Characterisation of Mineral Transformer Oil

by

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A thesis submitted to the University of Surrey for the award of
Doctor of Philosophy in the faculty of Chemistry

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June 26 2001
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Abstract

In recent years the electrical industry has begun to address the consequences of the environmental impact and the reduction in physical size of modern high-voltage equipment (such as transformers) on the use of mineral oil. Refiners have recently switched to new sources of crude to produce low-molecular weight, highly refined oils to insulate and cool transformers. To meet these pressures and changes, the National Grid Company (NGC) has begun a programme of analysis to characterise oils from various sources and to attempt to link changes in their composition and physical properties with their deterioration. Detailed analysis allows a more discerning choice among available oils; identification of the changes which occur before breakdown may provide an early warning of such difficulties.

The method chosen for fingerprinting transformer oil was gas-chromatographic (GC) analysis of the PAH (poly-aromatic hydrocarbon) fraction. The PAHs were extracted by a liquid-liquid and solid phase extraction (SPE) technique developed after exhaustive experimentation using different SPE cartridges. Unused transformer oils from different sources were used to demonstrate that the PAH fraction was sufficiently characteristic for its use as a source recognition method.

Accelerated ageing experiments were carried out to produce degraded oils under similar conditions to those found in large, power transformers. The oils were exposed to high temperature, high voltage and ultraviolet radiation. In each case the PAHs were extracted from the aged oils and analysed by GC.

The breakdown of transformer oil is known to produce acidity. Identifying the specific acids produced and monitoring their production in service would be an effective condition assessment tool. Artificially degraded oils with relatively high acidity values, measured by a standard technique, were analysed to identify acidic compounds.

A relatively new technique using array-based sensors, commonly referred to as electronic noses, was assessed as a tool for fingerprinting transformer oils.
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<td>ANN</td>
<td>Artificial Neural Network</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BAW</td>
<td>Bulk Acoustic Wave</td>
</tr>
<tr>
<td>BDV</td>
<td>Breakdown Voltage</td>
</tr>
<tr>
<td>BS</td>
<td>British Standard</td>
</tr>
<tr>
<td>BTA</td>
<td>Benzotriazole</td>
</tr>
<tr>
<td>CIGRÉ</td>
<td>Conférence Internationale des Grands Réseaux Electriques</td>
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<tr>
<td>CONCAWE</td>
<td>Conservation of Clean Air and Water Europe</td>
</tr>
<tr>
<td>DAD</td>
<td>Diode Array Detector</td>
</tr>
<tr>
<td>DBPC</td>
<td>Di-tert-butyl para cresol</td>
</tr>
<tr>
<td>DGA</td>
<td>Dissolved Gas Analysis</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethyl formamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulphoxide</td>
</tr>
<tr>
<td>DS</td>
<td>Durasyn</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<tr>
<td>E Agency</td>
<td>The Environment Agency for England and Wales</td>
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<tr>
<td>ECD</td>
<td>Electron Capture Detector</td>
</tr>
<tr>
<td>EDX</td>
<td>Electron Dispersive X-Ray</td>
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<tr>
<td>E-NOSE</td>
<td>Electronic Olfactory Sensory Equipment</td>
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<tr>
<td>EOS</td>
<td>Electrical Oil Services</td>
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<tr>
<td>EPA</td>
<td>Environmental Protection Agency (US)</td>
</tr>
<tr>
<td>FFA</td>
<td>Furfuraldehyde</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionisation Detector</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph(y)</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatograph – Mass Spectrometer</td>
</tr>
<tr>
<td>HP</td>
<td>Hewlett Packard</td>
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<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>HV</td>
<td>High Voltage</td>
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<tr>
<td>IEC</td>
<td>International Electrotechnical Commission</td>
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<tr>
<td>IP</td>
<td>Institute of Petroleum</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
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<tr>
<td>LV</td>
<td>Low Voltage</td>
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<tr>
<td>MS</td>
<td>Mass Spectrometer</td>
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<tr>
<td>MSD</td>
<td>Mass Selective Detector</td>
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<tr>
<td>NGC</td>
<td>National Grid Company plc</td>
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<tr>
<td>NIST</td>
<td>National Institute for Standards and Technology</td>
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<tr>
<td>NPD</td>
<td>Nitrogen Phosphorous Detector</td>
</tr>
<tr>
<td>NSD</td>
<td>Nitrogen Selective Detector</td>
</tr>
<tr>
<td>NST</td>
<td>Nordic Sensor Technologies</td>
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<td>PAH</td>
<td>Poly-aromatic hydrocarbon</td>
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<tr>
<td>PAO</td>
<td>Poly-alpha olefin</td>
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<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
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<tr>
<td>PCB</td>
<td>Poly-chlorinated biphenyl</td>
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<tr>
<td>PFTBA</td>
<td>Perfluorotributylamine</td>
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<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RI</td>
<td>Refractive Index</td>
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<tr>
<td>SAW</td>
<td>Surface Acoustic Wave</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>SFC</td>
<td>Super-Critical Fluid Chromatography</td>
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<tr>
<td>SIM</td>
<td>Single Ion Monitoring</td>
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<tr>
<td>SPE</td>
<td>Solid Phase Extraction</td>
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<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
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<tr>
<td>UV</td>
<td>Ultra-Violet</td>
</tr>
<tr>
<td>VI</td>
<td>Viscosity Index</td>
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<tr>
<td>VOC</td>
<td>Volatile Organic Compounds</td>
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Acknowledgements

I would like to acknowledge Roger Bolton, Alan Emsley and John Jones for their support and guidance throughout the duration of this thesis. The majority of the funding was provided by EPSRC, which was greatly appreciated.

National Grid provided financial support for the work and also made the GC-MS available. I would particularly like to thank Sue Fitton and Paul Jarman for their encouragement and Behrooz Pahlavanpour for his advice and the opportunity to share my work with the international community.

I would like to thank Malcolm Kersey formerly of SmithKline Beecham and Jonathan Slater at Birkbeck College for generously allowing me access to their electronic nose instruments. I would also like to thank Donald Hepburn at Glasgow Caledonian University for ageing oil samples and acting as a sounding board for ideas.

On a more personal note I would like to thank my family, friends and colleagues for their interest and support when things have not been going well. Most of all I would like to thank my wife Jo for her patience and encouragement.
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1.1. Introduction

In recent years the electrical industry has begun to address the consequences of the environmental impact and the reduction in physical size of modern high-voltage equipment (such as transformers) on the use of mineral oil. Traditionally, low-molecular weight, highly refined oils have been used to insulate and cool transformers, in recent years refiners have switched to new supplies of crude oil. To meet these pressures and changes, the National Grid Company (NGC) has begun a programme of analysis to characterise oils from various sources and to attempt to link changes in their composition and physical properties with their deterioration. Detailed analysis allows a more discerning choice among available oils; identification of the changes which occur before breakdown may provide an early warning of such difficulties.

Refined oils are very complex mixtures of hydrocarbons with up to 3000 components (Sierota and Rungis 1994) and up to 25% of the oil may be aromatic compounds. Oils for use in transformers, which conform to the industry standards set for electrical and rheological properties, may differ greatly in their chemical composition. On this account oils may fail in service and cause the transformer to fail long before the desired 40-year lifespan. Despite many analyses, only 10% of the components of many oils have been identified. Different oils cannot, therefore, be distinguished by the identification of every component. A “fingerprint” of some readily recognised components (e.g. aromatic compounds, heterocyclic compounds, etc.) can serve to differentiate oils without a full and detailed analysis.

Mineral oil was patented in Britain for use in transformers as early as 1891. The first oil used was paraffinic in nature but was replaced by naphthenic oil in the 1920s. Whilst many countries now use paraffinic oil with artificial oxidation inhibitors, the type of oil found in transformers and other oil-filled high voltage (HV) equipment throughout England and Wales is very similar to the oil first used 70 years ago. Modern refining techniques provide oil of higher quality at a price which allows the best compromise between cost and performance. Alternative liquid insulators, such as silicone oils and esters, are more expensive but have much higher flash and fire
points. Therefore, they can be cost effective if a transformer damage could cause the loss of human life or very expensive damage.

Oil is not the only electrical insulation found in a transformer; each copper conductor is wrapped in several layers of a special paper free from metallic and non-metallic ions. The paper has most of the lignin removed by treatment with sodium hydroxide and sodium sulphate by a procedure known as the Kraft process (Dahl, 1884). Paper, like oil, has been used in transformers for many years and continues to provide the cheapest and best option to transformer manufacturers.

A static transformer is essentially made up of a magnetic circuit, primary and secondary coils, terminals, cooling and insulation and in many cases external cooling apparatus and tap changing equipment to change voltages (Figure 1.2). They are very reliable and a low proportion of them fail due to electrical faults. However, mechanical failure may be the cause of many failures in auxiliary equipment and cause failure within the transformer (Emsley and Stevens, 1994).

![Figure 1.1: Photograph of a 400kv/275kv auto-transformer](image-url)
A study of failures in modern transformers (Franklin and Franklin) shows that between 70% and 80% of electrical failures are due to short-circuits between turns. The failure itself, in many cases, destroys the evidence of what caused the short-circuit and it is often a matter of conjecture. The responsibility for failure may be due to:

A. Faulty Manufacture
   a) Poor design
   b) Faulty materials
   c) Bad workmanship

B. Faulty or Abnormal Operation
   a) Careless drying out and installation
   b) Poor maintenance
   c) Abnormal transient or sustained operating conditions

Faults notwithstanding, during the service life of a transformer both forms of insulation suffer from degradation processes until they can no longer perform adequately and the unit is no longer fit for continued operation. Transformers in England and Wales, and many other countries, are not sealed systems and the oil can
be reconditioned or replaced if a problem arises. However, this is not true for the paper; it is not a renewable commodity within the transformer. It is fair to say, therefore, that the life of the transformer is equatable to the life of the paper. Since the breakdown products of the transformer oil are catalysts for the degradation of the paper (Nevell et al., 1985), it is also reasonable to say that the life of the paper is dependent on the stability of the oil. Even if the oil can be replaced, any damage caused to the paper by degraded oil is not reversed. Clearly, the quality of the oil in a transformer is important in its successful operation for a reasonable length of time - usually forty years.

1.2. Mineral Oil

Crude oil is made up of hydrocarbons, a small percentage of which contain oxygen or sulphur. The organic sulphur content can vary from 0.1% to 5%. Crude oil can be divided into three separate types: paraffinic, asphaltic and mixed-base. The paraffinic type crude is high in paraffinic compounds (alkanes) and consists of mostly lighter fractions - gasoline, gas oil and gases. The asphaltic type also contains paraffinic compounds but has a high concentration of naphthenic compounds (cycloalkanes).
fractions - gasoline, gas oil and gases. The asphalitic type also contains paraffinic compounds but has a high concentration of naphthenic compounds (cycloalkanes). Paraffinic crude provides most of the heavier fractions - bitumen and waxes. Mixed-base type crude is a mixture of asphalitic and paraffinic. All types of crude also contain aromatic molecules.

Crude oil of all three types has many uses, as can be seen in Figure 1.3, but it has to be refined to separate out the useful fractions. The different fractions are separated according to boiling ranges by distillation in a fractionating column. Insulating oils, including transformer oils, are produced from the fraction which has a boiling range between diesel fuel and automotive lubrication oils.

1.3. Transformer Oil

Regardless of the crude from which a transformer oil is refined, it will contain paraffinic and naphthenic hydrocarbons. With the exception of 'white oil', they will also contain aromatic compounds and various other molecules. The composition of the oil will depend on the choice of crude and on the refining procedure.

1.3.1. Chemical Composition

The many compounds present in crude oil have different effects on the properties of a refined oil; some will only benefit the oil and some are harmful, others will do both and balancing these compounds is part of the skill in refining an oil. Some of the compounds and their effects are here discussed.

1.3.1.1. Paraffinic Hydrocarbons

There are two types of paraffinic molecule in transformer oil: straight-chain and branched. Straight-chain paraffins or n-alkanes predominate, they are considered to have poor low-temperature properties as they crystallise as the oil temperature cools. Paraffins are poor solvents of water and oxidation products. As a result free water can be present and sludge (water/oil/solid suspension) will precipitate. Paraffins also have lower thermal stability than other hydrocarbons. It is fairly typical for oil refiners to
refer to all branched alkanes as “iso-paraffins”, rather than applying it to isoalkyl structures only.

![Paraffin](paraffin.png)

![Iso-Paraffin](iso-paraffin.png)

**Figure 1.4: Typical paraffinic molecules in transformer oil**

**1.3.1.2. Naphthenic Hydrocarbons**

Naphthenic molecules are cyclic alkanes. The ring structure can contain five, six or seven carbon atoms, but six is the most common. In contrast to the paraffins, naphthenes have excellent low temperature properties, which is important for transformers in lower climates. Naphthenic compounds are also better solvents for oxidation products. However, the naphthenic compounds found in the fraction used for transformer oils are more volatile than the paraffinic compounds. As a result oils with high naphthenic content tend to have lower flash points.

![Cyclopentane](cyclopentane.png)  ![Cyclohexane](cyclohexane.png)  ![Cycloheptane](cycloheptane.png)

**Figure 1.5: Typical naphthenic molecules in transformer oil**

**1.3.1.3. Aromatic Hydrocarbons**

Aromatic hydrocarbons are present in all but the most highly refined transformer oils. Most aromatic compounds in transformer oil contain at least one benzene ring. The chemical and physical properties of aromatic compounds differ greatly from
naphthenic compounds, but they have similar dielectric constants. There are many aromatic structures with only one benzene ring, called mono-aromatics, and benzene itself may be present. The aromatic fraction of a transformer oil is important because most of the natural inhibitors to oxidation are aromatic.

![Benzene and Biphenyl](image)

Figure 1.6: Typical aromatic molecules in transformer oil

Aromatic compounds, which contain two or more aromatic rings fused together, are called polycyclic aromatic hydrocarbons (PAHs) or polycyclic aromatics. Many PAHs are found naturally occurring in crude oil; several of these survive the refining process to form part of a transformer oil. The PAH content is usually higher if the boiling point range of the oil fraction is higher.

![Typical polyaromatic molecules in transformer oil](image)

PAHs are important in many ways and are discussed more fully later in this introduction.
1.3.1.4. Other Molecules

Transformer oil is not wholly composed of pure hydrocarbons. There are also some heteroatoms; typically nitrogen, oxygen and sulphur are present in small quantities. Nitrogen is present in only very small quantities, typically a few ppm, but can be found in two forms: basic (e.g. pyridine, quinoline) and non-basic (e.g. carbazole, pyrrole). Despite the low concentration, nitrogen-containing compounds can have a profound influence on the character of the oil. Some molecules can have unwanted characteristics - they can be charge carrying or oxidation initiators, or they can be extremely useful as oxidation inhibitors or metal passivators (especially of copper).

![Carbazole](image1)

![Acridine](image2)

Figure 1.8: Typical nitrogen-containing molecules in transformer oil

An unused transformer oil fresh from the refinery has few oxygen-containing molecules, although some dibenzofuran may be present. Furfuraldehyde (FFA) is occasionally left as a remnant from the refining process. Phenols can be found in some oils as synthetic additives, for example DBPC and BTA. Once an oil has been in service then oxygen-containing compounds are more common. Oxidation of oil, which is discussed in detail later, produces acids, ketones and phenols.

![Furan](image3)

![2-Furaldehyde](image4)

Figure 1.9: Typical oxygen-containing compounds in transformer oil
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Phenol based antioxidants

Figure 1.10: Typical oxygen-containing compounds in transformer oil

Although sulphur is more common in oil than nitrogen and oxygen it is still present at low concentrations. The structure of a sulphur-containing molecule greatly influences its effect on the oil. Most organo-sulphur molecules in transformer oil are either corrosive and cause damage to the copper in the transformer or they are antioxidants and destroy the peroxide intermediates; some may be both. For example arenethiols are effective oxidation inhibitors because of the stable arylthiooxy radical (ArS), but they also attack metals such as copper. Mercaptans are usually only present in particularly poor quality oils or as an intermediate oxidation product.

Dibenzothiophene  Mercaptan (Thiol)  Sulphide

Figure 1.11: Typical sulphur-containing molecules in transformer oil

1.3.2. Refining Techniques

In its natural state crude oil is of little use and must be refined by distillation or fractionation. The oil is separated into different distillates according to the boiling range. Depending on the crude this is done at normal pressure (paraffinic crudes) or at very low pressure (naphthenic crudes). Lowering the pressure allows separation of heavier molecules by lowering their boiling ranges. Normally fractionation does not take place above 350°C, as the oil will begin to decompose thermally.
Paraffinic crudes are commonly dewaxed (by low-temperature filtration) after distillation to give the oil reasonable low temperature properties. Naphthenic oils do not require dewaxing, as they do not usually contain many n-alkanes.

There are three methods used in refineries which remove unwanted components:

- Solvent Extraction
- Acid-Clay Treatment
- Catalytic Hydrogenation

The solvents used to extract impurities are sulphur dioxide or furfuraldehyde (FFA). Two phases are produced:
(i) The solvent phase containing the unwanted material
(ii) The raffinate phase, which is a purified oil

It is essential that all traces of the solvent are removed from the oil after extraction as the solvent can cause problems in the finished oil. For instance, transformer oil in service is analysed for FFA, as it is a breakdown product of paper, and any residual FFA from the refining would interfere with this monitoring process.

An increasingly less common technique is acid clay treatment. Depending on temperature and concentration, sulphuric acid can be used for solvent extraction. White oils (free from all aromatics and heteroatoms) can be produced using oleum - sulphuric acid containing free sulphur trioxide.

Acid clay treatment is gradually being phased out due to the environmental impact of its waste products. Activated clay is still occasionally used, however, to remove polar compounds from used oil.

Catalytic hydrogenation is gradually superseding acid clay treatment and solid phase extraction. The unwanted compounds are absorbed onto a catalyst at high temperature and pressure and they react with hydrogen dissolved in the catalyst. It is possible at this stage to increase the naphthenic content of a paraffinic oil at the expense of the aromatic fraction. The paraffinic oil gains the advantages of being a naphthenic oil, but loses the benefits of its aromatic fraction.
1.3.3 Paraffinic vs. Naphthenic Transformer Oil

A refined transformer oil may be paraffinic or naphthenic, which is usually dependent on the crude source and may impact on its performance. They each have their own advantages and disadvantages, and they are both used in transformers throughout the world. Some definitions are required to differentiate between the two types of oil. The US Bureau of Mines classifies oil by its density as shown in Table 1.1.

<table>
<thead>
<tr>
<th>Class</th>
<th>Density of Atmospheric Fraction (boiling range - 250°C-275°C)</th>
<th>Density of Vacuum Fraction (40mmHg, boiling range - 275°C - 300°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffinic</td>
<td>&lt; 0.825</td>
<td>&lt; 0.876</td>
</tr>
<tr>
<td>Intermediate</td>
<td>0.825 - 0.860</td>
<td>0.876 - 0.934</td>
</tr>
<tr>
<td>Naphthenic</td>
<td>&gt; 0.860</td>
<td>&gt; 0.934</td>
</tr>
</tbody>
</table>

This is not a particularly satisfactory demarcation between the classes, but a more definitive classification is yet to be established. A new method using differential scanning calorimetry (DSC) to detect wax is currently being considered by IEC (International Electrotechnical Commission).

A transformer oil which is paraffinic will have been produced from a paraffinic crude. It is high in n-paraffin and as such has a high pour point. Naphthenic transformer oil is produced from crudes lower in n-paraffin and which means that this type of oil has a lower pour point. Some of the advantageous properties of naphthenic oil stem from the higher aromatic content which is typically found in this type of oil.

A naphthenic oil can be produced from paraffinic crude if the aromatic fraction is converted to naphthenic compounds, the loss of the aromatic fraction means that this type of naphthenic is not as good as one produced from a naphthenic crude. The advantages of each type of oil are best discussed by considering the principal
properties which a transformer oil must have and which form the basis of BS148 specification:

- High Flash Point
- Low Pour Point
- Low Viscosity
- Low Density
- Chemical Stability
- Low Water Solubility
- High Electric Strength
- Good Appearance
- High Electrical Resistivity
- Low Dielectric Dissipation Factor

The flash point is the temperature at which a spark, just above the surface, will cause the oil to ignite. A transformer can produce electrical discharges, but they rarely cause ignition because they occur within the oil where there is not enough oxygen. Also, the operating temperature of a transformer is normally under 100°C, although occasionally faults in a transformer can cause hotspots, which can reach very high temperatures. Paraffinic oils tend to have higher flash points than naphthenic oils as they are less volatile.

Some transformers have to operate in colder climates and it is important that the oil does not become too viscous or it will not circulate freely and heat cannot be dissipated. The pour point is the temperature at which oil will no longer pour because it is too viscous. Paraffinic oils have a larger n-alkane fraction which crystallises and impedes oil flow. As such, they have higher pour points and sometimes require added pour point depressants to lower them.

Low viscosity is not only important at low temperatures. Low viscosity allows free flowing circulation within the transformer, which improves the cooling efficiency. Less viscous oil also enables better impregnation of the paper insulation. The viscosity of an oil decreases as the temperature increases. The measure of how much an oil changes with temperature is indicated by its viscosity index (VI). A high value for VI means that the oil demonstrates a small change in viscosity with temperature. An oil which is a good coolant has a low VI in combination with a low viscosity.

The density of an oil is important at lower temperatures. If there is free water present in a transformer then at very low temperatures (less than -10°C) the ice crystals will
float if the oil is too dense and this can cause instrument failure. The density of an oil is greatly influenced by the aromatic content of the oil. Therefore, paraffinic oil is less dense than naphthenic oil.

The chemical stability of the oil refers to its ability to resist oxidation. As well as higher temperatures, a transformer oil is also exposed to copper and iron which may catalyse oxidation. The source of the crude is usually the most significant factor in the chemical stability of the oil. A high aromatic content is usually beneficial to oil stability, thus naphthenic oils are often more stable than paraffinic oils. However, an oil can have an oxidation inhibitor introduced into it. The inhibitor is usually a phenol and is chosen because it is degraded in preference to the rest of the oil. Oils which are artificially inhibited are used in many countries, but these are not used in England and Wales.

Water and oil “do not mix”, but the solubility of water in oil is not zero. The amount of water which can dissolve in the oil depends on the temperature and the presence of polar molecules; unused oil is usually saturated by 60ppm of water at 30°C. An oil with a high aromatic content has the potential to hold more water. Experience shows that over long periods, ‘wet’ oil will oxidise more quickly and will have a lower breakdown voltage (BDV) (Pahlavanpour 1994). Before a transformer is filled the oil is always dried. However, the insulating paper usually contains a significant amount of water and equilibrium is reached between the phases shortly after the transformer is filled. The amount of dissolved water increases with the age of oil because oxidation products are polar. Water is a by-product of the oxidation process and it is preferable for the water to be dissolved in the oil rather than ‘free’ to create a short-circuit.

The best insulator is an oil which has been highly refined so that there is no aromatic content at all (white oil). The degree of refining has to be balanced against the other properties the oil should have. Whether either a naphthenic or a paraffinic oil has the best possible electrical properties depends on how much the refining has to be compromised to produce the required physical and chemical properties.
The appearance of an oil indicates the presence of heteroatoms (if it is dark) and the presence of particles if it is not clear. Naphthenic oils tend to be slightly darker as heteroatoms are more common in oils with higher aromatic content. Particles in an oil increase the probability of breakdown at low voltage but the amount is independent of the type of oil as they are usually contaminants from external sources such as oil containers.

The standard tests that form the BS148 specification are summarised in Table 1.2 and further details may be found in Appendix A. Clearly the specification takes little account of the chemical composition or the influence it may have on the performance of the oil.

Table 1.2: BS148:1998 Specification for unused and reclaimed insulating oils for transformers and switchgear for uninhibited class I oil.

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Method</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 40°C</td>
<td>BS EN ISO 3104:1996</td>
<td>≤16.5mm²/s</td>
</tr>
<tr>
<td>Viscosity at −15°C</td>
<td>BS EN ISO 3104:1996</td>
<td>≤800mm²/s</td>
</tr>
<tr>
<td>Flash Point</td>
<td>BS EN 22719:1994</td>
<td>≥140°C</td>
</tr>
<tr>
<td>Pour Point</td>
<td>BS 2000:Part 15:1995</td>
<td>≤−30°C</td>
</tr>
<tr>
<td>Appearance</td>
<td>BS 148:1998</td>
<td>Clear</td>
</tr>
<tr>
<td>Density</td>
<td>BS EN ISO 3675:1996</td>
<td>≤0.895kg/dm³</td>
</tr>
<tr>
<td>Neutralisation value</td>
<td>BS 148:1998</td>
<td>≤0.03mgKOH/g oil</td>
</tr>
<tr>
<td>Corrosive sulphur</td>
<td>BS 5680:1979</td>
<td>None</td>
</tr>
<tr>
<td>Water content</td>
<td>IEC 814:1995</td>
<td>≤20ppm (bulk)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>≤30ppm (drum)</td>
</tr>
<tr>
<td>Anti-oxidant additives</td>
<td>BS 5984:1980</td>
<td>Not detected</td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>BS EN 61125:1993 Method C</td>
<td>≤1.2mgKOH/g (acidity)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>≤0.8% sludge by mass</td>
</tr>
<tr>
<td>Breakdown voltage</td>
<td>BS EN 60156:1996</td>
<td>≥30kV</td>
</tr>
<tr>
<td>Dielectric dissipation</td>
<td>BS 5737:1979</td>
<td>≤0.005 at 90°C</td>
</tr>
<tr>
<td>factor</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### 1.3.4 Transformer Oil Supply

National Grid has traditionally bought unused transformer oil from Castrol (BS148 Grade) and Carless (Transol 1). Nynas started producing transformer oil for the UK market in the early nineties and National Grid began to use Nynas Nytro 10GB (latterly Nytro 10GBN) in 1994. Nynas oil was the first produced from Venezuelan crude, with Castrol and Carless following suit within a few years. Castrol and Carless have recently merged to form EOS (Electrical Oil Services) and National Grid has only two suppliers once more.

National Grid only uses unused oil in new transformers, however reclaimed oil is still purchased for older equipment. At one time the electricity companies in England and Wales removed oil and sent it for reclamation – removal of sludge and degradation products by filtration through Fuller’s Earth – and it would count as a credit in the ‘Pool’. Reclaimed oil from all the utilities would end up mixed and then would be resupplied as required. This practice has declined as problems with the ‘pooled’ oil became apparent.

- The oil became contaminated with PCBs (polychlorinated biphenyls)
- Reclaimed oil used to ‘top up’ a transformer can cause incompatibility problems, such as foaming under reduced pressure
- Doubts about the oxidation stability of reclaimed oil.

There are many other refiners of transformer throughout the world. Shell refineries in Germany and USA produce an oil which conforms to BS148, DialaB, but this is not currently used by National Grid. Other suppliers include those listed in Table 1.3
1.4. Transformer Oil Degradation

Transformer oil fails to fulfil its purpose if it conducts, either through electrical stress or through chemical degradation. Even an oil which passes the most stringent of specifications can fail in service due to one of these causes.

The electrical breakdown of transformer oil has been investigated by many researchers over more than half a century. No evidence of research into the chemical composition or degradation of transformer oil could be found. Some of the work into electrical breakdown is summarised here.

1.4.1. Conduction in Transformer Oil

An oil should, in theory, have an intrinsic conductivity i.e. it should be able to carry a current no matter how small (Zaky 1963). In practice, however, such a small conductivity is impossible to measure reliably as it is so easily affected by external factors, such as water, ionic impurities and dissolved gases.

Figure 1.12 shows a general curve which demonstrates how a conduction current is related to electrical stress for a uniform field.
In region A, the increase of current is Ohmic in nature, which means it is proportional to the field strength.

\[ J = \sigma F \]

where:  
- \( J \) = Current density,
- \( \sigma \) = Ohmic conduction
- \( F \) = Electric field

At a certain stress no more ions are produced and a current saturation is reached. Eventually at a very high stress a new source of charge carriers is produced and the current increases exponentially. The point at which this occurs depends on many factors, such as: electrode gap distance, type of liquid dielectric, electrode material and preliminary pre-conditioning (Tobazéon 1994). This point is unpredictable and the current rise cannot be satisfactorily explained. Clearly, the electrical stress in a transformer should not reach this point.

1.4.1.1. Space Charges

When a constant potential difference is applied between two electrodes across an insulating liquid an initial current flow is observed which may last from a few milliseconds to several hours. This initial flow is called the charging current. A charging current could be observed when a transformer is turned on for the first time but it is not measured. After this initial flow, the current decreases to an equilibrium value.
If the potential difference is removed once the equilibrium is reached then a discharge current is observed to flow in the opposite direction. The fact that this occurs is evidence of an electrode polarisation process i.e. the rate at which ions are discharged at the electrode surfaces is less than their rate of arrival. This causes space charges to form near to the electrodes (Jaffe 1953, Hart 1956)

Extensive study of space-charge phenomena (Guizonnier et al. 1956, 1957, 1962 and 1967) has led to the definition of two groups of insulating liquids - those with heterocharges and those with homocharges. Heterocharge liquids are those which produce space charges opposite in charge to the nearby electrode. The space charges in homocharge liquids have the same sign as the electrode at which they are formed. This grouping leads to three classes of oil:

A Homocharge: highly viscous, dry liquids - silicone oils/some mineral oils
B Heterocharge: low viscosity, dry liquids, charged particles of both signs present
C Both: Class B oils which are not dry

In a homocharge liquid the molecules are uncharged until a voltage is applied. When this happens the molecules close to the non-earthed electrode acquire a charge of the same sign by electron exchange and are repelled into the liquid.

In heterocharge liquids at low fields, charges having the same polarity as the non-earthed electrode are distributed exponentially in the gap between the electrodes. As the field strength increases the charge distribution in the vicinity of the non-earthed electrode remains exponential, but the influence of charges of the opposite polarity becomes more marked as they accumulate near the earthed electrode.

The determining factor in whether a liquid is homocharge or heterocharge is how quickly the homocharges are able to move away from the electrode. Experimental evidence has shown that homocharge liquids will all become heterocharge above a
certain temperature (typically 35-40°C) and that heterocharge liquids will become homocharge at sufficiently low temperatures (Figure 1.13). This suggests that viscosity of the liquid rather than any chemical affinity is principally responsible for the determining factor.

Figure 1.13: Effect of temperature on charge in dielectric liquids (Guizonnier 1957)

Using a probe electrode the potential can be measured at different distances from the live electrode. The potential falls more quickly with distance in a heterocharge liquid than in a homocharge liquid.

1.4.1.2. Low-Field Conduction Currents

Extensive low-field conduction-current experiments on heterocharge and homocharge liquids have been carried out (Guizonnier 1961). The currents in very dry heterocharge liquids quickly reached a quasisaturation level. However, the current was observed to increase rapidly with voltage as moisture levels rose. The higher the moisture content, the more steeply the current rises with voltage. It was also noted that the effect of temperature was similar to that of moisture content.
The variation of $i_0$, the initial or charging current, with temperature may be expressed by the following Arrhenius-type equation. Thus:

$$i_0 = Ae^{-W/kT}$$

where $i_0$ = Initial current

$A$ = Constant dependent on the liquid

$W$ = Activation energy

$k$ = Boltzmann constant

$T$ = Temperature (K)

For all heterocharge liquids tested (benzene, tetrachloromethane, transformer oil, silicone oil, paraffin – Forster 1962, 1963, 1964, 1967) the value for $W$ was found to be 0.41eV. It has been surmised that the charge carriers are water molecules in all cases, which would account for the conductivity of all the liquids having the same nature. Further evidence has been given by studies of deionised water: when the variation of the conductivity with temperature is measured the current is found to follow the equation above with a value of 0.41ev for $W$ (Guizonnier 1964).

Studies of homocharge liquids showed that, as expected, they performed like heterocharge liquids at higher temperatures. Below 35-45°C the current/temperature relationships were very complex (Guizonnier and Darve 1958).

1.4.1.3. High-Field Conduction Currents

Studies of conduction currents in liquid dielectrics at stresses in excess of 50kV.cm$^{-1}$ have shown that problems with stability and reproducibility are encountered. There are so many factors (electrode surface and geometry, fluid purity, hydrostatic pressure, moisture content dissolved gases etc.) which have to be overcome in order to study transformer oil that it is easy to see why problems arise. For example, in experimental studies at fields up to 200kV it has been observed that air absorbed in the oil increases the current (Figure 1.14) and the larger the voltage applied, the larger the currents measured (Sugita et al. 1960).
Field emission (Malik *et al.* 1998) and Schottky emission (Webster 1999) are usually regarded as the cause of high field conduction, however high field electrical dissociation (Coelho 1960) and collision ionisation (Nikuardse 1934) have also been postulated. These processes can be briefly summarised as:

A. Field Emission - Higher electric fields may cause increased electron emission from a conductor. Also called Fowler-Nordheim Field Emission or Quantum tunnelling

B. Schottky Emission – Thermionic emission from a metal electrode into the conduction band of a dielectric

C. High Field Electron Dissociation – Dissociation of polar impurities in a region of high field strength.

D. Collision Ionisation – One or more electrons bound to a target are removed as a result of a collision between a free energetic electron and a target molecule or atom to leave a charged species.

![Figure 1.14: Effect of gas on current voltage relationship (Sugita *et al.* 1960)](image)

Under high fields, conduction currents are usually accompanied by randomly occurring pulses or bursts of current. Ultrafast optical techniques have shown that
these pulses are associated with bubble formation (Qureshi and Chadband 1988) and the development and propagation of discharges called trees (Lessaint and Tobazéon 1988).

1.4.2 Electrical Breakdown Voltage in Mineral Oil

The study of breakdown mechanisms of transformer oils has been ongoing for several decades and has been the subject of many reviews (Batnikas 1994, Zaky and Hawley 1973, Gallagher 1975, Sharbaugh et al. 1978, Devin et al. 1981). However, the current state of knowledge is nowhere near that for insulating gases and solids, because it is much more complicated. Transformer oil is naturally a complex matrix and may also be contaminated with various impurities. The production of gases during the breakdown of the oil further complicates the issue.

Several plausible theories have been forward for the mechanism of electrical breakdown in transformer oil. However, the emergence of new experimental evidence often produces the need for their modification or rejection.

Assuming that a mineral transformer oil has been supplied which is pure and meets all the required specifications, it is well known that several external factors can affect the breakdown strength of the oil. These include: the presence of dissolved gases, ionic impurities and chemical additives, electrodes, temperature, pressure and duration of applied voltage. Currently there is no unified theory of breakdown which accounts for all of these factors. The effects of the most common factors are examined here.

1.4.2.1. Additives

There are many types of additives which can be found in oil, some of which are intentionally introduced and many others which are contaminants. The effects of some of these on the breakdown strength of the oil have been studied (Suzuki and Fujioka 1940, Ruhle 1941). Greases and lubricants are contaminants which may introduced by poor oil handling. They cause a significant decrease in breakdown voltage, even with very small quantities of contaminants.
Other investigations (Booth and Johnson 1954) have shown that wood resins, which at one time were introduced to increase oil viscosity, can actually increase the impulse breakdown voltage of mineral oil. This enables it to be used in conjunction with mineral oil as insulation in certain types of high voltage equipment without causing compatibility problems.

Studies of many insulating liquids have shown that PAHs also have a beneficial effect (Nederbragt 1936, Berberich 1938, Angerer 1963). Small concentrations increase breakdown strength and impulse strength. This is especially noticeable in paraffinic liquids with a naturally low aromatic content.

![Figure 1.15: Effect of aromatic content on breakdown voltage of transformer oil (after Nosseir and Lawrence 1965)](image)

In general, the additives which have been investigated can be separated into three groups (Angerer 1962):

1. Aromatic-type volatile compounds
2. Hydrogen acceptors which are less volatile and effective in the bulk fluid
3. Hydrogen acceptors as above which also form a protective coating on the electrodes.

The natural aromatic components of transformer oil and those added to it in experiments (e.g. benzophenone, azobenzene, azoxybenzene, benzil) fall into the first group. These aromatic compounds raise the dielectric strength by entering into the
gas bubbles formed in the oil, thereby reducing the probability that an electron will acquire sufficient energy in traversing the bubble to break a C-H bond and produce free hydrogen.

Electrons which do accelerate through bubbles cause the rupture of a C-H bond to produce $\text{H}_2$. This can be absorbed by the additives of the type found in groups 2 and 3. Group 2 additives do not contain oxygen e.g. naphthalene, group 3 additives contain oxygen e.g. p-nitrotoluene, p-benzoquinone and benzophenone. Therefore, the presence of naturally-occurring aromatic compounds and group 2 or 3 compounds (some can be naturally occurring), has the effect of raising both the breakdown voltage and gas absorbency of the oil. It has been demonstrated that gas evolution at high stress and breakdown voltage are related (Figures 1.15 and 1.16).

![Figure 1.16: Effect of aromatic content on gassing (after Nosseir and Lawrence 1965)](image)

1.4.2.2. Dissolved Gases

Gases dissolved in insulating liquids affect their breakdown voltage. Results from studies with hexane have shown that oxygen increases the electrical strength with an optimum content equivalent to an equilibrium partial pressure of 13N.m$^{-2}$ (Sletten 2023).
1959, 1960). This has been attributed to its electronegative properties - electrons emitted from the cathode create $O^2$ ions thus effectively reducing available electrons. Nitrogen and hydrogen have no effect, even at large concentrations. However, there appears to be some correlation between electric strength and carbon dioxide (Sletten and Lewis 1963).

Dissolved gases also affect the electrical properties of oil (Clark 1933). If electrical resistance of oil is monitored with increasing air concentration, the strength falls rapidly to a minimum, rises again to a maximum only to fall away gradually to a saturation level. Further studies show that it is the oxygen which causes the changes and there is a sharp rise in electrical strength as the $O_2$ level rises from a very low partial pressure to about 0.1N.m$^{-2}$ (Tropper 1964).

![Figure 1.17: Effect of oxygen and nitrogen dissolved in transformer oil on breakdown voltage at different electrode separations (after Gosling and Tropper 1964)](image)

1.4.2.3. Moisture

The solubility of water in transformer oil depends on the chemical nature of the oil and temperature. The saturation level for a typical, newly-refined transformer oil changes with temperature as shown:
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The relationship between water solubility and temperature can be expressed thus:
\[
\log w = \log w_0 + k\left(\frac{1}{T_0} - \frac{1}{T}\right)
\]
Where:
- \( w \) is the maximum solubility at temperature \( T \)
- \( w_0 \) is the maximum solubility at temperature \( T_0 \)
- \( T \) is the absolute temperature
- \( k \) is a constant

Oil will readily absorb moisture from the air. The amount absorbed is dependent on the temperature and equilibrium partial pressure of the water vapour. The linear relationship (Figure 1.19) indicates that uptake of water from the atmosphere is in accordance with Henry’s and Raoult’s Laws.
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The moisture should be removed from an oil before it is used in high-voltage equipment. The moisture found in free-breathing transformers, such as those used by National Grid, may be from oil degradation, but principally it will be from the paper. The equilibrium of moisture between the paper and the oil greatly favours the paper, however, it has been shown (Fallon and Thibault 1963) that this only holds for new oil and not for oxidised oils. The amount of water which will dissolve in oil is increased by the degree of oxidation. When considering action levels (monitor more frequently, dry, replace etc.) for moisture content in oil in transformers, beyond a certain degree of oxidation relative moisture content needs to be considered as well as the absolute water content.

There are three forms of free water in transformer oil:
(i) Dissolved (homogeneous solution)
(ii) Fine emulsion (dispersed - small droplets)
(iii) Coarse emulsion (dispersed - large droplets)

Normally there is a very low concentration of water in transformer oil. A typical unused oil contains less than 50ppm of water at 20°C. Most will disperse as free water and the rest will be in the form of bound or chemisorbed water (Baumann 1960, Fallou 1965). Water will bind to polar impurities present in an unused oil, to artificial inhibitors (phenolic) or to oxidation products. Bound water is very difficult to remove.

When the saturation level has been passed, the excess of water is present as an emulsion. This can occur if a transformer, which is saturated at the working temperature, is cooled. The droplet size depends on the amount of excess water and can vary from 0.1μm to 1.0μm. Beyond 500ppm the interfacial tension and viscosity of the oil can no longer keep the water in suspension and droplets will collect either at the bottom of the transformer or float to the top of the oil depending on the relative density of the oil to the water (Webb 1997).

It has been postulated that the presence of water in a transformer oil is not, of itself, a problem with regard to its electrical properties (Nikuradse 1934). The difficulty only arises when trace amounts of hygroscopic impurities are present in the water. This would account for the fact that measurements in different studies (See Figure 1.20) usually produce results which have qualitative but not quantitative agreement (Dickson 1951, Baumann 1960, Casper and Kemper 1963, Nelson et al. 1971).
Figure 1.20: Effect of water content on breakdown strength (electrode types and gap distances used by: 1 Spath 1923, 2 Zein Eldine 1956, 3 Kaplan and Kutchinski 1964, 4 Friese 1922)

A decrease in the breakdown strength is always observed when moisture is present. The decrease usually stabilises above 200ppm. Some experiments have suggested that there is stabilisation before the saturation point (ca. 50ppm) after which there is another sharp decrease when excess water becomes emulsified (Schober and Strittmater 1968).

Impurities which do not normally affect the breakdown strength will cause major problems in the presence of water. Cellulose fibres from the paper insulation can contaminate the oil. At low concentrations they have no influence on the breakdown voltage. Likewise 20ppm of water has only a small impact. However, this amount of water with 25ppm cellulose fibres can reduce the breakdown voltage by as much as 50%. This has been put down to the absorption of water from the oil into the fibres and their subsequent alignment in an electric field (Abed 1970).
Photographic evidence has suggested that fibres in oil will form a fibre bridge in the presence of water. This is because the relative permittivity of the moist fibres draws them into regions of high field where they become polarised and form dipole chains. This can occur with even very small quantities of impurities if there are sufficient free water droplets. A fibre bridge will lead to a short circuit and failure of the transformer. These bridges, however, are usually seen to form between electrodes which are only a few centimetres apart and the oil is static. They are unlikely to form in transformers where the gap is considerably larger and the oil is continuously circulated.

1.4.3. Chemical Breakdown of a Transformer Oil

The mechanisms by which transformer oil degrades chemically during service have not been well studied, although the effect of degradation on performance has been observed. As in most mineral oils, oxidation is the primary means of degradation in transformer oil (Lamarre and Gendron 1995, Wilson 1980). Crude oil and its derivatives are highly complex materials and, as such, create problems in attempts to study breakdown mechanisms. For this reason, experimental studies have been frequently carried out on n-paraffins (Blaine and Savage 1991), which are simpler, yet chemically relevant.

Previous studies have indicated the mechanisms and kinetics involved in the initial stages of oxidation in such model systems. The breakdown of a mineral oil usually takes place by a free radical reaction (Van Sickle et al 1973).

Formation of oxidation products via a free radical pathway:
Initiation
The reaction mechanism starts with the production of a free radical by homolytic fission – bond cleavage with both fragments retaining on electron from the covalent bond. The energy may be provided by ultraviolet radiation, heat, mechanical shear stress or electrical stress. The free radical is a highly reactive molecule (or atom) which has one or more unpaired electrons.
R - H → R·

Figure 1.21: Initiation step of a free-radical reaction
The free-radical will react with oxygen to form a peroxy radical, which will lead to the formation of oxidation products.

R·C·R' + O₂ → R·C·O·O·R'

Figure 1.22: Formation of a peroxy radical.

Propagation
The peroxy radicals continue the reaction by abstracting hydrogen to form oxidation products and new radicals. The hydrogen may come from other hydrocarbons or, if it is long enough, from itself to form bifunctional products.

Figure 1.23: Intermolecular hydrogen abstraction

Figure 1.24: Intramolecular hydrogen abstraction
Other propagating reactions are known as branching reactions. The oxidation products may also become radicals, giving different products.

**Termination**

The free-radical reaction is stopped when radicals react with each other to produce a molecule and no further free radical. Many different products may be formed by the termination step depending on the nature of the radicals which combine. Some examples are shown.
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Solids (sludge) are formed by polymerisation.

Smaller alkyl radicals can result in unsaturated products.

As previously stated, phenolic compounds are used as antioxidants, they may also be formed during breakdown. Phenols donate hydrogen radicals to a peroxy radical and terminate the free-radical process because the phenol is resonance stabilised.
Figure 1.30: Termination by substituted phenol

Thermolytic fission of hydrocarbons may take place at high temperature hotspots within a transformer; this is a likely source of free radicals. However, it is also possible that a fault resulting in a large amount of discharging may also initiate free-radical reactions because of the electrical energy and the ultraviolet radiation produced. Thus, a fault can accelerate the rate of oil degradation.

Under more severe oxidising conditions (e.g. very high temperature hotspots or high energy discharges) however, the picture is more complicated. This is because a larger number of oxidation products are produced and different reaction pathways occur. These new pathways include a reaction by which high molecular weight materials are produced. Such reactions also take place in transformer oil and are the source of sludge which is probably the single-most undesirable type of oil degradation product. The presence of sludge has the overall effect of raising the temperature of the transformer. This occurs in many ways: Sludge deposition impedes the conduction of heat away from the conductors and other parts of the transformer. The build up of sludge in oil ducts reduces the volume of oil passing over heating surfaces. Accumulation in the cooling areas of the transformer has the effect of lagging the cooling surfaces and also reduces the volume of oil passing through the cooling areas.
Analysis of paraffinic systems which have been subjected to severe oxidation conditions indicate that hydroperoxides are always the first degradation products to appear. Alcohols and esters reach a maximum value after a short time, but acids continue to increase with time. Esters are the last oxidation products to appear and are usually very low in concentration.
Chapter 2: Scope of the Present Work

2.1 Scope of the Present Work

2.1.1 Poly-Aromatic Hydrocarbons in Transformer Oil

   2.1.1.1 Extraction Method
   2.1.1.2 Analytical Techniques

2.1.2 Acids in Aged Transformer Oil

2.1.3 Ageing of Oil

2.1.4 Electronic NOSES

2.1.5 Summary of Objectives
Chapter 2: Scope of the Present Work

2.1 Scope of the Present Work

National Grid’s primary objective was to find a method for characterising oil as a way of checking the quality of new oils and ensure batch-to-batch consistency. The stability of the compounds used to characterise the oil was then to be investigated. The change of the compounds under service conditions could lead to a new method of condition monitoring for the oil. National Grid had already identified the PAH fraction as a possible candidate for use in fingerprinting. The objectives were set out thus:

A. Devise a qualitative method to determine the PAH content of transformer oil;
B. Investigate the use of the PAH content as a fingerprint to distinguish between oils from different sources;
C. Identify the changes to PAH fingerprint as a result of ageing;
D. Further investigate the chemistry of ageing.

The study of breakdown processes of PAHs in transformer oil in service is of particular interest to National Grid. This is because there is a limit of 0.1% carcinogens placed on waste by the Waste Management (Special Waste) Regulations 1996. An unused oil is not regarded as containing 0.1% carcinogens but it is believed that PAHs may be altered or created in service (Pahlavanpour 1995) and as a consequence diverter oils are considered special waste because of the increased electrical activity in a diverter.

Special waste has cost implications because it is more expensive to transport and dispose of – disposal of a tanker of uncontaminated used oil costs approximately £400, however if it is classified as special waste then the cost rises to approximately £4,400. In addition, more cost is involved in the storage of special waste on a site because, above 3,000 litres (or 23,000 litres on the waste-generating site), a special waste licence is required. There is a significant cost for each licence needed, including an application fee (anything from £425 to £2,500) and an annual payment (from £125 to £3,000). There are costs associated for the licence holder who needs to:
• Employ a technically competent manager;
• Make financial provision in case the waste escapes into the environment and causes pollution;
• Keep records, which must be available to the Environment Agency of England and Wales (E Agency) and provided to them periodically; and
• Have the facility that is licensed available for inspection at all times by the E Agency.

The costs for each of these is estimated at:
• £5,000 per manager in terms of training and registration for the technical competence award required;
• £600 per site per year financial provision for pollution prevention;
• 8 inspections per month and record keeping would cost approximately 17 days per annum (Booth 2001).

There are also costs involved with safe handling of used oil, which may be considered as a health hazard. Understanding how the PAHs are affected by degradation of the oil in service would enable National Grid to take the necessary steps to ensure appropriate handling and disposal of oil was in place.

2.1.1 Poly-Aromatic Hydrocarbons in Transformer Oil

Poly-aromatic hydrocarbons (PAHs) form a small but significant fraction of transformer oil (less than 3%) and can potentially be relatively easily extracted and then used to “fingerprint” the oil. It is intended that the fingerprints will a) identify oils from different sources and b) in the longer term, be correlated with oxidation properties. The carcinogenicity of some PAHs is also pertinent to the use and environmental impact of transformer oils. It should be noted that although some PAHs are referred to as carcinogens, they have to be biologically activated to form diol epoxides before they are truly carcinogenic.

Evidence from both epidemiological and experimental studies have shown that PAHs are highly suspect as causative agents in human cancer (Irvin et al. 1987, La Voce
Their carcinogenic activity can be divided into two aspects: a) mutagenic activity and b) interaction with nucleic acids. Both aspects will result in cancer formation in mammalian tissues. In general, the larger the PAH, i.e. the more rings it has, the greater the likelihood that it is carcinogenic. Benzo[a]pyrene, benzo[a]anthracene and 4-methylchrysene are three molecules which have been extensively studied because of their potency. Many of the smaller PAHs remain only suspected carcinogens but should still be treated with care.

Commercial transformer oils are typically assessed for PAH content as experimental observation has shown that below certain levels (commonly 3%) no statistical increase in the incidence of skin cancer in C3H mice is observed (Figure 2.1). Such a criterion presupposes a similar distribution of the component PAHs in all oil samples, regardless of their source, and the absence of adventitiously enhanced concentrations of more potent carcinogens.

![Figure 2.1: Correlation between IP346 results and the incidence of skin tumours in mice for paraffinic and naphthenic oils (CONCAWE data)](image)

This thesis reports the successful development of a new, quicker method for fingerprinting transformer oil by its PAH content.
There are numerous techniques by which PAHs might be extracted and analysed. The specific problem of removing and analysing PAHs in transformer oil, however, has not been investigated. There follows a discussion of references which present the most viable techniques which may be applied to this problem.

2.1.1.1 Extraction Methods
A standard method of PAH extraction, described by the Institute of Petroleum (IP346) is used by the electrical industry to assess the total poly-aromatic content of a transformer oil. The method involves liquid-liquid separation using dimethylsulphoxide (DMSO), measuring the PAH content by weighing. The experimental procedure must be followed precisely or errors can occur.

Another procedure, known as the Grimmer method (Grimmer and Böhnke 1972), is also commonly used by, although not originally designed for, chemists in the electrical industry. It can be broken down into three steps: the first is a liquid-phase separation, which is then followed by two clean-up stages by column chromatography. The resulting extract is typically analysed by gas chromatography (GC).

The environmental concern over PAHs has led to the development of many other extraction techniques, however, most of them are from aqueous media. These involve techniques such as solid-phase extraction (SPE), super-critical fluid extraction (SFE) and thin-layer chromatography (TLC). SPE has been used in several instances with crude oil derivatives and these methods will be investigated (Garrigues and Bellocq 1989).

2.1.1.2 Analytical Techniques
flame ionisation detector (FID) (Tóth 1983), fluorescence detector (Bagheri and Creaser 1988) and nitrogen selective detector (NSD) (Lee et al. 1975). Samples obtained from environmental sources are usually aqueous and lend themselves more readily to analysis by high-performance liquid chromatography (HPLC) with refractive index (RI), ultraviolet (UV) or diode array detection (DAD) (Lucke et al. 1985, Hayes and Anderson 1988, Dong et al. 1993, Lai and Vucic 1993, Gachanja 1993, Ewen et al. 1993, Akhlaq and Götze 1994).

Both gas and liquid chromatography have been used in an attempt to fingerprint transformer oils (Nichols Hazelwood 1955, Duval and Lamarre 1977, Petrovic and Vitorovic 1983). However, there is no pre-extraction of the oil.

Other techniques described involve the use of Fourier-transform infrared spectroscopy (FT-IR) (Olajire and Oderinde 1993), super-critical fluid chromatography (SFC) (Jenkins et al. 1991, Andersson et al. 1992), ultraviolet spectrophotometry (UV) and fluorimetry.

The work in hand has concentrated on the use of GC-MSD because it is able to resolve the PAHs and the software supplied is very useful in identifying the individual compounds. Other techniques have been evaluated and used as appropriate.

2.1.2 Acids in Aged Transformer Oils
The principal degradation products of transformer oil are carboxylic acids. The identification of the specific acids produced may provide important information about which compounds in the oil are most susceptible to oxidation. Identification of these compounds could lead to a more informed choice of transformer oil based on its chemical components.

The concentration of acid in transformer oil is an important test which is carried out as part of the maintenance of transformers in service. The test carried out at National Grid is a standard test method, their interest extends only to the level of acidity and not the identification of the acids present. Few acids have been identified in such
matrices and it is the intention of this study to develop methods to identify acid products of ageing and investigate mechanisms of formation.

2.1.3 Ageing of Oils

Analysis of transformer oils which have been in service will only yield information about changes in the composition if the original oil is available or its properties known. Transformers are typically in service for approximately forty years. During this time the oil is usually topped up and occasionally replaced. This makes it difficult to establish how the composition of PAHs, acids or other components may have changed during the course of the service life of an oil. In these circumstances it is preferable to set up accelerated ageing studies where an oil can experience forty years of degradation in a shorter period of time. Every effort should be made to ensure that the results are valid and that the oil is not at risk from degradation processes which could not possibly occur in a transformer.

A transformer can provide several sources of materials which could catalyse degradation and when it is in operation several phenomena could aid in the oil’s breakdown. This work will incorporate the most likely conditions which may effect a change in the PAH fraction of an oil. Copper, oxygen and water are all potential catalysts of oil oxidation. Electrical discharges, heat and ultraviolet radiation are possible sources of breakdown.

2.1.4 Electronic NOSEs

In recent years a new technique for rapid analysis and identification of a variety of substances has been developed; it is known as sensor technology. A proprietary name given to its product by Neotronics is E-NOSE (electronic olfactory sensor equipment) is often used to describe the instruments involved. The main application for this type of equipment is in the food industry, especially in brewing and production of coffee. This thesis will report the application of E-NOSEs to the fingerprinting of transformer oil. This would be a complement to the work already carried out using this type of equipment to assess the furan content of transformer oil.
2.1.5 Summary of Objectives

The original objectives set out at the beginning of the chapter can be broken down to show how the study was approached.

A. Devise a qualitative method to determine the PAH content of transformer oil:
   I Identify appropriate extraction techniques
   II Determine required conditions for chromatographic analysis of PAHs
   III Investigate alternatives to GC-MS for PAH analysis
   IV Measure extraction efficiency of method to ensure all PAHs are analysed.

B. Investigate the use of the PAH content as a fingerprint to distinguish between oils from different sources:
   V Extract and analyse PAH fraction from oils from all UK suppliers
   VI Obtain oils from suppliers outside of UK and analyse PAH fraction
   VII Investigate alternative fingerprinting techniques.

C. Identify the changes to PAH fingerprint as a result of ageing:
   VIII Set up controlled, ageing experiments to mimic and accelerate transformer ageing of oil.
   IX Observe changes to PAH fingerprint as a result of accelerated ageing

D. Further investigate the chemistry of ageing:
   X Investigate which factors have greatest effect on ageing of PAHs
   XI Examine service aged transformers for signs that laboratory ageing experiments have successfully copied reality
   XII Determine if fingerprinting techniques can be used to monitor state of oil in service
Chapter 3: Fingerprinting Method Development and Analysis of Unused Oils

3.1 Gas Chromatography
   3.1.1 GC-MS
      3.1.1.1 Mass Spectrometry of PAHs

3.2 Optimising the GC for PAH analysis
   3.2.1 PAH library

3.3 Fingerprinting Method Development
   3.3.1 Grimmer Extraction
   3.3.2 Solid Phase Extraction
   3.3.3 Solid Phase Extraction of PAHs

3.4 Fingerprints of Unused Transformer Oil
   3.4.1 Oils for the UK Market
   3.4.2 European Oils
3.1 Gas Chromatography

In gas chromatography (GC) separation of components in a mixture is achieved by passage of the vaporised sample in a gas stream through a column containing a liquid or solid phase. The components migrate at different rates due to differences in boiling point, solubility or adsorption (Fifield and Kealey, 1995).

GC is a powerful technique, ideal for the analysis of volatile compounds. Direct analysis by GC is limited to compounds with a molecular weight up to 400-500, but derivatives of non-volatile and/or polar compounds can be made, which are then suitable for subsequent analysis by GC (Braithwaite and Smith, 1996).

Gas chromatography theory, instrumentation and applications have been steadily improving. New and modified stationary phases are continually being introduced, together with developments on the engineering of the instruments and improved detection techniques, particularly mass spectrometry, to assist in identification of analytes. Electron capture (ECD) and nitrogen-phosphorus (NPD) detectors are widely used and more selective.

Figure 3.1: Schematic diagram of a GC system (adapted from Braithwaite and Smith, 1996)

Figure 3.1 shows the main components of a GC system. In this chromatographic technique, the mobile phase is a gas, and the columns are much narrower and longer than with high performance liquid chromatography (HPLC). In the late 1950s
capillary columns were introduced as an alternative to packed columns for GC. The revolutionary, open-tubular, narrower and longer columns (0.2–0.7 mm internal diameter (i.d.) and 10–00 m long) proved to be more efficient than the old packed columns (2–6 mm i.d. and 1–3 m in length) at separating mixtures, especially mixtures of volatile materials (Braithwaite and Smith, 1996).

3.1.1 GC-MS
Coupling a mass spectrometer (MS) to a GC produces a very powerful analytical technique. It provides the user with the ability to match the mass spectrum from an unknown substance eluted in a chromatogram with a library of spectra. In many cases the compound can then be identified.

The compounds eluting from the GC enter directly into the mass spectrometer. Ions are formed by bombarding the compounds with an electron beam. The ions are then separated according to their mass/charge ratio. The abundances of the ions are measured. The abundances of the fragments form the mass spectrum and the total abundance of all the fragments are used to produce the chromatogram. The sensitivity of the detector is dependent on the compounds but it is typically between $10^{-7}$ to $10^{10}$. This can be improved by using Single Ion Monitoring (SIM), which selects only a few mass/charge values for analysis. This improves the sensitivity range to $10^{-9}$ to $10^{-13}$.

The reproducibility of the mass spectrometer is improved by carrying out regular tuning. A standard compound is used to calibrate the instrument and set the mass axis for correct alignment. The compound used was perfluorotributylamine (PFTBA).

3.1.1.1 Mass Spectrometry of PAHs
The analysis of PAHs by mass spectrometry is relatively simple. The molecular ion ($M^+$) is usually the most intense. Between one and four H atoms may be lost to give the fragments ($M-1)^+$, ($M-2)^+$, ($M-3)^+$ and ($M-4)^+$. There is commonly a small quantity of ($M+1)^+$ due to 13-C. The abundance of the ($M)^{++}$ ion depends on the size of the molecule; more aromatic carbons enable stabilisation of the ion due to the $\pi$ electrons.
3.2 Optimising the GC for PAH analysis

A mixture of 16 different PAHs, identified by the EPA as priority pollutants from fuel combustion, were used to find the best column and temperature program for separation of PAHs (See Table 3.2). Figure 3.2 was obtained using an HP-1 column (see Table 3.1) the optimum temperature program for this column is shown in Figure 3.3.

![Figure 3.2: GC-MS analysis of EPA 16 -PAH standard with HP-1 column](image)

![Figure 3.3: Temperature program used to run PAH standards using HP-1 and HP-5MS](image)
Benzo[b]fluoranthene and benzo[k]fluoranthene are not resolved and the resolution for chrysene and benzo[a]anthracene is also poor. Peak separation was improved using column HP-5MS (See Table 3.1). All 16 compounds eluted and separated with the same temperature program.

Table 3.1: Comparison of columns used for PAH analysis

<table>
<thead>
<tr>
<th>Column Type</th>
<th>Length</th>
<th>Diameter</th>
<th>Film Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Column</td>
<td>HP-1 crosslinked methyl silicone gum</td>
<td>12.5m</td>
<td>0.2mm</td>
</tr>
<tr>
<td>Replacement Column</td>
<td>HP-5MS crosslinked 5% phenyl methyl siloxane</td>
<td>30m</td>
<td>0.25mm</td>
</tr>
</tbody>
</table>

Figure 3.4: GC-MS analysis of EPA 16–PAH standard with HP5-MS column
Table 3.2: Compounds corresponding to retention time in Figure 3.4

<table>
<thead>
<tr>
<th>Retention Time (min)</th>
<th>PAH</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.97</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>7.00</td>
<td>Impurity from solvent</td>
</tr>
<tr>
<td>7.51</td>
<td>Acenaphthylenne</td>
</tr>
<tr>
<td>7.66</td>
<td>Acenaphthene</td>
</tr>
<tr>
<td>8.08</td>
<td>Fluorene</td>
</tr>
<tr>
<td>8.99</td>
<td>Phenanthrene</td>
</tr>
<tr>
<td>9.04</td>
<td>Anthracene</td>
</tr>
<tr>
<td>10.64</td>
<td>Fluoranthene</td>
</tr>
<tr>
<td>11.06</td>
<td>Pyrene</td>
</tr>
<tr>
<td>14.00</td>
<td>Benzo[a]anthracene</td>
</tr>
<tr>
<td>14.13</td>
<td>Chrysene</td>
</tr>
<tr>
<td>17.53</td>
<td>Benzo[b]fluoranthene</td>
</tr>
<tr>
<td>17.61</td>
<td>Benzo[k]fluoranthene</td>
</tr>
<tr>
<td>18.60</td>
<td>Benzo[e]pyrene</td>
</tr>
<tr>
<td>23.06</td>
<td>Benzo[g,h,i]perylene</td>
</tr>
<tr>
<td>23.25</td>
<td>Dibenzo[a,h]anthracene</td>
</tr>
<tr>
<td>24.28</td>
<td>Indeno[1,2,3-c,d]pyrene</td>
</tr>
</tbody>
</table>

The temperature program was refined once samples had been prepared from transformer oil. A two-stage program, shown in Figure 3.5, was required; a slow temperature ramp rate to resolve the lower boiling point PAHs and a higher ramp rate to elute the remaining peaks. This gives a slightly misleading chromatogram as it appears there are two boiling ranges, but it allows all the compounds to be removed in a realistic time.
3.2.1 PAH library

The library of mass spectra included in the GC software contains several million spectra. However, the response of each system will differ slightly and given the similarity of mass spectra for many PAHs of the same mass differentiating between them is difficult. An increase in confidence of a match from the library with an unknown compound may be obtained if the library spectra are obtained on the same GC. To this end a variety of known PAHs with two, three and four rings were analysed and entered into a customised PAH library.

Standard solutions of each compound were made up in DMF (N,N-dimethyl formamide) and run on the GC-MSD, the resultant chromatograms were added to the library. Figure 3.6 shows a typical chromatogram and mass spectra for one of the standards.
3.3 Fingerprinting Method Development

3.3.1 Grimmer Extraction
The ‘Grimmer’ method (Grimmer and Böhnke, 1972) for extracting PAHs from oil is well known to insulating oil chemists. It involves liquid-liquid extraction and clean-up using column chromatography.

A brief outline of the method follows:

Aromatic hydrocarbons are separated from aliphatic and naphthenic hydrocarbons by extraction into a mixture of DMF (N,N-dimethylformamide) and water. The PAHs are separated from those components containing oxygen and nitrogen by extraction into cyclohexane. The extract is cleaned up on a silica column and then on a...
Sephadex column. The extract contains the PAHs and can be concentrated and then
diluted with DMF ready for injection into the GC-MS.

A chromatogram of a ‘Grimmer’ method extract of PAHs is shown in Figure 3.7 came
from a sample of unused Castrol oil transformer oil supplied in 1995. The
chromatogram shows over 150 peaks. The peaks which can be identified with
reasonable confidence are mostly two and three ring aromatic systems, e.g. biphenyl,
fluorene, anthracene and phenanthrene, frequently substituted with one or two methyl
groups. A second extract of the same sample (Figure 3.8) gave a nearly identical
chromatogram. The method appeared to be repeatable, but a third analysis of the
Castrol oil (Figure 3.9) did not repeat the previous two. A further two analyses of the
Castrol oil sample (Figure 3.10 and Figure 3.11) resembled but did not match the third
analysis.

Nynas is another significant supplier of transformer oil, and a sample of one of their
oils was also examined (Figure 3.12). Nynas oil showed a chromatogram, which
contained only a few PAHs similar to the later analyses of the Castrol oil.

Figure 3.7: Chromatogram of first Grimmer extract from Castrol oil with some
identified peaks
Figure 3.8: Chromatogram of second Grimmer extract from Castrol oil

Figure 3.9: Chromatogram of third Grimmer extract from Castrol oil
Figure 3.10: Chromatogram of fourth Grimmer extract from Castrol oil

Figure 3.11: Chromatogram of fifth Grimmer extract from Castrol oil
Chapter 3: Fingerprinting Method Development and Analysis of Unused Oils

The initial apparent repeatability of the 'Grimmer' method did not hold up to further examination. The method also has other drawbacks: the material costs are high and the clean-up procedure is labour intensive. At this stage it was not even clear if there is a difference between the PAH fractions of Castrol and Nynas oils. An alternative method was clearly required.

In an attempt to check the efficiency of the extraction, the oil residues from the 'Grimmer' extractions were analysed. The spectrum of the cyclohexane layer discarded in the liquid-liquid extraction is shown in Figure 3.13. The analysis of the discarded DMF:water layer from the extraction was not analysed. The discarded solvent from the silica column is shown in Figure 3.14, the column was then washed with DMF and this was analysed (Figure 3.15). Figures 3.16 and 3.17 show the analysis from the discard and the DMF wash from the Sephadex column.

The discarded cyclohexane eluent from the liquid-liquid extraction and the discarded solvent from the silica column showed poorly resolved spectra which resembled a simulated distillation. The wash contained much less material but its components were still poorly resolved. The only sample with discernible peaks was the initial 15ml from the Sephadex clean-up column. This sample contains many unidentified compounds but also many substituted naphthalenes, biphenyls and phenanthrenes. This means that the two-ringed PAHs and some of the three-ringed compounds are...
not being completely extracted in the Grimmer analysis. The wash from the Sephadex column contains very little.

**Figure 3.13:** Chromatogram of discarded cyclohexane layer from liquid-liquid extraction step of Grimmer extraction

**Figure 3.14:** Chromatogram of solvent discarded from silica column clean-up of the Grimmer extraction
Figure 3.15: Chromatogram of the cyclohexane wash of the silica column clean-up of the Grimmer extraction

Figure 3.16: Chromatogram of solvent discarded from sephadex column clean-up of the Grimmer extraction
3.3.2 Solid Phase Extraction

Probably the easiest, cheapest and quickest alternative to the ‘Grimmer’ method’ is solid phase extraction (SPE). This involves the use of cartridges containing a sorbent material with a particle size of about 40μm. The solid phase depends on the type of compounds to be extracted. By appropriate choice of the combination of sorbent and solvents, either the analyte(s) of interest can be retained while the matrix components pass through, or vice versa. The most common solid phases are long chain carbon systems (C₈-C₁₈) and silica.

A preliminary search through the literature failed to produce any instances where PAHs were extracted from an oil matrix by SPE. The Waters Limited bibliography of papers, where their Sep-Pak® cartridges (Figure 3.18) have been used, contains many examples of separating out PAHs. Among this list was a paper (Obuchi 1984) detailing the use of C₁₈ reversed-phase packed disposable columns (i.e. Sep-Pak cartridges) for separating PAHs in diesel oil.
Figure 3.18: A Waters SepPak® cartridge.

The method is outlined below:

"(1) Wash the preparation column (Sep-Pak C_{18}) with 5ml of acetonitrile-water (85:15, v/v).

(2) Permeate 50μl of test oil directly on the uppermost part of the Sep-Pak C_{18} with a microsyringe.

(3) Elute the oil with acetonitrile-water (85:15) and collect the initial 10ml effluent into a 10ml measuring flask."

A trial of the technique with transformer oil failed to separate the PAHs from the oil. Diesel oil and transformer oil are very different, diesel is a higher boiling mixture of many fewer compounds than transformer oil, and this may explain why this method failed to produce results.

A Waters Methods Development Kit was purchased for this project, which contained five SepPak® Plus cartridges each of C_{18}, Silica, Florisil®, Accell™ Plus QMA, Alumina A, Alumina B, Alumina N, NH_{2}, CN and Diol. There are three types of
elution protocols detailed in the Waters Sep-Pak Cartridge: Care and Use Manual depending on the type of phase. These are reverse phase, normal phase and ion exchange. A brief description of each technique follows, as PAHs are not ionic, nor even especially polar, species only the reverse and normal phase protocols were considered.

**Reverse Phase Protocol**

Non-Polar packing materials (C$_{18}$ and CN) are used in Reverse Phase chromatography. The sample is loaded dissolved in a polar solvent. Unwanted components are eluted with the same solvent. Compounds of interest are eluted using one non-polar solvent or in portions of progressively more non-polar solvents.

![Figure 3.19: Reverse-phase solid phase extraction](image)

**Normal Phase Protocol**

Normal Phase chromatography is used for the polar phases (Silica, Florisil®, NH$_2$, Diol and Alumina). The sample is loaded onto the cartridge. A non-polar solvent removes unwanted material. The components of interest are removed with one polar solvent or several solvents which are progressively more polar.
Chapter 3: Fingerprinting Method Development and Analysis of Unused Oils

Figure 3.20: Normal-phase solid phase extraction

Ion Exchange Protocol

Sep-Pak cartridges can also be used for Ion Exchange chromatography (with QMA or NH$_2$). The sample is dissolved in a solution of deionised water or a buffer and loaded onto the cartridge. The components of interest are removed using stronger buffers which change the pH or ionic strength.

3.3.3 Solid Phase Extraction of PAHs

Using reverse phase and normal phase chromatography, each of the ten types of cartridge were used in turn. The following procedures were used: (All sample elutions were accelerated by forcing through hexane under positive pressure using a syringe).

Reverse Phase Extractions

The cartridge was conditioned with methanol (10ml), which increases the interactions of the solid phase with the sample, and then the sample (250µl of unused transformer oil supplied by Castrol to BS148) was loaded onto the cartridge. All eluting solvents to this point were discarded as the cartridge holds 1ml of solvent and there was no chance that the solvent eluting would contain any of the oil sample. The cartridge was flushed with methanol (10ml) and the eluting solvent was collected in 1ml
aliquot for analysis. The cartridge was then washed with DMF (5ml) and cyclohexane (5ml). Both solvents were retained for analysis. The procedure was repeated with the oil dissolved in 2-propanol (1ml) to aid the loading of the oil on to the cartridge.

**Normal Phase Extractions**

The cartridge was conditioned with cyclohexane (10ml) and then the sample (250μl) was loaded onto the cartridge. All eluting solvent to this point were again discarded. The cartridge was flushed with cyclohexane 10ml and the eluting solvent was collected in 1ml aliquots for analysis. The cartridge was then washed with DMF (5ml) and methanol (5ml). Both washings were retained for analysis.

Subsequently, this procedure was modified as follows. The cartridge was preconditioned with methanol (10ml), as methanol conditions the solid phase more effectively than cyclohexane, and blown dry with air. The cartridge was then conditioned with cyclohexane as before but this time only to remove the methanol left on the cartridge. The oil sample was also dissolved in cyclohexane (1ml). The procedure was then carried out as before.

It was decided that ion exchange was not likely to produce the required separation.

The retained samples were analysed by GC-MS using the same temperature program as had been used for the ‘Grimmer’ extracts. Those solvents which had not been collected in several fractions were reduced using a rotary evaporator and made up to 0.5ml. In every case the first few aliquots of the first eluting solvent appeared to contain the entire oil sample. There was no apparent retention of sample on the cartridge and no apparent separation of compounds between the different aliquots of eluting solvent (examples of analyses of extracts shown in Figure 3.21 and 3.22.
Figure 3.21: Reverse phase results using aminopropyl (NH3) cartridge. Top: First elution with methanol. Bottom: Second elution with hexane.

Figure 3.22: Normal phase results using aminopropyl (NH3) cartridge. Top: First elution with hexane. Bottom: Second elution with methanol.
A single step extraction of PAHs by SPE seemed unlikely given the amount of resources already used. Instead of using neat or diluted oil as the sample the liquid-liquid extraction of ‘Grimmer’ method was used with the intention of replacing the long clean-up required with SPE.

Several liquid-liquid extracts were prepared and analysed by GC-MS (Figure 3.23). After the first attempts there remained only one of each type of cartridge although silica, C₁₈ and Florisil were readily available. The liquid-liquid extracts were each reduced in volume to 1ml. Reverse-phase extraction was carried out as before with C₁₈, CN, silica, and Florisil. The normal phase extraction was carried out on the silica, C₁₈ Florisil, NH₂, diol and alumina (A, B and N).

The only cartridges which showed any promise were the Alumina cartridges using normal phase chromatography. Alumina A and N both held back some PAHs in small quantities and released them when DMF was used to elute (Figure 3.24 and Figure 3.25). Using combinations of cartridges and solvents and collecting very small fractions the PAHs were not separated reliably.

![Figure 3.23: Liquid-liquid extract of oil used for SPE extraction method development](image)

Figure 3.23: Liquid-liquid extract of oil used for SPE extraction method development
A less common way of using SPE cartridges is as a direct replacement for columns. The 'Grimmer' method uses a 5g silica column for clean up. SPE Cartridges with silica packing are also able to perform this function. SPE cartridges gave successful and repeatable results when applied in the first chromatography clean up of the 'Grimmer' method (after appropriate scaling down). The extracts still needed further clean up after this step analogous to the Sephadex column used in the 'Grimmer' method. It was found this could be achieved using a C18 cartridge, which can be used as in normal phase chromatography, however the change in solvent releases contaminants from the cartridge. Contamination is avoided by using a single solvent

Figure 3.24: Chromatogram showing Alumina A clean up of liquid-liquid extract

Figure 3.25: Chromatogram showing Alumina N clean up of liquid-liquid extract
system to elute the required components.

The method is outlined below:

Table 3.3: SPE clean-up procedure

<table>
<thead>
<tr>
<th>Step</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Join 2 Sep-Pak Plus Silica Cartridges together and condition them using 10ml of AnalaR cyclohexane at a flow rate of 10-20ml/min.</td>
</tr>
<tr>
<td>2.</td>
<td>Load 1ml of diluted extract onto the cartridges and discard eluting solvent.</td>
</tr>
<tr>
<td>3.</td>
<td>Run cyclohexane through the cartridges at approximately 5ml/min. Discard the initial 5ml</td>
</tr>
<tr>
<td>4.</td>
<td>Collect the subsequent 5ml and reduce to 1ml.</td>
</tr>
<tr>
<td>5.</td>
<td>Condition a Sep-Pak Plus C18 cartridge with 5ml cyclohexane at a flow rate of approximately 5ml/min.</td>
</tr>
<tr>
<td>6.</td>
<td>Load 0.5-0.8ml of reduced eluent from silica cartridges and discard eluting solvent.</td>
</tr>
<tr>
<td>7.</td>
<td>Elute with cyclohexane and collect the first 1ml fraction.</td>
</tr>
<tr>
<td>8.</td>
<td>Reduce eluent to 0.2ml and run on GC.</td>
</tr>
</tbody>
</table>

The initial sample is prepared as the first step of the ‘Grimmer Method’. The solvent is removed under reduced pressure and made up to 10ml using cyclohexane. The resulting chromatogram contains approximately 100 peaks, of the identified peaks most are anthracenes, biphenyls, fluorenes, phenanthrenes, or pyrenes. See Appendix B for a list of compounds identified in Nynas 10GBN and other oils.

The extraction efficiency of the method was determined on two separate occasions. An extraction of Castrol oil was performed with benzo[a]anthracene as an internal standard and 9-bromofluorene as the external standard. Neither compound was found naturally occurring in Castrol oil. The extract from the liquid-liquid extraction step was found to contain 99% of the benzo[a]anthracene. After clean-up using SPE, the concentration had dropped to 79%.

The extraction efficiency was also investigated using a coal tar standard purchased from NIST. The standard contained many PAHs from biphenyl and naphthalene to
anthanthrene and coronene. The GC-MS was calibrated for all the PAHs and an extraction was carried out on the standard. The external standard was, once again, 9-bromofluorene. The average extraction efficiency was found to be 85% for 2- and 3-ring PAHs. Pyrene and chrysene were extracted at 80%. Coronene was not found in the extract.

Despite the efficiency of the method a shorter procedure would be preferable and other possibilities were investigated. Two single-step SPE extraction procedures appeared to have particular promise. One identified in the literature uses Florisil cartridges to extract PAHs from petroleum, the other uses silver ions held on a strong anion exchange SPE cartridge and was suggested at a Varian SPE workshop. These attempts are discussed here in detail.

Rapid extraction using Florisil cartridges

Florisil cartridges contain a solid phase that is a mixture of SiO₂ and MgO. In one reported instance (Garrigues 1989), Florisil cartridges were used to extract PAHs directly from petroleum. The complete extraction of neutral aromatic compounds is reportedly rapid and reliable, as verified by HPLC-UV.

Cartridge preparation and extraction procedure

The method described in the paper was followed exactly for transformer oil. The Florisil SepPak cartridge (supplied by Waters, phase weight 0.9g) was prewashed with methanol (20ml) and then hexane (20ml). The crude oil (200µl) was applied to the top of the cartridge. The paper demonstrates that all the 3-ring PAHs are eluted in the first 15ml of hexane. The first 1ml was not collected as the cartridge holds more than 1ml so this was just displaced solvent. Thereafter, 2ml aliquots of hexane (up to 20ml) were collected and analysed by GC-MS.

Principle of separation and results

The principal components of most crude oils are resins, asphaltenes and hydrocarbons (saturated, aromatic, polar and high molecular weight compounds). Resins and
asphaltenes precipitate on the Florisil and are adsorbed on the silica, as are the high molecular weight and polar hydrocarbons. The low molecular weight, non-polar hydrocarbons have a greater affinity for the non-polar hexane and are scarcely retained on the solid phase. The PAHs are eluted according to their aromaticity.

Figure 3.26 shows the chromatograms of the 2ml aliquots collected from the Florisil cartridge. The oil was predominantly eluted in the first aliquot and very little was seen in the subsequent aliquots.

The Florisil cartridge was rinsed with more polar solvents. There was no indication that any part of the sample had been retained on the cartridge.
Figure 3.26: Extraction of PAHs from transformer oil using a Florisil cartridge.
Discussion of Results

It has been demonstrated that the majority of the oil was not retained on the Florisil cartridge. This is because transformer oil is not like ‘most crude oils’ as they are highly refined oils containing naphthenic, paraffinic and aromatic hydrocarbons. Some of the more polar components might have been expected to be retained on the Florisil cartridge but this was not observed to be the case. This may have been because there are not many significantly polar molecules in unused transformer oil.

Silver ion chromatography (argentation)

The complexation of certain transition metals, including silver, to alkenes has been carried out for over a century (Birnbaum 1868). The relative stability, solubility and low cost of silver salts (as opposed to platinum, gold, palladium and rhodium) led to them being frequently used by many analytical chemists. In 1938, it was shown that the formation of silver alkene complexes was rapid and reversible (Winstein and Lucas 1938). It was only a matter of time before silver ions were incorporated into chromatographic separation of alkenes.

GC (Bradford 1955, Soto et al 1996) TLC (Barrett 1962), paper chromatography (Barretto and Enzel) and column chromatography (Goering 1961) all make use of silver ions for separation. But argentation has been most commonly used for HPLC (Heath 1975, Houx and Voerman 1976, van Beek and Lelyveld 1991). Recently attention has turned to silver ion chromatography using solid phase extraction cartridges (Christie 1989).

It would seem that argentation has been used almost exclusively for alkenes. But as aromatic compounds can also form complexes with silver (Coffey), then perhaps the technique could be extended. One report (Christie 1989) describes how an SPE cartridge can be prepared and used for argentation. It is this method which I have tried to adapt to separate aromatic compounds from saturated hydrocarbons.
Cartridge preparation and extraction procedure

A strong cation exchange cartridge (benzenesulphonylpropyl bonded to silica, provided by Varian) was used to hold the silver ions. The cartridge was wrapped in aluminium foil to prevent UV light deterioration of the solid phase.

A solution of silver nitrate (20mg) in acetonitrile:water (0.25ml, 10:1 v/v) was allowed to percolate through the cartridge. The cartridge was then flushed with acetonitrile (5ml), acetone (5ml) and dichloromethane (10ml) under slight pressure (pipette bulb).

Cartridges were also prepared in the same way using manganese (II) chloride (25mg) and chromium (III) nitrate (30mg), as these are also capable of forming aryl complexes (Cotton and Wilkinson).

Samples were prepared by the following method and analysed by GC-MS:

Samples were run through the silver cartridges. For the first, 200 μl of oil was applied to the cartridge. The sample was eluted under gravity with dichloromethane (5ml), a dichloromethane/acetone mixture (9:1 v/v, 5ml), acetone (5ml) and an acetone/acetonitrile mixture (1:1 v/v, 10ml). The second sample was a repeat of the first, except the elution was begun using cyclohexane (5ml) before the dichloromethane. The first scheme was copied for the manganese and chromium cartridges, but the samples were mixtures of PAH standards in THF (tetrahydrofuran).

Principle of separation and results

Certain transition metals can form complexes with alkenes because their d-orbitals possess the right symmetry for bonding (Powell). The formal bond can be considered to have a σ and a π component. In silver complexes, the σ component is an overlap of the ligand’s π-orbitals and the silver 5s orbital, while the π component is a ‘back bond’ formed by the filled silver 4d orbital and the π* (antibonding) orbital of the ligand.
Any compounds containing $\pi$ bonds in the sample passed through the cartridge should be held in a complex with the $\text{Ag}^+$ ions attached to the solid phase. The complex is not very strong, and the ligands should be easily removed by a more polar solvent. This method of separation works well for alkenes. Since, aromatic compounds could be considered as substituted alkenes, they may also be held by the silver. Transformer oils do not contain any alkenes, due to the vigorous nature of the hydrogenation process after refining, so aromatic compounds should be the only compounds that can be held by the silver ions.

The chromatograms resulting from the four samples that have been run are shown (Figures 3.27 – 3.32). In all four cases, the sample was totally eluted with the first and second solvents and by the third solvent no more material was extracted from the cartridge. The cartridges do not appear to have retained any of the sample.

![Figure 3.27](image1.png)

Figure 3.27: Extraction of PAHs from oil by argentation – chromatogram showing dichloromethane fraction (first solvent)

![Figure 3.28](image2.png)

Figure 3.28: Extraction of PAHs from oil by argentation – chromatogram showing acetone fraction (third solvent)
Figure 3.29: Extraction of PAHs from oil by argentation – chromatogram showing cyclohexane fraction (first solvent)

Figure 3.30: Extraction of PAHs from oil by argentation – chromatogram showing dichloromethane/acetone fraction (third solvent)

Figure 3.31: Extraction of PAH standards by manganese – chromatogram showing elution of PAHs by dichloromethane
3.4 Fingerprints of Unused Transformer Oils

3.4.1 Oils for the UK Market

In the six years from 1994 to 1999, National Grid purchased unused transformer oil from the three main suppliers to the UK market (i.e. conforms to BS148): Carless, Castrol and Nynas. The oils supplied by these companies were analysed and compared during the project.

The oils supplied by both Castrol and Nynas have been consistent within batches and with each other, according to their PAH fingerprints, every year from 1994 to 1999.
Carless, however gave a different fingerprint each year from 1994 to 1996, from 1997 onwards the fingerprints matched that of Castrol and Nynas.

Shell also produces oil for the UK market but it is not purchased by National Grid. A sample of Shell Diala B was analysed in 1997. The fingerprint was very different from any of the other oils previously analysed. The later eluting compounds are more dominant than in the oils used by National Grid.

In many cases the samples were analysed after the liquid-liquid extraction as well as after the clean up stages. The samples analysed are listed in Table 3.4, and the chromatograms can be found in Appendix C.

Table 3.4: Samples analysed by GC-MS after PAH extraction

<table>
<thead>
<tr>
<th>Manufacturer/Source of Sample</th>
<th>Year Supplied</th>
<th>Liquid-Liquid Extract</th>
<th>PAH Extract</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apar (India)</td>
<td>1999</td>
<td>✓</td>
<td>✓</td>
<td>C1/C2</td>
</tr>
<tr>
<td>Calumet (US)</td>
<td>1993</td>
<td>✓</td>
<td>✓</td>
<td>C3/C4</td>
</tr>
<tr>
<td>Carless Transol</td>
<td>1994</td>
<td>✓</td>
<td>✓</td>
<td>C5/C6</td>
</tr>
<tr>
<td>Carless Transol</td>
<td>1995</td>
<td>✓</td>
<td>✓</td>
<td>C7/C8</td>
</tr>
<tr>
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<td>1996</td>
<td>✓</td>
<td>✓</td>
<td>C9/C10</td>
</tr>
<tr>
<td>Carless Transol</td>
<td>1997</td>
<td>✓</td>
<td>✓</td>
<td>C11/C12</td>
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<tr>
<td>Carless Transol</td>
<td>1998</td>
<td>X</td>
<td>X</td>
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<tr>
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<td>1999</td>
<td>✓</td>
<td>✓</td>
<td>C13/C14</td>
</tr>
<tr>
<td>Castrol BS148</td>
<td>1994</td>
<td>✓</td>
<td>✓</td>
<td>C15/C16</td>
</tr>
<tr>
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<td>1995</td>
<td>✓</td>
<td>✓</td>
<td>C17/C18</td>
</tr>
<tr>
<td>Castrol BS148</td>
<td>1996</td>
<td>✓</td>
<td>✓</td>
<td>C19/C20</td>
</tr>
<tr>
<td>Castrol BS148</td>
<td>1997</td>
<td>✓</td>
<td>✓</td>
<td>C21/C22</td>
</tr>
<tr>
<td>Castrol BS148</td>
<td>1998</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Castrol BS148</td>
<td>1999</td>
<td>✓</td>
<td>X</td>
<td>C23</td>
</tr>
<tr>
<td>ESSO Univolt 52 (Portugal)</td>
<td>1998</td>
<td>✓</td>
<td>✓</td>
<td>C24/C25</td>
</tr>
<tr>
<td>ESSO Univolt 53 (US)</td>
<td>1986</td>
<td>✓</td>
<td>✓</td>
<td>C26/C27</td>
</tr>
<tr>
<td>Mol (Hungary)</td>
<td>1998</td>
<td>✓</td>
<td>✓</td>
<td>C28/C29</td>
</tr>
<tr>
<td>Nynas 10GBN</td>
<td>1994</td>
<td>✓</td>
<td>✓</td>
<td>C30/C31</td>
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</table>
Chapter 3: Fingerprinting Method Development and Analysis of Unused Oils

<table>
<thead>
<tr>
<th></th>
<th>Year</th>
<th>✔️</th>
<th>✗️</th>
<th>Compound</th>
</tr>
</thead>
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<tr>
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<td>✔️</td>
<td>✗️</td>
<td>C32</td>
</tr>
<tr>
<td>Nynas 10GBN</td>
<td>1996</td>
<td>✗️</td>
<td>✔️</td>
<td>C33/C34</td>
</tr>
<tr>
<td>Nynas 10GBN</td>
<td>1997</td>
<td>✔️</td>
<td>✔️</td>
<td>C35/C36</td>
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<tr>
<td>Nynas 10GBN</td>
<td>1998</td>
<td>✔️</td>
<td>✔️</td>
<td>C37/C38</td>
</tr>
<tr>
<td>Repsol Tension (Spain)</td>
<td>1998</td>
<td>✔️</td>
<td>✔️</td>
<td>C39/C40</td>
</tr>
<tr>
<td>Shell Diala B</td>
<td>1997</td>
<td>✔️</td>
<td>✔️</td>
<td>C41/C42</td>
</tr>
<tr>
<td>Technol Y300 (Slovenia)</td>
<td>1998</td>
<td>✔️</td>
<td>✔️</td>
<td>C43/C44</td>
</tr>
</tbody>
</table>

### 3.4.2 European Oils

The fingerprinting method was presented to CIGRÉ (Conferencia Internacional des Grands Réseaux Électriques) at the working group for “the study of techniques for fingerprinting oils” (Task Force 15.01.06) (Appendix F). As a result the method was included in a series of round robin tests looking at different oils from the European market: ESSO, Mol, Nynas, Repsol and Technol. A different temperature programme was used to reduce the effect of the change in temperature ramp.

The oils from ESSO and Repsol are paraffinic, Nynas and Technol are both naphthenic and Mol is an intermediate. This was determined by low temperature differential scanning calorimetry as part of the round robin study. The Mol and Technol samples are both inhibited with DBPC (di-tert-butyl-para-cresol) which is extracted by the PAH extraction method. The compound can be removed from the trace by the software so that the chromatograms can be compared.

The five oils gave five different fingerprints. Comparing the samples visually, the oil from Repsol is the only one which appears to have no similarities with any of the other four samples. The other four all have similar groupings of peaks at certain times. The groupings relate to different groups of similar structures and are also present in the Repsol sample but in the other four oils the peaks are also in similar ratios. The groupings and their related compounds are shown in Table 3.5.
Table 3.5: Observed groupings of PAHs in CIGRE round robin oils

<table>
<thead>
<tr>
<th>Retention Time (min)</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 – 11</td>
<td>Trimethylnaphthalene</td>
</tr>
<tr>
<td>11.5 - 13</td>
<td>Dimethylbiphenyl, Trimethylbiphenyl</td>
</tr>
<tr>
<td>14 – 15</td>
<td>Methylfluorene</td>
</tr>
<tr>
<td>18 – 20</td>
<td>Dimethylfluorene, Trimethylfluorene, Methyldibenzothiophene</td>
</tr>
<tr>
<td>21 – 22</td>
<td>Methylphenanthrene, Methylanthracene</td>
</tr>
<tr>
<td>22 – 24</td>
<td>Dimethyldibenzothiophene</td>
</tr>
<tr>
<td>25 - 26</td>
<td>Dimethylphenanthrene, Dimethylanthracene</td>
</tr>
</tbody>
</table>

The relative heights of the different groupings change from oil to oil and not all groups are found in all the oil samples. Also, other peaks show the oils to be different, for example Nynas contains pyrene and Mol contains chrysene, where the others do not and Technol does not contain 1,1'-biphenyl or any related structures.

The only other member of the CIGRÉ task force that was able to carry out the extraction procedure (Laborelec, Belgium) produced chromatograms with very different patterns. However, although all other factors were the same their column was 60m rather than 30m. This would mean that the peaks eluted later and the pattern would be changed by the different ramp rate in the temperature program.

The laboratory in Belgium also used the method to compare two different types of unused oils from the same supplier. The characteristics of the oil as determined by Laborelec are shown in Appendix D. Laborelec found that the fingerprints (Figures 3.33 and 3.34) closely resembled each other with “only some differences in peak height for some peaks.” (Reygaerts 1998) The oils were also sent to National Grid for examination and the chromatograms are shown below (Figure 3.35). The oils are not distinguishable by their PAH fingerprint.
Figure 3.33: Chromatogram of Laborelec sample A produced by Laborelec.

Figure 3.34: Chromatogram of Laborelec sample B produced by Laborelec.
Figure 3.35: Chromatograms of PAH extracts from Laborelec oils. Top: sample A. Bottom: Sample B.

Three other unused oil samples were analysed two from the USA (Calumet and ESSO) and one from Apar, India.

The two American samples are uninhibited naphthenic oils. The sample from Calumet shows a similar fingerprint to that of Nynas. The ESSO oil was the oldest oil fingerprinted. It is very different from the ESSO oil from Portugal which was supplied 12 years later. However it is very similar to the 1994 batch of oil supplied by Carless.

The sample from India is an attempt by a refiner to produce a naphthenic oil from a paraffinic crude oil. The PAHs are converted to naphthenic compounds and the consequent fingerprint shows very few PAHs.
Chapter 4: Transformer Oil Degradation Studies

4.1 Introduction

4.2 Accelerated Ageing Tests

4.2.1 Thermal and Oxidative Degradation

4.2.1.1 Factorial Experiments

4.2.1.2 Experimental Procedure

4.2.1.3 Observations

4.2.1.4 Analysis

4.2.1.5 Breakdown of PAHs in a Carrier Fluid

4.2.2 Electrical Breakdown Experiments

4.2.2.1 Silent Discharge in an Ozonizer

4.2.2.2 Breakdown Voltage Test

4.2.2.3 Breakdown in a Test Cell

4.2.2.4 Diverter Test Oil

4.2.3 Ultraviolet Radiation Experiments
4.1 Introduction

The next stage after developing a method for fingerprinting and comparing new oils is to look at used oil samples. Depending on the outcome of the study of aged oils there are different benefits to National Grid:

- If the PAH fingerprint is changed in service the breakdown processes of PAHs in transformer oil can be studied and this could lead to a technique for measuring oil quality. This would provide an alternative to the measurement of acidity for indicating when the oil needs to be changed. The flaw with studying acidity is that by the time it can be detected it may have begun to cause damage to the paper.
- If the PAH fingerprint is unaffected by service conditions then the fingerprint would be valid for all oils. In the event that an oil is found to be of poor quality in service then other oils with the same fingerprint can be assumed to be of the same poor quality. There would also be the potential for cost savings associated with waste disposal and health and safety precautions since there may not be an increase in the carcinogenicity of the oil.

Ideally, oils from different stages during the lifetime of a transformer would be studied. This is impossible in a three-year study given that transformer oil is expected to last in excess of twenty-five years. Oils which have been in service are subjected to unknown and usually varied conditions and have insufficient information on their original composition so we cannot identify what has been the major factor in the oil breakdown process. It is therefore necessary to carry out accelerated tests.

4.2 Accelerated Ageing Tests

Degradation requires energy and is accelerated by catalyst, so what are the conditions in a transformer that could cause oil degradation?

Sources of energy:

Heat

The amount of heat generated by the transformer is dependent on the load on the windings. Typically National Grid transformers are operated so that the internal
temperature does not exceed 90°C. However, localised areas, called hotspots, may be considerably hotter even if the transformer does not have a fault. Different faults cause localised overheating. In insulated conductors, overheating may cause temperatures up to 150°C. Temperatures above 150°C may be caused by a variety of effects such as small hotspots in the core, shorting links in the core, overheating of copper due to eddy currents, bad contacts or joints, and core and tank circulating currents (Rogers 1978). Many of these faults will reach temperatures high enough to cause pyrolysis of the oil to form carbon deposits. In the most severe cases the copper conductors may melt.

Electrical Faults
Discharges in transformers are the result of faults. They may be low energy partial discharges in gas-filled cavities or discharges as a result of continuous sparking due to bad connections or floating potentials. High energy discharges result in arcs with power follow-through. These can generate local temperatures of up to 1200°C and are the source of intense light energy.

Potential Catalysts:
Oxygen
National Grid's high voltage transformers are free breathing, i.e. they are in contact with the atmosphere so there is an unlimited supply of oxygen and the saturation solubility of oxygen in oil can be as high as 3% depending on the nature of the oil and temperature.

Copper
The conductors in the transformer are made of copper. These are wound with Kraft paper soaked in oil, so the oil is in direct contact with the copper.

Water
The moisture in a transformer is mostly in the paper, up to 3% of the weight of the paper may be moisture and in extreme case it may be as high as 8%. The moisture is in equilibrium between the paper and oil, with the moisture in the oil increasing as the temperature increases.
PAHs are stable with low chemical reactivity, but there are no reports in the literature of their stability or breakdown under transformer operating conditions. This study set out to investigate the degradation, or otherwise, of PAHs under the sort of environments of normal and fault conditions, in controlled, laboratory, accelerated experiments.

4.2.1 Thermal and oxidative degradation

The first series of investigations was thermal degradation, i.e. what is the effect of temperature on the stability of the PAHs in the oil? This was approached systematically by using factorial experiments.

4.2.1.1 Factorial Experiments

When designing a series of experiments it is important to establish their validity before drawing any conclusions from the results. Statistically designed experiments are efficient at giving meaningful results; they give a fixed amount of information considerably more easily than the laborious approach of changing one variable at a time. A further advantage of factorial experiments is that they give information about interactions between variables so they can be used to find optimum conditions for getting a required result from an experiment (Davies 1994).

Factors and Levels

The major contributory factors in oil degradation are believed to be water, temperature, oxygen and copper. These were tested at two levels (temperature at three) on one transformer oil as used by National Grid (Castrol BS148 Grade). The actual values used are shown in Table 4.2.

The initial levels chosen for water and oxygen were based on realistic levels for a transformer and those for temperatures were chosen to ensure accelerated oxidation. The temperatures were 120°C, 140°C and 160°C. At low temperatures oxidation may proceed too slowly; high temperatures may cause the ampoules to break due to gas evolution and pressure.
As received transformer oil generally contains up to 60ppm of water and drying is usually necessary before it can be used in the transformer. For the degradation experiments therefore, the moisture level of the oil was measured as received and served as the upper level. The oil was then dried with a flow of dry nitrogen gas and used as the lower level. A similar procedure was used for the oxygen levels, the level of dissolved oxygen in the oil, as received, was measured and served as the upper level. The oxygen was then removed from the oil at the same time as the water.

Copper is a good catalyst for oil oxidation. Copper in a transformer is in the form of thick wires and wrapped in paper, making it hard to determine a suitable surface area per volume of oil for use in the ageing experiments. Therefore, a similar amount of copper was used as is found in the standard oxidation stability test (IEC61125 Method C). The copper wire (2m x 1.5mm) was cut into shorter lengths (approximately 100mm) to fit the ampoule.

In summary, there are five variables: temperature, moisture, oxygen, copper and time. Three of these have two levels (water/oxygen/copper), one of them has three (temperature), and the third factor (time) has many levels. Clearly this makes the planning complicated, but a simple factorial table can be used as a basis for the planning of the experiments. If time is ignored, a table can be produced (Table 4.1) showing that 24 experiments are needed to cover all possible combinations. It is reasonable to assume that each experiment can be run for four time lengths, thus giving 96 experiments in total. In practice, after some experiments have been run some combinations became unnecessary and other experiments may need to be devised.
Table 4.1: Factorial Experiments

<table>
<thead>
<tr>
<th>Experiment</th>
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<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
</tbody>
</table>

Explanation of table:
-1 is the lower level for each factor
0 is the second level of three for temperature
+1 is the higher level for each factor
Table 4.2: Levels used for variables in factorial experiments

<table>
<thead>
<tr>
<th></th>
<th>-1</th>
<th>0</th>
<th>+1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0ppm*</td>
<td>N/A</td>
<td>as received – 58.2ppm</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0%*</td>
<td>N/A</td>
<td>as received – 3.067%</td>
</tr>
<tr>
<td>Temperature</td>
<td>120°C</td>
<td>140°C</td>
<td>160°C</td>
</tr>
<tr>
<td>Copper</td>
<td>none</td>
<td>2m cut into shorter lengths</td>
<td></td>
</tr>
</tbody>
</table>

*In practice the value is not zero, rather it is below the limit of detection for the measurement

4.2.1.2 Experimental Procedure

The oil was analysed for its ‘as received’ moisture content by Karl Fischer potentiometric titration and for its ‘as received’ oxygen content using a coulometric oxygen meter. The oil was degassed and dried using a flow of nitrogen through a gas bubbler into a Drechsel bottle full of oil for approximately 90 minutes until it gave a zero response on the oxygen meter.

The copper was prepared by dipping it in chromic acid and then rinsing with acetone. It was wrapped in clean medical wipes and handled, only when necessary, with gloves.

The experiments were carried out in glass ampoules with a volume of approximately 80cm³. The ampoules were flushed with nitrogen so that they were dry and free from oxygen, which would have affected the oxygen level in the oil. The oil (60cm³) was introduced to the ampoule through a thistle funnel with a long stem to prevent oil remaining in the neck of the ampoule; this would have carbonised when the ampoule was sealed giving a poor seal. Copper was then added as required. If the oil contained oxygen, these steps were carried out in a nitrogen-filled glove box. If the oil contained no oxygen then the ampoules were kept under vacuum until required, and the vacuum was re-applied for several hours after the oil was introduced. The ampoules were sealed with a glass-blowing torch; then placed in an oven.

Ultimately, not all of the experiments were set up because of availability of space in the nitrogen-flushed ovens. The ampoules that were prepared and the length of time for which they were aged are shown in Table 4.3.
### Table 4.3: Ageing experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Ageing Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400-480hrs</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>410</td>
</tr>
<tr>
<td>4</td>
<td>430</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
</tr>
<tr>
<td>6</td>
<td>410</td>
</tr>
<tr>
<td>8</td>
<td>430</td>
</tr>
<tr>
<td>9</td>
<td>400</td>
</tr>
<tr>
<td>10</td>
<td>410</td>
</tr>
<tr>
<td>12</td>
<td>430</td>
</tr>
<tr>
<td>13</td>
<td>450</td>
</tr>
<tr>
<td>14</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>480</td>
</tr>
<tr>
<td>17</td>
<td>450</td>
</tr>
<tr>
<td>18</td>
<td>430</td>
</tr>
<tr>
<td>20</td>
<td>480</td>
</tr>
<tr>
<td>21</td>
<td>450</td>
</tr>
<tr>
<td>22</td>
<td>400</td>
</tr>
<tr>
<td>24</td>
<td>400</td>
</tr>
</tbody>
</table>

### 4.2.1.3 Observations

Three of the samples that were prepared were not properly sealed. This permitted oxygen to get into the sample and cause oxidative as well as thermal breakdown. The three samples had been prepared for experiments 8, 13 and 24. The sample at 160°C (24) was very dark after just 350 hours and contained dark, solid sludge material. The two samples at lower temperatures (8 and 13) were allowed to run for 2850 hours and although they were also very dark, they were not as dark as sample 24 and they contained little sludge material. These samples were retained for fingerprinting as good examples of oils subjected to heavy oxidation.

All of the samples appeared to have condensation in the neck of the ampoule when
removed from the oven, which is an indication that some form of degradation has taken place.

In general, the samples appeared to be the same colour on removal as the original oil. The samples that had been held at 160°C showed some slight darkening especially in those that had been aged for longer.

In the experiments containing copper, an interesting effect was observed. The reddish colour of the copper was rapidly replaced by a dull grey; the rate of change depended on the temperature. The 160°C samples changed in the first 48 hours, the 140°C samples changed after one week and the 120°C samples took up to two weeks.

4.2.1.4 Analysis

The water and oxygen content of selected samples were measured. The results can be seen in Table 4.4. The acidity of every sample prepared was measured by automatic potentiometric titration and all were found to be less than 0.02mg KOH/g oil.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ageing Time hours</th>
<th>Original O₂ Content %</th>
<th>Final O₂ Content %</th>
<th>Original H₂O Content ppm</th>
<th>Final H₂O Content ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400</td>
<td>0</td>
<td>not measured</td>
<td>1</td>
<td>9.5</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>0</td>
<td>not measured</td>
<td>1</td>
<td>15.2</td>
</tr>
<tr>
<td>9</td>
<td>400</td>
<td>0</td>
<td>not measured</td>
<td>1</td>
<td>24.4</td>
</tr>
<tr>
<td>22</td>
<td>400</td>
<td>3.067</td>
<td>0.600</td>
<td>49</td>
<td>62.2</td>
</tr>
<tr>
<td>24</td>
<td>400</td>
<td>3.067</td>
<td>0.333</td>
<td>49</td>
<td>65.8</td>
</tr>
<tr>
<td>2</td>
<td>410</td>
<td>0</td>
<td>not measured</td>
<td>40</td>
<td>45.5</td>
</tr>
<tr>
<td>6</td>
<td>410</td>
<td>0</td>
<td>not measured</td>
<td>40</td>
<td>48.2</td>
</tr>
<tr>
<td>10</td>
<td>410</td>
<td>0</td>
<td>not measured</td>
<td>40</td>
<td>46.9</td>
</tr>
<tr>
<td>16</td>
<td>480</td>
<td>3.133</td>
<td>0.340</td>
<td>58.2</td>
<td>60.2</td>
</tr>
<tr>
<td>20</td>
<td>480</td>
<td>3.133</td>
<td>0.203</td>
<td>58.2</td>
<td>62.7</td>
</tr>
</tbody>
</table>

The first sample of oil analysed for oxygen after ageing was prepared for experiment 12. The sample was exposed to the air and showed that oxygen is rapidly dissolved as
the measurement was 3.05%. Later samples were analysed rapidly after breaking the seals and showed that little oxygen was present. It can be surmised that the oxygen is used up in oxidation of the oil, but the oxidation is limited because the oxygen is quickly consumed.

Visual examination of the dark-coated copper wires suggested that it was a dark grey, slightly reflective deposit on the surface. It was found insoluble in common organic solvents including acetone and chloroform, both of which can be used to dissolve oil sludge. Once the coating is removed the copper regains its previous lustre. One of the pieces of copper was immersed in ammonium hydroxide (2M). The resulting blue solution suggests copper in its +2 state.

The surface of the copper wires was examined at the National Grid forensic laboratories in Leatherhead. Visual examination under a light microscope showed that the wires were coated by a thin layer of dark grey or black material, which was relatively smooth and evenly coated. The coating is exemplified by the photographs in Figure 4.1. The elemental content of the coating was obtained by EDX (electron dispersive X-ray) analysis on the SEM (scanning electron microscope). Figure 4.3 demonstrates that only copper and sulphur are present in any significant quantity, with only a small amount of oxygen detected. Figure 4.2 shows the original copper for comparison. It would appear the coating is copper (II) sulphide, which is a black solid.
Figure 4.1: Black coating on copper wires

Figure 4.2: EDX of bare copper wire

Figure 4.3: EDX of black coating
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The first samples analysed for their PAH fingerprint were those which had been most severely treated. The three samples which had been in poorly sealed ampoules were analysed because they had been exposed to an excess of oxygen and were therefore the most likely to have been degraded. The sample aged at 140°C for more than 16000 hours was also analysed. The samples were analysed by GC-MS after the liquid-liquid extraction and after SPE clean up. The chromatogram from the most oxidised sample is shown in Figure 4.4 compared to the unused oil. Clearly there is no difference from the original sample and the PAHs have not been degraded in any way. The remaining samples, which had not been exposed to such severe conditions, were not fingerprinted as the PAH fingerprints would not have been any different.

![Chromatograms of PAH extractions from Castrol oil. Top: Unused oil. Bottom: Oxidised oil sample](image)

Figure 4.4: Chromatograms of PAH extractions from Castrol oil. Top: Unused oil. Bottom: Oxidised oil sample

4.2.1.5 Breakdown of PAHs in a carrier fluid

The PAHs in transformer oil would appear to be too stable to be noticeably altered by thermal or oxidative degradation at the temperatures used in the first series of accelerated ageing tests. The temperatures cannot simply be raised as the pressure in the ampoules may become dangerously high. To move to higher temperatures to investigate the thermal stability of PAHs in transformer oil a different approach is
required. Individual PAHs that have been identified in transformer oil were aged in a neutral carrier fluid.

The carrier fluid selected was a synthetic base oil, known as PAO (poly-alpha olefin). PAOs are produced by BF₃-catalysed oligomerisation of linear alkenes, generally of ten carbon chain lengths (Shubkin et al). The chosen PAO, Durasyn (DS) 164 supplied by Amoco, has similar rheological properties to transformer oil but it is known to have good oxidative stability (Gunsel et al. 1988) and will allow experiments to be carried out up to 200°C. The simple chemical composition of PAOs allows PAHs to be easily separated and it does not contain any PAHs which could interfere.

Two sets of standards (Table 4.5) were prepared in 5ml of THF (tetrahydrofuran) and added to 55ml of DS164. Samples of THF (5ml) in PAO (55ml) were also prepared as controls. The samples and controls were sealed in glass ampoules, under vacuum, and aged in an oven at 195°C.

Table 4.5: Sets of PAH standards used for thermal degradation experiments

<table>
<thead>
<tr>
<th>Set 1 (Retention time in brackets)</th>
<th>Set 2 (Retention time in brackets)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decafluorobiphenyl (3.94)</td>
<td>3,3'-Dimethyl-1,1'-biphenyl (7.53)</td>
</tr>
<tr>
<td>2,2'-Dimethyl-1,1'-biphenyl (6.40)</td>
<td>9,9-Dimethylfluorene (7.54)</td>
</tr>
<tr>
<td>9H-Fluorene (7.58)</td>
<td>9,10-Dihydrophenanthrene (8.28)</td>
</tr>
<tr>
<td>3-Methylfluorene (8.28)</td>
<td>4-Methylfluorene (8.43)</td>
</tr>
<tr>
<td>3,4-Benzofluorene (11.28)</td>
<td>Tricyclopentabenzene (9.04)</td>
</tr>
<tr>
<td>Benzo[a]anthracene (12.49)</td>
<td>2-Bromofluorene (9.57)</td>
</tr>
<tr>
<td>Triphenylene (12.55)</td>
<td>Pyrene (10.73)</td>
</tr>
</tbody>
</table>

Samples were removed after 65 and 115 days. The samples were doped with 9,9-dimethylfluorene (internal standard) and the PAHs were separated by the same liquid-liquid extraction as used for transformer oil. The PAHs were doped with 3,4-benzofluorene (external standard) and analysed by GC-MSD. The chromatograms of these standards are shown in Figure 4.5. The same standards after heating are then shown in Figure 4.6. The PAHs in the chromatograms do not appear to have changed.
as a result of the heating.

Figure 4.5: Chromatogram of PAH standards in PAO. Top: Set 1. Bottom: Set 2.

Figure 4.6a: Chromatogram of PAH standards (Set 1) aged 115 days in PAO.
4.2.2 Electrical Breakdown Experiments

The thermal and oxidation experiments failed to produce any change in the PAH fingerprint. The electrical effect on the fingerprint was then considered. Although insulating oil is frequently used in high voltage experiments no literature examples were found where the effect on the oil chemistry were investigated. Oils subjected to four different electrical ageing methods were examined.

4.2.2.1 Silent Discharge in an Ozonizer

An ozonizer was constructed (Figure 4.7) similar to that described by Augustine (Augustine 1975). A 10ml syringe was used as the cell. A piece of copper wire was inserted in one end of the syringe and held in place by PTFE tape; this was one electrode. The second electrode, also a piece of copper wire was held in place next to the syringe barrel by aluminium foil wrapped around the barrel. The syringe was filled with oil and the internal electrode was connected to a transformer capable of producing from 5kV to 15kV.
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Figure 4.7: Ozonizer cell used to electrically age transformer oil.

In order to ensure the apparatus was working properly, i.e. that it was capable of producing ozone, it was first used without oil. After a few hours the air was tested with moist starch-iodide paper which changed from white to blue-black showing that ozone had been formed.

The syringe was filled with Castrol BS148 transformer oil in order to see if silent discharge has any effect on the PAHs in oil. Samples were run at 5kV for 20 hours, at 10kV for 20 hours and at 15kV for 4, 20 and 40 hours. None of the samples showed any visible signs of ageing. There was a small increase in moisture content but no particular precautions were taken to prevent the oil from absorbing moisture from the atmosphere.

The PAHs were extracted from the samples and were analysed by GC-MS. Once
4.2.2.2 Breakdown Voltage Test

As discussed in the Introduction chapter there is a standard test performed on transformer oil known as Breakdown Voltage. The oil is held in apparatus similar to that shown in Figure 4.8. The voltage supplied to one of the electrodes is gradually increased until it is high enough to ‘jump’ across to the other electrode. In a standard test this is performed six times and the average is quoted as the breakdown voltage for that oil. However, the test can continue indefinitely.

![Breakdown voltage test cell](image)

Figure 4.8: Breakdown voltage test cell

One sample of unused Castrol BS148 transformer oil was left in the cell and subjected to 100 breakdowns in an attempt to create an observable breakdown in the PAH chemistry of the oil.

The oil was not visibly aged by this number of discharges, neither was the value for the breakdown voltage (in kV) significantly altered over the course of the test. The results for the full test are plotted below and show a slight downward trend.
The PAHs were extracted and analysed by GC-MS again with no significant effect on the fingerprint.

4.2.2.3 Breakdown in a Test Cell

Another method used to age transformer oil was devised at Glasgow Caledonian University. Dr Donald Hepburn of the Engineering Department aged unused Castrol BS148 transformer oil (a different batch to that used in experiments at Surrey University) using the test cell (Figure 4.10 and figure 4.11). The test is a glass cylinder clamped between two Perspex sheets. The high voltage electrode is a copper cone and the ground electrode is a flat piece of stainless steel.
Ageing experiments were set up with different materials covering the ground electrode but the discharge gap was maintained at 2mm. The materials used were:

- Uncovered stainless steel electrode (B)
- Thin copper foil coated with varnish (C)
- Thin aluminium foil coated with varnish (D)
- 1mm thick slice of ERIP (epoxy resin impregnated paper) coated with varnish (E)
- 1mm thick slice of ERIP unvarnished (F)
The voltage of the copper cone electrode was raised to a level where discharges took place. The experiment was then allowed to run for 4 hours.

Syringe samples (50ml) removed from the cell were sent to National Grid, Leatherhead for analysis along with a syringe sample of the unused oil (A).

The samples were analysed for their dissolved gas (DGA) content, moisture content, carbon composition and the PAH extracts were analysed by GC-MS.

The DGA results for sample B were lost because of a rig malfunction. The results for the CO\textsubscript{2} and the combustible gases for samples A and C – F are shown below (Table 4.6):

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO (ppm)</th>
<th>CH\textsubscript{4} (ppm)</th>
<th>CO\textsubscript{2} (ppm)</th>
<th>C\textsubscript{2}H\textsubscript{4} (ppm)</th>
<th>C\textsubscript{2}H\textsubscript{6} (ppm)</th>
<th>C\textsubscript{2}H\textsubscript{2} (ppm)</th>
<th>H\textsubscript{2} (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>&lt;10</td>
<td>2</td>
<td>633</td>
<td>1</td>
<td>&lt;1</td>
<td>&lt;0.2</td>
<td>7</td>
</tr>
<tr>
<td>C</td>
<td>15</td>
<td>13</td>
<td>531</td>
<td>28</td>
<td>2</td>
<td>339.2</td>
<td>105</td>
</tr>
<tr>
<td>D</td>
<td>18</td>
<td>37</td>
<td>549</td>
<td>83</td>
<td>8</td>
<td>914.9</td>
<td>232</td>
</tr>
<tr>
<td>E</td>
<td>13</td>
<td>8</td>
<td>559</td>
<td>6</td>
<td>2</td>
<td>24.8</td>
<td>43</td>
</tr>
<tr>
<td>F</td>
<td>66</td>
<td>17</td>
<td>625</td>
<td>30</td>
<td>3</td>
<td>248.7</td>
<td>91</td>
</tr>
</tbody>
</table>

The results for carbon typing showed that no significant effect was observed on these properties as they were all within experimental error.

The PAH extracts as analysed by GC-MS showed that this batch of Castrol contains a small amount of DBPC inhibitor which should not be present as the oil is classified as uninhibited. However, the level of the inhibitor is relatively low and is most likely the result of contamination at the refinery. There is no observed effect on the fingerprint due to this set of experiments.

### 4.2.2.4 Diverter Test Oil

The tests performed in the laboratory do not accurately reproduce the conditions an oil would typically experience in a transformer. However, oil in diverters and circuit breakers experience similar conditions to the rest of the transformer, but they are
usually more severe. They are subject to arcing and sparking and perhaps the PAH fingerprint would change under such conditions over an extended period of time.

A sample of oil was received which had been used in a diverter during its service duty and breaking capacity type tests. Prior to the tests the oil had been unused and was clear and very pale yellow (Figure 4.12 Bottle A). After the tests the oil was darker and green, with a suspension of carbon, which gave the oil the appearance of being black (Figure 4.12 Bottle C). The oil samples before and after the tests were analysed to obtain the PAH fingerprints and carbon typing values.

The before and after tests samples were analysed by FT-IR to determine the aromatic carbon content as described in IEC60590 and the paraffinic and naphthenic carbon contents were calculated according to ASTM D2140.

The oils were analysed by GC-MS after the liquid-liquid analysis stage and after complete extraction of the PAHs.

Figure 4.12: Effect of electrical ageing on appearance of oil. A - Sample before ageing; B - sample after ageing with carbon filtered out; C - sample as received after ageing.
Chapter 4: Transformer Oil Degradation Studies

The carbon typing results for the two oils are shown in the table below:

Table 4.7: Carbon typing results

<table>
<thead>
<tr>
<th>Oil Sample</th>
<th>Aromatic %</th>
<th>Density</th>
<th>Refractive Index</th>
<th>Naphthenic %</th>
<th>Paraffinic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before test</td>
<td>12.00</td>
<td>0.8849</td>
<td>1.48604</td>
<td>47.90</td>
<td>40.10</td>
</tr>
<tr>
<td>After test</td>
<td>11.88</td>
<td>0.8848</td>
<td>1.48603</td>
<td>47.64</td>
<td>40.48</td>
</tr>
</tbody>
</table>

The infrared spectra are shown below for the aromatic region (figure 4.13):

Figure 4.12: Infrared spectra of unused oil (black) and oil after diverter test (blue) in the aromatic region.

The carbon typing results are very similar, the density and refractive index are unchanged. The aromatic carbon content calculated by FT-IR decreases slightly after the lifetime test. The change is small and, given the nature of the test, it may be
considered within experimental error. However, under the conditions of the tests performed on the diverter it is plausible that a small but noticeable fraction of the aromatic molecules would be reduced to naphthenic form by the absorption of hydrogen gas. It is generally assumed that the molecules responsible for gas absorption are aromatic and that the poly-aromatic molecules are the most gas absorbing.

The PAH fingerprints after liquid-liquid extraction often show differences between samples that are not picked up by the full PAH extraction. This is because they contain mono-aromatic compounds and the polar compounds. The picture is often confused because they contain too much information. In this case, however, the two chromatograms are very similar. The only significant difference is observed in the peaks which elute between 36 and 46 minutes. This region contains larger molecules, such as the 3- and 4-ring PAHs (alkylated-phenanthrenes and pyrene) and even after just the liquid-liquid extraction usually contains only PAHs. This region appears to be lower in the ‘After Test’ sample than in the ‘Before Test’ (Figure 4.14).

![Chromatograms of the liquid-liquid extracts from transformer oil. Top: unused oil. Bottom: After test in diverter](image)

Figure 4.14: Chromatograms of the liquid-liquid extracts from transformer oil. Top: unused oil. Bottom: After test in diverter

The full PAH extraction fingerprints for both samples (Figure 4.15 and Figure 4.16) appear to be very similar to each other. As in the partially extracted samples the peaks in the region between 36 and 46 minutes are lower in the ‘After Test’ sample. The peaks around 22 minutes are also lower in the ‘After Test’ sample; these peaks correspond to methylated-fluorenes. It should be noted that the method is qualitative
and the numbers on the y-axis do not relate directly to the quantity of PAHs in the two oils.

Figure 4.15: Chromatograms of PAH extracts from transformer oil. Top: Unused oil. Bottom: After test in diverter.

Figure 4.16: Overlaid chromatograms of PAH extracts from transformer oil. Black: Unused oil. Green: After test in diverter.

4.2.3 Ultraviolet Radiation Experiments

Corona discharge in oil may cause UV radiation which is also responsible for degradation in oil, so, experiments were set up to investigate the effect of UV radiation on transformer oil.

The ultraviolet light source used was a linear, high-pressure mercury vapour lamp.
The lamp is made of a clear, fused quartz tube with tungsten electrodes, filled with mercury vapour and an inert gas. The lamp takes approximately five minutes to warm up while the mercury vaporises and reaches the operating pressure (1-2 atmospheres). The operating temperature can be up to 800°C; to prevent the oil from heating up the UV lamp was placed in an immersion well separated from the oil by cooling water (Figure 4.17).

![Photochemical Cell](image)

Figure 4.17: Photochemical Cell

In these experiments, single PAHs on their own were examined dissolved in toluene and cyclohexane, which were also studied separately. Approximately 60cm$^3$ of the solvents were aged for 120 hours. The solvent product was then analysed by GC-MS without any sample preparation.

The chromatograms of the solvents are shown in Figure 4.18 and Figure 4.19. The
cyclohexane solvent peak is not shown, the peak at approximately nine and a half minutes is shown in Figure 4.21

Figure 4.18: Chromatogram of UV-degraded cyclohexane

Figure 4.19: Chromatogram of UV-degraded toluene

Dicyclohexyl ether

Figure 4.21: Photochemical reaction product of cyclohexane
The chromatogram for toluene and its degradation products shows many more peaks. The identified peaks can be found in Appendix E.

Two single PAHs were aged in the photochemical cell for 120 hours each. Fluorene and pyrene were chosen as they are both common in the transformer oil. Few additional peaks were found in the photolysed fluorene but the compounds contained oxygen. The degradation products from pyrene were only hydrocarbons. The structures identified may be found in Appendix E.

Only one transformer oil was aged in the photochemical cell. The water cooling the cell dropped in pressure and caused the oil to overheat and char in less than 48 hours. The lamp was no longer operational and was beyond economical repair. The chromatograms from the extractions of this oil are shown in Figure 4.22 and Figure 4.23.

Figure 4.22: Chromatogram of a liquid-liquid extract of UV degraded transformer oil
Figure 4.23: Chromatogram of a PAH extract from UV degraded transformer oil
The extracts from the UV degraded oil are not significantly different from the unused oil. However, it is clear that ultraviolet radiation causes the breakdown of PAHs, but the level of UV radiation produced by a photochemical cell is far beyond that found in a transformer even under fault conditions. Further study of photochemical breakdown of PAHs may be of interest but is unlikely to be of significance to transformer oil breakdown in service.
Chapter 5: Analysis of Acids in Degraded Transformer Oil

5.1 Introduction

5.1.1 Literature Survey

5.2 Extraction and Analysis of Acids in Oil

5.2.1 Results

5.2.2 Extraction Efficiency and Alternative Methods
5.1 Introduction

The degradation studies covered in the previous chapter demonstrated that the study of PAHs in transformer oil was not going to be useful in monitoring the condition of oil in service. But, oils of all types produce organic acids when they oxidise. This is because most oxidation is by a free radical process, where hydroperoxides are produced, which are easily converted to acids in the oil. If the PAHs cannot be used to trace the ageing process, then perhaps the acid formation could be monitored instead.

Transformer oils are known to produce acid, so acidity measurements are routinely used in many industries to assess the condition of oil. The standard procedures for measuring the acidity are either by manual titration with a colour indicator or automatically by potentiometric titration. Oil oxidises at a rate dependant on the temperature and amount of available oxygen. The products are organic acids which can react with the copper, or more especially copper oxide. The resulting copper salts catalyse the formation of more acid. The levels of acid are usually very low and an increase usually indicates a fault in the transformer.

There is currently no effort made to identify the acids that are produced. If a more sensitive technique (current limit of detection is 0.01 mg KOH/g oil) was used to look for the presence of very low concentrations of acid, the oil could be replaced before its condition had deteriorated to the point where the acids were damaging the paper insulation.

5.1.1 Literature Survey

No previous instances of acid identification in oil could be found. This type of research may have been carried out and written in internal reports rather than being published in the literature. Contact was made with Colin Myers at National Power and Mike Myers at Castrol, both of whom have accumulated much experience in transformer oil analysis; neither was aware of work in this area,
5.2 Extraction and Analysis of Acids in Oil

The extraction procedure followed for the removal of acids from oil was as follows:

- Aqueous sodium hydroxide (3ml, 2M) was added to a sample of the oil (10ml).
- The two layers were mechanically stirred for two hours at room temperature.
- The resulting emulsion was placed in a separating funnel with 5ml of diethyl ether.
- The lower, aqueous, layer was run off and neutralised with hydrochloric acid.
- The liquor was then shaken with dichloromethane (5ml) to extract the organic acids.
- The dichloromethane layer was separated from the aqueous solution and dried with anhydrous MgSO₄.
- The dichloromethane was removed under reduced pressure.

The GC was not set up for polar compounds and the acids could cause damage to the column, so the acids were esterified for easier analysis:

- The aromatic, yellow residue left after the dichloromethane had been removed was dissolved in methanol.
- A single drop of acetyl chloride was added.
- The solution was stoppered and left for 48 hours at room temperature to allow the esterification to take place.
- The methanol was removed under reduced pressure and the remaining milky white solid was dissolved in dichloromethane and analysed by GC-MS.
This procedure was performed on three samples of oil:

A. The heavily oxidised Castrol oil produced during the thermal degradation experiments. Acidity measured by automatic potentiometric titration at 0.90mg KOH/g oil

B. The UV degraded oil from the photochemical cell. Acidity measured at 0.44mg KOH/g oil

C. A sample of Castrol oil aged for 2 years by natural light in a colourless glass jar containing 2g of copper wire. Acidity measured at 0.02mg KOH/g oil

5.2.1 Results

Figures 6.1 to 6.3 show the three chromatograms of the acid extracts.

![Chromatogram](image)

Figure 6.1: Chromatogram of esterified acids extracted from oxidised sample A
The three chromatograms have few resolved peaks and the badly oxidised samples have increased baselines, but after performing an automatic library search the following esters were detected:

Hexadecanoic acid, methyl ester was found in all three samples.
Sample A contains methyl esters of octanoic acid octadecanoic acids.
Sample B contains methyl esters of nonanoic, heptadecanoic and octadecanoic acids.
The analysis shows that acids are present in the oil and that they can be identified. However, the amounts appear to be very small and many other compounds are extracted.

5.2.2 Extraction Efficiency and Alternative Methods
The efficiency of the acid extraction method was investigated by dissolving decanoic acid and hexadecanoic acid in transformer oil then extracting as described previously. Very low concentrations of the methyl esters were detected in the final samples. The peaks were too small to enable quantification to have any meaning, indicating poor extraction efficiency.

The application of SPE to the removal of acids from transformer oil ought to be relatively straightforward since they are the only polar components of the oil, but silica, Florisil and C18 cartridges were tested in normal and reverse phase without success. Clearly, organic acids are formed during degradation, but, as with PAHs, their extraction is not straightforward and further work is needed to develop an effective extraction strategy.
Chapter 6: Evaluation of Array-Based Sensor Instruments for Fingerprinting Transformer Oil

6.1 Introduction
6.2 Sensors
   6.2.1 Piezoelectric Sorption Sensors
   6.2.2 Conductometric Sensors
      6.2.2.1 Metal Oxides
      6.2.2.2 Conducting Polymers
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6.6 Results
6.1 Introduction

During the course of the study, an opportunity arose to use array-based sensors to fingerprint transformer oils. Tests were carried out in collaboration with SmithKline Beecham who were evaluating electronic nose instruments for use in process control for manufacturing of flavouring products such as toothpaste and drinks. Some tests were carried out on their behalf and a protocol was developed which was then extended for use with transformer oils from different sources, both unused and aged.

Array-based sensors were inspired by human olfaction i.e. the sense of smell. The first attempt at machine olfaction was in the 1950s (Gardner, 1999) based on electrochemical cells. The cells comprised metal wire electrodes in contact with the surface of a porous rod saturated with dilute electrolyte. The machine used an array of 8 cells and was found to give different response patterns to different samples.

In the 1980s the term ‘Electronic Nose’ was first used and in the same paper a definition was given:

“An electronic nose is an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours.” (Gardner, 1994)

Both biological and machine olfactory systems are triggered by odorant molecules which are typically non-polar organic molecules with relatively low molecular weight. These are called volatile organic compounds (VOCs). Odours are frequently complex mixtures of many VOCs – up to several thousand. The threshold at which humans can detect odours can vary from a few parts per billion up to several parts per thousand (Craven, 1994).

The way in which machine olfaction attempts to mimic biological olfaction is shown in Figure 6.1.
6.2 Sensors

There are several types of sensors which have found applications in industry, an introduction to the most common types follows.

6.2.1 Piezoelectric Sorption Sensors

Piezoelectric sensors are typically constructed of coated quartz crystals. Quartz crystals are piezoelectric materials which means that they will generate a stable radio frequency resonance when subjected to acoustic waves. The coatings are similar to the materials used in GC columns and will absorb certain materials. The change in mass of the coating due to absorbed VOCs causes a change in the oscillation frequency which is characteristic of the mass absorbed. This type of sensor is called Bulk Acoustic Wave (BAW). Crystals which rely upon waves emitted along the surface by the electric field of surface-deposited aluminium electrodes are Surface Acoustic Wave (SAW) sensors. There are plenty of uses of SAW and BAW sensors covered in the literature (Zaromb and Stetter, 1984; Nakamoto et al., 1993; McAlernon et al., 1996) because they are so versatile, mainly because of the wide range of potential sorbent materials available in the form of gas chromatographic stationary phases.
6.2.2 Conductometric Sensors

6.2.2.1 Metal Oxides
Metal oxide semi-conductors can be used as sensors by observing the changes in resistance caused by vapours absorbed on the conductors (Dickinson). The oxide layer (e.g. tin oxide (Shurmer et al., 1989)) is coated on a ceramic pellet, which is usually heated to decrease response and recovery times. Oxygen is absorbed onto the oxide surface and removes electrons which increases the resistance of the semiconductor. The VOCs which are introduced, interfere with this process and cause the semiconductor to become more conducting. Metal oxide sensors are currently the most widely used, partly because they are relatively cheap to produce.

6.2.2.2 Conducting Polymers
Conducting polymer sensors are grown between two gold elements and bonded to a silicon substrate. The resultant polymer, commonly polypyrrole, has an innate electrical resistance called its baseline resistance. The baseline resistance changes in response to vapours which reversibly bond to the surface. This type of sensor is more diverse than the metal oxide sensors, but they are more expensive to produce and more difficult to accurately reproduce.

6.3 Pattern Recognition

The amount of data produced by a sample depends on the number of sensors and the time for sample analysis, but generally there are very large quantities of data produced. In order to get anything meaningful from this data special tools are required for interpretation. Most commercial instruments use either multivariate chemometrics such as principal component analysis (PCA) or artificial neural networks (ANN), or both.

6.3.1 Principal Component Analysis
The main aim of PCA is to reduce a large number of variables to a much smaller number of principal components (PCs) which capture the vast majority of variance in the data (Jackson, 1980). This reduces the dimensionality of data considerably,
enabling effective visualisation, regression and classification of multivariate data (Massart et al., 1988). PCA relies on the fact that a data matrix, $X$, can be decomposed into a matrix of scores, $T$, and loadings, $P$, such that,

$$X = T \cdot P$$

Many methods are available for deconvoluting the data matrix, the most popular being the NIPALS algorithm (Wold et al., 1969), which extracts one PC at a time, in order of significance. Typically, there is a great deal of correlation and redundancy in analytical responses so a small number of PCs is often sufficient to describe a large data set. By reducing instrumental responses comprising a large number of variables, $p$, to a smaller number, $n$, of principal components, each response can be represented as a point in $n$-dimensional PC space, and if $n$ is less than four, these points can be conveniently visualised. In a successful analysis, responses appear in distinct clusters in PC space according to their classification and the space can be divided into regions associated with the different classifications.

### 6.3.2 Artificial Neural Networks

Although many different types of ANN have been developed (Smits et al., 1994; Melssen et al., 1994), the vast majority of calibration and classification applications are most amenable to a multilayer feed forward network (Burns and Whitesides, 1993; Zupan and Gasteiger, 1991). The analytical uses, operation and training of such a network are documented in detail elsewhere (Duch and Diercksen, 1994; Gasteiger and Zupan, 1993). In short, a feed forward network becomes, after sufficient training, a model able to map responses presented to it to a corresponding set of outputs. If enough training data is provided and the network is not overtrained, the model will be sufficiently generalised to map unseen responses to appropriate outputs.

The basic ANN processing element is the neuron which is loosely based on the design of biological neurones (DARPA, 1988). Inputs $a_1..a_n$ are multiplied by corresponding weights, $w_1..w_n$, then summed together with a bias, $b$, before being mapped to an output, $t$, by a transfer function, $f$, which is selected according to the application. This process is summarised in the following equation:
\[ t = f(b + \sum_{i=1}^{n} w_i a_i) \]

A multilayer feed forward network consists of two or more layers of such neurons, with weighted interconnections from each neuron to every neuron in the next layer. Network training comprises adjusting the network weights and biases to give the most accurate model possible between the input and output pairs in the training data. This is most commonly achieved using back propagation of errors (McClelland and Rumelhart, 1988; Rumelhart et al., 1986), for which there are many different algorithms. The simplest method uses gradient descent, an iterative process where the weights and biases are moved in the direction which gives the most rapid decrease in the discrepancy between the actual and desired outputs. Each iteration of this process is referred to as an epoch. There are various refinements designed to improving the performance of the training, including adaptive learning rate and momentum.

6.4 Instrumentation

Four instruments were used during the course of this research:

- Arraytec Prototype
- NST 3220
- Birkbeck Prototype
- Neotronics e-NOSE 4000

The Arraytec instrument was made available by SmithKline Beecham where it was being evaluated. The sensor array consisted of 8 conducting polymer sensors, Arraytec provided very little other information about the sensors. The sample to be evaluated was contained in a 2ml capped, plastic vial. The sample needle was lowered into the vial, puncturing the cap in the process, and the headspace sampled. The gases in the headspace were passed across the sensors for 60 seconds. The sensors were then cleaned with air and the sensor resistances allowed to return to their baseline value before another sample could be run. The software supplied with the instrument contained a chemometric package capable of performing principal
Chapter 6: Evaluation of Array-Based Sensor Instruments for Fingerprinting Transformer Oil

Component analysis (PCA) and discriminant function analysis (DFA). The raw data could be exported to Microsoft (MS) Excel.

The software for the Arraytec instrument was licensed for a very short time and the company had to dissolve for legal reasons before the licence could be extended. The data collected on this instrument was therefore worthless, as it could no longer be accessed.

6.4.1 NST 3220
Developed by Nordic Sensor Technologies the NST 3220 is based on 15 metal oxide sensors. Ten of the sensors are called MOSFET sensors and respond to hydrogen containing species. The remaining five are referred to as MOS sensors and it is claimed they respond to all oxidising and reducing species and also to saturated hydrocarbons.

The instrument uses 250ml glass bottles which can be sampled automatically and repeatedly from a carousel. The samples are left sealed in the bottles for a minimum of thirty minutes to allow the VOCs to build up in the headspace to the point of equilibrium.

The data produced by the instrument was produced in a number of forms, but the processing that had taken place was not clear nor was it explained. The software did not contain any chemometric analysis nor any suggested graphical representation for the data.

6.4.2 Birkbeck prototype
The prototype instrument developed at Birkbeck College, University of London was built into the same case as the Arraytec instrument. Samples of approximately 0.5g are placed in 1.5ml plastic vials, which are allowed to equilibrate for 20 minutes. The vial is perforated by a needle which lowers into the vial and pumps the gas mixture in the headspace past the sensor array. The eight sensors in the array used for testing transformer oils were:

- U1 2a OV225 – cyano substituted polysiloxane
• U5 17a PECH – poly(epichlorohydrin)
• U2 12a OV25 – phenyl substituted polysiloxane
• U6 32a PEM – poly(ethylene maleate)
• U3 7a PPG – poly(propylene glycol)
• U7 22a PPE – poly(2,3,4-hexafluoropentane-1,5-diol-co-epichlorohydrin)
• U4 27a Allylbis – 2,2-bis(3-allyl-4-hydroxyphenyl)-hexafluoropropane
• U8 37a PIB – poly(isobutylene)

The samples were analysed for sixty seconds. The sensors were cleaned with air drawn through activated charcoal for 100 seconds. The data was analysed by a sample classification programme which uses a discriminant function analysis routine.

6.4.3 Neotronics e-NOSE 4000

The Neotronics instrument differs from the others used because the sensor is static rather than allowing continuous flow. Rather than sampling the headspace and passing it across the sensors, the head containing twelve semi-conducting polymer sensors (Figure 6.2) is lowered into the sample.

The sample is stirred during the analysis and the sample is kept at a constant temperature. The relative humidity can also be monitored. Including purging, heating, equilibrating and sampling time the analysis is completed in eight minutes.

The raw data could be plotted in several different graphical representations, but no chemometric analysis could be made.
6.5 General Approach to E-NOSE Evaluation

The different array-based sensors were made available at various periods and for different lengths of time throughout the study. It was not always possible to analyse the same oils on each instrument. The Arraytec prototype was provided for several days over the course of two months. It was possible to analyse several unused and aged samples of Nynas, Castrol, Carless and Shell oils all supplied between 1994 and 1996. It was also possible to investigate the repeatability of the analyses over the period.

When the NST instrument was available the work had to be completed over the course of a few consecutive days. The same oils were available as for the Arraytec instrument and were all analysed. However, most could only be analysed once or, at most, twice. The raw data was made available for later examination in MS Excel.

The Birkbeck prototype was available for just a few hours. There was only the opportunity to analyse seven different oil samples in two batches. One sample of
each of Castrol, Carless and Shell oils and an aged Castrol oil were analysed in the first batch. The second batch consisted of Castrol oil from Glasgow Caledonian University, the first being the unused oil, the second after ageing at 90°C for 400 hours and the third had been exposed to UV radiation for 24 hours. The raw data were not available for interpretation at a later date.

The Neotronics instrument was available for a similar length of time as the NST. Oils from the same suppliers were analysed as for the NST and Arraytec instruments but they were supplied in 1998. An inhibited oil was also analysed.

### 6.6 Results

**Arraytec prototype**

It is not possible to show results from the Arraytec instrument for reasons explained earlier. The data were analysed at the time of sampling and it is worth noting that the best results, in terms of grouping and discrimination, were obtained when using DFA rather than PCA. Unused oils from different batches were easily distinguished, however the separation of the Castrol oil from its oxidised analogue was not so clear. The repeatability of the instrument over the course of several weeks was excellent.

**NST 3220**

The raw data obtained by the NST instrument had to be exported to MS Excel. The MOS (or TGS) sensors generally gave bigger responses to the oil samples than the MOSFET sensors. The average MOS responses are shown below.

<table>
<thead>
<tr>
<th>Name</th>
<th>TGS 1</th>
<th>TGS 2</th>
<th>TGS 3</th>
<th>TGS 4</th>
<th>TGS 6</th>
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<tbody>
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<td>3.54</td>
<td>2.89</td>
<td>0.30</td>
<td>0.17</td>
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<td>29.33</td>
<td>38.16</td>
<td>4.96</td>
<td>2.25</td>
</tr>
<tr>
<td>Shell Diala B</td>
<td>3.51</td>
<td>13.34</td>
<td>17.13</td>
<td>1.98</td>
<td>0.71</td>
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<tr>
<td>Castrol '97</td>
<td>9.69</td>
<td>66.04</td>
<td>61.53</td>
<td>6.46</td>
<td>0.57</td>
</tr>
<tr>
<td>Carless -Cl</td>
<td>8.44</td>
<td>63.97</td>
<td>58.59</td>
<td>5.98</td>
<td>0.40</td>
</tr>
<tr>
<td>Carless Rec</td>
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<td>55.41</td>
<td>56.54</td>
<td>6.22</td>
<td>1.34</td>
</tr>
<tr>
<td>Castrol Aged</td>
<td>19.46</td>
<td>77.85</td>
<td>93.36</td>
<td>10.75</td>
<td>2.31</td>
</tr>
</tbody>
</table>
Chapter 6: Evaluation of Array-Based Sensor Instruments for Fingerprinting Transformer Oil

<table>
<thead>
<tr>
<th></th>
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<th>2.49</th>
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<th>0.02</th>
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</thead>
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<td>12.98</td>
<td>11.58</td>
<td>1.08</td>
<td>-0.03</td>
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<tr>
<td>DS168</td>
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<td>36.71</td>
<td>43.12</td>
<td>4.60</td>
<td>0.66</td>
</tr>
<tr>
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<td>32.85</td>
<td>38.04</td>
<td>4.05</td>
<td>0.67</td>
</tr>
<tr>
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<td>29.11</td>
<td>35.69</td>
<td>4.29</td>
<td>1.58</td>
</tr>
<tr>
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<td>15.64</td>
<td>17.23</td>
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</tr>
<tr>
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<td>34.07</td>
<td>3.77</td>
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</tr>
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<tr>
<td>Carless '96</td>
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<td>Hexane</td>
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<td>194.59</td>
<td>38.94</td>
<td>11.24</td>
</tr>
<tr>
<td>Shell Diala B</td>
<td>5.33</td>
<td>14.99</td>
<td>6.90</td>
<td>1.57</td>
<td>0.30</td>
</tr>
<tr>
<td>DS168</td>
<td>1.31</td>
<td>16.44</td>
<td>5.55</td>
<td>0.48</td>
<td>-0.39</td>
</tr>
<tr>
<td>Castrol Aged</td>
<td>12.60</td>
<td>53.37</td>
<td>25.78</td>
<td>3.02</td>
<td>1.47</td>
</tr>
</tbody>
</table>

The average responses of the MOS sensors are shown in Figures 6.3 to 6.7.

Figure 6.3: MOS sensor results for Nynas oils

Figure 6.3 shows the repeatability of the instrument since the Nynas samples should be identical. Sensors 2 and 3 give the largest response but also have a large range, giving the impression that the sensors are not especially repeatable.
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Figure 6.4: MOS sensor results for Castrol oils

The results for Castrol are more promising. The Castrol 1996 sample shows good repeatability and, unlike Nynas, a difference between the samples was expected as Castrol oil was less consistent between 1994 and 1996.

Figure 6.5: MOS sensor results for Carless oils

The Carless oils ought to exhibit the greatest variety in results. The repeated Carless 1996 sample shows good repeatability. The dechlorinated and reclaimed samples give a greater response on all sensors.
Figure 6.6: MOS sensor results for unused and heavily oxidised sample Castrol 1995
The difference in response between unused Castrol and heavily oxidised Castrol oil is clear. Sensors 1 to 4 all give a much bigger response to the oxidised oil.

Figure 6.7: Average MOS sensor results for unused oils
The average response to Nynas, Castrol and Carless oils from Figures 6.3 to 6.5 are shown in Figure 6.7 along with the response to Shell oil, the synthetic oil DuraSyn 168 and hexane. The sensors give a very large response to hexane, which is shown for comparison, but requires a logarithmic scale so that the differences between the
other samples can still be seen. The responses to the transformer oils all give very similar patterns but the size of response is different, with Nynas giving the largest response and Shell giving the smallest.

**Birkbeck Prototype**

The first oils studied using the Birkbeck prototype were the unused oils from Castrol, Carless and Shell along with the badly oxidised sample of Castrol oil. The data were analysed using Discriminant Function Analysis (DFA). The results are shown in Figures 6.8 to 6.14.

![Figure 6.8: Comparison of E-NOSE response to oil using DFA at 59 seconds](image)

The largest response to a sample is frequently at the end of the run. In the case of the Birkbeck instrument the sampling time was 60 seconds and comparisons were first made at 59 seconds. Figure 6.8 shows that the unused Castrol, Carless and Shell oils and the oxidised Castrol oil are showing a bunching of the data but there is poor discrimination between them. The plot at 59 seconds gave the best possible discrimination.
In Figure 6.9 the software has been instructed to ignore the data produced from the analysis of the oxidised oil in grouping the other three samples. If the plotted points for the oxidised oil are ignored it can be seen that there is now better resolution and grouping of the unused oils. The oxidised samples are then treated as ‘unknown’ data points which are not the same as any of three ‘known’ samples.

Figure 6.10: Comparison of E-NOSE response to oil using DFA at 50 seconds
Figure 6.10 shows the same analysis but at 50 seconds rather than 59 seconds. It demonstrates that the grouping and discrimination can be improved or degraded depending on the selection of the data. The oxidised samples are still being treated as 'unknown' and are not grouping with any of the other clusters.

Figure 6.11: Comparison of E-NOSE response to oil using DFA at 59 seconds. The last analysis of this batch of oils shows the discrimination between the unused and oxidised Castrol oil. The Carless and Shell oils have been excluded. The instrument has grouped the data and shows very good discrimination between the two clusters.

Figure 6.12: Comparison of E-NOSE response to oil using DFA at 59 seconds.
Chapter 6: Evaluation of Array-Based Sensor Instruments for Fingerprinting Transformer Oil

The Birkbeck instrument again shows that it can discriminate between samples of the same oil that has been aged. Figure 6.13 shows the same analysis but at 50 seconds, showing that the best discrimination is not always at the latest point of analysis.

Figure 6.13: Comparison of E-NOSE response to oil using DFA at 50 seconds.

The last analysis shows that the instrument can recognise a sample introduced to it that is ‘unknown’. The UV aged oil was analysed but the instrument was not provided any information about it and has correctly positioned it with the ‘UV aged’ cluster.

Figure 6.14: Comparison of E-NOSE response to oil using DFA at 50 seconds.
Neotronics e-NOSE 4000

The results from the Neotronics instrument could not be interpreted by an analysis package. The sensor responses over the course of the 2 minute sampling time could be plotted and various graphical representations were possible. Representative results are shown in Figures 6.15 to 6.23

![Graph showing sensor responses to Castrol oil](image)

Figure 6.15: Sensor response to Castrol oil using Neotronics e-NOSE 4000

Figure 6.15 shows the response of the Neotronics sensors to Castrol transformer oil. This is a typical plot for a sensor array with all the sensors responding to some extent. It is interesting to note that the response may be temperature dependent: an analysis of the data at 20 seconds would be very different than at 100 seconds. Figures 6.16 to 6.18 show how the responses of the sensors at 110 seconds in the above graph may be plotted.
Figure 6.16: Bar view of sensor responses to Castrol oil at 110 seconds

Figure 6.17: Offset polar view of sensor responses to Castrol oil at 110 seconds
Figure 6.18: Polar view of sensor responses to Castrol oil at 110 seconds

Figure 6.19: Sensor response to Nynas oil using Neotronics e-NOSE 4000
Figure 6.20: Sensor response to Carless oil using Neotronics e-NOSE 4000

The sensor responses of Nynas and Carless oils are almost identical to those of Castrol oil. This is not so surprising as the oils analysed by Neotronics instrument were supplied in 1998 and the oils from the three suppliers were very similar.

Figure 6.21: Subtraction of sensor response of Castrol oil from Nynas oil using Neotronics e-NOSE 4000
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A facility not available with the previous instruments is the ability to compare sensor responses of different samples by subtracting one from another. The graph in Figure 6.21 shows the sensor response of the Castrol oil subtracted from that of Nynas oil. It demonstrates that the oils are very similar, except for a deviation in the first 20 seconds where the sensors have shown a greater initial response to the Castrol oil.

Figure 6.22: Sensor response to Mol oil using Neotronics e-NOSE 4000

The sensor response to the inhibited oil produced by Mol is also very similar to that of the other three suppliers. The difference, however, is in the magnitude of the response. The Mol oil has produced a larger response than any other oil. There are also more subtle differences in the relative responses of some of the sensors. These differences can be more easily demonstrated by subtraction.
Figure 6.23: Subtraction of sensor response of Castrol oil from Mol oil using Neotronics e-NOSE 4000

The subtraction of Castrol from Mol shows that sensor Type 263 responds more to Mol than Castrol and that Type 258 responds more to Castrol than Mol. These differences, although small, are significant. If a chemometrics package had been available it is likely that it would have shown that Mol is easily distinguished from Castrol.
Chapter 7: Conclusions and Further Work

7.1 Discussion of Objectives
   7.1.1 Evaluation of Electronic NOSES

7.2 Suggestions for Further Work
7.1 Discussion of Objectives

Devise a qualitative method to determine the PAH content of transformer oil

The first objective of the project was to find or develop a method to extract the PAHs from transformer oil. Despite the large number of extraction procedures in the literature detailing the extraction of PAHs from environmental samples, no accounts were found of their extraction from such highly refined mineral oils as transformer oil. There were extraction procedures found for other matrices also refined from crude oil, such as diesel, petroleum and lubrication oil. These methods were attempted with varying success. Ultimately, a method developed by Grimmer (Grimmer and Böhnke 1972) for extracting three-ring PAHs from lubrication oils was successfully adapted using solid phase extraction (SPE) to perform the required extraction.

The analysis using GC-MS was relatively straightforward. Once the chromatographic conditions were optimised for the separation of PAHs the extracts could be successfully analysed and compared. Alternatives to GC-MS for analysis of the PAHs were considered and are presented in the literature review. However, GC-MS seemed to be as appropriate as any technique. Future fingerprinting could be carried out using GC with a flame ionisation detector (FID), which is much less expensive, as it is not necessary to identify the individual peaks. National Grid also elected to pursue fluorescence detection of PAHs independently of this project.

The extraction efficiency of the method was determined on two separate occasions. An extraction of Castrol oil was performed with benzo[a]anthracene as an internal standard. The GC-MS was calibrated for benzo[a]anthracene with 9-bromofluorene as the external standard. Neither compound was found naturally occurring in Castrol oil. The extract from the liquid-liquid extraction step was found to contain 99% of the benzo[a]anthracene. After clean-up using SPE, the concentration had dropped to 79%.
Chapter 7: Discussion and Further Work

The extraction efficiency was also investigated using a coal tar standard purchased from NIST. The standard contained many PAHs from biphenyl and naphthalene to anthanthrene and coronene. The GC-MS was calibrated for all the PAHs and an extraction was carried out on the standard. The external standard was, once again, 9-bromofluorene. The average extraction efficiency was found to be 85% for 2- and 3-ring PAHs. Pyrene and chrycene were extracted at 80%. Coronene was not found in the extract.

Investigate the use of the PAH content as a fingerprint to distinguish between oils from different sources

National Grid uses oil supplied by Carless and Castrol (now combined to form EOS) and Nynas. Several oils supplied by these companies and spanning several years were fingerprinted and compared. In the early part of the project the Carless, and to a lesser extent Castrol, oils were found to be of varying composition. More recently oils supplied by all three companies were indistinguishable and it is perhaps significant that this occurred after National Grid let it be known that they were fingerprinting the oils. Nynas oils were consistent throughout the project.

A single oil supplied by Shell, which is produced for the UK market but not purchased by National Grid, was also fingerprinted. The resulting chromatogram was very different from the other three UK suppliers with a higher concentration of larger PAHs. This batch of oil had been sold as BS148 standard, but this fingerprint was used with other tests to prove it was poor quality and likely to fail in service in a transformer.

The fingerprinting technique was used in a round robin study within CIGRÉ, which is a collaborate research organisation that feeds in to IEC (International Electrotechnical Committee). The oils were supplied by members of CIGRÉ and came from various European countries. Some of these were inhibited paraffinic oils and were found to have few, small PAHs. Others were naphthenic but not from the same crude source as the UK naphthenic oils.
However, although three other laboratories took part in the study, only one member of
the CIGRÉ task force had used the extraction procedure correctly. The two sets of
fingerprints were very different and this may be attributed to the different column
lengths used. This would have had less effect if the temperature program only used a
single temperature ramp. The same member had also used the method to examine two
oils from the same supplier but with different characteristics, most noticeably in
viscosity and performance in oxidation stability tests. No difference was observed. It
would appear that the fingerprinting technique identifies the crude source but cannot
detect subtle changes in refining.

Identify the changes to PAH fingerprint as a result of ageing

Accelerated ageing experiments were set up to investigate the effects of heat,
electrical stress and ultraviolet radiation. The thermal experiments were designed to
exclude oxygen but it was eventually determined that heat with or without oxygen had
no effect on the PAH fingerprint.

Progressively more severe electrical experiments were performed to observe the effect
of electrical stress on the PAHs. The silent discharge and breakdown voltage test did
not have any effect on the PAH fingerprint. There was some suggestion that a few
PAHs had reduced slightly in concentration after the diverter service duty and
breaking capacity type test.

The effect of ultraviolet ageing on PAHs in transformer oil could not be investigated
properly. However, the photochemical cell clearly had an effect on the PAH
standards. It could be surmised that the PAHs in the transformer oil would be
likewise affected. The photochemical cell is very far from reality and may not be
considered to be a realistic ageing test for transformer oil.

At the start of this study, it had been surmised that the breakdown of PAHs in
transformer oil would occur during the ageing. Then the fingerprinting technique
could have been used to monitor the health of the transformer oil in service and act as an early warning for the end of its useful life before it could cause damage to the paper insulation. In practice it was found that the PAHs are so stable that the PAH fingerprint does not change during the service life of the oil in a transformer. Although this prevents the use of PAHs to characterise ageing, it does mean that the source of an oil can be identified even after it has been in service.

Further investigate the chemistry of ageing:

The degradation experiments did not have any effect of PAHs in transformer oil. Transformers are known to produce acid as a degradation product. No evidence was found in the literature of identification of the acids formed from transformer oil degradation. Acids would have damaged the column used for PAHs so they were esterified first. It was demonstrated that linear esters of between six and sixteen carbon atoms could be detected. The extraction of acids posed a similar problem to that of the extraction of PAHs. Several SPE methods were attempted and evidence of a few acids was found.

7.1.1 Evaluation of Electronic NOSES

The results of four different array-based sensor instruments, or Electronic NOSES, were reported. The first suffered a software problem and the results could not be reproduced. The results of the instruments are greatly enhanced by the use of chemometric software packages and other instruments on the market make use of artificial intelligence software. The raw data can be of use but it is not always obvious how best to display it to appreciate what the data is showing.

The NST instrument produced large quantities of data, but the software did not contain any means for displaying it. The metal oxide sensors that are susceptible to hydrogen containing species (MOSFET) were generally unresponsive to the mineral oils. The other metal oxide sensors (MOS), described as responsive to oxidising and reducing substances and also saturated hydrocarbons, were relatively more responsive, but the results were not particularly repeatable. The differentiation between oils from
different suppliers seemed to rely heavily on the magnitude of the response as the pattern of response was very similar for all the oils. All of the MOS sensors responded much more to the oxidised oil than to the unused oil.

The Birkbeck instrument uses conducting-polymer sensors; it was only used for a few samples. The advantage of chemometric analysis was clear. The unused oils clustered in their own areas and were well separated. The inclusion of the oxidised oil may have confused the picture too much but the oils were still clustered, but not well separated. The distinction between unused oils and their aged analogues was very good.

The Neotronics instrument also uses conducting polymer sensors. The data could be plotted in different ways but the chemometric analysis was not available. The sensors gave very similar responses to the naphthenic oils. The inhibited paraffinic oil gave a similar response but the differences could be seen.

7.2 Suggestions for Further Work

The fingerprinting method that has been developed achieves the original goal of producing a fingerprinting technique. It has several advantages over the original ‘Grimmer’ method:

- It is cheaper as it uses lower cost materials and smaller quantities of solvents
- It reduces the extraction time because SPE is much faster than column chromatography
- In the experience of this author it is more repeatable.

However, the extraction time is still too long to be a viable routine technique with a single sample taking approximately four hours. This fingerprinting technique could be used to validate future fingerprinting methods. The power of chemometrics as applied to the E-NOSE data suggests that it could be applied to a different technique to produce a more rapid fingerprinting technique. If it could be applied to the oil without pre-extraction it would be a very powerful technique.
The array-based sensor technology appears to have potential for the analysis of transformer oils. It would appear that polymer sensors are more appropriate than the metal oxide sensors. Ultimately, if the oil could be accessed, an instrument could be designed to monitor the condition of oil in a transformer without removing a sample. This could significantly reduce National Grid's maintenance costs.
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8.1 References

8.2 Bibliography
8.1 References

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"Transformer Book" 11ed., Franklin A.C. and Franklin D.P


APPENDIX A


Tests

Kinematic Viscosity

Flash Point

Pour Point

Appearance
Examine a representative sample of the oil in transmitted light under an oil depth of approximately 100mm and at ambient temperature. Oil must be clear and free from sediment and suspended matter.

Density
BS EN ISO 3675:1996: Crude petroleum and liquid petroleum products. Laboratory determination of density or relative density. Hydrometer method.

Neutralisation Value
Water Content

Anti-oxidant additives
BS5984:1980: Method for detection and determination of specified anti-oxidant additives in insulating oil

Oxidation Stability

Breakdown Voltage
BS EN 60156:1996: Insulating liquids – Determination of the breakdown voltage at power frequency – Test method

Dielectric Dissipation Factor
BS 5737:1979: Methods for the measurement of relative permittivity, dielectric dissipation factor and d.c. Resistivity of insulating liquids.

Gassing Tendency
BS 5797:1986: Method for measurement of the rate of gassing of cable and capacitor insulating oils under electrical stress and ionisation.

Total PCB Content
BS EN 61619:1997: Insulating liquids – Contamination by polychlorinated biphenyls (PCBs) – Method of determination by capillary column gas chromatography.

Total Furans
Polycyclic Aromatics
APPENDIX B

PAHs Identified in Selected Transformer Oils
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**APPENDIX C**

PAH Fingerprints of Unused Transformer Oils

<table>
<thead>
<tr>
<th>Code</th>
<th>Oil Type</th>
<th>Extract Type</th>
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<td>C1</td>
<td>Apar</td>
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<td>C2</td>
<td>Apar</td>
<td>PAH Extract</td>
</tr>
<tr>
<td>C3</td>
<td>Calumet</td>
<td>Liquid-Liquid Extract</td>
</tr>
<tr>
<td>C4</td>
<td>Calumet</td>
<td>PAH Extract</td>
</tr>
<tr>
<td>C5</td>
<td>Carless Transol 1994</td>
<td>Liquid-Liquid Extract</td>
</tr>
<tr>
<td>C6</td>
<td>Carless Transol 1994</td>
<td>PAH Extract</td>
</tr>
<tr>
<td>C7</td>
<td>Carless Transol 1995</td>
<td>Liquid-Liquid Extract</td>
</tr>
<tr>
<td>C8</td>
<td>Carless Transol 1995</td>
<td>PAH Extract</td>
</tr>
<tr>
<td>C9</td>
<td>Carless Transol 1996</td>
<td>Liquid-Liquid Extract</td>
</tr>
<tr>
<td>C10</td>
<td>Carless Transol 1996</td>
<td>PAH Extract</td>
</tr>
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<td>Carless Transol 1997</td>
<td>Liquid-Liquid Extract</td>
</tr>
<tr>
<td>C12</td>
<td>Carless Transol 1997</td>
<td>PAH Extract</td>
</tr>
<tr>
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<td>Carless Transol 1999</td>
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</tr>
<tr>
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</tr>
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<td>C15</td>
<td>Castrol BS148 1994</td>
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</tr>
<tr>
<td>C16</td>
<td>Castrol BS148 1994</td>
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<td>C17</td>
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<td>C18</td>
<td>Castrol BS148 1995</td>
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<td>C19</td>
<td>Castrol BS148 1996</td>
<td>Liquid-Liquid Extract</td>
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<td>C20</td>
<td>Castrol BS148 1996</td>
<td>PAH Extract</td>
</tr>
<tr>
<td>C21</td>
<td>Castrol BS148 1997</td>
<td>Liquid-Liquid Extract</td>
</tr>
<tr>
<td>C22</td>
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<td>PAH Extract</td>
</tr>
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<td>Castrol BS148 1999</td>
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<td>ESSO Univolt N52</td>
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<td>C29</td>
<td>Mol</td>
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<tr>
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<td>Nynas 10GBN 1994</td>
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<td>C31</td>
<td>Nynas 10GBN 1994</td>
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<td>Nynas 10GBN 1997</td>
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<td>C34</td>
<td>Nynas 10GBN 1997</td>
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<td>C41</td>
<td>Shell Diala B</td>
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<td>C42</td>
<td>Shell Diala B</td>
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</tr>
<tr>
<td>C43</td>
<td>Technol Y300</td>
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</tr>
<tr>
<td>C44</td>
<td>Technol Y300</td>
<td>PAH Extract</td>
</tr>
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</table>
Figure C1: Chromatogram of liquid-liquid extract from Apar oil
Figure C2: Chromatogram of PAH extract from Apar oil
Figure C3: Chromatogram of liquid-liquid extract from Calumet oil
Figure C4: Chromatogram of PAH extract from Calumet oil.
Figure C5: Chromatogram of liquid-liquid extract from Carless Transol (1994)
Figure C6: Chromatogram of PAH extract from Carless Transol (1994)
Figure C7: Chromatogram of liquid-liquid extract from Carless Transol oil (1995)
Figure C8: Chromatogram of PAH extract from Carless Transol oil (1995)
Figure C9: Chromatogram of liquid-liquid extract from Carless Transol oil (1996)
Chromatogram C10: Chromatogram of PAH extract from Carless Transol oil (1996)
Figure C11: Chromatogram of liquid-liquid extract from Carless Transol oil (1997)
Figure C12: Chromatogram of PAH extract from Carless Transol oil (1997)
Figure C13: Chromatogram of liquid-liquid extract from Carless Transol oil (1999)
Figure C14: Chromatogram of PAH extract from Carless Transol oil (1999)
Figure 15: Chromatogram of liquid-liquid extract from Castrol BS148 oil (1994)
Figure C16: Chromatogram of PAH extract from Castrol BS148 oil (1994)
Figure C17: Chromatogram of liquid-liquid extract from Castrol BS148 oil (1995)
Figure C18: Chromatogram of PAH extract from Castrol BS148 oil (1995)
Figure C19: Chromatogram of liquid-liquid extract from Castrol BS148 oil (1996)
Figure C20: Chromatogram of PAH extract from Castrol BS148 oil (1996)
Figure C21: Chromatogram of liquid-liquid extract from Castrol BS148 oil (1997)
Figure C22: Chromatogram of PAH extract from Castrol BS148 oil (1997)
Figure C23: Chromatogram of liquid-liquid extract from Castrol BS148 oil (1999)
Figure C24: Chromatogram of liquid-liquid extract from ESSO Univolt N52 oil
Figure C25: Chromatogram of PAH extract from ESSO Univolt N52 oil
Figure C26: Chromatogram of liquid-liquid extract from ESSO Univolt N53 oil
Figure C27: Chromatogram of PAH extract from ESSO Univolt N53 oil
Figure C28: Chromatogram of liquid-liquid extract from Mol oil
Figure C29: Chromatogram of PAH extract from Mol oil
Figure C30: Chromatogram of liquid-liquid extract from Nynas 10GBN oil (1994)
Figure C31: Chromatogram of PAH extract from Nynas 10GBN oil (1994)
Figure C32: Chromatogram of liquid-liquid extract from Nynas 10GBN oil (1995)
Figure C33: Chromatogram of liquid-liquid extract from Nynas 10GBN oil (1997)
Figure C34: Chromatogram of PAH extract from Nynas 10GBN oil (1997)
Figure C35: Chromatogram of liquid-liquid extract from Nynas 10GBN oil (1998)
Figure C36: Chromatogram of PAH extract from Nynas 10GBN oil (1998)
Figure C37: Chromatogram of liquid-liquid extract from Nynas 10GBN oil (1999)
Figure C38: Chromatogram of PAH extract from Nynas 10GBN oil (1999)
Figure C39: Chromatogram of liquid-liquid extract from Repsol Tension oil
Figure C40: Chromatogram of PAH extract from Repsol Tension oil
Figure C41: Chromatogram of liquid-liquid extract from Shell Diala B oil
Figure C42: Chromatogram of PAH extract from Shell Diala B oil
Figure C43: Chromatogram of liquid-liquid extract from Technol Y300 oil
Figure C44: Chromatogram of PAH extract from Technol Y300 oil
APPENDIX D

Physical, Chemical and Electrical Properties of Unknown Laborelec oils
Table 3.4: Physical, Chemical and Electrical characteristics of two unused oils from the same (unknown) supplier.

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Test Method</th>
<th>Sample A</th>
<th>Sample B</th>
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<tr>
<td><strong>Physical</strong></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Appearance</td>
<td></td>
<td>IEC60296</td>
<td>Clear</td>
<td>Clear</td>
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<tr>
<td>Colour</td>
<td></td>
<td>ISO2049</td>
<td>0.5</td>
<td>0.5</td>
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<tr>
<td>Density @ 20°C</td>
<td>kg/dm³</td>
<td>ISO3675</td>
<td>0.881</td>
<td>0.883</td>
</tr>
<tr>
<td>Flash Point (PMC)</td>
<td>ºC</td>
<td>ISO2719</td>
<td>146</td>
<td>142</td>
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<td>Cloud Point</td>
<td>ºC</td>
<td>ISO3015</td>
<td>&lt;42</td>
<td>&lt;42</td>
</tr>
<tr>
<td>Pour Point</td>
<td>ºC</td>
<td>ISO3016</td>
<td>&lt;51</td>
<td>&lt;57</td>
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<tr>
<td>Kinematic Viscosity @ 40°C</td>
<td>mm²/s</td>
<td>ISO3104</td>
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<tr>
<td>20°C</td>
<td></td>
<td></td>
<td>8.9</td>
<td>7.8</td>
</tr>
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<td>-15°C</td>
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<td>19.9</td>
<td>16.9</td>
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<tr>
<td>-30°C</td>
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<td>186</td>
<td>146</td>
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<td></td>
<td></td>
<td></td>
<td>876</td>
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<td><strong>Chemical</strong></td>
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<tr>
<td>Neutralisation Value</td>
<td>mgKOH/g</td>
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<td>Water Content</td>
<td>mg/kg</td>
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<td>Carbon Type Composition</td>
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<tr>
<td>Aromatic Hydrocarbons</td>
<td>%</td>
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<td>14.7</td>
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**Gassing Tendency (+ = gas evolving; - = gas absorbing)**

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APPENDIX E

Photochemical degradation products of Toluene, Fluorene and Pyrene
The following compounds were identified by GC-MS after toluene was aged for 120 hours in the photochemical cell described in Chapter 4:

- Benzyl alcohol
- Benzoic Acid
- 2-Methyl-1,1'-biphenyl
- 2,2'-Dimethyl-1,1'-biphenyl
- 3,3'-Dimethyl-1,1'-biphenyl
- Phenyl acetic acid
- 1-Methyl-2-phenylmethoxybenzene
- Benzyl ether
- 1,2-Diphenylethanol
- Benzylbenzoate
- Phenylbenzoate
- 2-Hydroxy-5-methylbenzophenone
The following compounds were identified by GC-MS after fluorene (in cyclohexane) was aged for 120 hours in the photochemical cell described in Chapter 4:

9H-Fluorene

Fluoren-9-one

Diphenylmethane

Dibenzonfuran
The following compounds were identified by GC-MS after fluorene (in toluene) was aged for 120 hours in the photochemical cell described in Chapter 4:

- Pyrene
- 3,4-Dihydropyrene
- 4H-Cyclopenta[def]phenanthrene
- Phenanthrene
- Fluoranthene
- 1H-1-Phenylmethylene indene
- 1-Phenynaphthene
APPENDIX F

Related Publications and Reports

*Fingerprinting of Transformer Oils by GC-MSD* – Report for CIGRE 15.01.06 ‘Study of techniques for fingerprinting oils (A)

*Mineral Insulating Oil Fingerprinting: A Tool for maximising Oil Filled Equipment Lifetime* – CIGRE 2000 Publication (B)

*Classification of Transformer Oils from Fluorescence Measurements Using Chemometrics and Artificial Neural Networks* – Submission to Analytical Chemistry (C)

*The Effect of Arcing on the PAH Fingerprint* – National Grid internal report (D)

*Maximising Information: Application of Chemometrics to GC-MS Data* – Report by Henryk Herman for National Grid using GC-MS fingerprinting data (E)
CIGRE 15.01.06

Study of techniques for fingerprinting oils

Third meeting, Leatherhead 15/1/99

FINGERPRINTING OF TRANSFORMER OIL BY GC-MSD

Bruce Pahlavanpour and Gordon Wilson
Appendix F

Fingerprinting of Transformer Oils by GC-MSD

Introduction

At the last meeting of CIGRE 15.01.06 in Slovenia, a Round Robin study of transformer oils was agreed upon using GC-MSD (gas chromatography-mass selective detection) and HPLC (high performance liquid chromatography). This report describes the extraction procedure for the GC-MSD and the results obtained by the National Grid Company Plc.

Equipment and Samples

The work was carried out on a Hewlett Packard (HP) GC5890 Series 2 with an HP MSD 5971A detector. The column was an HP5-MS (cross-linked methyl silicone gum – 30m x 0.25mm x 0.25µm film thickness). The software package, Enhanced Chemstation G1701AA V3, was used to control the GC and analyse the results.

The solid phase extraction (SPE) cartridges used were Waters’ SepPak Plus silica (690mg) and C18 (360mg). The AnalaR cyclohexane was provided by Rathburn Chemicals, and the AnalaR DMF (dimethyl formamide) by BDH. The magnesium sulphate was supplied by Fischer.

Members of the CIGRE 15.01.06 group provided the samples for analysis and were as follows:
A (SEA-Marconi - before reclamation)
B (SEA-Marconi - after reclamation)
ESSO Univolt 52
Mol
Nynas 10GBN
Repsol Tension
Technol Y3000

Note: SEA Marconi oils were sent in four syringes labelled A1, A2, B1 and B2. A1 and A2 were assumed to be the same, likewise B1 and B2. Oil from A2 and B2 was analysed.

Experimental Procedures

Extraction

Liquid – Liquid Extraction: Cyclohexane (20cm³), DMF (45cm³) and de-ionised water (5cm³) are shaken together with a 5g sample of the oil in a 100cm³ separating funnel. The upper (organic layer is discarded). The aqueous layer is added to water (40cm³) and cyclohexane (90cm³) in 250cm³ separating funnel. The funnel is shaken and the lower aqueous layer is discarded. The organic layer is washed twice with water (15cm³).

Appendix F

The organic layer is then dried with magnesium sulphate and gravity filtered before being concentrated under reduced pressure.

SPE clean-up: The sample is made up to 1 cm³. Two silica SepPak Plus cartridges are joined together and preconditioned with cyclohexane (10 cm³). The sample is loaded onto the top of the cartridges and the eluting solvent is discarded. Cyclohexane is eluted through the cartridges at approximately 10 cm³ min⁻¹. The first 5 cm³ fraction is discarded and the second fraction is retained. The sample is concentrated to 0.5 cm³ under reduced pressure. A single C₁₈ cartridge is preconditioned with cyclohexane (5 cm³). The sample is loaded onto the cartridge and the eluting solvent discarded. The sample is removed from the cartridge by cyclohexane (1 cm³) flowing at approximately 5 cm³ min⁻¹.

Chromatographic Analysis

For each PAH extraction analysis, 0.1 μl is injected into the split/splitless injector. The He flow is kept at 40 cm³ min⁻¹ and the split/splitless ratio is 20:1. The injector temperature remains at 290°C and the detector is at 310°C. The initial oven temperature is 90°C, which is maintained for four minutes. The detector is bypassed for the first three minutes so that the solvent peak does not damage the filament. After four minutes, the oven temperature increases at 12.5°C min⁻¹ for four minutes (i.e. to 140°C). The temperature then increases at 2.5°C min⁻¹ for 32 minutes (i.e. to 220°C). The final gradient returns to 12.5°C min⁻¹ for another four minutes (i.e. to 270°C). The final temperature is held for five minutes.

Results

The seven samples were analysed using the previously described method. The chromatograms are shown together on the next page. They are shown separately, in more detail in Appendix I.

NB. The liquid-liquid extracts were also analysed using GC-MSD. This has been shown to be useful for comparing oils in some cases. These results are shown in Appendix II.

Peak Analysis of the Chromatograms

The main advantage of mass selective detection over other GC detectors is the ability to easily identify the compounds in a chromatogram. Chemstation software allows a report to be produced listing all the compounds found in a chromatogram and an indication of the certainty of the identification. Experience has shown that peaks can be more exactly identified individually, but for this report the automatic identification was used on each chromatogram.
The extraction method is known to separate PAHs from the oil, it also extracts groups of compounds which are not strictly poly-aromatic, namely Naphthalenes, Biphenyls, Phenyl-indenes, Fluorenes and Dibenzothiophenes. A summary of the compounds found in each oil can be found in Appendix II (along with mass spectra for the two identified inhibitors).

**Discussion of the Results**

**Initial Comparisons of the Chromatograms**

The two chromatograms of SEA Marconi oil are clearly very similar. The reclamation appears to have left the fingerprint unchanged. The chromatograms of the Nynas, Repsol, Esso and SEA Marconi oils all have their own characteristic set of peaks which could be described as a fingerprint.

The chromatograms of Mol and Technol Y3000 are overwhelmed by the amount of inhibitor in the oil. The inhibitor peak can be removed or the software can be made to focus in on the considerably smaller peaks. Focusing in on these chromatograms shows them to be very similar to each other and very different from the other five oils.

**Comparisons of the content of PAHs**

It can be clearly seen in the chart in Appendix II that the two oils from SEA-Marconi contain very similar compounds. The liquid-liquid extractions appear to show greater difference between the two oils. It is interesting to note that 1,2,4-trichlorobenzene was found to be present in the liquid-liquid extract of the unreclaimed sample.

The inhibitor in Mol and Technol chromatograms can be easily identified as a phenol. However, the Technol sample appears to have fewer of the higher molecular weight aromatics this could account for the presence of a second inhibitor identified in the liquid-liquid extract of Technol oil (a methylenebis phenol).

As expected, the chemical compounds present in the oils are characteristic. For example: Nynas has no anthracene structures and no dibenzothiophenes, which are common in most of the other samples. Technol Y3000 contains no biphenyl structures and the Repsol sample has no naphthalenes at all, but has many dibenzothiophenes. ESSO Univolt also has many dibenzothiophenes, but no pyrene or chrysene. The SEA Marconi oils contain a significant amount of each group of compounds.

Displaying the distribution of compounds (as in Appendix III) has potential as a fingerprint. However, it would need to be combined with some form of quantitation.

**Conclusions**

This method of extraction and chromatographic analysis is capable of distinguishing between oils from different companies. It has shown the two oils from SEA-Marconi to be from the same source. The PAH extraction seems unable to conclusively...
differentiate between the two oils, however the liquid-liquid extractions are similar but not the same.

The fingerprinting technique has also identified that the Mol and Technol oils are from the same original source, but they are not the same oil, probably due to different refining conditions.

One unexpected result has been that the method can identify any inhibitors present. However, the liquid-liquid extract had to be analysed to detect the second inhibitor in Technol.
Appendix F1
Appendix F

File: C:\HPCHEM\DATA\PHDRES-1\CIGRE\PAHEXT-1\CTENSION.D
Operator: G.Wilson
Acquired: 20 Oct 1998 11:08 using AgcMethod CIGRE1
Instrument: GC/MS Ins
Sample Name: CIGRE - Technol Y3000 PAH extract
Misc Info: Solvent: Cyclohexane
Vial Number: 1
Appendix F

File: C:\HPCHEM\DATA\PHDRES~1\CIGRE\LIQ-LI~1\CA2.D
Operator: G. Wilson
Acquired: 1 Oct 1998 9:43 using AcqMethod GORDON1
Instrument: GC/MS Ins
Sample Name: CIGRE - SEA-Marconi (A) liquid-liquid extract
Misc Info: Solvent: Cyclohexane
Vial Number: 1

[TIC: CALD]

Abundance

Time->

0 500000 1000000 1500000 2000000 2500000 3000000 3500000 4000000 4500000

4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00 36.00 38.00 40.00 42.00 44.00 46.00 48.00
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Operator : G.Wilson
Acquired : 1 Oct 1998 8:50 using AcqMethod GORDON1
Instrument : GC/MS Ins
Sample Name: CIGRE - SEA-Marconi (B) liquid-liquid extract
Misc Info : Solvent: Cyclohexane
Vial Number: 1

Abundance

TIC: CB2.D

Time (min)
Appendix F
Appendix F

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Instrument: GC/MS Ins
Sample Name: CIGRE - Nynas liq-liq extract
Misc Info: Solvent: Cyclohexane
Vial Number: 1
Appendix F

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Abundance
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Appendix F

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![Graphical representation of the molecular structure](image-url)
MINERAL INSULATING OIL FINGERPRINTING: A TOOL FOR MAXIMISING OIL FILLED HV EQUIPMENT LIFETIME

G. WILSON and B. PAHLAVANPOUR
The National Grid Company plc
United Kingdom

ABSTRACT

Developments in transformer and other oil-filled equipment design have allowed a reduction in the amount of oil required. The resultant increase in stresses on the oil means that it is now a more critical component of the insulation system, particularly at higher voltages. This increased stress may lead to a reduction in the effective service life of the oil and without remedial action, any reduction in the oil’s properties may cause damage to the equipment itself. It is hoped that by understanding the chemical nature of the oil it is possible to make the equipment last longer either by better selection of the oil or by more accurate condition monitoring. A ‘fingerprinting’ technique has been developed to help distinguish between good and bad oils.

This paper describes the method used for fingerprinting oil based on extraction of the PAH (polycyclic aromatic hydrocarbon) fraction and subsequent GC analysis. This method has shown potential for determining which oils are not suitable for use in transformers and other HV equipment.

The analysis of the PAH fraction also allows for improvements to be made in the labelling, handling and disposal of oil to reduce health risks.

1. INTRODUCTION

Over the years, there have been significant advances in the engineering of transformers and insulating systems leading to smaller designs and a reduction in the amount of oil used. Whereas 80 years ago there were seven litres of oil for each kVA it is now less than half a litre. With less oil the requirements upon it have increased and its performance is under closer scrutiny. Developments in refining processes have improved the properties of the oil, although it is essentially the same as the oil that was used a century ago. Further developments of the oil could be achieved by understanding which components of the oil are beneficial and which are detrimental. This would enable oils to be produced which would last longer in service and, consequently, lengthen the life of oil-filled equipment. Another benefit of understanding the components better would mean that the way in which they change during service could be monitored. Monitoring components which change means that the equipment can be run for as long as possible before removing it from the system and maintenance can be more accurately scheduled.

The prevailing emphasis in oil specifications and testing is to establish its electrical, physical and general chemical properties and to decide whether it is capable of insulating and cooling HV equipment. Clearly, this is necessary but it does not provide for the oil continuing to perform as an insulator in service. How the oil changes over time and in different conditions is defined by its molecular chemistry. Oxidation stability testing can perform a limited assessment of oil performance and sulphur content has also proved to be of use, however the chemical structures in the oil have been largely ignored by HV equipment users.

A refined mineral oil, such as insulating oil, typically contains around 3,000 different hydrocarbon

*Figures quoted are for distribution transformers. Values for transformers used for transmission are lower.

*THE NATIONAL GRID COMPANY Plc – Kelvin Avenue, Leatherhead, KT22 7ST, UK
compounds of which only about 10% have been individually identified\(^1\). These compounds are commonly divided into three main groups: paraffinic, naphthenic and aromatic. The relative amount of carbon in each group can be measured to give a gross characterisation of the oil and an indication of the oil's ability to absorb gas. It can also be used to determine whether the crude oil was naphthenic or paraffinic, although this may be better determined by LT-DSC (low temperature – differential-scanning calorimetry). A more detailed knowledge of the compounds in the oil would allow the selection of the compounds of greatest benefit to oil stability and performance and also the elimination of those which can cause harm to the HV equipment. These harmful compounds may be present in unused oil or produced as a result of degradation processes; in this case the precursors could be eliminated before degradation.

Fingerprinting is a term applied in many areas of chemical analysis; it is usually a means of recognising the source of a material. Fingerprinting involves the identification of a compound or compounds which are characteristic of a sample. Fingerprinting transformer oil should lead, initially, to the categorising of oils which experience has shown to be particularly stable or unstable. However, it may also lead to the identification of compounds critical to the performance or properties of oil. Optimisation of oil in this fashion will lead to the extension of its useful life and, consequently, the useful life of oil-filled HV equipment.

2. EXPERIMENTAL

The class of compounds identified as being most suitable for fingerprinting and most likely to yield useful information about transformer oil was the polycyclic aromatic hydrocarbons (PAHs). The concentration of PAHs in insulating oil is carefully considered in the refinery process. The presence of PAHs improves the ability of an oil to absorb gases produced in a transformer. This positive effect has to be balanced against the negative impact of PAHs on impulse breakdown. The PAH fraction is typically less than 1%.

This class of compounds has also been identified by the Environmental Protection Agency (EPA) as containing some compounds which are hazardous to human health. It would be preferable to remove these compounds from insulating oil. However, as mentioned PAHs improve the gas absorbency of oil and they are also known to act as natural oxidation inhibitors, so their removal would be detrimental. Therefore, it would clearly be useful if PAHs could be measured and monitored.

2.1 Extraction of PAHs

There is a standard test method, BS2000 Part 346, for the analysis of the total polycyclic aromatic (PCA) content of transformer oil\(^2\). This is carried out to assess the carcinogenicity of unused oil. PAHs and PCAs are commonly used interchangeably but PAHs differ from PCAs in that all the aromatic rings in PAHs are fused and have at least 3 rings. It has also been suggested that, while the standard method gives valuable information about carcinogenicity, it does not give an accurate value for PCA content\(^3\). BS2000 Part 346 was not used for fingerprinting.

Grimmer\(^4\) describes a method known to be capable of extracting PAHs from transformer oil. The 'Grimmer' method involves extraction by liquid-phase transfer and clean-up by chromatography. The procedure is both labour-intensive and expensive in terms of materials. Careful choice of solvents and replacement of column chromatography by solid-phase extraction have developed this method so that it is much quicker and cheaper to perform.

2.2 Liquid – Liquid Extraction

Cyclohexane (20cm\(^3\)), DMF (45cm\(^3\)) and de-ionised water (5cm\(^3\)) are shaken together with a 5g sample of the oil in a 100cm\(^3\) separating funnel. The upper (organic layer is discarded). The aqueous layer is added to water (40cm\(^3\)) and cyclohexane (90cm\(^3\)) in 250cm\(^3\) separating funnel. The funnel is shaken and the lower aqueous layer is discarded. The organic layer is washed twice with water (15cm\(^3\)). The organic layer is then dried with magnesium sulphate and gravity filtered before being concentrated under reduced pressure.

2.3 SPE clean-up:

The sample is made up to 1cm\(^3\). Two silica cartridges are joined together and preconditioned with cyclohexane (10cm\(^3\)). The sample is loaded onto the top of the cartridges and the eluting solvent is discarded. Cyclohexane is eluted through the cartridges at approximately 10cm\(^3\) min\(^{-1}\). The first 5cm\(^3\) fraction is discarded and the second fraction is retained. The sample is concentrated to 0.5cm\(^3\) under reduced pressure.

A single C\(_{18}\) cartridge is preconditioned with cyclohexane (5cm\(^3\)). The sample is loaded onto the cartridge and the eluting solvent discarded. The sample is removed from the cartridge by cyclohexane (1cm\(^3\)) flowing at approximately 5cm\(^3\) min\(^{-1}\).

2.4 Chromatographic Analysis

The work performed at The National Grid Company plc has involved the use of gas chromatography (GC) coupled to a mass selective detector (MSD). This provides information about the actual PAHs in the transformer oil; a flame-ionisation detector (FID) would be expected to produce identical fingerprints of the extracts.
For each PAH extraction analysis, 0.1μl of the extract is injected into the split/splitless injector. The helium flow is kept at 40cm³ min⁻¹ and the split/splitless ratio is 20:1. The injector temperature remains at 290°C and the detector is at 300°C. The initial oven temperature is 90°C, which is maintained for two minutes. The detector is bypassed for the first three minutes so that the solvent peak does not damage the filament.

After two minutes, the oven temperature increases at 12.5°C min⁻¹ for four minutes 48 seconds (i.e. to 150°C). The temperature then increases at 1°C min⁻¹ for 30 minutes (i.e. to 180°C). The final gradient returns to 12.5°C min⁻¹ for another seven minutes and twelve seconds (i.e. to 270°C). The final temperature is held for five minutes.

![Figure 1: Temperature Program for GC-MSD for PAH Extract Analysis](image)

The chromatograms of the PAH extracts are considered to be fingerprints of the original oils. Different fingerprints can be overlaid in order to make comparisons. The peaks within the fingerprints can be matched to the compounds they represent by their mass spectra.

3. RESULTS AND DISCUSSION

3.1 Paraffinic vs. Naphthenic oils

The PAH fingerprint is affected most by the original source of the oil. Paraffinic and naphthenic transformer oils have markedly different profiles when analysed using this method. Typically, paraffinic oils have fewer PAHs, especially the smaller structures. Paraffinic oils usually contain additives, which are extracted by this method.

![Figure 2: Comparison of Typical Naphthenic and Paraffinic (additive removed) Oils.](image)

This has proved useful in the analysis of oils produced by a new manufacturer. Successive oil samples were claimed to be naphthenic and carbon typing carried out by the supplier indicated this was the case. Carbon typing carried out by NGC disagreed with the results of the supplier. PAH fingerprints of the oils showed they were, in fact, paraffinic in nature and also inhibited.

![Figure 3: Example of Oil Claimed to be Naphthenic.](image)

3.2 Identification of Bad Oil

If a particular batch of oil is shown by experience to perform badly in service it is necessary to identify the equipment containing the oil. It is not always possible to trace the source of oil in a transformer and even harder to locate all pieces of equipment containing the same oil.

It is not practical to fingerprint the oil from every piece of equipment, as it would take too long and be very expensive. However, oils suspected of causing a fault can be tested to compare with those that are known to be deficient in some way. An oil known to produce sludge in certain types of electrical equipment after a short period of time in service has been identified. Comparison of its PAH fingerprint with those of unused samples has enabled the identification of the original supplier. This means that other equipment suspected of containing the same oil could have the oil fingerprinted and, if necessary, replaced before sludging occurs.
Several oils from various sources have been fingerprinted and matched to the poor quality oil. In some cases the oil appears to have been blended or had certain components removed.

Because of the time involved in carrying out a fingerprint, it would be helpful if a more rapid method could be used to identify oils which may also cause sludging problems. The carbon composition of oil does not give a fingerprint but it can be used to distinguish oils which are clearly different. The majority of NGC transformers have had their oil analysed for carbon composition; analysis of these results can identify oils that are the same or similar. Further comparison with oils known to be of poor quality reduces the number of oils that need to be fingerprinted.

However, it is not yet certain whether the carbon composition remains constant throughout the service life of an oil. Whereas the fingerprint is believed to be unchanged even under very harsh conditions.

3.3 Year-by-Year Consistency

In addition to identifying bad oils already in service there is also a need to ensure the continued quality of the supply of unused oils. It is not possible to fingerprint oil before it is put into a transformer as an oil usually needs to be accepted at the site so the tests must be relatively quick and portable. However, random samples of unused oils are chosen each year from suppliers to the British market to be fingerprinted. In this way, the oil can be monitored for major changes, which may affect the performance.

Some oil supplied has been very consistent over the last five years and some has been more variable. More recently an improved consistency of supply has been observed.

3.4 Prediction of Oil Properties

The nature of the data which produces a PAH fingerprint lends itself relatively easily to manipulation by chemometrics. A limited study of PAH fingerprint data by chemometrics has been carried out. Using principal component regression (PCR), the PAH fingerprint has been shown to correlate to certain properties of the whole oil. Physical properties such as density, refractive index and viscosity can be predicted as can the total sulphur content.

4. CONCLUSIONS

The application of a fingerprinting technique to transformer oil has proved beneficial to oil forensic work. By examining the PAH fingerprint, the source of the crude oil can be identified and gross changes in refining can be observed.

Subtle changes in refining do not cause a significant change to the PAH profile as they are very stable. This stability is useful because it means that the PAH fingerprint remains unaffected by most of the conditions or treatment that a transformer oil experiences e.g. high temperature, electrical stress, reclamation etc.

The fingerprint of an unknown oil can be compared to those of oils with known in-service performance, and if an adequate match is found its likely performance can be predicted. This is especially important if they are shown to match oils which are known to perform badly in service. Once identified, these oils can be dealt with appropriately before they cause irreparable damage to the HV equipment.

Chemometric analysis of the GC-MSD data has shown that the PAH fraction can be correlated to physical and chemical properties of the whole oil.

5. FURTHER WORK

A great deal of work is planned in this area. This will be carried out in conjunction with other members of CIGRE working group 15.01.06 as well as National Grid Company plc. It is hoped that PAH fingerprinting will be performed more quickly, perhaps using a different analytical technique, whilst providing the same information.

Further work on the interpretation of the PAH fingerprints will involve:

1. Relation of particular compounds to oxidation stability of the whole oil. Determining which PAHs contribute to the oxidation stability of the oil and therefore increase the lifetime of the oil and hence that of HV equipment in service.
2. Relation to gas absorbency of the whole oil and identification of compounds which may be particularly beneficial to the absorption of gas.
3. Further chemometric analysis to identify relationship between PAHs in oil and physical and electrical properties of the whole oil.
Correlation with carcinogenicity of whole oil and quantification of total and individual carcinogenic PAHs. This will allow oil to be properly labelled according to the health risk it poses to those who come into regular contact with it.

6. ACKNOWLEDGEMENTS

This work forms part of the PhD thesis by Gordon Wilson at the University of Surrey under the supervision of Dr Roger Bolton to whom acknowledgement is due.

The involvement of colleagues at the National Grid Company plc and the members of CIGRE 15.01.06 is also appreciated.

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Classification of Transformer Oils from Fluorescence Measurements Using Chemometrics and Artificial Neural Networks

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Abstract

This paper describes the evaluation of fluorescence spectroscopy as a means of classifying mineral insulating oils used in high-voltage electrical equipment. Principal component analysis (PCA) and artificial neural networks (ANNs) are used to investigate the value of fluorescence spectra for the determination of oil type, manufacturer, regulatory conformance and age. The work was carried out in two stages, on two batches of oils. The first batch consisted of twelve oils subjected to a short period of use in new transformers. These twelve oils are representative of transformer oils supplied to National Grid Company plc (NGC) in 1994. The second batch was of 68 oils, comprising mostly of oils of unknown origin taken from transformers, but also some unused and reconditioned oils. PCA proved to be a useful tool for exploring databases of oil fluorescence spectra, although it did not provide the resolution necessary to identify individual oils from their spectra. However, an ANN was found to be able to achieve this goal for the first batch of twelve oils. Preliminary examination of the fluorescence data obtained from the second batch of oils suggests that the spectra can be used to determine whether or not an oil has been used and that it is possible to distinguish between oils which meet required specifications and those that do not. A clear correlation between spectra and oil colour, which can be an indication of oil degradation, was also found.

Keywords: Transformer oil, fluorescence spectroscopy, principal component analysis, artificial neural networks.
Introduction

Oil is used for insulation and cooling in high-voltage electrical transformers. Power transformers are expected to last for at least forty years and since oil has been used for this purpose for a hundred years there are a vast array of different transformer oils to be found even within an electricity distribution network operated by a single organisation. The oils in use vary widely in origin, age, manufacturer, and consequently in chemical composition. This results in oils which initially pass the specifications but then perform differently in service. Ideally, a procedure capable of yielding a complete characterisation of the chemical composition of an oil would lend itself to the decision-making process especially where certain chemical properties could be directly related to key operational characteristics, such as resistance to oxidation. In practice however, this would be an extremely ambitious task, almost certainly requiring large amounts of time and a mélange of analytical techniques. Even determining a few key components of oil can be difficult, for example polyaromatic hydrocarbons (PAHs). PAHs are found naturally in mineral oil and have been analysed because they have an important effect on the electrical performance of transformer oil and on its stability, they are also of environmental concern. Current techniques are limited to a standard test method for measuring the total content of polycyclic aromatics (1) in unused oil and a qualitative procedure involving liquid-phase partition and solid-phase extraction with subsequent analysis by GC-MS (2).

An alternative way of approaching the problem is to liken an oil of unknown history to an oil with known origin and performance characteristics by comparing multivariate
measurements that yield sufficient information to enable an accurate comparison to be made. This suggested the use of a suitable spectroscopic technique capable of characterising the complex transformer oil matrix. For UV/visible excitation wavelengths at room temperature, the fluorescence emission of transformer oil is due to the presence of numerous aromatic structures. These structures range from alkylated monoaromatics through substituted polyphenyl compounds to fused unsubstituted and substituted polyaromatic structures. All of these types of compounds have particular regions of the UV/visible waveband at which they tend to absorb and emit electromagnetic energy, depending on the arrangement of the rings contained within the molecule and whether or not they are fused. Spectrofluorimetry has been widely used in the characterisation of hydrocarbons in environmental analysis (3-7) and in process monitoring applications (8,9) and the technique was adopted in this work.

The multivariate signals generated by spectroscopy present more of a challenge for interpretation than univariate signals, but the additional data available in such signals has much greater potential for extracting information and differentiating between responses. Of the many mathematical techniques that have been developed for the analysis of multivariate data, there are two major types: unsupervised and supervised. Unsupervised techniques, such as principal component analysis (PCA), allow visualisation and clustering of unseen responses and are useful for initial exploration of data. Supervised techniques, such as multivariate regression and feed-forward artificial neural networks (ANNs) are trained on known analytical responses. In the case of ANNs, this allows unseen responses to be classified into previously defined groups.
The aim of this work was to investigate the use of PCA to explore the relationship between the multivariate analytical signals provided by fluorescence spectroscopy. Artificial neural networks (ANNs) were then evaluated for their ability to classify oils into pre-defined groups according to their fluorescence spectra. PCA has been used several times for the analysis of fluorescence spectra (10-14). ANNs are frequently used for classification and calibration of spectra (15,16), although application to fluorescence data (17,18) is not widely reported in the literature.

The work was carried out in two stages on different batches of oils. The first batch consisted of twelve oils subjected to a short period of use in new transformers. These twelve oils are representative of transformer oils supplied to National Grid Company plc (NGC) in 1994. The aim of this part of the work was to determine to what extent the fluorescence spectra are related to the oil type and manufacturer, and to try to devise a way of identifying individual oils or manufacturers from the spectral signatures. The second batch was of 68 oils, comprising mostly of oils of unknown origin taken from transformers, but also some unused and reclaimed oils. This enabled the effects of ageing on the fluorescence spectra of the oils to be investigated. Additionally, the second batch of oils included some from mainland Europe. These samples were analysed to determine whether they could be distinguished from oils which comply with British specifications (19).

**Experimental**

Transformer oils

All oils were supplied by National Grid Company Plc (Leatherhead, UK).
Acquisition of fluorescence spectra for oils

**Synchronous Scanning Measurements:** All fluorescence measurements were carried out using an Instruments SA Fluoromax II spectrofluorimeter. This is a completely automated instrument using single-grating monochromators for excitation and emission wavelength regulation. The standard scan used for oil classification was a synchronous scan with a wavelength interval, $\Delta \lambda$, of 4nm. This is not a straightforward type of scan, such as the emission scan where one monochromator is fixed and the other scanned, rather it involves scanning both emission and excitation simultaneously, with the emission detection set at a wavelength always 4nm longer than the excitation wavelength. This produces a two-dimensional spectrum giving an indication of fluorescence response of the sample for a range of excitation wavelengths. For this study, fluorescence was recorded for excitation between 250nm and 500nm.

**Fluorescence Collection Method:** Fluorescence collection was performed in reflectance (180°) mode in order to minimise sample reabsorption. The tendency with concentrated samples is for fluorescence occurring at shorter wavelengths to be reabsorbed very effectively within the body of a liquid sample. Collecting emission from the surface of a sample means that the light travels through only a very small fraction of the sample, reducing reabsorption to a minimum.

**Cuvettes:** It was necessary that the cuvette material was as near transparent as possible in the UV part of the spectrum, making UV fused quartz cuvettes the obvious choice. However, the high sample throughput necessary to generate the large databases of spectra required in this work would prohibit this type of cuvette due to the high unit cost and rigorous and time consuming cleaning method required between each new sample. Hence it was decided that disposable UV methacrylate cuvettes would be used for all
measurements, and these would be used for one sample and then discarded. The reduced precision in signal observed from the use of methacrylate cuvettes was countered by taking a fluorescence measurement through each of the cuvette's four faces, so that the typical variations could be taken into account by PCA and the ANNs.

Data analysis

Data analysis was performed under the Windows 98 operating system (Microsoft, USA) on a 333MHz Pentium II PC with 128MB of SDRAM (Dell, Republic of Ireland). Exploratory data manipulation and visualisation was carried out in Matlab 5.2.1 (Mathworks, USA). PCA was carried out using PLS Toolbox 1.5 for Matlab (Eigenvector Research, USA). Neural networks were trained and simulated using the Matlab Neural Network Toolbox 3.0 (Mathworks, USA). For convenience, all data interpretation was performed off-line, separately from the fluorescence measurements, although the two activities could be integrated on the same PC, or in a dedicated microcontroller in an integrated instrument, at a later date.

Data Analysis Methods

The two primary data analysis methods used to analyse the oil spectra were principal components analysis (PCA) and artificial neural networks (ANNs). These techniques are introduced very briefly below. Much more thorough descriptions can be found in the large amount of literature available.

Principal Components Analysis

The main aim of PCA is to reduce a large number of variables to a much smaller number of principal components (PCs) which capture the vast majority of variance in the data (20). This reduces the dimensionality of data considerably, enabling effective
Appendix F

visualisation, regression and classification of multivariate data (21). PCA relies on the fact that a data matrix, $X$, can be decomposed into a matrix of scores, $T$, and loadings, $P$, such that,

$$X = T \cdot P$$  \hspace{1cm} (1)

Many methods are available for decomposing the data matrix, the most popular being the NIPALS algorithm (22), which extracts one PC at a time, in order of significance. Typically, there is a great deal of correlation and redundancy in analytical responses so a small number of PCs is often sufficient to describe a large data set. By reducing instrumental responses comprising a large number of variables, $p$, to a smaller number, $n$, of principal components, each response can be represented as a point in $n$-dimensional PC space, and if $n$ is less than four, these points can be conveniently visualised. In a successful analysis, responses appear in distinct clusters in PC space according to their classification and the space can be divided into regions associated with the different classifications.

**Artificial Neural Networks**

Although many different types of ANN have been developed (23,24), the vast majority of calibration and classification applications are most amenable to a multilayer feed forward network (25,26), and this is the type used here. The analytical uses, operation and training of such a network are documented in detail elsewhere (27,28). In short, a feed forward network becomes, after sufficient training, a model able to map responses presented to it to a corresponding set of outputs. If enough training data is provided and the network is not overtrained, the model will be sufficiently generalised to map unseen responses to appropriate outputs.
The basic ANN processing element is the neuron, shown in Figure 1, which is loosely based on the design of biological neurones (29). Inputs $a_1..a_n$ are multiplied by corresponding weights, $w_1..w_n$, then summed together with a bias, $b$, before being mapped to an output, $t$, by a transfer function, $f$, which is selected according to the application. This process is summarised in Equation 2.

$$t = f(b + \sum_{i=1}^{n} w_i a_i)$$  \hspace{1cm} (2)

A multilayer feed forward network consists of two or more layers of such neurons, with weighted interconnections from each neuron to every neuron in the next layer. Network training comprises adjusting the network weights and biases to give the most accurate model possible between the input and output pairs in the training data. This is most commonly achieved using back propagation of errors (30,31), for which there are many different algorithms. The simplest method uses *gradient descent*, an iterative process where the weights and biases are moved in the direction which gives the most rapid decrease in the discrepancy between the actual and desired outputs. Each iteration of this process is referred to as an *epoch*. There are various refinements designed to improving the performance of the training, including adaptive learning rate and momentum. Detailed descriptions of training schemes are ubiquitous in the reviews and tutorials on neural networks (23,26,28).

**Results**

The synchronous scan only collects fluorescent emission from the waveband where the absorption and emission bands of a species *overlap by the specified wavelength interval*. This reduces the complexity of absorption and fluorescence spectra of a species into a
single trace, often with one main fluorescence component present in the form of one peak. For mixtures of fluorescent species, each fluorophore is represented by its own peak, although if very many species are present the distinction becomes less clear as in the case of transformer oil. In addition, fluorophore concentration greatly affects the spectrum. At low concentrations the intensity of fluorescence is directly proportional to the concentration of a fluorophore, but at higher concentrations a degree of reabsorption occurs, so that the intensity read at the detector is less than might be expected. This reabsorption is not uniform over the entire peak. Rather, the shorter wavelengths are preferentially reabsorbed over longer wavelengths. However, these aspects were not considered a problem for the purposes of this work, as a quantitative determination of each individual species present was not the aim. The use of reflectance measurements vastly reduced quenching problems compared to the more conventional right angle fluorescence collection method. Examples of the spectra obtained from transformer oils are shown in Figure 2.

Principal component analysis of first 12 oils

PCA was conducted on fluorescence spectra obtained from the original twelve oil samples. For each oil, eight spectra were taken over two consecutive days. Four spectra were acquired for each oil by rotating the cuvette through all four faces each day. A plot of the first two principal component (PC) scores for each oil is shown in Figure 3. Between them, these two PCs capture 91% of the variance in the spectra. The main observation is that the oils appear to fall into three distinct groups, as marked on the figure. Furthermore, these groups are broadly related to the oil manufacturer, so all but one of the oils from supplier A fall into group one while all those from supplier C are in
group two. Group three contains an oil of unknown origin and the remaining oil from supplier A - this is a consequence of the more variable nature of the oil from supplier A. The only oil from supplier B falls in the middle of the cluster of oils from supplier C.

Within the main three clusters, individual oils generally form a pair of four point sub-clusters, due to instrumental drift between the two days on which the measurements were made. The sub-clusters are clearly sufficiently separated in PC space to allow identification of individual oils within groups one and three, but are too heavily overlapped in group two. The first three PCs were found to capture 95% of the variance, but the extra dimension was not found to improve the resolution of individual oils.

**Neural network classification of first 12 oils**

Since PCA did not provide the basis for identifying the individual oils from their fluorescence spectra, ANNs were evaluated for the task instead. The network employed for the interpretation of fluorescence spectra was of a feed forward architecture and was trained using backpropagation with adaptive learning rate and momentum. The input to the network was a 251-point spectrum (250-500nm) obtained from an oil and the outputs represent the individual oil groups. We adopted the convention that the output for a specific oil type will be high (close to 1) when the measured oil falls into that group and low (close to 0) otherwise. The output layer consists of neurons with a sigmoidal transfer function, defined by Equation 3, which encourages the outputs towards limiting values of 0 or 1.
The neurons in the hidden layer also have sigmoidal transfer functions, which is critical in allowing the network to cope with the possibility of non-linear relationships between inputs and outputs.

The data used were the same 96 spectra as analysed using PCA. These were split into two sets of 48 by taking two repetitions of each oil from each of the two days, so spectra 1 to 4 were from the first oil, spectra 5 to 8 from the second oil, etc. The first data set was used for network training while the second was used as an unseen set for network testing. Networks with different numbers of hidden neurons and training times were evaluated. Figure 4 shows the output matrix achieved when presenting the training and test sets to a network comprising 100 hidden neurons, trained for 100,000 epochs. Inevitably, outputs are rarely exactly 0 or 1, but making the output layer competitive (so that only the neuron with the highest output is set to 1 and all the others are considered to be 0) results in 100% accurate classification.

Principal component analysis of second batch of oils

Despite the encouraging results obtained using ANNs, PCA was employed for exploration of the spectra acquired from the second batch of oils because the characteristics of many of the oils were unknown so no specific classification goal could be defined. As in the previous section, four spectra were obtained for each oil by rotating the cuvette and taking a measurement through each of its four faces. The large number of oils meant that spectra were acquired over a number of days. The first three
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PCs were found to capture 94% of the variance in the spectra (54% for PC1, 29% for PC2 and 11% for PC3) so visualisation of the data concentrated on these components. Figure 5 shows the scores plot for the first two PCs of all the oils. As with the previous batch, the four spectra for each oil form distinct clusters. The division between unused oils (those with labels beginning with letters) and used oils (numbered labels) is very clear, with used oils falling together in a region in the top right quadrant of the plot. The only exception is the unused oil labelled H, which falls in the used region. It is interesting to note that the spectra of oils R1 and R2, which are reconditioned, are grouped with the old oils.

Plotting PC1 against PC3 (Figure 6) provides additional information. The used oils form a linear feature, with the position of each oil indicating the amount of fluorescence observed, which is also closely correlated to the colour of the oil. Colourless oils lie near the top of the PCA plot, while dark oils have lower PC3 scores and higher PC1 scores. The oils are also seen to fall into two distinct groups: those on the main linear feature are used oils or non UK oils (from suppliers other than A, B, or C) while those to the lower left of the main group are unused oils from UK suppliers (with the exception of used oil 111157). This is a potentially useful result, as it provides a way of differentiating between those oils which can be employed in new transformers (i.e. those complying with UK specifications) and those which cannot (i.e. used oils and foreign oils).

Discussion

PCA proved to be a useful tool for exploring databases of oil fluorescence spectra,
although it did not provide the resolution necessary to identify individual oils from their spectra. However, a relatively straightforward ANN was able to achieve this goal for the first batch of twelve oils. It is interesting to note that the ANN could classify oils correctly despite instrumental drift and the relatively poor quality of the spectra acquired when using disposable plastic (rather than quartz) cuvettes. These are useful findings for the practical application of this work.

It could be argued that the ability of the ANN to identify individual oils is actually too specific for the intended purpose, and that a more general classification system would be more appropriate. However, it should be noted that this work serves to show that the maximum possible discrimination between oils is achievable, and that a broader classification system for identifying, for example, the oil manufacturer from a spectrum is entirely feasible. Exploration of the fluorescence spectra obtained from the second batch of oils proved productive, as it showed that the spectra can be used to determine whether or not an oil has been used and further showed that it is possible to distinguish between oils which meet BS148 and those that do not. A clear correlation between spectra and oil colour (which can be an indication of oil age) was also found. Of course, a simple colorimeter could be used to determine the age from colour but it is important to note that this represents only one part of the information provided by the more advanced fluorescence technique.

While the work in this project has focused on the qualitative classification of oils, there is no reason why a similar approach could not be used to attempt quantitative analysis using multivariate calibration. Obvious techniques to consider include principal
component regression (PCR), partial least squares (PLS) and ANNs (with different architecture to that used here). These methods have the potential to permit the extraction of physical parameters, such as refractive index, from the fluorescence spectra provided that the spectra contain information sufficiently related to those parameters. This would require a database of fluorescence spectra obtained from oil with a range of known physical parameters.

**Conclusions**

It has been demonstrated that multivariate data arising from fluorescence spectroscopy can be used to delineate different transformer oils according to origin and extent of use. The categorisation is achieved using established chemometrics based on principal component analysis, while use of a feed-forward artificial neural network provides further refinement in resolution. The information provided can be used as a rapid screening test of an oil's suitability for use in a new transformer or its continued use in a transformer in service. This is useful to transformer operators who have to schedule outages to make maintenance work as efficient as possible. The technique is all the more attractive because of the ease of data acquisition - fluorescence collection from an undiluted sample, using front face reflectance measurements, makes the technique straightforward and amenable to on-site field testing. As a final note, unravelling the underlying chemistry of oils and relating this to the classifications unearthed here is worthy of further investigation and may provide new insight to the ageing process in transformer oils.
References

(1) BS2000 (Pt 346) — “Determination of PCA content in unused lubricating base oils and asphaltene-free petroleum fractions — DMSO extraction/Refractive Index method

(2) Gordon Wilson, private communication


(4) Picer, M.; Picer, N. *Chemosphere* 1992, 24, 1825-1834


(19) BS148 - Specification for unused mineral oils for transformers and switchgear


Figures

Figure 1: A single neuron, as used in ANNs. Inputs $a_1..a_n$ are multiplied by the corresponding connection weights, $w_1..w_n$, then summed together with a bias, $b$, before being mapped to an output, $t$, by a transfer function, $f$.

Figure 2: Fluorescence spectra for a selection of the first twelve transformer oils. The initial letter of each label indicates oil supplier (A, B or C).

Figure 3: First two principal component scores for the first twelve oils. The initial letter of each label indicates oil supplier (A, B or C). The divisions between groups were added manually to emphasise the resulting clusters.

Figure 4: Neural network output matrix for a network comprising 100 log sigmoidal hidden neurons, trained for 100,000 epochs, when presented with the training and test sets.

Figure 5: First two principal component scores for the second batch of oils. Labels beginning with letters indicate unused oils, with the letter indicating the supplier (A, B and C are UK-based, others are from continental Europe). The division between unused and used oils was added manually to emphasise the natural clustering.

Figure 6: Scores for PC1 and PC3 for the second batch of oils. Key as Figure 3.
Figure 1
Figure 2

Intensity vs. Wavelength / nm

- C1
- A1
- A5
- Unknown
Figure 3
Figure 4
Figure 5
Figure 6

Unusable oils
(old or foreign)

Scores on PC# 3

Darker oils

Usable oils

Scores on PC# 1

x10^3

266
Summary

The increasing concern about the effect of carcinogens, such as PAHs, on human health has led to a change in the regulations regarding the disposal and carriage of PAH containing materials. Transformer oils contain PAHs because of their source and because they are beneficial to its operation. Although oils can be tested in a meaningful way for toxic effects by IP346 this test is not applicable to used oils. There is a belief that the PAH content of oils changes in service and that this is especially true for diverter and circuit breaker oils.

An oil which had been used in diverter during its service duty and breaking capacity type tests was analysed before and after the test to monitor any change which may occur in the PAH profile. The oil samples were also analysed for carbon composition.

The results would appear to suggest that the PAHs are largely unaffected and that, if anything, the PAH content is reduced and thus it can be assumed that the carcinogen content is also reduced. Further work to confirm this is recommended.
Appendix F

The Effect of Arcing on the PAH Fingerprint

Introduction

Two major and interrelated concerns of modern society are the need for adequate energy supply and the relationship between environmental quality and human health and welfare. Some of the compounds which are omnipresent and abundant pollutants of the environment and are also highly suspect as causative agents in human cancer are the organic molecules known as PAHs (polycyclic aromatic hydrocarbons) [1]. PAHs are naturally occurring in fossil fuels and, unless they are specifically removed or destroyed, they are usually present in refined products of crude oil. This is the case with insulating oil and is where the concern over PAHs in the environment becomes relevant to the National Grid Company plc.

NGC owns many thousands of pieces of oil-filled HV equipment. There is a significant risk that a company owning and transporting so much oil will lose a certain quantity into the environment. There will also be daily occurrences where NGC employees work with oil and much of it will have been subjected to ageing of some kind. Both of these issues present the possibility of exposure of people and the environment to PAHs, so it is necessary for NGC to establish the threat posed by the PAHs within its oil, either unused or used.

There is a requirement in BS148 [2] that all unused oils have a value of less than 3% for IP346 [3] analysis. This test is frequently considered to be a measure of the PAH content. This is not the case; IP346 measures the fraction of the oil which is soluble in DMSO described as the polycyclic aromatic content (PCA). The PCA content includes PAHs but also many other compounds which contain hetero-atoms (sulphur and nitrogen). However, it has shown good correlation with the incidence of skin cancer in mice (Figure 1) making it a useful measurement. Unfortunately it has no value for used oils because the correlation has not been established and it is not sensitive enough to the chemical changes which may occur during use. In fact a value of 3% obtained by IP346 approximates to a PAH content of 0.1% [4]. There is currently no standard method which gives a value of PAH content, and tests for
carcinogenicity are not carried out by or for NGC because they involve experiments on animals and the results take two years.

Figure 1: Correlation between IP346 results and the incidence of skin tumours in mice for paraffinic and naphthenic oils (CONCAWE data)

In a previous report a method of fingerprinting transformer oil by its PAH fingerprint was described [5]. The fingerprint is robust to attempts to degrade the oil in the laboratory. Oil has been aged at high temperatures (up to 160°C) in the presence of oxygen and copper, subjected to UV light with and without cooling and exposed to repeated discharge in a test cell; all of these oils have given the same PAH fingerprint before and after degradation. This means that no PAHs are produced in significant quantities and none of the existing PAHs are preferentially reduced.

If the PAH fingerprint is unchanged during the service life of the oil and its IP346 value before use was below 3% then the oil should not become carcinogenic,
mutagenic\textsuperscript{*} or teratogenic\textsuperscript{†}, unless the PAH fraction is not the only contributor to the carcinogenicity of the oil. This would also mean that waste oil would pass the requirement of Waste Management Regulations, which require materials with greater than 0.1% carcinogenic matter should be treated as special waste [6].

The tests performed in the laboratory do not accurately reproduce the conditions an oil would typically experience in a transformer. However, oil in diverters and circuit breakers experience similar conditions to the rest of the transformer, but they are usually more severe. They are subject to arcing and sparking and it has been suggested that the PAH fingerprint would change under such conditions.

A sample of oil was received which had been used in a diverter during its service duty and breaking capacity type tests. Prior to the tests the oil had been unused and was clear and very pale yellow. After the tests the oil was darker and green, with a suspension of carbon, which gave the oil the appearance of being black (Appendix F4). The oil samples before and after the tests were analysed to obtain the PAH fingerprints and carbon typing values.

Experimental

The before and after tests samples were analysed by FT-IR to determine the aromatic carbon content as described in IEC60590 [7] and the paraffinic and naphthenic carbon contents were calculated according to ASTM D2140 [8].

The PAH fingerprints were obtained by the procedure previously described [5]; a method developed at NGC. The oils were analysed by GC-MSD after the liquid-liquid analysis stage and after complete extraction of the PAHs.

Results

The carbon typing results for the two oils are shown in the table below:

\* Capacity for affecting DNA, the worst mutagens cause hereditary defects.  
\textsuperscript{†} Affects human fertility or unborn children.
<table>
<thead>
<tr>
<th>Oil Sample</th>
<th>Aromatic %</th>
<th>Density</th>
<th>Refractive Index</th>
<th>Naphthenic %</th>
<th>Paraffinic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before test</td>
<td>12.00</td>
<td>0.8849</td>
<td>1.48604</td>
<td>47.90</td>
<td>40.10</td>
</tr>
<tr>
<td>After test</td>
<td>11.88</td>
<td>0.8848</td>
<td>1.48603</td>
<td>47.64</td>
<td>40.48</td>
</tr>
</tbody>
</table>

Table 1: Carbon typing results

The resulting chromatograms, which represent the PAH fingerprints, can be found in Appendix F5.

Discussion

The first thing to note is that the carbon typing results and the PAH fingerprint are very similar to that of Nynas N10GBN. It is likely, therefore, that the oil is from the same crude source, it is hydrotreated naphthenic oil with low PAH content.

The carbon typing results are very similar, the density and refractive index are unchanged. The aromatic carbon content calculated by FT-IR decreases slightly after the lifetime test. The change is small and given the nature of the test it may be considered within experimental error. However, under the conditions of the tests performed on the diverter it is plausible that a small but noticeable fraction of the aromatic molecules would be reduced to naphthenic form by the absorption of hydrogen gas. It is generally assumed that the molecules responsible for gas absorption are aromatic and that the poly-aromatic molecules are the most gas absorbing.

The PAH fingerprints after liquid-liquid extraction often show differences between samples that are not picked up by the full PAH extraction. This is because it contains mono-aromatic compounds and the polar compounds. The picture is often confused because it contains too much information. In this case, however, the two chromatograms are very similar. The only significant difference is observed in the peaks which elute between 36 and 46 minutes. This region contains larger molecules, such as the 3- and 4-ring PAHs (alkylated-phenanthrenes and pyrene) and even after just the liquid-liquid extraction usually contains only PAHs. This region appears to be lower in the ‘After Test’ sample than in the ‘Before Test’.
The full PAH extraction fingerprints for both samples appear to be very similar to each other. As in the partially extracted samples the peaks in the region between 36 and 46 minutes are lower in the ‘After Test’ sample. The peaks around 22 minutes are also lower in the ‘After Test’ sample, these peaks correspond to methylated-fluorenes. It should be noted that the method is qualitative and the numbers on the y-axis do not relate to the quantity of PAHs in the two oils.

Conclusions

The overall impression of the PAH fingerprints for the two samples is that they are the same:

- The ‘After Test’ sample does not contain any new peaks and all of the previous peaks are present.
- The peaks are generally in the same ratios, so that the patterns of the fingerprints are similar.

The differences between the two samples appear to indicate that PAHs may be reduced during the diverter test. As the test is not quantified there remains the possibility that the majority of the PAHs have increased and the only a few peaks have remain unchanged. However, it is unlikely that so many peaks would increase by the same amount, such that the general pattern is unchanged.

The types of PAHs may also be significant, if they have been reduced by absorption of gas they would be the PAHs most beneficial to insulating oil, i.e. making it more gas absorbing

It is unlikely that a reduction in the PAH content would account for a significant change in the aromatic carbon content. Although PAHs account for 0.1\% by weight and would correspond to more than 0.1\% of the carbon content, the observed reduction of PAHs would not amount to as much as 0.1\% of carbon content.
Appendix F

Future Work

Research into the carcinogenic potency of oil is already taking place at the Cranfield Biotechnology Centre. It is hope that a relatively simple test will be developed to assess used and unused oil samples for there carcinogenic content. The initial step is to find a method to produce the same results as IP346 but more simply.

The possibility that PAHs are reduced by gases produced during high electrical activity can be explored using the gassing tendency test. Once the equipment is operational then a programme of work can be produced using different PAHs and different conditions.

References

2. BS148 Specification for Unused Mineral Insulating Oils for Transformers and Switchgear
4. Naphthenics special issue on transformer oil 1999 (Nynas market magazine)
6. Environmental Protection (Special Waste) Regulations 1996
7. IEC60590 Determination of the Aromatic Hydrocarbon Content of New Mineral Oils 1st edition 1977
8. ASTM D2140-81 Carbon Type Composition of Insulating Oils of Petroleum Origin
Appendix F

APPENDIX F4

A Sample of oil before test
B Sample of oil after test (filtered)
C Sample of oil after test
APPENDIX F5

Liquid-liquid extract of 'Before Test' sample

Liquid-liquid extract of 'After Test' sample
PAH extracts of 'Before Test' (bottom) and 'After Test' (top) samples

PAH extracts of 'Before Test' (Yellow) and 'After Test' (Green) samples

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