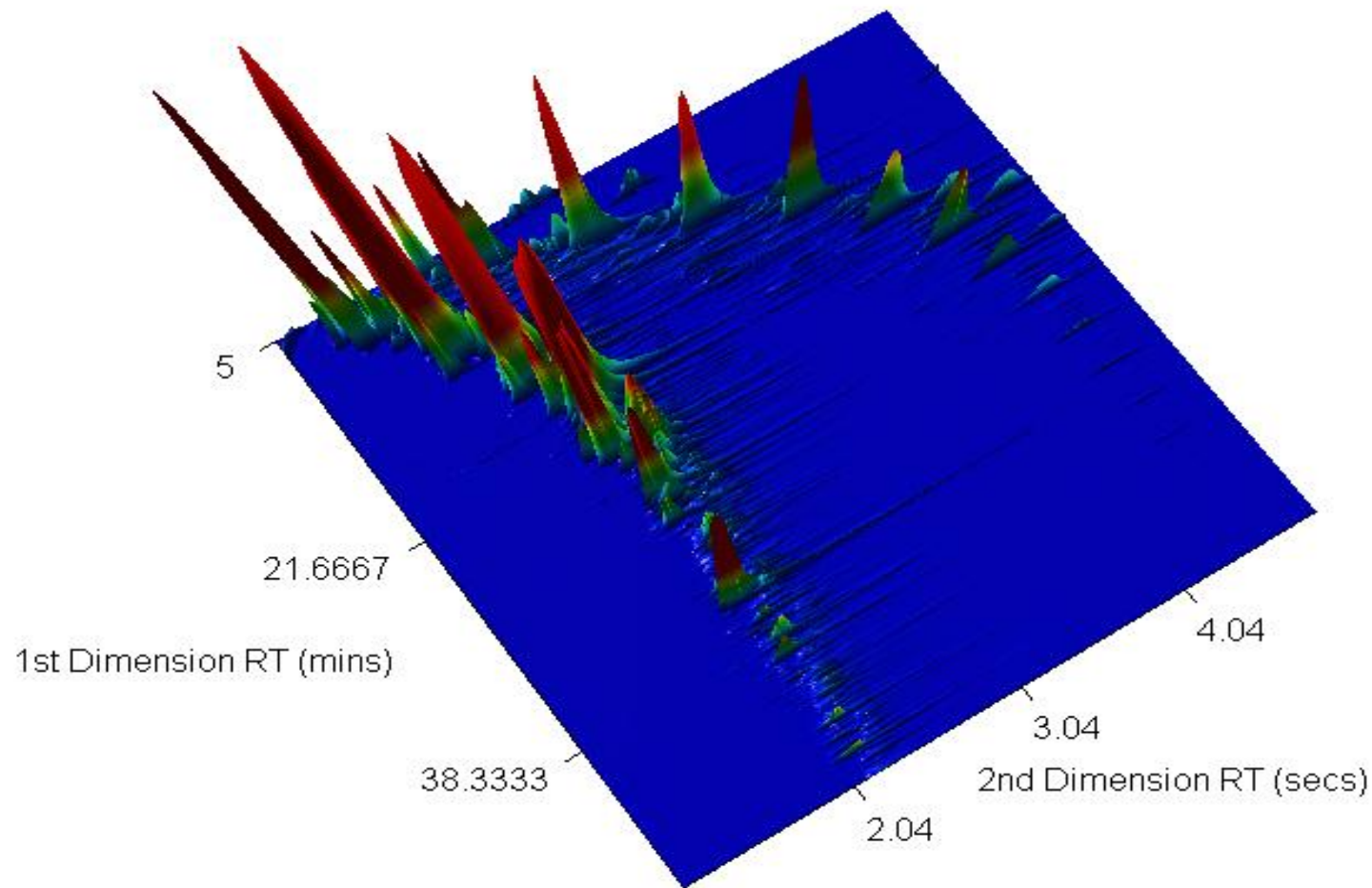


# GCXGC ANALYSIS OF COAL TAR



- Generates a very large dataset

# GCXGC ANALYSIS OF COAL TAR



- The large dataset is assessed using Principle Component Analysis (PCA).
- A statistical method that emphasises trends and patterns in the data.

# CASE STUDIES

## US Case Study

- Samples of DNAPL Tar were obtained from a former landfill site in the US.
- The tar was suspected to originate from a former Gasworks operating between 1910 & 1960's - used 2 different processes CWG & Hasche.
- The tar was suspected to have been dumped in the early 1950's.
- GCxGC was used to produce a database of compounds, diagnostic ratios and Multivariate statistics (PCA and HCA) that were used to establish the source and production process used.

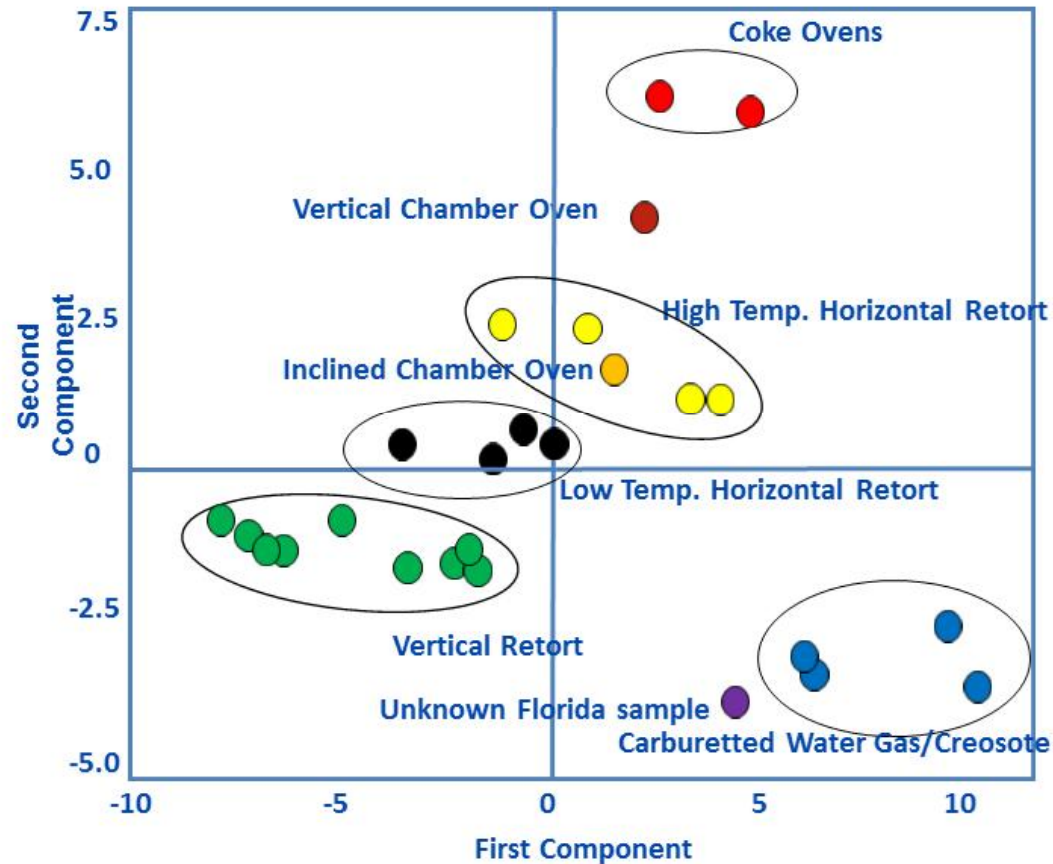
## Netherland Chamber Oven Sample

- Sample obtained from the Arnham Gasworks, Netherlands.
- The tars originated from a chamber oven process - unusual in the UK but extensively used in Europe for gas making from coking coals



# DO TARS PRODUCE UNIQUE SIGNATURES

PCA score plot of the coal tar data set, allows the coal tars to be assigned to the different processes used to manufacture them.



# WHAT DOES THIS TELL US?

- The PCA can interpret the data to show clearly defined groupings for coal tars of similar origins.
- GCxGC analysis was able to identify 865 individual compounds within the US sample – far more than traditional GC methods could accomplish.
- GCxGC analysis was able to demonstrate :
  - The US tar was produced by the carburetted water gas process.
  - The Sample from the Netherlands had a unique signature attributable to a chamber oven process.
- This is the first time these methods have been applied to samples from outside of the UK.

# TAR COMPOUND DATABASE

- Research into tar is not uncommon, however:
  - Research papers often focus on limited samples;
  - Unknown production processes. e.g. Culp *et al.*; &
  - Limited suite of analysis. e.g. PAH
- Databases do exist which list the compounds within coal tars:
  - BoMB Bulletin 606 (Properties of Compounds in Coal-Carbonization Products) published in 1963;
  - Known Components of Coal Tar – Coal Tar Research Association;
  - This information has not advanced since 1960's
- The application of GCxGC to coal tar samples provides a unique opportunity for the production of a database of compounds present within coal tar analysed using modern analytical techniques.



# COMPOUND DATABASE

- Produces a database of compounds present within tar samples:
  - 16 tar samples
  - representing 5 different major production processes.
- The database is unique due to:
  - the number of samples tested; and
  - the number of production processes represented.
- A total of 2369 unique compounds were detected within the samples

# COMPOUND DATABASE

- The 2369 compounds included:
  - 948 Aromatic compounds;
  - 196 Aliphatic compounds;
  - 380 Sulphur containing compounds;
  - 209 Oxygen containing compounds;
  - 262 Nitrogen containing compounds;
  - 15 Mixed heterocycles;
  - 359 Hydroxylated compounds;
- Of the 2369 unique compounds detected – only 163 were detected within all tar samples (coal & oil based tar samples).
- These 163 compounds provide a key to Identify gasworks derived tars.

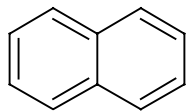
- Polycyclic Aromatic Hydrocarbons – PAHs
- Alkyl Polycyclic Aromatic Hydrocarbons – Alkyl PAHs
- Heterocyclic compounds
  - Oxygen containing PAHs – Oxy-PAHs
  - Sulphur containing PAHs - PASHs
  - Nitrogen containing PAHs – NPACs
  - Mixed heterocycles



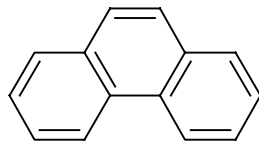
# POLYCYCLIC AROMATIC HYDROCARBONS - PAH

- PAH - a common persistent organic pollutant & formed through pyrolytic, petrogenic and biological sources.
- PAH toxicity varies greatly and is determined by the number of fused rings. For example 4 and 5 ring PAHs have a tendency to be carcinogenic and mutagenic.
- The US agency for toxic substances lists 18 PAHs as being of concern.
- Long term modelling of Coal tar plumes predicts that even after 1000 years 89% of the initial mass of Phenanthrene will still be present, and for the moderately and sparingly soluble components 60% and 98% respectively.

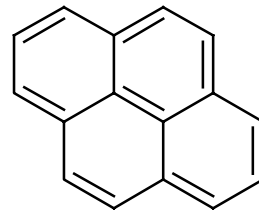
Naphthalene



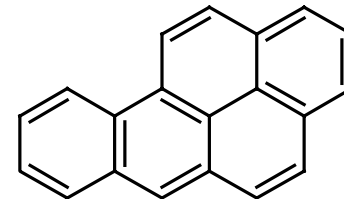
Phenanthrene



Pyrene

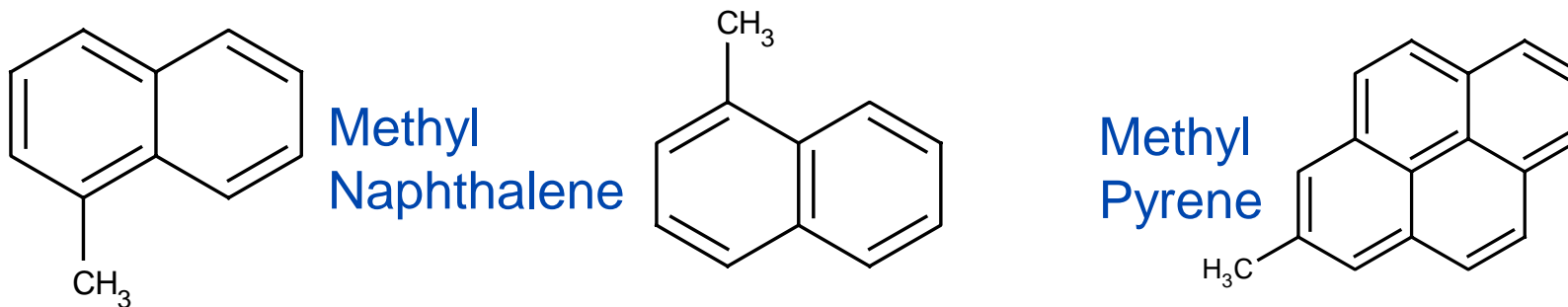


Benzo(a)pyrene



# ALKYL PAH

- Alkyl PAH an important group of compounds often ignored during environmental analysis due to difficulties in accurate measurements.
- The EPA has created a list of 16 groups of C1 to C4 alkyl PAH and combined them with the 18 EPA PAH to give the EPA 34.
- The 16 groups of alkyl PAH actually contain several hundred different compounds.
- GCxGC can resolve more alkyl PAH than traditional GC analysis.



# DOES IT MATTER?

- Alkylated PAHs can significantly contribute to the toxicity of PAH mixtures, in some cases accounting for 80% of the toxic burden.
- In crude oil alkyl PAHs can account for 99% of the total PAH content.
- In coal tars alkyl PAH can account for 35 to 42%.
- Risk assessment continues to rely solely on parent PAH data – this may suggest that risks could be underestimated for both coal tar and oil polluted sites.
- Of the 163 compounds detected within all tar samples 74 (45.4%) were in the form of Alkyl PAHs.

# WHAT ARE HETEROCYCLIC COMPOUNDS?

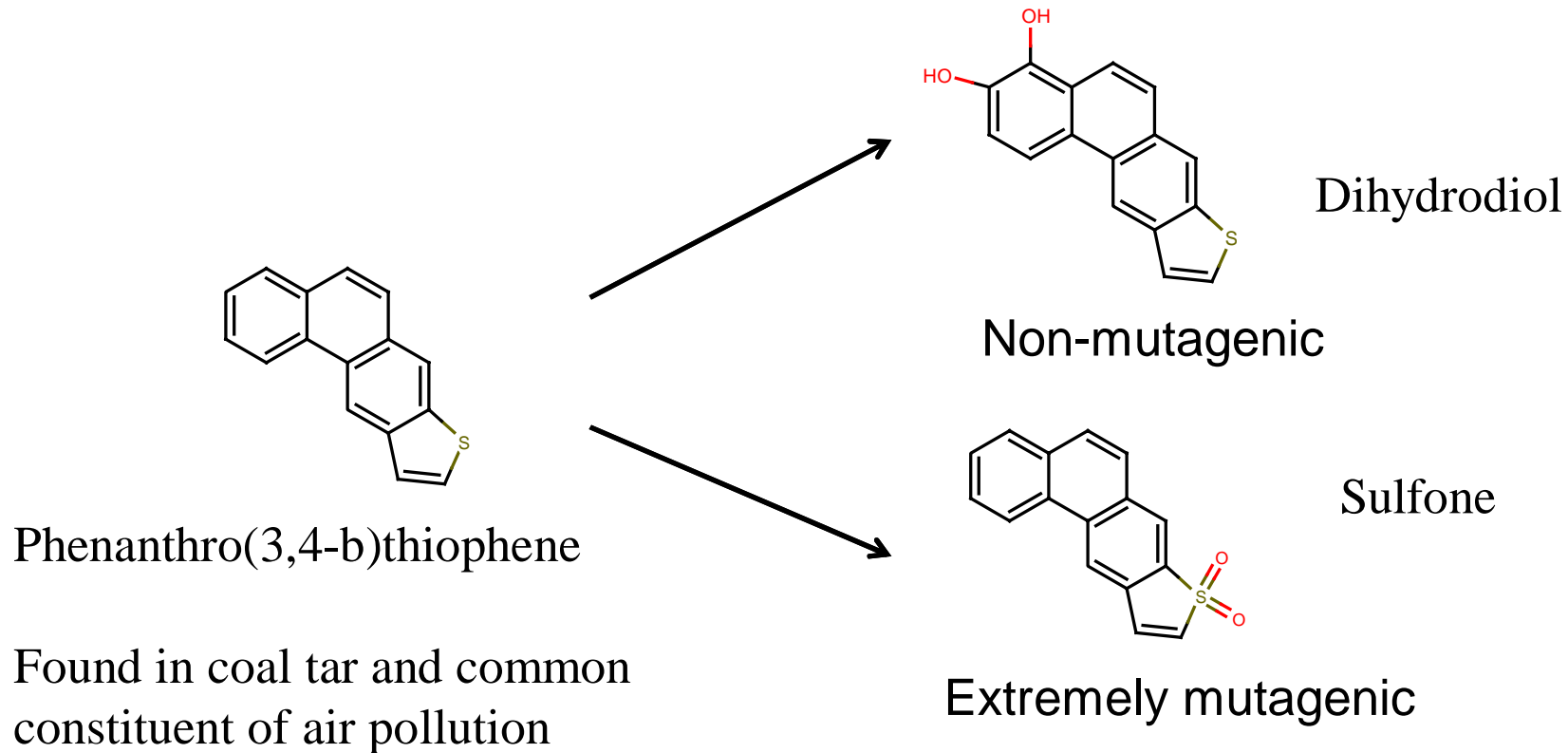
- A heterocyclic compound is a compound that has at least two different elements as members of its ringed structure.
- Of particular interest in coal tar, are those containing:
  - Oxygen;
  - Sulphur; and
  - Nitrogen.
- Sulphur and Nitrogen containing PAHs are largely determined by their presence in the parent coal, with some temperature dependant alterations.
- Oxygen containing compounds are likely to be defined by the temperature of the carbonisation/gasification process and can be used as potential forensic biomarkers.



# SULPHUR CONTAINING PAH - PASH

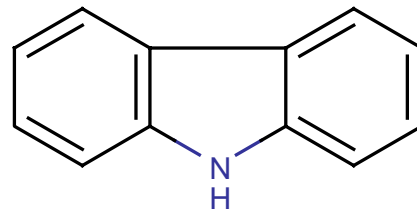
- Organic sulphur occurs in coal tar;
- Of most importance are heterocycles such as thiophenes or dibenzothiophenes;
- Due to the presence of sulphur PASHs exist in an even greater variety of structures compared to PAHs with alkylated isomers being dominant;
- PASHs co-elute with PAHs - a fractionation or isolation step is required to correctly measure PASHs – achieved with the use of GCxGC;
- PASHs and their metabolites can be carcinogenic or mutagenic;
  - Benzo[2,3]phenanthro[4,5-bcd]thiophene > mutagenic than Benzo[a]pyrene.
- PASHs are readily metabolised by bacteria and higher organisms;
  - Metabolites can have increased mutagenic or carcinogenic activity.

# METABOLISM OF PASH



# NITROGEN CONTAINING PAH – NPAC

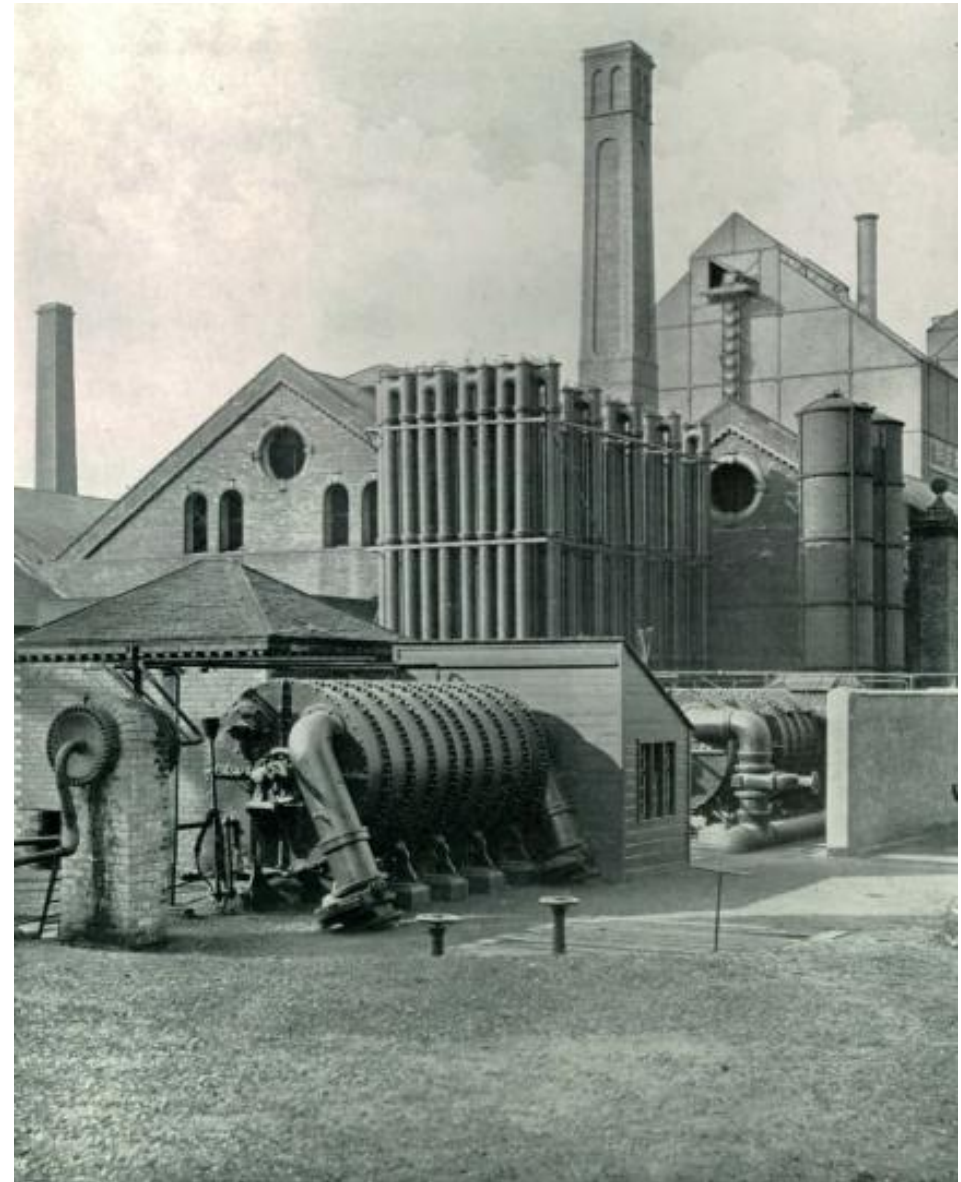
- Nitrogen is present in all fossil fuels and is associated almost exclusively with the organic portion of the crude material.
- Nitro & amino groups can enhance toxicity by up to 100-fold.
- A number of heterocyclic nitrogen compounds are known, or suspected, carcinogens.
- Even though the concentration of NPAC in coal tar could be relatively low, the possible health effects from (NPAC) cannot be ignored.
- NPACs could be of special concern in groundwater at gasworks due to their increased water solubility.



carbazole

# CLOSING REMARKS

- Tar was produced by multiple processes.
- Variation in composition is quite considerable >2000 detectable compounds.
- GCxGC provides a method to understand the complexity of chemistry.
- Only a 163 are common across all the tars analysed.
- Wide diversity between different tars beyond the 163 compounds
- A series of three papers is due to be published putting the unique database into the public domain.
- A series of other related papers will follow.







- Thanks to:
- Chris Taylor - National Grid - funding
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- University of Strathclyde:
  - Prof. Bob Kalin – Principal Investigator
    - Dr Chris Gallacher
    - Dr Fabrizio Colosimo
    - Dr Laura McGregor
- Those who have participated in providing samples for the research.

# Thank You

Please contact us if you have any further questions.



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