PORTABLE OPTICAL PROBE FOR MONITORING OF TRANSFORMER OILS

A thesis submitted to The University of Manchester for the degree of Master of Philosophy in the Faculty of Engineering and Physical Sciences

2014

ZONG WEN YAN

SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING
CONTENTS

DECLARATION .............................................................................................................. 1
COPYRIGHT .................................................................................................................. 1
ACKNOWLEDGEMENTS .............................................................................................. 2
ABSTRACT .................................................................................................................... 3
LIST OF FIGURES AND TABLES ................................................................................ 8
NOMENCLATURE ........................................................................................................ 13
ABBREVIATIONS ........................................................................................................ 13

1.0 CHAPTER I: INTRODUCTION ............................................................................ 14

1.1 BACKGROUND ....................................................................................................... 14
  1.1.1 Electrical Power Transmission Distribution Systems and Transformers .......... 14
  1.1.2 Crude Oils ......................................................................................................... 15
  1.1.3 Applications of Oils in Transformers ................................................................. 15
  1.1.4 Fluorescence Spectroscopy ............................................................................... 16

1.2 PROJECT AIMS AND OBJECTIVES .................................................................... 17

1.3 THESIS LAYOUT ................................................................................................... 18

2.0 CHAPTER II: TRANSFORMER OILS ............................................................... 20

2.1 INTRODUCTION ................................................................................................... 20

2.2 EXTRACTION, REFINING AND PRODUCTION OF TRANSFORMER OILS ....... 21

2.3 TRANSFORMER OIL PROPERTIES, OPERATIONAL ENVIRONMENT AND AGEING .............................................................. 23
  2.3.1 Dielectric Strength ............................................................................................ 24
  2.3.2 Oxidation Stability and Ageing ......................................................................... 24
  2.3.3 Thermal and Flow Properties ........................................................................... 25
  2.3.4 Consideration of the Operational Environment and General Requirement on Oil 25

2.4 CHEMICAL STRUCTURE OF TRANSFORMER OIL ......................................... 28
  2.4.1 Paraffins .......................................................................................................... 28
  2.4.2 Napthenes ........................................................................................................ 29
  2.4.3 Aromatic Hydrocarbons .................................................................................... 30
  2.4.4 Nitrogen Containing Molecules ....................................................................... 30
  2.4.5 Sulphur Containing Molecules ........................................................................ 30
  2.4.6 Oxygen Containing Molecules ........................................................................ 31

2.5 CHEMICAL REACTIONS AND REACTION CONDITIONS ............................. 31

2.6 EXISTING MONITORING TECHNIQUES FOR TRANSFORMERS ............... 33
4.3 SYSTEM B .............................................................................................................64
  4.3.1 The DPU Module ..........................................................................................65
  4.3.2 The Battery Module ....................................................................................65
  4.3.3 The JAZ-INTLED Module ..........................................................................66
  4.3.4 The Spectrometer Module ..........................................................................66
4.4 SPECTRASUITE® PARAMETERS .................................................................68
  4.4.1 Consideration and Setting of System Parameters .....................................68
4.5 MAP OF EXPERIMENTATION .......................................................................70
  4.5.1 Transformer Oil Ageing and Experimentation .........................................70
  4.5.2 Oil Preparation ..........................................................................................71
  4.5.3 Ageing of Oil (Air-Circulating Thermal Ageing) .........................................72
  4.5.4 Timely Removal of Oils from the Thermal Oven and Measurements ........73
4.6 EXPERIMENTATION WITH SYSTEMS A AND B .......................................74
  4.6.1 System B ....................................................................................................74
  4.6.2 System A ....................................................................................................75
  4.6.3 Comparison with existing techniques in future .........................................75
5.0 CHAPTER V: PRINCIPAL COMPONENT ANALYSIS .......................................76
  5.1 INTRODUCTION ..............................................................................................76
    5.1.1 Mathematical basis of PCA .......................................................................77
    5.1.2 Description of IBM SPSS Statistics 20 and its Parameters .......................81
    5.1.3 Key Analytical Descriptives .....................................................................83
    5.1.4 Differences between PCA and Factor analysis .........................................86
6.0 CHAPTER VI: RESULTS AND ANALYSIS .....................................................87
  6.1 INTRODUCTION ..............................................................................................87
  6.2 EXPERIMENTAL ERRORS AND REPEATABILITY .....................................88
  6.3 THERMALLY AGED DIALA S2-ZUI ............................................................91
    6.3.1 Experimental Results ...............................................................................91
    6.3.2 Analysis of Results for DIALA S2-ZUI .................................................94
  6.4 THERMALLY AGED NYTRO LIBRA .............................................................101
    6.4.1 Experimental Results ...............................................................................101
    6.4.2 Analysis of results for thermally aged Nytro Libra .................................104
  6.5 THERMALLY AGED 10 GBN .........................................................................107
    6.5.1 Section I: 10 GBN Experimentation ......................................................107
ABSTRACT
Transformer oils, which are used for cooling and insulation, need to be monitored in order to ensure that their performance is reliable and safe, so that maintenance can be carried out when necessary. Therefore techniques that help to define the ageing status of transformer oil are essential.

In the present work fundamental research has been carried out to study the fluorescence emission spectra of three types of transformer oils (Shell Diala S2-ZUI, Nytro Libra and 10 GBN). Two optical systems were used. The first system (A) uses a 404 nm Gallium Nitride (GaN) semi-conductor laser diode as the excitation source while the second system (B) uses a 365 nm LED.

Baseline data on the fluorescence emission of the three types of oils were obtained first. Based on detailed analysis of the spectral profiles changes in oil samples aged over a range of time intervals, a new method based on the sum of two normalised peak intensities was proposed and tested. Taking into account of the experimental errors, this method has been shown to be able to resolve the changes in the oil conditions.

The performance of the Principal Component Analysis method was also assessed by applying it to the different types of oils. Results show that although it is capable of differentiating the overall changes in oil conditions, it is less effective for oils that emit fluorescence spectra profiles differing only in the overall intensity. Thus care has to be taken in the application of this method for oil monitoring. The method based on the sum of normalised peak intensities is preferred because it is effective, fast and convenient to apply.

The applicability of the portable system (System B) as an alternative to the laboratory based condition monitoring system (System A) has been discussed, based on the results.
DECLARATION

No portion of this work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institution of learning.

COPYRIGHT

i. The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”) and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

ii. Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

iii. The ownership of certain Copyright, patents, designs, trademarks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

iv. Further information on the conditions under which disclosure, publication and commercialisation of this thesis, the Copyright and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP Policy (see http://documents.manchester.ac.uk/DocuInfo.aspx?DocID=487), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see http://www.manchester.ac.uk/library/aboutus/regulations) and in The University’s policy on Presentation of Theses.
ACKNOWLEDGEMENTS

I would like to thank my supervisor Professor Krikor Ozanyan and my co-supervisor Professor Zhongdong Wang for their valuable time and guidance throughout this MPhil. I am also extremely grateful to Dr Xiao Yi and my colleagues for their assistance and advice. I would also like to thank my family for their continual support which has made this possible.

I am also very grateful to the University of Manchester, Electricity North West (ENW) and Engineering and Physical Sciences Research Centre (EPSRC) for the funding of this project.
LIST OF FIGURES AND TABLES

FIGURES

Figure 1.1 Simplified UK Electrical Power Transmission System [1] ........................................ 14
Figure 2.1 Typical flow chart of an oil refinery [14] ................................................................. 21
Figure 2.2 Different types of Paraffins: methane (left) and ethane (right) ................................ 29
Figure 2.3 Different types of napthenes: cyclopentane (left) and cyclohexane (right) .......... 29
Figure 2.4 Different type of aromatic hydrocarbons ................................................................ 30
Figure 2.5 Diagram showing elementary steps in hydrocarbon auto-oxidation [34] .......... 32
Figure 2.6. Diagram of 2-furfuraldehyde ................................................................................. 37
Figure 3.1. Diagram showing an example of emission spectrum in the study of fluorescence light emission ...................................................................................................................... 42
Figure 3.2. Diagram showing different energy levels in a molecule ........................................ 43
Figure 3.3. Stokes shift in wavelength of the exciting and emitted radiation. The vertical axis is Intensity and the horizontal axis is Wavelength (nm) .................................................. 45
Figure 3.4 Diagram showing the differences in spin for various electronic states .............. 46
Figure 3.5 - Partial Jablonski diagram for absorption, fluorescence and phosphorescence [51] ........................................................ ......................................................... 48
Figure 3.6. Graph showing the average gasoline spectrum for all samples measured, excited at 404 nm [25] ................................................................................................. 53
Figure 3.7. Graph showing summary of the liquid gasoline samples showing similar spectral features [57] ................................................................................................................. 54
Figure 3.8. Experimental setup by Tan in order to obtain fluorescence spectra of gasoline and transformer oils at various wavelengths [60] .......................................................... 55
Figure 3.9. Graph showing the fluorescence spectra of new transformer oil which has been normalised at 499.9 nm [60] ................................................................. 56
Figure 4.1. Diagram of different geometrical setups. (A) and (C) being the perpendicular geometry; (B) the front surface geometry and (D) the inline geometry [60] .......... 59
Figure 4.2. Photo showing the experimental setup to measure the fluorescent radiation from transformer oils ................................................................................................................. 63
Figure 4.3. Image of the modular measurement system (System B) used in the project ...... 65
Figure 4.4. The control and display panel of the DPU module .................................................. 65
Figure 4.5. Experimental setup of System B .............................................................................. 67
Figure 4.7. Photo showing where optical probe and oil insertion in System B ................... 74
Figure 5.1 PCA transformed orthogonal coordinate system in 3D space for a cluster of points. The origin of the new coordinate system passes the “middle” point of the cluster ....... 77
Figure 5.2. Parameters to select in PCA .................................................................................. 82
Figure 5.3 Results displaying the Correlation Matrix, KMO and Bartlett’s Test and Communalities ....................................................................................................................... 83
Figure 5.4 Results displaying the Total Variance ................................................................... 84
Figure 5.5 Example of Scree Plot ......................................................................................... 85
Figure 5.6. Component Matrix given in this example ............................................................... 85
Figure 6.1 Repeatability test by System A of fresh Nytro Libra. The integration time is set to 100 ms. ................................................................................................................................. 90
Figure 6.2 Repeatability test by System A of Nytro Libra aged for 3 weeks. The integration time is set to 100 ms.

Figure 6.3 Enlargement of Figure 6.1 for details of repeatability of fluorescence spectra measurement of fresh Nytro Libra.

Figure 6.4 Intensity of fluorescence emission of Diala S2-ZUI in arbitrary unit from 400 nm to 700 nm with cuvette label given in Table 6.1 as keys to the curves, obtained from System A with an excitation wavelength of 404 nm. The colour patches from the top are in same order as the legend.

Figure 6.5 Intensity of fluorescence emission of Diala S2-ZUI in arbitrary unit from 400 nm to 700 nm with the cuvette label given in Table 6.1 as keys to the curves, obtained from System B with an excitation wavelength of 365 nm. The colour patches from the top are in same order as the legend.

Figure 6.6 Change of normalised fluorescence light emission of Diala S2-ZUI at 442 nm and 490 nm from System A as a function of ageing time. For comparison the colour patches of the aged oil are also given. This figure corresponds to the original results shown in Figure 6.4.

Figure 6.7 Change of fluorescence light emission of Diala S2-ZUI from System B at 408 nm and 490 nm as a function of ageing time. This figure corresponds to the original results shown in Figure 6.5.

Figure 6.8 Change of fluorescence light emission at 408/442 nm and 490 nm as a function of ageing time. The error bar is 2.5 % in either direction.

Figure 6.9 Showing Diala S2-ZUI results in Figure 6.6 (System A) scaled at 490 nm.

Figure 6.10 Showing Diala s2-ZUI results in Figure 6.7 (System B) scaled at 490 nm.

Figure 6.11 Scaled intensity of Diala S2-ZUI at 408/442 nm and 490 nm as a function of ageing time for results from System A in Figure 6.6 and System B in Figure 6.7. The ratio and sum of the two peaks is also shown. The error bar is 2.5 % in either direction.

Figure 6.12 PCA Component plot in rotated space for results from System A (Figure 6.4), i.e. ageing results for Shell Diala S2-ZUI.

Figure 6.13 PCA Component plot in rotated space for results from System B (Figure 6.5).

Figure 6.14 Angle of degradation for Shell Diala S2-ZUI as a function of ageing time. The sums of the normalised intensities are also displayed for comparison. The error bar is 2.5 % in either direction.

Figure 6.15 Intensity of fluorescence emission for Nytro Libra in arbitrary unit from 400 nm to 700 nm with cuvette labels given in Table 6.2 as keys to the curves, obtained from System A with an excitation wavelength of 404 nm. The samples were sealed. The colour patches from the top are in same order as the legend.

Figure 6.16 Intensity of fluorescence emission for Nytro Libra in arbitrary unit from 400 nm to 700 nm with cuvette labels given in Table 6.2 as keys to the curves, obtained from System B with an excitation wavelength of 365 nm. The samples were sealed. The colour patches from the top are in same order as the legend.

Figure 6.17 Change of normalized fluorescence light emission intensity at 430/442 nm and 490 nm as a function of ageing time. For comparison the colour patches of the aged oil are also given. The error bar is 2.5 % in either direction.
Figure 6.18 Results in Figure 6.15 (System A) scaled at 485 nm. ............................................... 105
Figure 6.19 Results in Figure 6.16 (System B) scaled at 485 nm..................................................... 105
Figure 6.20 Scaled intensity at 430/442 nm and 490 nm as a function of ageing time for results from System A in Figure 6.15 and System B in Figure 6.16. The ratio and sum of the two peaks is also shown. ............................................................................................................. 106
Figure 6.21 Component plot in rotated space for (a) results from System A (Figure 6.15), and (b) System B (Figure 6.16), i.e. ageing results for Nytra Libra. ................................................................. 107
Figure 6.22 Fluorescence spectra from 400 nm to 700 nm of cuvette samples A1-A5, no acid, dry; obtained from System A with an excitation wavelength of 404 nm. The colour patches from the top are in same order as the legend showing change in their colour as the oil samples become aged. ............................................................................................................................... 110
Figure 6.23 Fluorescence spectra from 400 nm to 700 nm of cuvette samples A6-A10, LMA, dry; obtained from System A with an excitation wavelength of 404 nm. ........................................... 110
Figure 6.24 Fluorescence spectra from 400 nm to 700 nm of cuvette samples A11-A15, HMA, dry; obtained from System A with an excitation wavelength of 404 nm. ...................................... 110
Figure 6.25 Fluorescence spectra from 400 nm to 700 nm of cuvette samples B1-B5, no acid, wet; obtained from System A with an excitation wavelength of 404 nm. The colour patches from the top are in same order as the legend showing change in their colour as the oil samples become aged. ............................................................................................................................... 111
Figure 6.26 Fluorescence spectra from 400 nm to 700 nm of cuvette samples B6-B10, LMA, wet; obtained from System A with an excitation wavelength of 404 nm. ........................................... 111
Figure 6.27 Fluorescence spectra from 400 nm to 700 nm of cuvette samples B6-B10, HMA, wet; obtained from System A with an excitation wavelength of 404 nm. ........................................... 111
Figure 6.28 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples A1-A5, no acid, dry. For comparison the colour patches of the aged oil are also given................................................................................................................. 113
Figure 6.29 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples A6-A10, LMA, dry. ................................................................. 113
Figure 6.30 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples A11-A15, HMA, dry. ................................................................. 113
Figure 6.31 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples B1-B5, no acid, wet................................................................. 114
Figure 6.32 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples B6-B10, LMA, wet ................................................................. 114
Figure 6.33 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples B11-B15, HMA, wet................................................................. 114
Figure 6.34 Component plot in rotated space for results from System A of 10 GBN samples A1-A5, no acid, dry. ................................................................................................................. 118
Figure 6.35 Component plot in rotated space for results from System A of 10 GBN samples A6-A10, LMA, dry. ................................................................................................................. 118
Figure 6.36 Component plot in rotated space for results from System A of 10 GBN samples A11-A15, HMA, dry................................................................................................................. 118
Figure 6.37 Component plot in rotated space for results from System A of 10 GBN samples B1-B5, no acid, wet. ................................................................................................................. 119
Figure 6.38 Component plot in rotated space for results from System A of 10 GBN samples B6-B10, LMA, wet.

Figure 6.39 Component plot in rotated space for results from System A of 10 GBN samples B11-B15, HMA, wet.

Figure 6.40 PCA Component plot in rotated space of A1 - A15 and B1 - B15 using System A with the different aged samples circled in their various colours.

Figure 6.41 Angle of degradation for 10 GBN as a function of ageing time for samples A1-A5. The sum of the intensity is also displayed for comparison.

Figure 6.42 Angle of degradation for 10 GBN as a function of ageing time A6-A10.

Figure 6.43 Angle of degradation for 10 GBN as a function of ageing time A11-A15.

Figure 6.44 Angle of degradation for 10 GBN as a function of ageing time B1-B5. The sum of the intensity is also displayed for comparison.

Figure 6.45 Angle of degradation for 10 GBN as a function of ageing time B6-B10.

Figure 6.46 Angle of degradation for 10 GBN as a function of ageing time B11-B15.

Figure 6.47 Fluorescence spectra from unsealed 10 GBN without copper, obtained from System A (404nm laser, (a)) and System B (365 nm LED, (b)).

Figure 6.48 PCA plot of fluorescence spectra from unsealed 10 GBN without copper, obtained from System A (404nm laser, (a)) and System B (365 nm LED, (b)).

Figure 6.49 Fluorescence spectra from sealed 10 GBN without copper, obtained from System A (404 nm laser, left) and System B (365 nm LED, right).

Figure 6.50 PCA plot of fluorescence spectra from sealed 10 GBN without copper, obtained from System A (404 nm laser, left) and System B (365 nm LED, right).

Figure 6.51 Fluorescence spectra from unsealed 10 GBN with copper, obtained from System A (404 nm laser, left) and System B (365 nm LED, right).

Figure 6.52 PCA plot of fluorescence spectra from unsealed 10 GBN with copper, obtained from System A (404nm laser, left) and System B (365 nm LED, right).

Figure 6.53 Fluorescence spectra from sealed 10 GBN with copper, obtained from System A (404nm laser, left) and System B (365 nm LED, right).

Figure 6.54 PCA plot of fluorescence spectra from sealed 10 GBN with copper, obtained from System A (404 nm laser, left) and System B (365 nm LED, right).

TABLES

Table 2.1. Measured Breakdown Voltages for Fresh and Contaminated Shell Diala Oil [18]

Table 2.2. Properties in accordance with the functions of the transformer oil.

Table 2.3. Recommended Safe Values for Gases in DGA.

Table 2.4. Key gases which can be generated by transformer faults [41].

Table 2.5. Indication of transformer condition from Furfuraldehyde content and DP value [38].

Table 2.6 Expected Properties of Transformer Oils.

Table 3.1 Wavelength and energy range of different radiation spectra.

Table 3.2. Difference between Fluorescence and Phosphorescence.

Table 3.3. Different optimal wavelengths for excitation of oil samples [60].

Table 4.1 Characteristics of the two Systems A and B used in the present work.
Table 4.2 List of sample conditions and thermally ageing temperature. For 10 GBN tests were performed in two groups which are shown in green and blue background colours.

Table 6.1 Ageing time of oils and their cuvette number.

Table 6.2 Ageing duration and cuvette labels for Nytro Libra.

Table 6.3 Showing the different parameters and the period in which the oils were aged under.

Table 6.4 Angles in PC plot for different cuvette samples.

Table 6.5 Angles in PC plots for each cuvette sample listed according to types of sample.

NOMENCLATURE

- \( c \) (page 44): Concentration (mol Litre\(^{-1}\))
- \( c \) (page 45): Speed of light (m s\(^{-1}\))
- \( E \): Total energy of molecule
- \( E_{abs} \): Energy of light absorbed by molecule during excitation
- \( E_{el} \): Electronic energy
- \( E_{fluor} \): Energy of emitted fluorescence light
- \( E_{rot} \): Kinetic energy of rotation
- \( E_{solv.relax} \): Energy due to solvent cage
- \( E_{tr} \): Translation energy
- \( E_{vib} \): Energy lost by molecule during vibrational relaxation
- \( h \): Planck’s constant (J.s)
- \( I \): Intensity of light transmitted
- \( I_o \): Intensity of incident light
- \( k_d \): Dissociation rate constant (s\(^{-1}\))
- \( k_{ec} \): External conversion rate constant (s\(^{-1}\))
- \( k_f \): Fluorescence rate constant (s\(^{-1}\))
- \( k_i \): Intersystem rate constant (s\(^{-1}\))
- \( k_{ic} \): Internal conversion rate constant (s\(^{-1}\))
- \( k_{pd} \): Predissociation rate constant (s\(^{-1}\))
- \( l \): Path length (cm)
- \( l \) (page 45): Subshell
- \( m_l \): Energy shift
- \( m_s \): Electron spin
- \( n \): Shell
- \( T \): Transmittance
- \( \varepsilon \): Molecular absorptivity (Litre mol\(^{-1}\) cm\(^{-1}\))
- \( \phi \): Quantum yield

ABBREVIATIONS

- A/D: Analog-to-Digital Converter
- ADU: Analog-to-Digital Unit
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BS</td>
<td>British Standards</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>CUO</td>
<td>Clean Used Transformer Oil</td>
</tr>
<tr>
<td>DGA</td>
<td>Dissolved Gas Analysis</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of Polymerization</td>
</tr>
<tr>
<td>DUO</td>
<td>Dirty Used Transformer Oil</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GaN</td>
<td>Gallium Nitride</td>
</tr>
<tr>
<td>HMA</td>
<td>Higher Molecular Acid</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>IEC</td>
<td>International Electrotechnical Commission</td>
</tr>
<tr>
<td>IFT</td>
<td>Interfacial Tension</td>
</tr>
<tr>
<td>INRAD</td>
<td>International Radio</td>
</tr>
<tr>
<td>KMO</td>
<td>Kaiser-Meyer-Olkin value</td>
</tr>
<tr>
<td>LED</td>
<td>Light - Emitting Diode</td>
</tr>
<tr>
<td>LMA</td>
<td>Lower Molecular Acid</td>
</tr>
<tr>
<td>LRP</td>
<td>BP Lead Replacement Petrol</td>
</tr>
<tr>
<td>N/A</td>
<td>Not Applicable</td>
</tr>
<tr>
<td>NO</td>
<td>New Transformer Oil</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light-Emitting Diode</td>
</tr>
<tr>
<td>PAH</td>
<td>Poly Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>PC</td>
<td>Principal Components</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
</tr>
<tr>
<td>S/N</td>
<td>Signal to Noise Ratio</td>
</tr>
<tr>
<td>SUL</td>
<td>BP Super Unleaded</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
</tbody>
</table>
CHAPTER I: INTRODUCTION

1.1 BACKGROUND

1.1.1 Electrical Power Transmission Distribution Systems and Transformers

A transmission and distribution system is a network of electrical conductors, insulators, electrical apparatus, and monitoring and control equipment that work together to deliver electrical power from its source (generation plants) to its customers. Transformers are critical components in the network and are one of the most expensive ones in terms of cost and maintenance. They are required to manipulate the parameters of electrical power over an alternating current (a.c.) transmission system in order to maximize the efficiency of bulk electricity transmission and to ensure safe and secure operation of the network.

![Simplified UK Electrical Power Transmission System](image)

Figure 1.1 Simplified UK Electrical Power Transmission System [1]

In the UK, transformers are rated at: 400 kV, 275 kV, 132 kV, 33 kV and 11 kV (as shown in Figure 1.1) [1]. The ability of these transformers to work continuously generally relies on their insulation and cooling systems being in a good condition. Transformer oils fit the role of an insulating medium appropriately at the different voltage levels. It is also an excellent coolant which has balanced heat transfer capabilities to carry the heat generated in the current carrying conductors out of the system and into the environment. Hence the temperature of the
transformer and especially the solid insulation materials, which is often regarded as the life of
the transformer, is maintained at sufficiently low values. The condition of the transformer oils,
in terms of its physical and chemical properties, are therefore of upmost importance and need
to be monitored in a convenient, reliable and safe way to provide important information for
maintenance. By applying such a technology a secure, timely and economic supply of
electricity is made possible to the consumers (industrial, commercial and domestic).

1.1.2 Crude Oils

Crude oil is a naturally occurring mixture of either liquid or gas found mainly in the pores of
rocks and the upper layers of the earth’s crust. It is formed over a long period of time,
possibly millions of years according to the more commonly accepted biogenic theory, by the
decay and compression of the remains of dead animals, plants and ocean micro-organisms. Its
importance as a resource can be highlighted by the fact that it is extracted, processed and
refined to produce a very diverse range of products that are used in many applications in
industry and daily life. Some examples are: aviation oils, car engine oils, electrical oils
(transformer oils), hydraulic fluids, lubricating oils, turbine oils, and so forth. Crude oil is
also refined to produce fuels, such as petrol and diesel, which are a vital energy source. In
2012 fossil fuels alone contributed to approximately 78% of the total energy consumption in
the UK [2]. It is a highly condensed energy source which is the result of continuous
decomposition and compression of organic remains under high pressure and heat conditions.
For example the energy density of diesel is 35.8 MJ kg$^{-1}$ more than that of wood although
wood is 4 times denser [3]. The origin of this energy is often regarded as solar and
geothermal; where the former refers to the stored energy in animals and plants obtained
originally from the sun while the latter associates with the thermal conditions which enable
the chemical reactions for the crude oil processes to take place.

1.1.3 Applications of Oils in Transformers

Transformer oils are produced from crude oil. In a number of applications, they are often
required to have a condition and quality that has to be maintained at high standards at all
times. For example, oils used in transformers are required to have strong and sustained
dielectric strength (approximately 60 kV mm$^{-1}$ for breakdown tests for mineral oils at 23 °C
[4]) and good oxygen stability (no greater than 0.2 mgKOH gOil$^{-1}$ [5]) [6]. The dielectric
strength of a transformer oil is also known as the breakdown voltage per unit gap length. This
is a measure of the voltage needed to cause a spark between two electrodes submerged in the oil which is separated by a specific gap (can range from 0.025 - 0.08 cm). A spark is potentially hazardous as it might ignite the oil and would therefore undermine the safe operation of the transformer. Oxidation stability is the ability to withstand moisture and temperature effects decaying the oil over time. This is required for long lasting operation. There are numerous tests with the most common being acidity level, sludge and water content (see Section 2.6).

Nevertheless, no matter how resilient transformer oils are, they will decay over time and will eventually need to be replaced. In transformers electrical stresses, thermal stresses and contamination are the main causes of oil degradation [7], which to a certain extent can be minimised but not avoided. Therefore, the problem is ‘how can degradation be quantified?’ How can the conditions of the oil be classified as being in a state that warrants a replacement? This is a very arduous and complex task, which has resulted in considerable amount of research and development work being carried out to investigate different methods of monitoring the condition and quality of oils.

1.1.4 Fluorescence Spectroscopy

In this dissertation, we study a method that has great potential, most notably in being deployed on field probes working in the real grid transformers - fluorescence spectroscopy.

Fluorescence spectroscopy is an optical analytical method based on the interaction of electromagnetic radiation with matter, such as molecules. The phenomenon of fluorescence was first noticed in the 16th century by a Spanish physician known as Nicolas Monardes and by a Franciscan missionary called Bernardino de Sahagún [8]. They both noticed a blue colour or a “blue opalescence”, as one of them describes it, when water was infused with wood from a small Mexican tree. Many similar phenomena were noticed later, however it was only during the 19th century when it started to become more developed and understood. During this period Sir George Stokes (1864) first proposed that fluorescence spectroscopy could be used as an analytical tool [8]. It was also discovered at this time by Edmond Becquerel (1842) [8] that fluorescence emissions were at a longer wavelength than that of the original excitation source, which provided a strong basis for understanding the phenomenon. Fluorescence spectroscopic technology has since advanced greatly and is now well
established and frequently used in many scientific disciplines for qualitative and quantitative analysis. For example, it is used in the diagnostics of combustion engines, gasoline or fuel fingerprinting [9, 10]; and is often used for the detection of PAH levels in ground soil [11].

In this project fluorescence spectroscopy will be studied for its suitability as a technique for monitoring the condition of transformer oils. It is hoped that, in future, by using such a test method the deterioration condition of the oil can be quickly identified. This expectation is based on several advantages of the technique. For example, it has a sensitive response to certain chemical groups, such as Poly Aromatic Hydrocarbons (PAHs), which are commonly found in transformer oils. It also has a simple set-up and is most likely to be a cost effective and less time consuming alternative to condition analysis methods that already exist (see Section 2.6).

1.2 PROJECT AIMS AND OBJECTIVES

In this project, the focus is mainly on analysing oils used in transformers to achieve insulation and cooling. The aim is to investigate and, develop a method and design a portable instrument to fingerprint the thermally accelerated ageing condition of transformer oils. This project will particularly concentrate on an optical fluorescence method using an UV 404 nm laser diode excitation source in a laboratory setup, and a 365 nm UV LED light source, which is to be coupled to a portable spectrometer and data acquisition system to act as a ‘shoulder strap’ probe for examination of oil. The equipment set-ups will be discussed in detail in Section 4.0.

The objectives throughout this project will be:

- Literature review of: thermal accelerated ageing in lab conditions; fluorescence fingerprinting methods; and the chemistry behind the ageing mechanism. Other existing methods for transformer oil monitoring will also be briefly reviewed.
- Designing new portable equipment to study the fluorescence method for fingerprinting transformer oil condition.
- Using alternative types of transformer oils; for example, Diala S2 ZU-I and Nytro Libra.
- Testing the reliability and performance of the portable probe.
- Identification of required future work and improvements
1.3 THESIS LAYOUT

This thesis consists of 7 chapters. This chapter serves as a general introduction to the background of the project and the structure of the thesis. The other chapters are briefly described below.

Chapter II: Transformer Oils
This chapter gives a description of transformer oils, their properties and uses; their chemistry and ageing characteristics. It also talks about the background theory and applications of existing monitoring techniques.

Chapter III: Fluorescence Spectroscopy
This chapter focuses on the theory of fluorescence and the conditions for the application of this method. It also describes methods that have been used previously and new methods for transformer oil diagnostics.

Chapter IV: Experimental System
This chapter describes the method for oil analysis and the different equipment set-ups used; the oils used and the procedures that followed.

Chapter V: Principal Component Analysis
This chapter will introduce the analysis method known as “Principal Component Analysis” which is used to analyse the data. It will also give a description of the software used to implement this method.

Chapter VI: Results and Analysis
This chapter presents the results from the experiments and the analysis of the results using manipulated data and PCA.
Chapter VII: Conclusion and Further Work

The final chapter of the thesis concludes the work that has been carried out and suggests any additional work that can be done in future. It will also discuss the feasibility and potential of the ‘shoulder strap’ method for online system monitoring of transformer oils.
CHAPTER II: TRANSFORMER OILS AND EXISTING MONITORING TECHNIQUES

2.1 INTRODUCTION

Oils are used in power transformers for cooling, electrical insulation and carrying information [6]. They are commonly known as ‘transformer oils’ and are used in conjunction with cellulose paper and pressboard to form a vital cooling and insulation system to keep transformers in long term, safe operation. Transformer oils are also often thought of as the ‘life-blood’ in transformers. Their purpose is strengthened by the fact that they provide approximately 80 % of the dielectric strength in a transformer [7] and about 70 % of the diagnostic information for transformer maintenance [12]. The conditions of these transformer oils are therefore of major importance and have been a rapidly growing concern among the grid operators both in the UK and worldwide. There are two main reasons for this. Firstly, an exponential increase in the demand of electrical power over the last decade has resulted in rapid industrialisation, infrastructural expansion, and increases in the affordability and usage of electrical appliances. Secondly, there are aged apparatus that cannot be replaced immediately over a short period and would thus require time and money for long term planning. These circumstances cumulatively impose a large strain on the oils in operation, which are also effectively out-dated and ‘old fashioned’ in meeting the design criteria and requirements of the present age. As a result, transformer oils in operation are approaching the end of their operational life ahead of time and have to be replaced. In order to regulate and quantify this problem of ‘operational life’ many monitoring and diagnostic methods were explored and devised. At present, the commonly used methods include: colour testing, dissolved gas analysis, furan analysis, etc. The requirements for these methods are normally specified in the national standards, such as BS EN 60422: 2006 [13].

Transformer oils have been in existence since the beginning of the 20th century [7] and are continuously being developed in order to adapt to the ever increasing demand of electrical power from the consumers. They are produced by refining crude oil through a number of extraction and purifying processes. This chapter will mainly describe the production processes of transformer oils; its properties, ageing process and chemical background. There
will also be a description of traditional and commonly used methods for transformer and oil diagnosis.

### 2.2 EXTRACTION, REFINING AND PRODUCTION OF TRANSFORMER OILS

Crude oil is extracted from the earth and then subjected to a series of physical and chemical processes to produce more useful products. This takes place in an oil refinery which is usually custom designed for only a particular type of crude oil. A typical flow chart of an oil refinery is shown in Figure 2.1. When raw crude oil is first extracted from the earth it will contain a lot of contaminants, such as salt and water, which has to be washed out and removed before the oil can be processed any further. This is done in a unit known as a ‘de-salter’. This unit utilises hot water as an extraction agent (note the salt is dissolved in the

![Figure 2.1 Typical flow chart of an oil refinery](image_url)
water and not the crude oil). The raw feed is first mixed with approximately 4 – 6 % water and is heated to about 120 °C before it enters the de-salter unit. In the unit the water is separated from the crude oil by an electric field. A well performing de-salter aims to remove approximately 90 % of the salt in the raw oil. The oil is then pumped to an ‘atmospheric distillation tower’ which separates the oil further into different levels or fractions by manipulating the different boiling points of the chemicals. Species with relatively low boiling points will be separated first. These intermediate products are further processed to produce fuels and solvents. The residue from the atmospheric distillation tower is pumped to a ‘vacuum distillation tower’ where it is also further separated to produce electrically insulating and lubricant oils. Any further residue from the vacuum distillation tower can be processed to produce fuels, asphalts and bitumen. It is to be noted that the distillate products from the vacuum distillation tower need to be further refined before they can be used as insulating and lubricant oils. This is to remove any contaminants and unwanted chemicals that are still present in the products; for example waxes, sulphur, nitrogen and oxygen containing compounds.

These purifying and separation processes from the vacuum distillation tower include:

- Selective solvent extraction – This process aims to remove any unwanted contaminants or impurities from the product stream by dissolving it in a solvent or through precipitation.
- Sulphuric acid extraction – This process aims at removing sulphuric impurities originally in the crude oil by dissolving it in a fluid to form sulphuric acid or hydrogen sulphide.
- Earth filtration – There are often a lot of physical impurities in the oil when it is extracted from the earth. These impurities are removed via filtration which uses specifically sized pores to separate the fluid from the solids.
- Hydrogenation – Unsaturated hydrocarbons are of little use as fuels and are converted into saturated hydrocarbons in this process. Unwanted impurities are also removed during this stage.
- Re-distillation – This process is the repeated distillation of crude oil to remove any unwanted fluids.
- Filtration – This is similar to the earth filtration process. It aims at removing solid impurities which still remain in the crude oil after earth filtration.
• **Dehydration** – This process aims at removing water and other impurities through evaporation.

In the production of electrical oils special attention is paid to their electrical properties, oxidation stability and gas absorbing properties (see next section). Contaminants such as sulphur, nitrogen and aromatic content are also regulated and kept to a minimum. In producing transformer oils sometimes not all these processes are necessarily needed. A selection of these processes are chosen, simulated and then analysed in order to find an economical solution to produce the desired quality of oil.

Currently, the most common type of oil being produced and used in transformers is probably ‘mineral oil’. Although lubricating and transformer oils are both composed of mineral oils that are produced in the same fraction of the refinery, their application and chemical compositions are different. Lubricating oils are designed to reduce the friction between moving surfaces whereas transformer oils are designed for cooling and insulation. With this in mind their physical and chemical properties are therefore quite different. Nevertheless, the popularity of using mineral oils in transformers is slowly changing as the concerns of pollution and global warming attract more attention. The idea of more sustainable and eco-friendly alternatives is much more appealing. This has led to the development of alternative cooling and insulation fluids, such as vegetable oils and natural esters [15]. Research conducted has shown that in general these fluids have a comparable performance and exhibit similar properties to mineral oil [15, 16]. Nonetheless, the processes required to produce these fluids are still considered quite expensive and not as versatile. Therefore they are still not as favoured as mineral oils yet which are cheaper and more available. Despite this, it is hoped in future as the technological advancements in this area becomes more developed the availability and economical costs will be much more accepted.

### 2.3 TRANSFORMER OIL PROPERTIES, OPERATIONAL ENVIRONMENT AND AGEING

In order for transformer oils to provide sufficient cooling and electrical insulation it must have effective, functional and appropriate properties that are compatible with the system that it works in. It should also not be interfered by maintenance analysis and meet the legal
requirements for health, safety and environmental legislation. Four fundamental properties that are crucial to transformer oils as a dielectric fluid are discussed below.

2.3.1 Dielectric Strength
Dielectric strength is a measure of the ability of a material to withstand an externally applied voltage (a.c. or d.c.) across it without causing a significant electrical current passing through it suddenly (breakdown). It is normally expressed in units of kV cm\(^{-1}\). It is a property of the material and the measured value for transformer oil may be dependent on particle content, type of particles, water content and the test method used. Transformers operate at high voltages which require good electrical insulation between conductors at different voltage levels to avoid electrical breakdown or large leakage current. The dielectric strength of the insulating oil has to be maintained when the transformers operate in continuous mode for years under varying weather conditions. It is related to the chemical composition and purity of the oil. The typical values of the dielectric strength of new transformer oil and used oil can be compared and are shown in Table 2.1 for a sphere to plane test gap of 1 mm gap length. The oil used in the test was Shell Diala A/AX oil which was widely used in industry. The table shows results that were determined at 60 Hz and are in accordance with ASTM D 1816-84a [17] which specifies the breakdown voltages of fresh oil and contaminated oil. The year specifies the year in which the oil was tested. From Table 2.1, it can be seen that the value of the breakdown voltage of the new fresh oil has decreased by approximately 56 % once it has become contaminated which is very significant and can be hazardous to the safe operation of the transformer. Therefore this property has to be monitored in order to avoid such problems.

<table>
<thead>
<tr>
<th>Year</th>
<th>Average Breakdown Voltage (kV) for 1 mm sphere plane gap</th>
<th>Standard Deviation (kV)</th>
<th>Oil Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>34.0</td>
<td>6.1</td>
<td>Fresh</td>
</tr>
<tr>
<td>2010</td>
<td>14.8</td>
<td>2.3</td>
<td>Contaminated</td>
</tr>
<tr>
<td>2011</td>
<td>40.3</td>
<td>4.0</td>
<td>Fresh</td>
</tr>
</tbody>
</table>

2.3.2 Oxidation Stability and Ageing
Oxidation stability can be seen as the ability of the oil to slow down or stop the chemical reactions that will deteriorate the oil in the presence of oxygen throughout its operational life,
which may lead to the production of acids and sludge as the final decay products. This is achieved by the oil because it contains inhibitors that react instead of the oil. Transformer oils are said to be of either two types, inhibited or uninhibited, however in essence all oils are inhibited. Inhibited oils will contain synthetic compounds such as phenols (e.g. DBPC and DBP) which act as inhibitors. Uninhibited oils will contain natural inhibitors which are mainly composed of peroxide destroying compounds. Chemical reactions relating to oxidation will be described later in this chapter. Ageing stability, likewise, is the result of the oil being oxidized and effectively decomposing or ‘growing old’.

Transformer oils decompose because of the electrical and thermal stresses imposed on it. As this happens the insulation and thermal conduction behaviour of the oil will change and its effectiveness will decrease. A quantitative indication of oxidation stability is given by the amount of sludge and acid products formed in the oil. The most commonly used oxidation tests are IEC methods which have been compiled in IEC 61125 ed1.0 (A, B and C which were formerly IEC 74, 474 and 813, respectively) [19]. To summarize, chemical reactions are responsible for the deterioration of the stability of the oil. Therefore, a good oxidation stability is required to slow these chemical processes down so the oil service life can be maximized.

2.3.3 Thermal and Flow Properties

Oils used in transformers provide not only good insulation but also efficient thermal conduction and convection to remove heat from its sources. Convection here means the transfer of energy as a result of the motion of mass. A higher heat capacity, namely the thermal energy stored in a unit mass of oil, will result in more heat energy being removed from the transformer system through convection. A lower viscosity would mean less friction. Thus potentially a higher velocity of the oil flow can be achieved which will allow more heat to be removed from the transformer if necessary.

2.3.4 Consideration of the Operational Environment and General Requirement on Oil

During operation, transformers will be put under electrical, thermal and physical stresses (see below). Thermal stresses in particular are a major problem because they can slowly decompose the organic materials used in cooling and insulation. They are generated when
energy is dissipated in the form of heat from steel sheet cores, copper windings, hysteresis, eddy currents and magnetic flux leakages [20].

There are two types of energy losses; ‘load losses’ and ‘no load losses’ [21]. ‘Load losses’ are generated by electrical currents flowing in the coils; whilst ‘no load losses’ are associated with energy losses from magnetic fields alternating in the core. During normal and peak times of operation these stresses will surge up and down. This continual wear and tear will gradually degrade the cooling and insulation systems reducing its potential life which is essentially the life of a transformer. Transformer oil properties therefore play a key role in the functionality of transformers.

Apart from the properties introduced in the above sections, transformer oils have a variety of other properties. They are categorised as either physical, chemical or electrical properties. However, the boundaries are sometimes not as clear cut and often there are some that can be regarded in multiple categories. In general, physical properties, such as thermal and flow characteristics, are considered important during the design stage. During the operation stage electrical and chemical properties become more dominant and it is thus necessary to monitor the condition of the oil both before and in service.

For transformers to be reliable whilst in operation the insulation system must have certain basic oil characteristics, some of which have been introduced above with details. These properties are:

- Sufficiently low viscosity so that its ability to circulate and transfer heat is not impaired;
- High electric strength to withstand the electrical stresses whilst in operation;
- Adequate low temperature properties in order to survive extreme climate conditions expected at the installation site;
- Proper oxidation resistance to ensure long life in service;
- Good resistance to emulsion to prevent holding water in suspension in the oil;
- Free from inorganic acid, alkali and corrosive sulphur which causes corrosion of metal parts and insulation which can accelerate the production of sludge;
- High flash/fire points (combustion);
- Low pour point (melting point);
- Low water content.
Table 2.2 provides a detailed idea of what different properties are expected to be specified for the various functions in which the oil has.

<table>
<thead>
<tr>
<th>Cooling</th>
<th>Electrical Insulation</th>
<th>Life time</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Viscosity</td>
<td>• Breakdown voltage</td>
<td>• Oxidation stability</td>
</tr>
<tr>
<td>• Pour point</td>
<td>• Power factor</td>
<td>• Inhibitor content</td>
</tr>
<tr>
<td>• Viscosity index</td>
<td>• Impulse breakdown</td>
<td>• Solubility</td>
</tr>
<tr>
<td></td>
<td>• Resistivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Water content</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material Compatibility</th>
<th>Health, Safety, Environment</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Sulphur content</td>
<td>• Flash point</td>
<td>• Density</td>
</tr>
<tr>
<td>• Acidity</td>
<td>• DMSO extractable compounds, IP346</td>
<td>• Interfacial tension, IFT</td>
</tr>
<tr>
<td>• Corrosive sulphur</td>
<td></td>
<td>• Furanic compounds</td>
</tr>
<tr>
<td>• Aromatic content</td>
<td></td>
<td>• Gassing tendency</td>
</tr>
</tbody>
</table>

In the UK, transformer oils in operation can vary extensively in age, chemical composition, manufacturer and origin. Some of these are quite old with incomplete data which can often pose a major problem when they have to be treated. International standards were published by the ‘Commission électrotechnique international’ (IEC), an international organisation made up of different national committees, in order to regulate the oils. For the UK, the British committee imposed the standard BS 148 [22] as a guide for transformer oils in the UK. This information is very important, as the operator can then decide safely and efficiently how maintenance should be carried out or in what way leaks should be treated. Other standards are ASTM D 3487 (American Standard) and IEC 60296. This is to reduce the risk of dangerous accidents and damages taking place which can ruin the environment and surrounding community during oil spills, transformer failure or decommissioning. Nonetheless these standards only state the minimum requirements for transformer oils, whereas many transformer producers, electricity companies and boards have their own stringent specifications based on the operational conditions such as transformer size, operating load, local climate, etc. With advanced refining techniques, it is possible to have transformer oil tailor-made to suit the exact requirements for such specifications.
2.4 CHEMICAL STRUCTURE OF TRANSFORMER OIL

Mineral oils are made up of a diverse range of hydrocarbon structures. They contain carbon chains which can range between C\textsubscript{15} to C\textsubscript{40}. There are also a small percentage of heteroatoms, such as nitrogen, oxygen and sulphur, which are usually bonded to the aromatic hydrocarbons. The carbon structures are made up of three types of basic structural groups, which are represented by the letters P (Paraffinic), N (Naphthenic) and A (Aromatic). A common method of categorising the oil type is to calculate the total percentage of carbon in P, N and A regardless of whether it is an individual compound or with a functional group attached to it [6, 20]. It should be noted that the aromatic content in oils is considerably lower than that of paraffins or naphthenes. Oils are therefore not classified as aromatic. Their content is limited because they are carcinogenic, mutagenic and toxic [6, 23-25]. In the past, carbon analysis mainly depended on the physical properties of the oil such as: the refractive index, density and molecular weight. However this was very basic and not very accurate. The method was later developed and incorporated with spectrographic analysis i.e. infra-red spectroscopy (IEC 590) [20]. Using infrared analysis, if the measured C\textsubscript{P} content is less than 50 % the oil is said to be very paraffinic. If the C\textsubscript{P} content is greater than 56 % the oil is said to be naphthenic [6].

The variety of different molecular structures in transformer oil is very vast and extremely complex, this has the consequence that it is very difficult to identify them all. For example, in one particular crude it took Hobson (1973) approximately 40 years to identify 234 hydrocarbons present in the oil which only represented about 45 % of the entire composition [20]. Nevertheless, this task is not impossible and many scientists have strongly questioned what molecules actually exist and how they react. In addition, many modern techniques, such as chromatography and mass spectrometry, if used correctly, can allow the examination of the oils if given enough time.

2.4.1 Paraffins

Paraffins are saturated hydrocarbons. They have single bonds and contain the maximum number of hydrogen atoms that can be accommodated in a hydrocarbon structure. They have the general chemical formula C\textsubscript{n}H\textsubscript{2n+2} (where n = number of carbon atoms) and can be either branched or straight. The straight chains are normal-alkanes which are also known as
waxes. When these molecules are cooled down their flow becomes restricted. This mostly affects oils that are used in cold climates and therefore it must be removed if it is to be used in such conditions. These molecules also have low solubility in water and lower thermal stability than aromatics and naphthenes. They also have oxidation products that tend to precipitate sludge. Figure 2.2 gives an example of different paraffins: methane (CH\textsubscript{4}) and ethane (C\textsubscript{2}H\textsubscript{6}).

![Figure 2.2 Different types of Paraffins: methane (left) and ethane (right)](image)

### 2.4.2 **Napthenes**

These saturated hydrocarbon molecules are also known as cycloalkanes and those with greater than 20 carbon atoms are typically known as cycloparaffins. They have the general chemical formula C\textsubscript{n}H\textsubscript{2n}. The molecules are connected in a ring structure with 5, 6 or 7 carbon atoms connected by single bonds. However, the 6 ring structure exists more commonly. They have excellent low temperature properties which are ideal for cold climates. Figure 2.3 shows two examples of napthenes: cyclopentane (C\textsubscript{5}H\textsubscript{10}) and cyclohexane (C\textsubscript{6}H\textsubscript{12}).

![Figure 2.3 Different types of napthenes: cyclopentane (left) and cyclohexane (right)](image)
2.4.3 Aromatic Hydrocarbons

These molecules have the general formula \( C_nH_{2n-6} \) and are made up of large molecules of benzene rings. The rings contain 6 carbon atoms connected by alternating double and single bonds. All mineral oils contain aromatic hydrocarbons to some extent. They are perhaps the most important group of molecules in transformer oils as they have important chemical and physical properties. Alkylated monoaromatics have good electrical and gas absorption properties. Polyaromatics are active in the oxidation process and form phenols which act as oxidation inhibitors. They also have strong gas absorption properties. However there are some drawbacks, for example it reduces the impulse breakdown strength and they are carcinogenic. Figure 2.4 shows some examples of aromatic hydrocarbons.

![Different type of aromatic hydrocarbons](image)

2.4.4 Nitrogen Containing Molecules

These molecules usually have a mixed effect on transformer oils but they can still impact its characteristics significantly. Some of these molecules can act as inhibitors to the oxidation process whilst some others can accelerate the process. Some of the molecules can act as charge carriers in electrical fields. Others can help passivate the copper and other types of metals.

2.4.5 Sulphur Containing Molecules

Sulphur, likewise, has a similar effect to nitrogen. It can be both advantageous and disadvantageous depending on the type of molecule. But it should be noted that there are probably hundreds of different types of molecules making it very difficult to discern which is which. Some sulphur containing molecules can capture reactive compounds as peroxides from the oxidation reactions and will improve the oxidation stability of the oil. However the
negative side is that there are also others which can be corrosive to metals. Therefore it is important to optimise the refinement of the oils in such a way that the oxidation stability is non-corrosive.

2.4.6 Oxygen Containing Molecules

The amount of oxygen containing molecules is generally low but it will increase over time as the oil oxidizes. Some oxidation products are: acids, ketones and phenols. Phenols are useful for acting as oxidation inhibitors. There is often a misconception between chemically bonded oxygen and physically dissolved oxygen. These differ because the latter can be removed by degassing.

2.5 CHEMICAL REACTIONS AND REACTION CONDITIONS

Even though there have been relentless efforts from refiners to enhance the quality of transformer oils a small proportion of unstable hydrocarbons always exist due to their convoluted chemical nature. Although the mechanisms of ageing have not been fully understood it can be said that oils age due to the electrical stresses, high temperatures and catalytic copper equipment which exist in transformers [26]. Under these effects the vulnerable hydrocarbons will inevitably decompose homolytically, due to certain weak covalent bonds, to form free radicals [27]. Free radicals have a free electron which causes them to be very unstable and reactive. They play an important role in ‘oxidation reactions’ which lead to the formation of decay products and incipient electrical failures. Apart from oxidation reactions there are also other reactions taking place on a lesser scale. These are hydrolysis and peroxide reactions [28].

It is difficult for decay products to be formed if the hydrocarbon chains do not decompose. Energy is required to break the covalent bonds in the hydrocarbon chains. This is mainly supplied by two sources [7, 29-33]. The first source is from the effects of a strong electromagnetic field which can supply the energy (approximately 4 eV) to cleave a covalent bond and trigger the injection of a free electron into the transformer oil. The second source is the thermal energy being generated by the ‘energy losses’ in overheated areas in the transformer or namely hot-spot areas. Currently, the maximum allowable hot spot temperature in transformers is limited to 140 °C for conventional oil/paper insulation.
Decay products which are commonly formed from ageing are: acids, polar compounds and sludge [26]. These products can have detrimental effects on the properties of transformer oils. They can cause increased viscosity, di-electric loss and reduced breakdown strength [16].

The mechanism of hydrocarbon oxidation is an auto-catalytic reaction. This means that at least one of the reactants is also a product, which thereby creates a chain of reactions that can be self-sustained [34]. The reaction starts off with electrical and thermal stresses in an oxidizing environment leading to the production of a hydrocarbon radical. This radical reacts with available oxygen to produce a peroxy radical, which then removes hydrogen from another hydrocarbon molecule to produce hydroperoxide. The removal of hydrogen from a hydrocarbon will also lead to the production of a new radical and will inadvertently restart the process. Hydroperoxides are very unstable and will decompose to form ketones and water. Ketones can also be further oxidized to form carboxylic acids or split to make aldehydes. Alternatively the presence of hydroxyl groups will lead to the production of alcohols and phenols. These reactions are the core of the auto-oxidation chain reactions and are only really limited to the concentration of oxygen available once the reaction has initiated [26, 34]. Figure 2.5 shows the steps of auto-oxidation.

![Diagram showing elementary steps in hydrocarbon auto-oxidation](image)

Figure 2.5 Diagram showing elementary steps in hydrocarbon auto-oxidation [34]

Most products of oxidation will have an adverse effect on the properties of the oil and transformer. For example, carboxylic acids will either dissolve in the oil or volatilize into the headspace of the transformer. The dissolved acids will damage the paper and copper
windings whereas the volatile acids will corrode the mechanical structure it is in contact with [26].

Catalysts
Oxidation reactions can also be influenced by external catalysts. In transformers there are copper windings and iron cores that will be submerged in transformer oil. These metals will act like catalysts to provide an alternative route of oxidation reaction with lower activation energy. The rate of catalysis does not depend on the mass of the metal catalysts but on the size of the surface area of contact between the metal and the oil. A larger surface area will mean a greater rate of reaction as more hydrocarbon molecules can access the catalytic sites.

High Temperatures
Apart from temperature acting as a source of energy to break the covalent bonds in the molecules they also have a catalytic effect on the transformer oil. More molecules will have the activation energy required for oxidation. Also, molecules will have more kinetic energy leading to more molecular collisions and an increase in the rate of reaction. Temperature will also cause hydrocarbon molecules to decompose into radicals leading to auto-oxidation reactions mentioned before. Therefore a higher temperature will contribute to more radicals being formed.

High temperatures are governed by how much electrical load the transformers are under and so is the service life of the oil. Energy is lost mainly in the form of heat from steel sheet cores, copper windings and other conductive parts of the transformer. The energy loss is generally small and results from less than 5 % of the power input. Typically the temperature rises encountered in transformers are between 30 °C to 60 °C. This is quite big when considering that an approximate increase in temperature by 7 °C doubles the rate of degradation [35].

2.6 EXISTING MONITORING TECHNIQUES FOR TRANSFORMERS

The term ‘monitoring’ is a basic parameter used to describe the measurements which allow threshold alarms. Sometimes this is referred to as ‘diagnostic analysis’. A variety of methods are available to evaluate the condition of the transformers and their insulation systems. The
more traditional methods (dissolved gas analysis, furan analysis, colour, etc.) have been widely used for many years and the more modern methods range from methods that have been used only recently or are still in the research stage.

The existing methods for condition monitoring are:

- Dissolved Gas Analysis (DGA)
- Furan Analysis
- Colour
- Water Content
- Acidity
- Dielectric Strength
- Interfacial Tension (IFT)
- Dielectric Dissipation Factor
- Inhibitor Content
- Sediment and Sludge
- Particles

### 2.6.1 Dissolved Gas Analysis

Dissolved gas analysis as one of the more important oil analysis techniques allows the possibility of distinguishing electrical faults such as partial discharge (corona), over-heating, and arcing in oil insulated equipment. This is because insulating oils under electrical and thermal stresses decompose to release small quantities of gas as it decays. DGA aims to take a number of small samples over a certain period of time to analyze the trends in order to determine the severity and condition of the faults. The tests will analyze the concentration of gases such as: hydrogen, methane, acetylene, ethylene, ethane, carbon monoxide, carbon dioxide, nitrogen and oxygen. The relative volume ratios and amount of different types of gases will then be used to determine the nature of the fault [36-38].

Oil-impregnated cellulosic paper decomposition will generally produce carbon oxides (CO and CO₂), some hydrogen (H₂) and methane (CH₄), which is due to the presence of oil. Transformer oil decomposition processes are more complex. As the oil is heated it will mainly produce ethylene (C₂H₄).
The information provided by DGA is very valuable in analysing the health of the transformer. The results from the data provide the following:

- Advanced warning of developing faults;
- Monitoring of the rate of fault development;
- Confirmation of the existence of faults in the transformer;
- Allowing convenient planning of maintenance;

However, the DGA method has its limitations. Firstly, because of its very good sensitivity, there is difficulty to draw a line between normal and abnormal results, i.e. to be sure that a fault really exists. More information is required in order to make a thorough evaluation of the transformer such as manufacturing details, history of transformer maintenance, loading practice and previous faults. Secondly, DGA analysis is not able to tell the location of the fault although it can indicate what type of fault it is. The conditions inside transformers are not constantly homogenous. The temperature, pressure gradients and different flow characteristics define the complexity of the system. Therefore this imposes limits to the effectiveness of the analysis of the results obtained from DGA. Thirdly, the effective use of DGA as a preventive monitoring technique requires accumulated operational data on real transformers, such as on large power transformers at transmission levels. For example difficulties and confusion arises for distribution transformers as a result of lack of industry standards and relative lack of DGA experience.

In addition, there are distinctive differences between the DGA method and the portable optical probe under investigation in the present work. Firstly, because of the accurate measurement needed for each gas component, gas extraction from oil requires precision, operation and is subject to human errors leading to gas loss. It is not possible to extract all the gases due to the solubility coefficient of each gas. In contrast, with the optical probe method, aged or contaminated oil samples are directly tested. There is no need to extract the gas components. It has a sensitive response to certain chemical groups. Secondly, the whole set of test instrumentation for DGA cannot easily be made into a mobile test platform in comparison with the fluorescence monitoring system. The fluorescence based system can however be made compact to be used as a mobile system. Thirdly, the procedure with fluorescence based monitoring is simpler and the results can be obtained within a shorter time compared with the DGA system.
In general, three steps are required to determine the condition of the transformer. Firstly, it is necessary to establish whether a fault exists or not. Normally there are always some fault gases expected to be dissolved in the oil. When these fault gas levels exceed the recommended safe values a fault is determined. Some safe values of these are shown in Table 2.3 [39].

<table>
<thead>
<tr>
<th>Transformer Type</th>
<th>H₂  (ppm)</th>
<th>CO (ppm)</th>
<th>CO₂ (ppm)</th>
<th>CH₄ (ppm)</th>
<th>C₂H₆ (ppm)</th>
<th>C₂H₄ (ppm)</th>
<th>C₂H₂ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power transformer</td>
<td>75 - 150</td>
<td>400 - 850</td>
<td>5300 - 12000</td>
<td>35 – 130</td>
<td>50 - 70</td>
<td>110 - 250</td>
<td>&gt; 270</td>
</tr>
<tr>
<td>Distribution Transformer</td>
<td>100</td>
<td>200</td>
<td>5000</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>5</td>
</tr>
</tbody>
</table>

The next step is to determine the type of fault. The two most common methods to do this is by studying the key gases and gas ratios [40]. The key gas method requires the plotting of all the Total Dissolved Combustile Gas (TDCG) as a percentage of their total value in a histogram in order to see if there are any distinctive patterns. Different types of faults are expected to give different distinctive patterns of key gases released. For example, for a partial discharge high levels of hydrogen are expected to be present with low levels of other gases. The ratio method is where the ratio is calculated for gases with respect to other gases. The ratios can then be used to determine the severity of the fault by comparing it with recommended safe levels for gases. Table 2.4 shows the faults and the related key gases that are generated.

The final step is to calculate the rate of fault generation. To do this at least two consecutive samples with two consecutive results are required.

<table>
<thead>
<tr>
<th>Material</th>
<th>Condition</th>
<th>Key Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulosic insulation</td>
<td>Overheated &gt; 150 °C</td>
<td>CO, CO₂ and H₂O</td>
</tr>
<tr>
<td>Oil</td>
<td>Overheated &gt; 110 °C</td>
<td>CH₄, C₂H₆, C₂H₄ and organic gases</td>
</tr>
<tr>
<td></td>
<td>Electrical stresses (partial discharge and arcing to 1000 °C)</td>
<td>H₂, C₂H₂, waxes and H₂O</td>
</tr>
</tbody>
</table>
2.6.2 Furan Analysis

In transformers, cellulose is used as a raw material in the production of its solid insulation paper, which is a natural polymer of glucose. This material, being organic, will decompose slowly during service and will release decayed products into the oil. When this happens its mechanical strength, which is one of its vital properties, will start to diminish. Eventually when it loses most of its mechanical strength and is susceptible to mechanical damage the integrity of the system will be undermined. Therefore in order to quantify the mechanical strength of the cellulosic insulation paper the measurement of its mechanical properties is required. This can be done by directly measuring the tensile strength, also known as Degree of Polymerisation (DP), of the insulation paper [42]. However, a major disadvantage of this method is that in order to measure the DP value the insulation paper will have to be removed from the transformer, which is usually done during transformer maintenance. Therefore this method is very impractical and has found many disfavours with people interested in monitoring the condition of the transformer.

The presence of these thermal decay products can be detected through extracting the oil and measuring their concentration by High Performance Liquid Chromatography (HPLC) [43]. During thermal degradation of the cellulosic insulation it is found that the most prominent component of the paper decomposition is 2-furfuraldehyde (Figure 2.6) [44]. The composition of this chemical can be directly related to the DP value of the paper insulation. Moreover the levels of 2-furfuraldehyde can also relate to the average deterioration of the paper insulation. However, the rate of ageing in the paper is not uniform. Different locations have different rates of degradation because of a temperature gradient in the transformer.

![Diagram of 2-furfuraldehyde](image)

Figure 2.6. Diagram of 2-furfuraldehyde

Apart from 2-furfuraldehyde there are also other furanic derivatives such as 5-hydroxymethylfurfuraldehyde, 5-methylfurfuraldehyde, acetylfuran, furoic acids and furfurylalcohol, which are produced on a smaller scale. The concentration of these furans can be measured and the DP can be calculated. The rate of change of the concentration of these furans will
indicate the rate of ageing of the paper. The main advantage of this method is that it will indicate the condition of the paper because the degradation products cannot be produced by the oil. Table 2.5 shows the significance of the different 2-furfuraldehyde levels for a typical power transformer with an oil to paper ratio of 20 : 1.

Table 2.5. Indication of transformer condition from Furfuraldehyde content and DP value [38]

<table>
<thead>
<tr>
<th>Furfuraldehyde content (ppm)</th>
<th>DP value</th>
<th>Condition of transformer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 0.1</td>
<td>1200 – 700</td>
<td>Healthy transformer</td>
</tr>
<tr>
<td>0.1 - 1.0</td>
<td>700 – 450</td>
<td>Moderate deterioration</td>
</tr>
<tr>
<td>0 - 10</td>
<td>450 – 250</td>
<td>Extensive deterioration</td>
</tr>
<tr>
<td>&gt; 10</td>
<td>&lt; 250</td>
<td>End of life criteria</td>
</tr>
</tbody>
</table>

2.6.3 **Colour Tests**

The colour tests are used as a visual reference for the condition of the oil. This is done by comparing the colour of the oil to a colour chart provided by many oil manufacturers. These charts have a colour scale ranging from 0.5 to 8.0 (based on ASTM D 1500) with new oil having a colour number of 1.0 or less and will appear to be clear to a light straw colour. Aged oil will have a dark red to black colour and may indicate contamination such as sludge.

2.6.4 **Water Content**

The measurement of the water content is explained in detail in IEC 814 and 422. Depending on the amount of water present in the oil different methods may be utilised. In general, water even in small quantities can be harmful in transformers because it is present in areas with high electrical stress. Water can accelerate the decay of both the insulating oil and the paper insulation which will release more water as a side reaction. This is a repetitive cycle which will never end until the insulation has been degraded. Once this happens the paper insulation can never (unlike the oil) be returned to its original condition. Water can be present either through internal sources in the transformer or through external sources such as the atmosphere. Externally water can come from silica gel breathers or from leaks in the transformer (e.g. cracked insulation). Internal sources of water are from paper and oil degradation.
2.6.5 Acidity
Acids are decay products from the oxidation reactions and a small proportion may be due to
atmospheric contamination. The measurement method is described in ASTM D974. Acids
can damage the insulation system which may induce corrosion inside the transformer in the
presence of water. If an increase in the acidity is experienced then the rate of deterioration of
the oil will increase. This will lead to the inevitable decay product of sludge. The maximum
acidity of the transformer oil should never exceed 0.25 mgKOH gOil\(^{-1}\). This is known as the
critical acid number. If the acidity is higher than this value, rapid increases in the
deterioration are to be expected.

2.6.6 Dielectric Strength
This method is specified in IEC 156. It is measured by observing at what voltage a sparking
exists between two electrodes that are separated by a specific gap when submerged in oil.
The gap will be specified when conducting the test. For example, for a gap of 2.5 mm the
voltage level will be increased slowly between the electrodes. The rate of rise of voltage is
usually controlled at 2 kV s\(^{-1}\). When the oil breaks down, i.e. when it sparks, the test will
stop and the voltage is recorded. This measurement is repeated 3 to 6 times and the average
value is normally taken. A low breakdown voltage value will indicate the presence of
moisture content and conducting substances in the oil. It is expected that dry and clean oil
will ideally give better results than oil with moisture content and conducting impurities. It is
commonly accepted that the minimum breakdown voltage transformer oils should have is
approximately 30 kV. This test is fairly simple however it is quite popular and frequently
used as it gives a primary indication of the health of transformer oil and the equipment is
fairly portable.

2.6.7 Interfacial Tension (IFT)
The test method for IFT is described in ASTM D971. This method aims at measuring the
tension between the interfaces of oil and water which do not mix. This test is also sensitive to
particularly oil decay products and soluble polar contaminants which are the result of
decayed insulation material. The results are expressed in dyne/cm with good oil having an
interfacial tension of between 40 and 50 dynes cm\(^{-1}\) (equivalent to 0.04 N m\(^{-1}\) and
0.05 N m\(^{-1}\) respectively); and badly deteriorated oil having an IFT of 18 dynes cm\(^{-1}\)
(equivalent to 0.018 N m\(^{-1}\)) or less. In general, the greater the concentration of contaminants
the lower the IFT will be. This is because the oxidation products will lower the interfacial tension which will cause it to have an affinity for both water and oil. This will lower the IFT.

2.7 SUMMARY

Transformer oils and cellulosic paper insulation are vital to the cooling and insulation system in the transformers. Without these systems in place the transformers will fail which result in economic loss and disruption of services which rely on electrical power. Transformer oils therefore need many specialised properties which will allow safe and reliable operation of its system. Some of these properties that are expected of transformer oils are shown in Table 2.6.

<table>
<thead>
<tr>
<th>Properties Expected of Transformer Oils</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Compatibility with transformer equipment and materials</td>
</tr>
<tr>
<td>2. Ageing stability</td>
</tr>
<tr>
<td>3. Lack of maintenance analysis interference</td>
</tr>
<tr>
<td>4. Fulfillment of health, safety and environmental legislation</td>
</tr>
</tbody>
</table>

Transformers being one of the most expensive power equipments used in industry will also need regular maintenance and are expected to have a long service life. For this to happen the transformers will need stable and strong electrical, chemical and physical properties. For transformer oils particularly strong dielectric strength, good oxidation stability and low viscosity is required. These properties would be required to withstand the electrical and thermal stresses that are present in the transformer to a certain extent.

Transformer oils will decay slowly due to chemical reactions, such as oxidation, taking place in the oil during service. However the decay of the oil is not uniform in the transformer as ‘hotspot’ areas tend to have a faster rate of deterioration. Nevertheless as the oil circulates the deteriorated oil will quickly spread over the whole volume. Therefore intelligent and well-planned diagnostic monitoring and maintenance is required. However the more traditional methods that are frequently used, such as DGA and furan analysis, usually require long periods of time to obtain results and use large equipment that is both costly and non-portable. This is not very convenient and efficient. Therefore a more portable, cheap, and less time consuming method that can give a good indication of the transformer oil condition is needed.
CHAPTER THREE: FLUORESCENCE SPECTROSCOPY

3.1 INTRODUCTION

Fluorescence is a deactivation process whereby luminous energy is emitted from an atom or molecule due to the absorption of electromagnetic radiation, typically in the UV and visible range of the electromagnetic spectrum, which can be seen in Table 3.1 [45].

<table>
<thead>
<tr>
<th>Radiation</th>
<th>Wavelength range (nm)</th>
<th>Energy quantum (electron volts)</th>
<th>Absorption or emission of radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma rays</td>
<td>&lt; $10^{-2}$</td>
<td>$&gt; 1.24 \times 10^5$</td>
<td>Nuclear reactions</td>
</tr>
<tr>
<td>X-rays</td>
<td>$10^{-2} - 1$</td>
<td>$1.24 \times 10^5 - 1.24 \times 10^3$</td>
<td>Transitions of inner atomic electrons</td>
</tr>
<tr>
<td>Ultraviolet</td>
<td>1 – 400</td>
<td>$1.24 \times 10^3 \sim 3$</td>
<td>Transition of outer atomic electrons</td>
</tr>
<tr>
<td>Visible</td>
<td>400 – 700</td>
<td>3.11 – 1.77</td>
<td></td>
</tr>
<tr>
<td>Infrared</td>
<td>700 – (5 × $10^4$)</td>
<td>$1.77 \sim 2.48 \times 10^{-2}$</td>
<td>Molecular vibrations</td>
</tr>
<tr>
<td>Far infrared</td>
<td>$5 \times 10^4 - 10^6$</td>
<td>$2.48 \times 10^{-2}$</td>
<td>Molecular rotations</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sim 1.24 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Microwaves</td>
<td>$10^6 - 10^8$</td>
<td>$1.24 \times 10^{-3}$</td>
<td>Oscillation of mobile or free electrons</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sim 1.24 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Radio waves</td>
<td>$&gt; 10^8$</td>
<td>$&lt; 1.24 \times 10^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>

Fluorescence is one of the two phenomena categorized as photoluminescence. The alternative process is known as phosphorescence and the distinction between the two will be discussed briefly later in this chapter. The fluorescence emissions are collected, analysed and represented by excitation or emission spectra. An emission spectrum is the distribution of emission intensity as a function of wavelength induced by an excitation source with a single constant wavelength. Conversely, an excitation spectrum is the dependence of emission intensity at a single wavelength upon different excitation wavelengths. These two types of spectra are normally obtained with a monochromator. They are useful because substantial changes in the spectra provides information about the composition of aged or contaminated...
oil which is then correlated to the dielectric strength and other properties of the oil. In the present work the emission spectra from oil samples using a chosen excitation light source (such as LEDs) are recorded and studied. It is a plot of relative intensity as a function of wavelength ($\lambda$) or energy (eV or cm$^{-1}$); an example is shown in Figure 3.1.

![Emission Spectrum Diagram](image)

Figure 3.1. Diagram showing an example of emission spectrum in the study of fluorescence light emission.

The emission of luminous energy can be summarised in three steps: the absorption of electromagnetic radiation; the excitation of electrons and the emission of photons. This is explained in further detail in Section 3.2.

The excitation of electrons in molecules is slightly different from that in atoms. Atoms can only be excited to different electronic levels whereas molecules can have additional changes in vibrational and rotational levels [23]. This is because molecules have several atoms bonded together and the relative positions of the atoms can influence the electronic properties of the molecules. As a result there is a grouping of levels in which only one structural parameter changes, which is also evident in Figure 3.2.

Figure 3.2 gives a visual representation of these different energy levels which electron transitions can take place in a molecule. It can be better understood by further looking into the energy levels of a molecule.
In principle, the total energy of a molecule is:

\[ E = E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} + E_{\text{tr}} \]  

(1)

where \( E_{\text{rot}} \) is the energy of rotation. This is the energy for the rotation of a molecule as a unit body. \( E_{\text{vib}} \) is the energy of vibration of atoms about their equilibrium positions. \( E_{\text{el}} \) is the electronic energy which is the potential energy due to the electron arrangement in the molecules. \( E_{\text{tr}} \) is the translational energy of the molecule. The hierarchy for the energy required for the excitation of the molecular levels is: electronic levels > vibrational levels > rotational levels. Fluorescence spectroscopy is primarily concerned with electronic and vibrational states.

![Diagram showing different energy levels in a molecule](image)

**Figure 3.2.** Diagram showing different energy levels in a molecule

### 3.2 ABSORPTION, EXCITATION AND EMISSION IN MOLECULES

The first step in the emission of fluorescence and phosphorescence is photon absorption. Electromagnetic radiation at an appropriate wavelength is irradiated onto molecules. These molecules then absorb the radiation as energy and become excited. Molecules can only absorb radiation at specific wavelengths corresponding to their energy levels therefore different molecules will absorb radiation at different wavelengths. From Beer-Lambert’s law (2) it can be seen that the fraction of the incident radiation absorbed by the molecules is independent of the intensity of the light and is only proportional to the concentration of the
absorbing species and the length of the light path. It can be seen that there is a logarithmic relationship between the transmittance \( T \) of light through a medium; the product of the absorption coefficient of a substance and the path length of the light \( I \).

\[
\frac{I}{I_o} = 10^{-\varepsilon cl}
\]

where:
\[
\begin{align*}
I & = \text{Intensity of transmitted light} \\
I_o & = \text{Intensity of incident light} \\
\varepsilon & = \text{Molecular absorptivity coefficient (Litre mol}^{-1} \text{ cm}^{-1}) \\
c & = \text{Concentration (mol Litre}^{-1}) \\
l & = \text{Pathlength of sample (cm)}
\end{align*}
\]

The transmittance is a ratio of the intensity of the transmitted radiation to the incident radiation (3).

\[
T = \frac{I}{I_o}
\]

Taking logs of (2) we get:

\[
\log_{10} \frac{I_o}{I} = \varepsilon cl
\]

\( \log_{10} \frac{I_o}{I} \) is known as the absorbance or the optical density. Absorption spectra are a plot of absorbance against the wavelength.

The second step is the excitation of the outer electrons in the molecules. They are excited from a ground energy level to one of many vibrational energy levels in the excited electronic states.

The final step is the relaxation of the molecules. The excited electrons are unstable and will relax back to the ground energy state via several processes releasing photons. This emission is normally at a longer wavelength than the original excitation light.
Shorter wavelength radiation emissions can happen when an intense excitation beam is used, causing the electrons to absorb two photons instead of one. Therefore, when it deactivates the emission is at a shorter wavelength than the original source. However the probability of this happening is very low and is normally neglected. Emissions that take place at longer wavelengths are the result of the emitted photons having less energy than the original source. This is possible if an excited molecule relaxes to an energy level that is higher than that before it is excited. This is given by Planck’s relation [46]:

\[ E = \frac{hc}{\lambda} \]

where \( E \) is energy, \( h \) is Plank’s constant (6.63×10\(^{-34}\) J s); \( c \) is the speed of light (2.99792×10\(^8\) m s\(^{-1}\)) in vacuum and \( \lambda \) the wavelength of radiation in a specific medium.

The wavelength of the emitted light cannot be shorter than the wavelength of the original excitation source (in the same medium); correspondingly, the emission wavelength (\( \lambda \)) is longer. This shift in wavelength is known as Stokes shift [47], which can be seen in Figure 3.3.

\[ \text{Figure 3.3. Stokes shift in wavelength of the exciting and emitted radiation. The vertical axis is Intensity and the horizontal axis is Wavelength (nm).} \]

### 3.2.1 Fluorescence Transitions Determined by Spin

The concept of electron spin is crucial to the understanding of the fluorescence process and the difference it has to phosphorescence. It is briefly explained in this paragraph. From basic quantum physics, it is commonly known that electrons can only have two spin states, either up (\( +\frac{1}{2} \)) or down (\(-\frac{1}{2} \)). In addition to this, the Pauli Exclusion Principle states that any two electrons in the same atom cannot have the same four quantum numbers, which are: shell (n), subshell (l), energy shift (m\(_l\)) and electron spin (m\(_s\)). It also states that only two electrons may occupy an electron orbit at any one time and that they must have the opposite spin state. This
is known as spin pairing and is the reason why most molecules do not exhibit a magnetic field. These molecules are called diamagnetic and are also not affected by static electric fields. Molecules which contain free radicals are paramagnetic because they have unpaired electrons. Unpaired electrons have magnetic moments which can be attracted to magnetic fields.

Singlet and triplet electronic states exist when an electron is excited to a higher energy level. For electrons to be considered in a singlet state their electron spins must be paired and their electronic levels do not split when exposed to a magnetic field. For electrons to be considered in a triplet state the electron spins are the same as the other unpaired electrons i.e. parallel spin. shows the differences in electronic spins between the different electronic states.

![Diagram showing the differences in spin for various electronic states](image)

Figure 3.4 Diagram showing the differences in spin for various electronic states

Fluorescence and phosphorescence both result in light emission in the visible range, however they differ in many aspects. For example for fluorescence emissions the electronic energy transitions due to excitation has the same electron spin as its previous state. Electron spin is important as it is the main reason why singlet and triplet electronic states exist (Figure 3.5). This is described in more detail later in this chapter. A list of other differences is highlighted in Table 3.2.
Table 3.2. Difference between Fluorescence and Phosphorescence

<table>
<thead>
<tr>
<th></th>
<th>Fluorescence</th>
<th>Phosphorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time for emission</td>
<td>Within $10^{-9}$ s to $10^{-6}$ s</td>
<td>At least $10^{-4}$ s and up to $10^2$ s</td>
</tr>
<tr>
<td>Energy transitions</td>
<td>Singlet excited states</td>
<td>Triplet excited states</td>
</tr>
<tr>
<td>Probability of emission</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Other</td>
<td>N/A</td>
<td>Forbidden transitions</td>
</tr>
</tbody>
</table>

Fluorescence has a very short life time allowing it to compete favourably with other energy relaxation processes in molecules. The wavelength of the emitted light is determined by the energy gap between the ground state and the singlet state. Since a fluorescence photon is always less than the energy absorbed by a given molecule as a prerequisite for this transition, the emitted light has always a longer wavelength than the excitation source. The overall energy balance for fluorescence can be written as:

$$E_{fluor} = E_{abs} - E_{vib} - E_{solv.relax}.$$  

where, $E_{fluor}$ is the energy of the emitted light; $E_{abs}$ is the energy of the light absorbed by the molecule during excitation; and $E_{vib}$ is the energy lost by the molecule from vibrational relaxation. The $E_{solv.relax}$ term arises from the need for the solvent cage (i.e. the molecules around a particular molecule in a solvent) of the molecule to reorient itself in the excited state and then again when the molecule relaxes to the ground state.

Phosphorescence on the other hand has a rather long lifetime and slower light emission process which can range from approximately $10^{-4}$ to $10^2$ seconds. This is reflected by the fact that by quantum mechanical criteria, they are forbidden transitions. For phosphorescence the molecules relax from the triplet excited state to the singlet ground state. This results in phosphorescence intensity usually being much weaker, with the exception of a special group of molecular systems, referred to as phosphors [48-50].

Apart from fluorescence and phosphorescence there are also other processes which compete with fluorescence in order for excited molecules to relax to ground level. They are: internal
conversion, external conversion and intersystem crossing. This explained in more detail in Section 3.3.

![Figure 3.5 - Partial Jablonski diagram for absorption, fluorescence and phosphorescence [51]](image)

### 3.3 PROCESSES COMPETING WITH LIGHT EMISSION AND INFLUENCING FACTORS

The alternative relaxation processes competing with fluorescence are described below with the aid of Figure 3.5. This section is to provide further information on the mechanisms and influencing factors for fluorescence light emission. It will be useful to the interpretation of the results and observed phenomena.

#### 3.3.1 Internal Conversion

This is an inter-molecular process in which a molecule changes to a lower electronic state without the emission of radiation. It is a crossover of two states with the same multiplicity meaning singlet-to-singlet or triplet-to-triplet states. The internal conversion is more efficient when two electronic energy levels are close enough so that two vibrational energy levels can overlap as shown in Figure 3.5 between levels S1 and S2. The lifetime for internal conversion to take place is approximately $10^{-12}$ seconds making it a fairly rapid process. Nearly all molecules occupying an electronic state higher than the second level will exhibit internal conversion.
3.3.2 **External Conversion**

This is also known as collisional deactivation. This happens when a molecule in an excited electronic state collides with other molecules causing energy to be transferred between the colliding molecules and ultimately leads to the deactivation of the excited molecule. Low temperature and high viscosity leads to enhanced fluorescence because they reduce the number of collisions between molecules, thus slowing down the deactivation process.

3.3.3 **Intersystem Crossing**

Intersystem crossing is a process where there is a crossover between electronic states of different multiplicity as demonstrated in the singlet state to a triplet state (S1 to T1) in Figure 3.5. The probability of intersystem crossing is enhanced if the vibration energy levels of the two states overlap. Intersystem crossing is most commonly observed with molecules containing heavy atoms such as iodine or bromine. The spin and orbital interaction increase and the spin becomes more favourable. Paramagnetic species enhances intersystem crossing, which consequently decreases fluorescence. This process takes about $10^{-9}$ seconds.

3.3.4 **Factors and Processes Influencing Fluorescence**

Fluorescence emissions can be affected by different control variables. The molecular structure and chemical environment (species in the system and their density and temperature) of the molecules are good examples. The likelihood of a molecule to fluoresce can be described by the value known as the Quantum Yield ($\phi$). This is a ratio of the number of molecules that luminesce to the total number of excited molecules. Equation (7) shows that quantum yield is determined by different rate constants ($k$):

\[
\phi = \frac{k_f}{k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d}
\]

with,

- $k_f$ being the fluorescence rate constant ($s^{-1}$);
- $k_i$ the intersystem rate constant ($s^{-1}$);
- $k_{ec}$ the external conversion rate constant ($s^{-1}$);
- $k_{ic}$ the internal conversion rate constant ($s^{-1}$);
- $k_{pd}$ the predissociation rate constant ($s^{-1}$) and
- $k_d$ the dissociation rate constant ($s^{-1}$).
The value of constants $k_f$, $k_d$ and $k_{pd}$ are related to the chemical structure and $k_i$, $k_{ec}$ and $k_{ic}$ to the chemical environment. Strong fluorescent molecules have a quantum yield of one and for non-fluorescent molecules their value approaches zero. For example, crude petroleum oils have a fluorescence lifetime of 4 to 5 ns, giving a fluorescence rate constant of $2.0 \times 10^{-10}$ s$^{-1}$ [52]. The quantum yield of the components in petrol ranges from 0.07 to 0.41 [52, 53] with a typical value of 0.07 for Benzene, 0.12 for 1,3,5-Trimethylbenzene, 0.17 for Meta-xylene, 0.17 for Toluene, 0.18 for Ethyl benzene, 0.19 for Ortho-xylene, 0.40 for Para-xylene, and 0.14 for 1,2,4-Trimethylbenzene.

For clarity, below is a description of different factors that might influence the fluorescence emissions.

### 3.3.5 Chemical Structure

The most intense signals of fluorescence are found in compounds that contain aromatic groups. Transformer oils contain polycyclic aromatic hydrocarbons (PAHs) in small concentrations which are believed to exhibit strong fluorescence signals [24, 54, 55]. This high sensitivity and selectivity is an important characteristic in sensor applications, which indicates the possibility of using fluorescence in transformer oil monitoring. Aliphatic, alicyclic and highly conjugated double-bond structures also display fluorescence. There are also other compounds that fluoresce, however they will not be listed because the possibility of their existence in transformer oil is unlikely. There are also chemical groups that inhibit fluorescence, for example carboxylic acids or carbonyl groups on an aromatic ring.

### 3.3.6 Temperature

The quantum yield of fluorescence will decrease as the temperature increases. This is because as temperature increases the frequency of molecular collisions will increase causing the probability of molecules relaxing via external collisions to increase. This process is known as thermal quenching or collisional quenching.

### 3.3.7 Viscosity

A compound with a high viscosity will exhibit better fluorescence because the movement of molecules are restricted and thus will reduce deactivation via collision.
3.3.8 Other Processes

The presence of oxidizing agents, such as dissolved oxygen or traces of peroxides, can reduce the intensity of the fluorescence signal.

Usually excitation sources are in the form of high energy beams (high energy per photon). This can cause the sample to decompose into other chemical molecules. This will reduce the concentration of molecules (photodecomposition) that can fluoresce and will therefore cause a decrease in wanted fluorescence signals.

3.4 EXISTING APPLICATION OF FLUORESCENCE IN MONITORING AND MEASUREMENT

The application of fluorescence spectroscopy has the potential to be used in many areas. Its fundamental principle is to identify molecules or substances that exhibit fluorescence. This allows fluorescence spectroscopy to be used for identification, tracking, monitoring and in many other ways. For example, fluorescence spectroscopy has been used in the detection of PAH contamination of soil or ground water [56] and in the monitoring of hydrocarbon fuels in combustion engine diagnostics [25, 57, 58]. PAHs are known to be carcinogenic and mutagenic. They are extremely dangerous chemicals and if ingested the result could be fatal. Therefore monitoring techniques, such as fluorescence spectroscopy, are essential in order to identify and treat the PAH chemicals. Yeo et al. investigated the applicability of using a 404 nm semi-conductor laser diode for monitoring commercial gasoline.

3.4.1 Monitoring of Commercial Gasoline Using Fluorescence Spectroscopy

In [25], the aim was to investigate and characterize the fluorescence behaviour of commercial gasoline, using at that time, a new, ‘reliable and relatively low-cost’ gallium nitride (GaN) based semi-conductor laser diode. The results were then compared to conventional excitation and optical absorption methods to try and examine the possibilities of using portable instrumentation in future.

Gasoline and mineral oils are both crude oil derivatives that contain complex hydrocarbon molecules. The lighter component, gasoline, contains aromatic compounds that tend to highly
fluoresce. Heavier aromatic molecules are expected to have lower excitation and emission energies although this is dependent on the structure of the molecules to some degree. For example, the lighter components benzene, toluene, and xylene can be excited in the range of 230 to 270 nm and possibly emit between 270 to 330 nm; whilst the heavier components anthracene (C\textsubscript{14}H\textsubscript{10}) and perylene (C\textsubscript{20}H\textsubscript{12}), are excited in the ranges 290 to 390 nm and 340 to 440 nm, respectively. Their emissions ranges are at 370 to 500 nm and 420 to 580 nm [59]. The fluorescent behaviour of gasoline has proven to be very informative because the analysis of its behaviour has been successfully extended into other applications, such as the analysis of emitted pollutants from motor vehicles [9, 10], detection of fuel spills and fuel fingerprinting. Therefore theoretically it can be expected that other substances with similar chemical compositions may exhibit resembling behaviour and can be applied in analytical detection or fuel fingerprinting. As a result transformer oils, which have a chemical composition akin to gasoline, are expected to exhibit similar fluorescence behaviour. Ideally, methods such as condition monitoring or fingerprinting of transformer oils using fluorescence spectroscopy can also be applied.

The equipment set-ups used in [25, 57, 58] were very similar. In [25] two excitation sources were used. The first set-up was used in all three papers. It consisted of a 404 nm GaN based semi-conductor laser diode (Power Technology) with a power output of 30 mW. This was coupled to a 30 dB optical isolator (Optics For Research: IO-3-404-PHU). The fluorescence signals from the samples were fed into a Czerney-Turner grating monochromator (Bentham Instruments: M300), which uses a 69 mm by 69 mm holographic diffraction grating. This has a blaze wavelength of 250 nm in order to perform the spectral scans. The signals from the monochromator are then collected in a photomultiplier tube (Electron Tubes Inc: P30CWAD5-08) which was operating in photon counting mode with a dark count of 40 counts per second in order to provide a spectral resolution of 1.8 nm. This tube was placed at the exit slit that has a slit width of 1 mm in order to improve the sensitivity of the system.

The second setup used was a 75 W high-stability Xe arc lamp (Hamamatsu). The signals were then passed through 6 mm of Schott UG11 filter. This provided 2.4 mW of excitation power. A monochromator and photomultiplier tube, similar to the first setup, was used as well.
The samples used were obtained from major UK suppliers. They were standard unleaded, ultra-low sulphur unleaded and lead-replacement gasoline.

The efficiency of collecting fluorescence emission from a substance greatly depends on the setup of the equipment used. The focus is mainly on the layout of the optical instruments and the position of the sample used. There are many different set-ups such as: perpendicular geometry, inline geometry and front surface geometry. It was found that perpendicular geometry was the most efficient geometry from previous experimentation. Nevertheless it should be noted that this will always depend on the type of experiment that is being done and what the final aim is. In this thesis an alternative method of the front surface geometry will be used whereby we directly inject the optical laser and sensor into the sample. This is explained in more detail in chapter IV.

Figure 3.6 shows the average gasoline spectrum of all the samples measured using the 404 nm setup. It can be seen from this graph that there are peaks around 420 and 440 nm, which are in the visible spectrum range. This means that there are molecules present which consistently have strong fluorescence emissions at around these wavelengths. This can also be seen in Figure 3.7, which shows the emission spectra of different gasoline samples excited using the 404 nm semi-conductor laser diode. The main difference between the spectra of these gasoline samples is the intensity. The results here show that different types of gasoline may be differentiated by their fluorescence spectra.
Figure 3.7. Graph showing summary of the liquid gasoline samples showing similar spectral features [57]

3.4.2 Selection of Excitation Wavelength

The optimum wavelength in which different oils are expected to fluoresce was investigated by Tan [60], using the setup shown in Figure 3.8, which is a perpendicular geometry where the laser was used to excite the sample in the cuvettes directly.

A mode locked titanium: sapphire laser (Mira Optima 900-D), which can be tuned from 710 nm to 1000 nm, was used as the excitation source. In the pulsed mode, it has a repetition rate of 82 MHz and pulse duration of 180 femtoseconds. The laser beam diameter is 0.8 mm. No coupling optic fibre was used between the laser and the sample. The laser directly excited the sample. The Mira 900 was tuned from 800 nm down to 700 nm with an interval of 10 nm. To obtain shorter wavelengths, a second harmonic generator was used to halve the input wavelength. The INRAD ultra-fast harmonic generation was used to provide the second harmonic required to excite the hydrocarbons down to 350 nm. The output power from the second harmonic generator is kept at a constant of 15 mW to ensure consistency throughout the experiment. An Ocean Optics USB2000 spectrometer was used to measure the induced fluorescent light. This spectrometer is based on the Czerny-Turner configuration with a high performance and low cost 2048 linear silicon CCD array (Model ILX511) from Sony. The system has a sensitivity of 86 photons per count and a signal to noise ratio of 250 : 1. For a CCD detector, the incoming photons are first converted into photoelectrons. Their ratio is quantified by the Quantum Efficiency (number of photoelectrons to incoming photons). The photoelectrons for a pixel are then converted into a voltage signal (readout) before being digitised via an A/D converter. The Gain means the number of photoelectrons needed to
produce one count, i.e. one analog-to-digital unit (ADU). The number of photons per count reflects the sensitivity of the CCD detector.

Figure 3.8. Experimental setup by Tan in order to obtain fluorescence spectra of gasoline and transformer oils at various wavelengths [60]

Using this setup six different samples were used. They were:

- BP Lead Replacement Petrol (LRP)
- BP Super Unleaded (SUL)
- BP Unleaded (UL)
- New transformer oil (NO)
- Dirty Used transformer oil (DUO)
- Clean Used transformer oil (CUO)

An example of the results obtained is shown in Figure 3.9 where the results have been normalised at 499.9 nm. By normalisation it is meant that the emission spectra from different excitation wavelengths are scaled so that their readings at 499.9 nm all equal to the corresponding value of a selected spectrum. Therefore the absolute values do not bear much significance after the normalisation process. It is the relative differences that matter. It can be seen that transformer oils exhibit similar fluorescence emissions to that of gasoline (around 420 nm and 440 nm). The results suggest that fluorescence methods used in gasoline monitoring can be possibly applied to transformer oils.
Figure 3.9. Graph showing the fluorescence spectra of new transformer oil which has been normalised at 499.9 nm [60]

Table 3.3. Different optimal wavelengths for excitation of oil samples [60]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optimal Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirty Used Oil (DUO)</td>
<td>380</td>
</tr>
<tr>
<td>Cleaned Used Oil (CUO)</td>
<td>360</td>
</tr>
<tr>
<td>New transformer oil (NO)</td>
<td>380</td>
</tr>
<tr>
<td>Lead Replacement Petrol (LRP)</td>
<td>380</td>
</tr>
<tr>
<td>Super Unleaded (SUL)</td>
<td>385</td>
</tr>
<tr>
<td>Unleaded (UL)</td>
<td>380</td>
</tr>
</tbody>
</table>

By changing the excitation wavelength from 400 to 380 nm there was a 20 % increase in the peak signal and 10 % on the integrated signal, based on the spectra without normalisation. However, it was also found that using excitation wavelengths shorter than 400 nm would cause the optical fibres to attenuate heavily because the attenuation of an optical fibre is a function of wavelength. Therefore a compromise must be made between the excitations wavelength and the signal quality so that the fibres can be efficiently coupled. In the work of [60] as discussed in this section, no optical fibre was used in obtaining the results such as those shown in Figure 3.9 because of the attenuation problem of the optical fibre as a function of wavelength. The excitation wavelength was identified to be 380 nm based on the increase of the peak signal and integrated signal mentioned above, consideration of the attenuation issue of optical fibres, and also the fact that the spectra with 380 nm as the
excitation wavelength is most feature-rich in the range of 400 nm to 500 nm. Table 3.3 gives the identified optimum excitation wavelength for different types of oils in [60].

In addition, a study was carried out by Hindle and McCann [53] on the fluorescence of a gasoline sample diluted in Iso-octane stimulated by a blue LED (with peak emission wavelength of 460 nm) by performing a spectral analysis of both the source and the emitted light using a computer-controlled scanning monochromator. The spectrum is rather smooth spanning from 440 nm to 650 nm centred at 510 nm. This is different from the spectra shown in Figure 3.9. There are two possible reasons for this difference. Firstly, the samples have different chemical compositions and secondly the excitation light sources have very different wavelengths. It is to be noted that an optimal excitation wavelength of 330 nm is determined for gasoline.

3.5 SUMMARY

From previous work it can be seen that transformer oils which exhibit similar properties to gasoline can also exhibit similar fluorescence. They have peaks around 420 and 440 nm which are both in the visible spectral range. For transformer oils the optimal excitation wavelength is suspected to be around 360 to 380 nm. As the oils age the chemical compounds in the oil are also expected to change. In particular it is hoped that the fluorescence emitting compounds, aromatic hydrocarbons, will decrease as they are also decayed. When this happens the intensity of the fluorescence exhibited should decrease as the concentration of these molecules decrease. By analysing this trend it is expected a relationship can be deduced so that the ageing condition of the transformer oil can be monitored. In addition using portable fluorescence systems will allow the possibility of online system monitoring. This would reduce the need of relying on more traditional methods that are both time consuming and expensive.
CHAPTER IV: EXPERIMENTAL SYSTEM

4.1 INTRODUCTION

The detection and analysis of fluorescent radiation emitted by a substance greatly depends on the setup of the equipment used. The measurement hardware has to meet a number of requirements, as listed below:

- Ability to induce and sense the fluorescence emission from the test samples with reasonable sensitivity. This will require the selection of proper excitation light source so that fluorescence emission from the sample is detectable and easily distinguishable from the rest of the spectrum.
- Ease of operation. The test procedure should not contain difficult and complex handling of the samples and equipment to ensure the correctness of the results.
- Reasonable repeatability. Good repeatability allows a degree of confidence and reliability in the results to be established. This is particularly important when a large number of samples over an extended period are to be tested. It is also an indication of the robustness of the measurement system.

To ensure the proper operation of the hardware system, the focus is on the layout of the optical instruments, the spectral response of the detection system, and the position of the sample used.

There are different set-ups which can be used in order to measure the fluorescence of a sample. There is perpendicular geometry, inline geometry and front surface geometry. These types of geometry influence the efficiency of the fluorescence collected due to the positioning of the instruments and their samples. In particular it is found that perpendicular geometry has the best possible performance. Figure 4.1 shows the position of the equipment in perpendicular and front surface geometry.
4.1.1 Perpendicular Geometry

In this setup, the excitation source is placed perpendicular to the collection fibre. This setup allows the collection of fluorescence signals without much interference from the backscattering of the excitation beam. It has been shown that the forward and backward direction of the incident radiation experiences the strongest back scattering [60]. This is why perpendicular geometry is preferred as to reduce the back scattering of the incident beam.

4.1.2 Inline Geometry

In inline geometry the detector is placed opposing the excitation source on the same line. This is usually used for absorption measurements as any signal which is not attenuated by the sample will be collected by the collection fibre. It is expected in this geometry that the fluorescence signals will be collected with the excitation signal. This can cause problems if the sample is very dilute or concentrated. In very dilute samples the signals collected from the excitation beam may be much stronger than the signal from the fluorescence. Likewise if the sample is very concentrated an inner filter effect will take place and the emission is likely to take place close to the excitation source causing a reduction in the signal collected by the detector.
4.1.3 Front Surface Geometry

In front surface geometry the collection fibre is positioned alongside the excitation source. This geometry is preferred when the sample is a very strong absorbing species. The disadvantage of this setup is that there is very strong back scattering which is also collected by the collection fibre.

4.1.4 Chosen Experimental Setup

The perpendicular geometry was the most efficient geometry as there were fewer problems with backscattering. This is true only when the excitation light is able to penetrate into sufficient depth in the oil to induce fluorescence emission that can be collected by the fibre. In addition, the emitted fluorescence light is able to transmit through the oil sample to reach the collection fibre. It is therefore true that the choice of the experimental arrangement is best based on consideration of the optical properties (absorption coefficient, quantum yield, etc) and the type of results that is desired.

Transformer oils are mixtures consisting of up to 2900 alkane, naphthenic and aromatic hydrocarbon molecule [55] with 25 % of aromatic hydrocarbons being fluorescent species. Alkane and naphthenic compounds do not absorb in the near UV region (200 - 380 nm). It is the aromatic compounds in the transformer oil that absorb at in this region. The quantum yield of aromatic compounds range from 0.1 to 0.4 [59]. There is work on the measurement of the absorbance of silicone oil [61] and transformer insulation oil, the optical path length is however not explicitly given. There is little work to directly measure the absorption coefficient of aged transformer oil at different degree of degradation. The composition of the transformer oil changes substantially during the ageing process, including the appearance of copper particles suspended in oil. It has not been able to quantitatively estimate the conversion efficiency. Despite this, it is still worth pointing out that the effect of a high optical density of the transformer oil under aged condition on the fluorescence intensity is the main drawback of the perpendicular geometry with relatively large optical path length. By moving the excitation and collecting fibres closer together, the efficiency of collection is improved as inner filter effects are reduced. By inner filter effects we mean that the attenuation of excitation source light and absorption of emitted fluorescence light.
For this project a similar geometry to the front surface geometry is chosen whereby we directly inject the optical laser and sensor into the sample instead of placing it in front of the cuvette. Alternatives to front surface geometry were not considered in detail because they were not included in the aim of the project and were much less suitable for a portable and infield deployable probe. This choice is based on the following considerations:

- Aged transformer oil loses its transmittance to visible light and in the extreme case (severely aged oil) induced fluorescence light can hardly reach the collection fibre in the perpendicular geometries in Figure 4.1, especially Geometry (A).
- The front surface geometry has the advantage of being able to collect the fluorescence induced near the immersed excitation source, especially for heavily aged transformer oil with dark colour.

There is a need to experiment whether the application of front surface based sensors which is simpler in structure can be directly placed on transformers for online monitoring.

The experimental system employed two types of optical systems which were both obtained from Ocean Optics. For the ease of reference, the first system will be known as ‘A’ and the second system will be known as ‘B’. Both of these systems were used for spectral analysis of transformer oils in order to characterise their fluorescence emissions. Nevertheless their excitation light source and the reasons for their application are quite different.

System A has a more traditional setup with separate components connected to each other. It was larger and bulky so therefore was not ideal for portable usage. System B was much more modern and with a very portable setup. The applicability and feasibility of both systems are discussed in more detail in Chapter VI.

In order to perform basic spectral analysis some essential components are needed; these are:

- Excitation light source: to provide the light that can cause fluorescence to be emitted from the transformer oil. The wavelengths used are 365 nm (System B) and 404 nm (System A).
- Opto-isolator: used to protect the laser module by preventing any backscatter radiation from reaching the excitation source.
• Spectrometer: to separate the spectra of the emitted fluorescent light into well resolved wavelengths.
• Optical detector: to detect the intensity of radiation at selected wavelengths.
• PC for data acquisition and analysis

It should be noted that some of these components may not always be clearly visible and may be integrated into one instrument. However they are still existent and required for basic spectral analysis.

4.2 SYSTEM A

This system is different to other systems used to measure the fluorescence of engine oils, hydrocarbons, lubricants, PAHs, etc. [23, 25, 57, 58]. The system includes a 30 mW Gallium Nitride (GaN) based semi-conductor laser diode (Power Technology: PPM-LD-1380-T) operating at 5 mW level. It emits a 404 nm blue beam which is used to excite the hydrocarbon molecules in a sample. An internal cooling system keeps the emission wavelength variation within ±0.15 nm. The FWHM of the laser diode is not known. However, Power Technology which delivered the laser at that time was using blue nitrogen gallium nitride laser diodes which were manufactured by Fabry–Pérot Technology and therefore the line width corresponds to a multi-mode cavity.

The laser is coupled to an optical isolator (Optics for Research: IO-3-404-PHU) to block any back reflections generated. The isolator is able to provide a maximum of -43.6 dB attenuation of the reflected light and a forward transmission of 0.89 at 488 nm. For the present system operating at 404 nm it actually provides a backward isolation of -29 dB (0.126 %) and a forward transmission of 0.4.

These instruments are connected to an optical probe. The probe (QR400-7-VIS) consists of a 2m long fibre bundle with a core diameter of 400 µm for each fibre and a probe ferrule of 6.35 mm diameter. The central fibre is used to channel the measured signal beam which is surrounded by six 400 µm fibres to channel the laser beam. The relative transmittance of the fibres in the spectral range of 400 – 800 nm is better than 90 %.
The intensities of the fluorescence generated at different wavelengths are measured by a spectrometer (Ocean Optics USB 2000) and photo detector (a 2048 elements Sony ILX511B linear CCD array) which then sends the data to a computer for analysis.

The actual power reaching the sample is affected by a few factors, such as the forward transmission of the isolator and the efficiency of the optical fibre (types of glass, purity of glass, fused interface between the core and clad, the quality of the end finishing and assembly of the parts). The optical fibres are normally locked in the equipment box and its length cannot be measured accurately.

Before the start of the experiment the laser power delivered by probe was 0.18 mW and because of the character of the setup it was not possible to measure this value in the oil volume. However at the end of the experiment it was confirmed the power had not degraded notably. Therefore we can assume that all the samples have been investigated with the same level of excitation power. The particular power delivered by the laser has less importance because our assessment is not quantitatively in terms of fluorescence intensity.

The arrangement of System A is shown in Figure 4.2.

From earlier works [25], the laser module was used because at that time it had one of the narrowest emission wavelength bandwidths on the market for good portability, compactness and inexpensiveness. The wavelength of this system may not be ideal to excite large range of hydrocarbons. However it does provide a compromise between the optimal wavelength for hydrocarbon excitation and the shortest excitation wavelength bandwidth preferred. Further advancements in spectral analysis instrumentation have led to even more portable and cheaper equipment. This led to the design of System B as described in the next section.
The sensitivity of this system is 86 photons / count. In the obtained results the intensity of spectra were varying between 300 and 3000. This suggests a range of radiative energy of $1.3 \times 10^{-14}$ to $1.3 \times 10^{-13}$ J at 440 nm was received by the CCD detector in 100 ms of integration time, which is equivalent to the range of $1.3 \times 10^{-13}$ to $1.3 \times 10^{-12}$ W within a short interval of wavelength corresponding to the CCD pixel spectral resolution of 0.33 nm. There is very strong backscatter light from ultraviolet laser which may exceed the range of sensitivity of the USB 2000 system. Thus the backscatter intensity is very strong but is not possible to quantify.

4.3 SYSTEM B

The optical probes and the spectrometers used in System A and System B are the same. However System B has a much more compact design.

This system is a newly designed optical system known as the Jaz™ (Ocean Optics Inc.). It has the essential characteristics for cost-effective, portable online monitoring of transformer oils and many other applications (e.g. field applications, remotely controlled, process flow and quality assurance). It has stacked modules along with autonomous components which can combine to form up to a maximum of eight modules. The purpose of this equipment and setup was to check whether the traditional spectral methods of analysis, i.e. System A, could be used on more portable and compact instruments with shorter wavelengths, i.e. LEDs. LEDs are used because they are cheaper, more compact and easily portable.

The Jaz™ (Ocean Optics Inc.) setup used in the experiments throughout this project was specifically chosen and its configuration was specified to meet the needs of the project. It consisted of four modules as these were the most essential components. This meant the design was compact and lightweight which was most suitable for the aim of portable or online performance. The Jaz™ (Ocean Optics Inc.) modules are connected together internally when they are stacked together. The design is shown in Figure 4.3. These constituting modules were:

1) DPU module for data processing
2) Battery module
3) JAZ-INTLED 365 nm light source module
4) Spectrometer module
There is also an optical probe used to mediate the excitation beam and collected signal.

![Image of the modular measurement system (System B) used in the project](image)

**Figure 4.3.** Image of the modular measurement system (System B) used in the project

### 4.3.1 The DPU Module

This module serves as the user interface. It contains a Blackfin™ embedded microprocessor which directs the interactions between the modules and also handles data processing, logging and distributed computing. This eliminates the need for a PC. It has the dimensions 109.2 mm by 63.2 mm by 14.2 mm and has a $128 \times 64$ OLED display which offers a clear and perceptible display of the measurements. The module is also quite light and weighs only 90.72 g. It also allows custom programmed scripting. The display is flexible and can be turned by 180° to allow visual convenience during portable usage. The module only consumes approximately 1 to 2 W. The display is shown in Figure 4.4.

![The control and display panel of the DPU module](image)

**Figure 4.4.** The control and display panel of the DPU module

### 4.3.2 The Battery Module

This module is stacked underneath the DPU module and contains a rechargeable lithium-ion battery which can allow autonomous data collection with a power-conserving sleep mode for
long-term measurements and can be used for up to 8 hours. It has a voltage of 5 V maximum and a capacity of 14.8 W h. It can be recharged through Ethernet, USB or external power supplies. It also contains two SD card slots which can store the data collected simplifying data transfer to the PC.

4.3.3 The JAZ-INTLED Module
This module is stacked underneath the DPU module and contains an interchangeable 365 nm blue LED used to excite the sample under examination. This module has the dimension 109.2 mm by 63.5 mm by 28.58 mm. The time required for a stable output is approximately 30 minutes. This module contains a connector for an optical fibre (fibre optical probe) to carry the light source. The power is provided by the battery module and consumes approximately 0.2 W. This can be controlled using the DPU module. The LED is connected to a 400 µm reflection probe (QR400-7-VIS), the same as that used in System A. It has a monocoil jacketing. The relative transmission in the spectral range of 400 – 800 nm is better than 90 %. A comparison of the characteristics of the two systems is given in Table 4.1.

4.3.4 The Spectrometer Module
This module is functionally the same as that used for System A. It is the last module and is stacked underneath the LED light source module. It has replaceable slits and a Czerny-Turner optical bench design. This spectrometer module is very flexible because it has gratings and external slits that are easily switched out by qualified users. It uses a 2048 elements Sony ILX511B linear CCD array (200 - 1100 nm) detector with 14 gratings (UV through to Shortwave NIR). The entrance slits can be chosen from a range of 5, 10, 25, 50, 100 or 200 µm widths. It has an optical resolution of approximately 0.3 - 10.0 nm (FWHM) depending on the grating and slit width. The integration time of the optical detector can be adjusted between 870 µs to 65 seconds. This module also has a slot for the connection of the optical probe.

The slit width of the spectrometer was fixed to 50 µm when it was delivered and subsequently used in the experiments. A 600 line grating was used. This gives a spectral resolution of approximately 3 nm. The integration time 1 second with a sampling interval of 10 seconds.
The dynamic range of a system is defined as the full scale signal divided by the minimum resolvable signal. For the spectrometer in use, the minimum resolvable signal is taken as the standard deviation of the dark signal. Contributions to the dark signal include readout noise and other system electronics noise. The given dynamic range is 1300 : 1 (approximately 31 dB). It is to be noted that the dynamic range is different from the A/D converter’s resolution. The dynamic range is a measurement of the spectrometer’s performance without involving detecting any light. It is therefore not an indicator of the quality of the signal in the measurement of spectra.

On the other hand, the signal to noise ratio (S/N) indicates how precisely the spectrometer can measure a certain light level. The S/N is defined as the energy of the signal to that of the noise. The given S/N for the spectrometer is 250 : 1. This value is much lower than the dynamic range of 1300 : 1 or 31 dB. This is due to the probabilistic nature which governs light measurements, i.e. when light is measured the total noise level in the signal is higher than the dark noise of the system.

It has a sensitivity of 75 photons per count at 400 nm which allows the counts delivered by the software to be converted into intensity. Under normal circumstances the background elimination resulted in background noise of the order of 300 counts.

For the purpose of easy data analysis the Jaz™ (Ocean Optics Inc.) module was connected to a laptop and the optical probe was inserted into a specially made dark box so that there was minimal interference to the readings. This can be seen in Figure 4.5.

A comparison of the characteristics of the two systems is given in Table 4.1.
Table 4.1 Characteristics of the two Systems A and B used in the present work.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>System A</th>
<th>System B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power of light source</td>
<td>GaN laser diode (PPM-LD-1380T) from Power Technoogy Inc. Maximum output power of 25 mW, operated at 5 mW in experiment.</td>
<td>JAZ-INTLED-365 from Ocean Technology with output power of 1 mW.</td>
</tr>
<tr>
<td>Estimated optical power reaching sample</td>
<td>0.18 mW</td>
<td>0.18 mW</td>
</tr>
<tr>
<td>Central wavelength (nm)</td>
<td>404</td>
<td>365</td>
</tr>
<tr>
<td>FWHM (nm)</td>
<td>Blue nitrogen gallium nitride laser diode from Fabry–Pérot Technology with multi-mode cavity.</td>
<td>9</td>
</tr>
<tr>
<td>Mode of operation</td>
<td>Continuous</td>
<td>Continuous at 12VDC and 500 mA, or pulsed mode at 1000 mA with a duty cycle of 50 %.</td>
</tr>
<tr>
<td>Optical fibre connection</td>
<td>UV-VIS fibre with a flat transmittance of 90 % over the range of 400 – 800 nm. 6×400 μm (diameter of core) for delivering laser beam and 1×400 μm for detected light emission.</td>
<td>Not necessary</td>
</tr>
<tr>
<td>Optical connector / coupler</td>
<td>Optical isolator (IO-3-404-PHU) with -29 dB reflected light attenuation and a measured forward transmittance of 0.4.</td>
<td>Not necessary</td>
</tr>
<tr>
<td>Spectrometer</td>
<td>USB 2000 Czerny-Turner spectrometer with bandwidth of 400 – 850 nm and 600 lines grating blazed at 500 nm. The inlet slit width is 50 μm, giving a spectral resolution of 2 nm.</td>
<td>Sony CCD array (ILX511B).</td>
</tr>
</tbody>
</table>

4.4 SPECTRASUITE® PARAMETERS

Ocean Optics SpectraSuite (2008) was the software used to display spectrometer readings of both System A and B. An installation CD was supplied along with both systems however the software can be found on the Ocean Optics website if required (http://www.oceanoptics.com/technical/softwaredownloads.asp) [62].

4.4.1 Consideration and Setting of System Parameters

After the system is properly initialised, it is necessary to set the system parameters before any measurements can be taken. These parameters are:
• Integration time
• Scans to average
• Boxcar width

The integration time is defined as the length of time during which the photo detector is exposed to the spectrum resolved by the spectrometer. It is similar to the role of a shutter in a camera. The higher the specified value the longer the detector will be exposed to the incoming photons. For the experiments performed on each of the two systems the integration time was kept constant, if possible, to show the relative changes in the graphs during scope mode. The strength of the output signal from the detector is proportional to the integration time as long as the output is not saturated. Because of the oil samples were aged for different period, their ability to emit and transmit fluorescence is rather different. To obtain output with reasonable counts yet without saturation, the integration time for System A was chosen to be different for different samples: 50 ms, 100 ms, and 1 s. The integration time shorter than that used for System B because its light source is more powerful than the latter. For System B the power of the light source is 1 mW and that reaching the sample is around 0.18 mW, indicating that this system has a better optical coupling efficiency. It was found that a single integration time of 10 s is acceptable for most of the samples.

The ‘scans to average’ parameter sets the number of discrete spectral acquisitions that are accumulated before the spectrometer receives data. This means a user-defined number of scans will be taken and averaged before a waveform is sent to the PC. The larger the value the better the signal to noise ratio (S : N). The S : N will improve by the square root of the number of spectra averaged. This value was set to 1 for all the measurements.

The ‘boxcar smoothing width’, as it is also known, is a technique which averages the spectral data. This method averages a group of adjacent detector limits. For example, a value of 5 would average 5 points to each of the left and right sides. A higher value would provide smoother data and a greater S : N ratio. However if the value is too large there is a loss of spectral resolution. The S : N ratio will improve by the square root of the number of pixels averaged. For the measurements of both System A and B the boxcar width was set to 5 as this provided a reasonable smoothness in the data without much loss in spectral resolution. To verify this, the number of points was varied between 2 and 10 and the spectral resolution for
the fluorescence signals obtained in the present work was not noticeably affected. The 5 point boxcar averaging was also used in previous studies [63].

4.5 MAP OF EXPERIMENTATION

There are three objectives of the experiment. Firstly, a number of commonly used transformer fluids are to be tested for their ability to emit fluorescence light. Secondly, different ageing environment is to be replicated in the laboratory in view of the fact that it is difficult to obtain oil samples with different aged conditions from real operational transformers. Thirdly, the fluorescence emission data of oils with different ageing conditions are to be obtained to provide baseline information for further analysis and characterisation.

A well-planned experimental procedure is required because of the large amount of preparation and short length of time involved. The procedure from start to end can be divided into six sections, which are:

1) Experimental planning
2) Equipment preparation
3) Oil preparation
4) Air-circulated ageing
5) SpectraSuite setup
6) Timely removal of oils from the thermal oven and measurements

4.5.1 Transformer Oil Ageing and Experimentation

In the present work there were three different types of oils that were used for fluorescence measurements; they were:

- Shell Diala S2-ZUI
- Nynas Nytro Libra
- Shell 10 GBN

Diala S2-ZUI, Nytro Libra, and 10 GBN are uninhibited transformer oils. Uninhibited oils were the main samples for experimentation because the majority of transformer oils still in operation in the UK are uninhibited and therefore the results would be more related to the present circumstances.
4.5.2 Oil Preparation

Diala S2-ZUI and Nytro Libra were stored in large liquid containers of approximately 100 L in a cool (approximately 15 °C outdoors) and dark environment. The oils were extracted using a large plastic pipette and stored in 250 ml bottles.

These oils were aged for a period of six to eight weeks at elevated temperatures. The choice of the ageing period and temperature is based on results observed in previous work and by trial tests performed in the present work. A compromise between the ageing period and temperature has to be made to ensure safety of experimentation, comparable ageing effects to real environment, and an ageing period as short as practically possible to minimise the experimental cost. Temperature of 110 °C and 120 °C had been used in previous experiments. In the present work a different temperature is to be used for ageing two types of oils. However the ageing temperature has to be lower than the flashpoint (140 °C). Thus an ageing temperature of 130 °C was chosen in the experiment. With this temperature a period of 6 - 8 weeks is sufficient to achieve considerable ageing of the oil samples.

Each sample was contained in an individual bottle. Firstly, each bottle sample was filtered to remove any solid particles in the oil. A Fischer 250 ml filter was used. The pores of the filter were 0.2 µm and it took about 3 - 4 hours to finish the filtering under natural conditions. With the aid of a vacuum pump the filtering process was sped up and the required time was reduced by approximately half. Once all the oils were filtered they were put into a thermal vacuum oven at 75 °C in order to be dried.

The vacuum oven is often used to remove any bubbles in the oil before experimentation. Bubbles may influence the fluorescence measurements of the oil by either deflecting or changing the path of the irradiation beam and hence the number of transmitted photons.

The samples were left in the oven for approximately 48 hours to ensure that the oils were thoroughly dried so that moisture is not a major influence on the acceleration of the ageing process.

Once the above process was over the pressure of the oven was restored to atmospheric level and the heating in the oven was switched off to let the oven cool for 4 hours. This allowed the
sealing around the oven door to shrink back to its original shape and the oils to be removed safely. At this stage the drying process was completed. It is to be noted that the drying process was to remove the moisture from the oil, it was not an ageing process. The oil bottles were then removed. The caps of the bottles were removed and copper in the form of sheets of the surface area of 4 cm² (1 cm by 1.9 cm by approximately 0.1 cm) per 250 ml of oil was added to imitate oils in operational transformers. Sealing tape was then applied to the mouth of the bottle (to prevent moisture, air and gases entering or leaving the bottle) before the caps were put back to close the bottles. In doing so the number of variables affecting thermal ageing was limited and accelerated ageing is controlled to a certain extent. The oil can now be thermally aged.

All samples were prepared following the same procedure as described above. The total number of samples prepared is 45 with 8 Diala S2-ZUI, 7 Nytro Libra and 30 10 GBN samples. Each sample was contained in a separate bottle.

### 4.5.3 Ageing of Oil (Air-Circulating Thermal Ageing)

The 250 ml bottle samples were placed at the centre of the oven. They were rotated anticlockwise every 3 days. This was because there was a temperature gradient inside the oven and by doing this the samples were exposed to a more balanced thermal ageing process. The hottest areas were closest to the interior metallic walls and the cooler areas were close to the centre of the oven and the door. Using a thermometer the temperature difference was shown to be approximately 4 - 5 °C less around the centre of the oven and close to the door. Figure 4.6 depicts this process.

![Figure 4.6. Top view of the location of the oil sample bottles for thermal ageing inside an oven](image)

The three types of oils were aged under different conditions. This is shown in Table 4.2. It should be noted that 10 GBN had the most conditions. This was because there were two
separate experiments for these oils. For Diala S2-ZUI and Nytro Libra the conditions were minimal because the aim was to see the temperature influence on the fluorescence of the oils. The blue and green highlighted conditions under 10 GBN depict separate experiments.

The two experiments for 10 GBN were carried out to compare and study the effect of copper and acid in the ageing process separately. For 10 GBN previous work [63] has suggested that a thermal ageing temperature of 115 °C produces speedy ageing of the samples. It was therefore selected in the present work. The green group samples have been tested with both systems while the blue groups tested with System A only which was the only system available at the time of test.

Table 4.2 List of sample conditions and thermally ageing temperature. For 10 GBN tests were performed in two groups which are shown in green and blue background colours.

<table>
<thead>
<tr>
<th>Diala S2-ZUI (8 samples)</th>
<th>Nytro Libra (7 samples)</th>
<th>10GBN (30 samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130 °C</td>
<td>130 °C</td>
<td>115 °C</td>
</tr>
<tr>
<td>Copper, Dry, Sealed, No acid</td>
<td>Copper, Dry, Sealed, No acid</td>
<td>Unsealed, dry, no copper, no acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unsealed, dry, copper, no acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sealed, dry, no copper, no acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sealed, dry, with copper, no acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sealed, dry, no copper, no acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sealed, dry, no copper, LMA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sealed, dry, no copper, HMA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sealed, wet, no copper, no acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sealed, wet, no copper, LMA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sealed, wet, no copper, HMA</td>
</tr>
</tbody>
</table>

4.5.4 Timely Removal of Oils from the Thermal Oven and Measurements

When the oils reached their given ageing time they were removed from the oven and immediately used in the 365 nm Jaz™ (Ocean Optics Inc.) and 404 nm laser experiments. The experiments were finished on the same day. The oil samples from each bottle were placed in small cuvettes of 4.5 ml with a 10 mm path length, which were all stored in a labelled box. The cuvettes were transparent with a cubic shape of flat faces, which simplifies
any optical analysis due to its simple shape. They had been commonly used in previous oil ageing tests with different probe arrangements.

A cuvette was then put into the system B to be tested. After testing with System A is finished, another cuvette of each type of relevant oil was prepared from the original bottle containing the aged oil and put into System A for testing.

4.6 EXPERIMENTATION WITH SYSTEMS A AND B

4.6.1 System B

The system designed for Jaz™ (Ocean Optics Inc.) can be seen in Figure 4.7. A non-metallic box, which was created by the University’s mechanical workshop, held a small box that held the cuvette in place. The optical probe that was connected to the stacked Jaz™ (Ocean Optics Inc.) modules was locked in place at the top of a box. The probe was dipped slightly into the cuvette up to the triangular vertex as shown in Figure 4.7. This was to ensure that the probe would be inserted into the oil to represent online testing and would be submerged at a same level in each of the tests to increase consistency.

![Figure 4.7. Photo showing where optical probe and oil insertion in System B](image)

The box was then closed with a removable door before the experiment can start. This was to exclude the ambient light to prevent it interfering with the measurements. The Jaz™ (Ocean Optics Inc.) was then connected to a laptop and SpectraSuite was used to display the fluorescence readings. Once the fluorescence of the oil was measured the cuvette was placed
back in the original place in the sample box. This process is then repeated for all samples using this system.

4.6.2 System A

The method of this experimentation is very similar to that of the Jaz™ (Ocean Optics Inc.). Cuvette samples were taken out of the bottles using a plastic pipette and stored in a cuvette. The cuvette was placed in a holder inside the box (see position of cuvette in Figure 4.2). The holder is screwed to tighten the hold and then pushed up so the laser is slightly dipped into the cuvette. The door is then closed by turning. The laser is then switched on and the measurements is displayed and recorded on SpectraSuite. Once measurements are done the cuvettes are placed back into the cuvette box. The cuvette label, oil type and conditions are noted down for future reference. It is to be noted that the probe for both systems is the same. The induced fluorescent light was collected by the middle optical fibre while the six fibres surrounding the middle one delivers the excitation light to the sample.

4.6.3 Comparison with existing techniques in future

It was hoped that a comparison of results from acidity measurements and fluorescence measurements could have been done to show any correlations however due to time constraints and availability of equipment this could not be done.
CHAPTER V: PRINCIPAL COMPONENT ANALYSIS

5.1 INTRODUCTION

Principal Component Analysis (PCA) was used in the project as a data reduction and information extraction method in order to analyse the vast amount of spectral data and be able to find a correlation between the oil conditions and their fluorescence emission. The method was implemented in a widely available software known as ‘IBM SPSS Statistics 20’. A description on how this was performed and what parameters were chosen will be given in this chapter.

It has been more than 100 years since the first use of PCA in research. The most famous early paper on PCA was by Pearson [64]. It aims at extracting the most relevant information from a complex set of data and transforming it into a lower dimension of data. A dimension in engineering discipline means a freedom or a variable. This is achieved by reducing a large set of variables into ‘artificial’ variables known as ‘principal components’. These principal components would account for most of the variance in the original data.

For example, if there are 10 correlated variables in a typical data set; PCA could be applied to reduce the amount of variables to a lesser number of principal components but still retain most of the most variance in the data. If two components were extracted and accounted for 70% of the total variance; it is said that two dimensions in component space account for 70% of the variance. Therefore the utmost amount of information in the data can be contained in fewer ‘artificial variables’. This would make the data more manageable for analysis.

PCA can be performed on many different types of data e.g. raw data, correlations, or covariance matrices. In this project specifically PCA is performed on a large amount of raw spectral data. Another important requirement for PCA analysis is the volume of raw data available. This is because it is a statistical method based on correlation matrices of the variables so a reasonably large sample size is required if the analysis is to stabilize and be fairly accurate. According to Tabachnick et al. [65, 66] a sample size of 300 is good and 1000 or more is excellent. The amount of spectral data for each graph is more than 1000. Therefore PCA is very suitable and can be applied to the spectrographic data obtained in this project.
5.1.1 Mathematical basis of PCA

Principal Component Analysis (PCA) is a method of coordinate transformation in multivariable space. The word “coordinate” here means a dimension of freedom corresponding to an independent variable in a multivariate system.

For example, in a \((x,y,z)\) 3-dimensional space, the three orthogonal coordinate axes can be rotated and translated around their origin. A point of \((x_1,y_1,z_1)\) corresponding to the original coordinate system will have new values of \((x_2,y_2,z_2)\) in the transformed (rotated) space.

- If there is only one point, then the best transformation will result in the point being at the origin of the new coordinate system.
- If there are more points lying on a line segment, then the best transformation will lead to a new coordinate system whose origin is at the middle of the line segment with one axis passing the points.
- When there are a cluster of points as shown in Figure 5.1, PCA analysis will define the axis along the largest extent of the cluster as principal component 1 (PC1), along the second largest extent as PC2, and the other direction as PC3. This means within the new coordinate system the largest variation in the cluster is more straightforwardly correlated with the axis of PC1, thus the pattern in the data can be much more clearly seen.

![Figure 5.1 PCA transformed orthogonal coordinate system in 3D space for a cluster of points. The origin of the new coordinate system passes the "middle" point of the cluster.](image-url)
When a system has more than three independent variables, the transformation will become more complicated. The mathematics is described below.

A system has N variables or dimensions and their values for the $i^{th}$ sample (a sample means a round of measurement) are represented by a row vector $X_i$

$$X_i = [ x_{i1}, x_{i2}, \ldots, x_{in} ]$$

(9)

where $x_{ij}$ (j here means the second subscript of the element), $j = 1, N$, are the values of the variables and each round of sampling of the system variables results in such a vector. Assuming M samples have been taken, then there will be M vectors of $X_i$ type. The results can then be expressed as a matrix of

$$V = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1N} \\ x_{21} & x_{22} & \cdots & x_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ x_{M1} & x_{M2} & \cdots & x_{MN} \end{bmatrix}$$

(10)

which has M rows and N column. Thus each column vector in V represents a set of values for a variable. The relationship among the variables or dimensions is quantified by the variance for a single vector and covariance between two column vectors.

The variance and covariance for column vector $j$ and column vector $k$ can be written as

$$c_{jk} = c(V_j, V_k) = \frac{\sum_{i=1}^{M} (x_{ij} - \overline{V_j})(x_{ik} - \overline{V_k})}{M-1}$$

(11)

Where $V_j$ and $V_k$ are two column vectors, and $\overline{V_j}$ and $\overline{V_k}$ are the average of the two column vectors. When $j = k$, $c_{jj}$ is the variance, otherwise it is the covariance between two different column vectors.

The variance of a set of data measures its spread, i.e. the average of distance squared of each point to the centre of the data set (average of all points). The covariance of two sets of data measures the probability of two variables changing together, i.e. if the corresponding points in the two sets take the same position in relation to the centres of the data sets. A large covariance means the two variables have a more linear relationship while a low covariance means the two variables are more independent. By calculating the variance and covariance
for each column vector in relation to all other vectors, a covariance matrix of $N \times N$ elements can be obtained:

$$
C = \begin{bmatrix}
c_{11} & c_{12} & \cdots & c_{1N} \\
c_{21} & c_{22} & \cdots & c_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
c_{N1} & c_{N2} & \cdots & c_{NN}
\end{bmatrix}
$$

(12)

The objective of using PCA is to obtain a new system of orthogonal coordinates to re-represent the data, therefore it is necessary to find out the $N$ axes. This can be done by finding out the eigenvectors of the matrix. $P_j$ as an eigenvector of matrix $C$ is defined as

$$
C P_j = P_j
$$

(13)

and

$$
P_j = \begin{bmatrix}
p_{1j} \\
p_{2j} \\
\vdots \\
p_{Nj}
\end{bmatrix}
$$

(14)

where $\lambda$ is the corresponding eigenvalue of $P_j$. $C$ here can be regarded as a transformation matrix. The distinct feature of an eigenvector is that transformation by matrix $C$ results in a scaling of itself.

For an $N$ by $N$ square matrix, there can be a maximum of $N$ eigenvectors. If there are $K$ eigenvectors, then all these eigenvectors can be arranged as columns of another matrix starting with the vector corresponding to the largest eigenvalue, the following relationship is arrived:

$$
\begin{bmatrix}
c_{11} & c_{12} & \cdots & c_{1N} \\
c_{21} & c_{22} & \cdots & c_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
c_{N1} & c_{N2} & \cdots & c_{NN}
\end{bmatrix} \begin{bmatrix}
p_{11} & p_{12} & \cdots & p_{1K} \\
p_{21} & p_{22} & \cdots & p_{2K} \\
\vdots & \vdots & \ddots & \vdots \\
p_{N1} & p_{N2} & \cdots & p_{NK}
\end{bmatrix} = \begin{bmatrix}1 & 2 & \cdots & K
\end{bmatrix} \begin{bmatrix}
p_{11} & p_{12} & \cdots & p_{1K} \\
p_{21} & p_{22} & \cdots & p_{2K} \\
\vdots & \vdots & \ddots & \vdots \\
p_{N1} & p_{N2} & \cdots & p_{NK}
\end{bmatrix}
$$

(15)

In PCA method, each $P_j$ is called a principal component (PC), playing the role of an orthogonal axis after PCA transformation. If there are only $K$ eigenvectors, it means that all
the variation in the original M sets of data each with N dimension can be fully expressed in terms of the K axes.

Multiplying each of the original row vector of type $X_i$ with the matrix formed by the eigenvectors, i.e.

$$
\begin{bmatrix}
  x_{i1}, x_{i2}, \ldots, x_{iN}
\end{bmatrix}
\begin{bmatrix}
  p_{11} & p_{12} & \cdots & p_{1K} \\
  p_{21} & p_{22} & \cdots & p_{2K} \\
  \vdots & \vdots & \ddots & \vdots \\
  p_{N1} & p_{N2} & \cdots & p_{NK}
\end{bmatrix}
= \begin{bmatrix}
  y_{i1} \\
  y_{i2} \\
  \vdots \\
  y_{iK}
\end{bmatrix}
$$

(16)

where $Y_i = [y_{i1} \ y_{i2} \ \cdots \ \ y_{iK}]$ contains the new values after transformation corresponding to $X_i$. The values of $P_j$ as given in (14) are called the loadings for the original data values, and the values in $Y_i$ are the scores of $X_i$ (new coordinate values in the transformed space) corresponding to different PCs (new axes).

One of the objectives of using PCA is to reduce the dimensions of the system, i.e. to use a lesser number of PCs to express the data and to identify the patterns, for engineering problems it is hoped that the dominant variations, or features, in the original data can be visualised by the use of only a few PCs. The PCs can be chosen by inspecting a Scree plot that displays the eigenvalues. An example is given in Figure 5.5 which can be found in Section 5.1.3.

Upon obtaining the scores, the new set of data can be plotted in the space defined by the selected PCs, such as PC1 against PC2, the two largest principal components. However, the loadings of this set of principal component (PC1 and PC2) may not give an easy interpretation of the results. The pattern in the original data may not be clear. A further arithmetic processing of the loadings and scores is needed to further simplify the interpretation of the patterns buried in the original data.

Perhaps the most widely used method for rotation is the Varimax method. It seeks a new set of rotated loadings that maximize the variance, $W$, of the squared loadings of the first set of principal components. This can be achieved by maximising the following variance:

$$
W = \sum_{ij} \left( p_{ij}^2 - \bar{p}_{ij} \right)
$$

(17)
where $P_{ij}$ represent the individual values in (15) and $\overline{p_{ij}^2}$ is the average value of the squared loadings in a principle component $j$ (Equation 14) with summation over $i$. This new set of loadings is then used to fingerprint the patterns and features in the original data.

### 5.1.2 Description of IBM SPSS Statistics 20 and its Parameters

SPSS is an established software package used profusely in many fields for statistical analysis. The software package contains a vast amount of functions and statistical methods. This section will focus on giving a description of the process of the PCA method used in SPSS and the important parameters that were selected. An example using samples 2.3 to 2.9 were used throughout this description.

In SPSS the PCA method is found under the Factor Analysis method, in which ‘Principal Components’ should be chosen under the ‘Method’. This is the only method for PCA; the rest of the methods are for factor analysis. Before a simulation for PCA can be run various parameters have to be selected first.

In the ‘Analyze’ box (Figure 5.2) there are two options: ‘Covariance matrix’ and ‘Correlation matrix’. Covariance matrix is for original non-standardised data. For original data the importance of a variable is dependent on the relative size of its variance. A higher variance would mean a higher importance for that variable. If the variability of a variable is not the aim then the data is standardised and the ‘Correlation matrix’ is used. A correlation matrix is obtained in a way similar to the covariance matrix except the calculation of the values of the element of the matrix. Mathematically the correlation between two vectors is equal to the covariance of the two vectors divided by the product of the variances of the two vectors. The division by the product of the variances is called “standardisation”. If the variables are more or less equally important then usually ‘Covariance matrix’ is used. For the spectral data ‘Covariance matrix’ was used.

‘Unrotated factor solution’ and ‘Scree plot’: The data is unrotated first in order to see which variables are of importance and how many components should be extracted. The Scree plot is a visual representation of the eigenvalues that are calculated for each of the components.
In ‘Extract’ box the number of components to be displayed can be chosen and the cut-off
eigenvalue can be set. First select ‘Based on Eigenvalues’ and set the value to 1. This is the
default standard value for both standardized and non-standardised data. This is to see how
many factors to extract later.

Figure 5.2. Parameters to select in PCA

‘Descriptives’: These parameters show what statistics should be calculated and displayed.
‘Univariate descriptives’ and ‘Initial solution’ are selected so that the descriptive statistics
and the initial solution of all components are shown. ‘Coefficients’ and ‘KMO and Bartlett’s
test of sphericity’ are also selected because they are a measure of sampling adequacy and will
indicate the strength of connection between the variables. The values are between 0 and 1.
However values closer to 1 are more desirable as this means the variables show greater
connection.

Once the number of components to be extracted has been chosen an ‘Varimax’ rotation is
done.

Rotation is done to improve the solution in order to get a clearer picture. Using a varimax
rotation in SPSS will give an orthogonal rotation that minimises the number of variables that
have high loadings on each factor. This will simplify the interpretation of factors.
5.1.3 Key Analytical Descriptives

The PCA analysis will generate a lot of statistical data and results. Some key analytical descriptions are explained in this section.

**Correlation Matrix**

<table>
<thead>
<tr>
<th></th>
<th>C23</th>
<th>C24</th>
<th>C25</th>
<th>C26</th>
<th>C27</th>
<th>C28</th>
<th>C29</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation</td>
<td>1.000</td>
<td>.999</td>
<td>.986</td>
<td>.981</td>
<td>.932</td>
<td>.733</td>
<td>.577</td>
</tr>
<tr>
<td>C24</td>
<td>.999</td>
<td>1.000</td>
<td>.961</td>
<td>.986</td>
<td>.942</td>
<td>.740</td>
<td>.505</td>
</tr>
<tr>
<td>C25</td>
<td>.986</td>
<td>.961</td>
<td>1.000</td>
<td>1.000</td>
<td>.979</td>
<td>.630</td>
<td>.532</td>
</tr>
<tr>
<td>C26</td>
<td>.981</td>
<td>.991</td>
<td>1.000</td>
<td>1.000</td>
<td>.995</td>
<td>.648</td>
<td>.711</td>
</tr>
<tr>
<td>C27</td>
<td>.932</td>
<td>.942</td>
<td>.979</td>
<td>1.000</td>
<td>.900</td>
<td>.925</td>
<td>.816</td>
</tr>
<tr>
<td>C28</td>
<td>.733</td>
<td>.749</td>
<td>.833</td>
<td>.846</td>
<td>.925</td>
<td>1.000</td>
<td>.972</td>
</tr>
<tr>
<td>C29</td>
<td>.577</td>
<td>.595</td>
<td>.692</td>
<td>.711</td>
<td>.816</td>
<td>.972</td>
<td>1.000</td>
</tr>
</tbody>
</table>

**KMO and Bartlett’s Test**

<table>
<thead>
<tr>
<th>Kaiser-Meyer-Olkin Measure of Sampling Adequacy</th>
<th>811</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bartlett’s Test of Sphericity</td>
<td>Approx. Chi-Square</td>
</tr>
<tr>
<td>of</td>
<td>Sig</td>
</tr>
</tbody>
</table>

**Communalities**

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C23</td>
<td>1.000</td>
<td>.988</td>
</tr>
<tr>
<td>C24</td>
<td>1.000</td>
<td>.913</td>
</tr>
<tr>
<td>C25</td>
<td>1.000</td>
<td>.972</td>
</tr>
<tr>
<td>C26</td>
<td>1.000</td>
<td>.960</td>
</tr>
<tr>
<td>C27</td>
<td>1.000</td>
<td>.955</td>
</tr>
<tr>
<td>C28</td>
<td>1.000</td>
<td>.931</td>
</tr>
<tr>
<td>C29</td>
<td>1.000</td>
<td>.644</td>
</tr>
</tbody>
</table>

Figure 5.3 Results displaying the Correlation Matrix, KMO and Bartlett’s Test and Communalities

The ‘Correlation Matrix’ (Figure 5.3) shows how well each graph is correlated to each other with all diagonal values equal to one indicating perfect correlation. In principal component analysis it is required that there are correlations greater than 0.3. From the table it can be seen that all the variables have a correlation greater than 0.3. Therefore the analysis is valid.

‘KMO and Bartlett’s Test’ (Figure 5.3) is a measure of sampling adequacy and shows the strength of the correlations between the variables as well. For PCA it is required that the Kaiser-Meyer-Olkin value is greater than 0.5 in order for the analysis to be accurate and reliable. From the table it can be seen that the KMO is 0.811. This value is close to 1 which is very desirable. PCA also requires that the probability associated with Bartlett's Test of Sphericity be less than the level of significance. In this case the probability associated with the Bartlett test is < 0.001. This also satisfies the requirement.
‘Communalities’ (Figure 5.3) represents the proportion of the variance in the original variables in the initial iteration. The communality value for each variable should be 0.50 or higher. If the variables do not satisfy this condition the variable will have to be deleted and the simulation will be run again until all the variables have an extraction value of greater than 0.5.

<table>
<thead>
<tr>
<th>Component</th>
<th>Initial Eigenvalues</th>
<th>Extraction Sums of Squared Loadings</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>% of Variance</td>
</tr>
<tr>
<td>1</td>
<td>6.233</td>
<td>88.044</td>
</tr>
<tr>
<td>2</td>
<td>0.753</td>
<td>10.753</td>
</tr>
<tr>
<td>3</td>
<td>0.013</td>
<td>1.899</td>
</tr>
<tr>
<td>4</td>
<td>0.001</td>
<td>0.111</td>
</tr>
<tr>
<td>5</td>
<td>0.000</td>
<td>0.002</td>
</tr>
<tr>
<td>6</td>
<td>2.36E-005</td>
<td>0.000</td>
</tr>
<tr>
<td>7</td>
<td>1.48E-005</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Extraction Method: Principal Component Analysis.

Figure 5.4 Results displaying the Total Variance

‘Total Variance Explained’ (Figure 5.4) shows the number of components which should be extracted. The calculated eigenvalues of each component is shown along with the percentage of variance each component of the original data has. The cumulative percentage of variance is shown next to it. Ideally components with eigenvalues of greater than 1 should be extracted. In the table you can see only component one satisfies this condition and component 2 is close. Although component 2 does not have an eigenvalue greater than 1 it still should be extracted. By extracting these two components a cumulative variance of 99.797 % is achieved. This value is adequate and is ideal for analysis. Also a minimum of two components is needed for rotation analysis. Any further extraction is unneeded and the eigenvalue of other components is not high enough.
The Scree plot (Figure 5.5) is a visual representation of the eigenvalues. From the graph it can be clearly seen that the first two components should be extracted.

![Scree Plot](image)

Figure 5.5 Example of Scree Plot

‘Component Matrix’ (Figure 5.6) contains component loadings. The columns under the heading component are the principal components that have been extracted. In this table it can be seen that the simulation only showed one extracted component. This is because SPSS only extract components with an eigenvalue greater than one. These values are the correlations between the variable and the component. Due to the fact that these values are correlations, the values can range from -1 to +1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>C23</td>
<td>.949</td>
</tr>
<tr>
<td>C24</td>
<td>.955</td>
</tr>
<tr>
<td>C25</td>
<td>.986</td>
</tr>
<tr>
<td>C26</td>
<td>.993</td>
</tr>
<tr>
<td>C27</td>
<td>.990</td>
</tr>
<tr>
<td>C28</td>
<td>.911</td>
</tr>
<tr>
<td>C29</td>
<td>.903</td>
</tr>
</tbody>
</table>

Figure 5.6. Component Matrix given in this example
5.1.4 Differences between PCA and Factor analysis

Although the logic of both these methods are different they are both supported in the same SPSS function. PCA, unlike factor analysis, is not commonly used to identify any underlying variables. The loadings on the components are therefore not interpreted as factors. PCA is used to analyse the total variance whereas factor analysis analyses the common variance. PCA also assumes that each original measure is measured without equipment error.
CHAPTER VI: RESULTS AND ANALYSIS

6.1 INTRODUCTION

The experimental results of the fluorescence emission measurements on transformer oils under different thermal ageing conditions are presented in this chapter. It is to be noted that no measurement of acidity of the aged oils has been taken because the relevant equipment was unavailable during the project period. A total of three types of fluid were used, which are Diala S2-ZUI, Nytro Libra, and 10 GBN. The samples were mainly provided by large UK suppliers, Royal Dutch Shell plc and Nynas AB.

There are several objectives to the ageing and measurements, which were mentioned in the previous chapter:

• The first objective is to acquire substantial baseline data of the fluorescence emissions of various types of transformer oils which were thermally aged using both Systems A and B. This type of measurement is time consuming and requires attending the samples at regular intervals and carrying out the measurements.
• The second objective is to gain an understanding of the features associated with transformer oil ageing under thermal stress, in terms of the profile of the emitted fluorescence spectra of Systems A and B, and its change with time when thermally aged.
• The third objective is to apply the method of principal component analysis (PCA) to the measured fluorescence spectra and assess its effectiveness in characterising the condition of degraded transformer oils. The method of PCA has been introduced in Chapter V.
• The final objective is to evaluate whether the application of portable and online fluorescence assessment can be feasible. This will also include a discussion on the drawbacks in using this method and how they can be offset.

Two systems with excitation wavelength of 404 nm (System A) and 365 nm (System B), respectively, have been used in the measurement. The measured intensity of the fluorescence radiation is not in its absolute value because the systems are not calibrated against a standard
radiation source. Therefore the unit of intensity in all diagrams is labelled as arbitrary. The values are the counts of the data acquisition system which can be interpreted as being scaled by a constant. The spectral response of the systems has been taken into account in producing the output of the measurement system.

It is well known that temperature affects the rate of oxidation which approximately doubles for each 7 °C rise [20]. In real transformer operation, bulk oil temperatures are normally in the region of 60 - 70 °C. Taking an operational temperature of 70 °C, the oxidation acceleration factor would be 624 at 130 °C and 86 at 115 °C. A 7 week ageing would be equivalent to 51 and 11.6 years of operation, at 130 °C and 115 °C, respectively. A transformer is expected to last 40 years. It can be seen that the choice of 7 week ageing period is reasonable, which is supported by experimental results where the fresh oil had been severely aged over the period of 6 - 8 weeks. Very high ageing temperatures under abnormal conditions can result in increased evaporative loss, thermal cracking, secondary and tertiary chemical reactions. The use of 130 °C in the present work represents the most severe case of overheating, which is just below the flash points of 140 °C (Diala) and 152 °C (Libra). The focus in this chapter is on the emission of fluorescence light from aged transformer oils.

Sections 6.2 to 6.5 are devoted to the results for all three types of fluids together with a description and analysis of the features of the measurements and results from PCA. In each section the results will be first presented in a subsection and the analysis given in a separate subsection. This separation of the presentation and the analysis of the results into two subsections have the benefit of separating the original results as a fact from analysis which may contain personal views. Section 6.5 presents a summary of the work in this chapter.

6.2 EXPERIMENTAL ERRORS AND REPEATABILITY

Before presenting and discussing any results the experimental uncertainties need to be assessed to provide confidence in the analysis and conclusions drawn. The experimental uncertainties include systematic errors and random errors. In the measurement of fluorescence emission of aged oils, experimental uncertainties come from dark noise, readout noise, background noise and experimental back scatter due to environmental interference or test procedure (repeatability).
The systematic error introduced by the probe and the optical detection system was measured first in the absence of oil in a closed test cabinet. An integration time of 1 second was used. The output of the CCD detector shows a rather constant reading of 1526 counts with a fluctuation of 300 counts. The test was repeated a number of times and the offset stayed the same. The average of this offset is caused by dark current. Therefore the value of 1526 was deducted from the original data before the results are analysed.

For the present optical arrangement and fluorescence detection system, most of the random uncertainties including the scatter come from background noise and the experimental procedure. For example in performing fluorescence measurements the relative position of the probe in the cuvette may be slightly different from sample to sample, causing certain difference in scattering. The value of 300 counts obtained above reflects the background noise.

However, the above analysis did not involve any fluorescence light. It is therefore necessary to test the system’s repeatability when fluorescence light is present. For this purpose measurement of the fluorescence strength of a fresh Nytro Libra sample (Figure 6.1) and a Nytro Libra sample aged for 3 weeks (Figure 6.2) were repeated several times. The fluorescence spectra of the second sample are also shown by Curve 5.3 in Figure 6.12.

Part of Figure 6.1 is enlarged in Figure 6.3. All data were obtained with an integration time of 100 ms. The maximum difference between two scans in Figure 6.1. is 350 counts (measured at 442 nm in Figure 6.3) while that in Figure 6.2 is 25 (measured at the highest peak).

The observed noise in the spectrum in Figure 6.1 is 0.021 of the signal value while that in Figure 6.2 is 0.023, consistent with each other. In the case of no exciting light the noise is about 300 counts with integration time of 1 second. With fluorescence emission a maximum noise of 350 counts was obtained with an integration time of 100 ms yields noise levels of approximately 2.5 %. Thus, the error induced in both bases were of the same order of magnitude and comparable to the noise amplitude in the spectra (comparing 445 nm) in both figures.
Figure 6.1 Repeatability test by System A of fresh Nytro Libra. The integration time is set to 100 ms.

Figure 6.2 Repeatability test by System A of Nytro Libra aged for 3 weeks. The integration time is set to 100 ms.
6.3 THERMALLY AGED DIALA S2-ZUI

6.3.1 Experimental Results

Diala S2-ZUI is a type of uninhibited electrical insulating oil with specifications satisfying IEC 60296. It is manufactured from mineral oils and is non-corrosive to copper. Its density at 20 °C is 875 kg m⁻³. For information, the acidity of the product supplied by Shell is around 0.01 mg KOH g⁻¹; sludge has a measure of 0.3 % (mass) and the aromatic content is approximately 9 %.

It is a good dielectric medium with a higher breakdown voltage (60 kV rms value for a 2.5 mm electrode gap) than required by industry standard (30 kV for used oils). It has good oxidation stability (induction time of 164 hours per 120 °C) and is efficient in heat transfer. It also has excellent low temperature properties (pour point of -57 °C, kinematic viscosity of 940 mm² s⁻¹ compared with industrial standard of 1800 mm² s⁻¹ at -30 °C).

Diala S2-ZUI was tested in an artificial thermal ageing environment for 8 weeks at 130 °C in an air circulating oven. A total of 16 cuvettes were used in 2 tests as listed in Table 6.1. Cuvette 6.1 and Cuvette 3.1 were both taken from the same bottle (sample) which was aged for one week. Cuvette 6.1 was used in System A test and Cuvette e 3.1 used in System B test. The procedure has been described in Chapter IV.
Table 6.1 Ageing time of oils and their cuvette number

<table>
<thead>
<tr>
<th>Ageing time (Weeks)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1 (System A): Cuvette No.</td>
<td>6.1</td>
<td>6.2</td>
<td>6.3</td>
<td>6.4</td>
<td>6.5</td>
<td>6.6</td>
<td>6.7</td>
<td>6.8</td>
</tr>
<tr>
<td>Test 2 (System B): Cuvette No.</td>
<td>3.1</td>
<td>3.2</td>
<td>3.3</td>
<td>3.4</td>
<td>3.5</td>
<td>3.6</td>
<td>3.7</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Both System A and System B were used to measure the fluorescence emissions of each type of aged oil. The results are shown in Figure 6.4 and Figure 6.5. Figure 6.4 shows the emission in the wavelength range of 400 to 700 nm from the cuvette samples at different stages of ageing using an excitation wavelength of 404 nm (System A). It is apparent that there are two peaks, one at 442 nm and the other at 490 nm, which agrees with previous observations [60, 63]. The change in spectra within the second week (Key label 6.2 in Figure 6.4) is only in the range of 455 to 530 nm with a 5 % drop. At the end of Week 3, emission at 442 nm is already lower than at 490 nm. There is a drop of 48 % at 442 nm but only 31 % at 490 nm. In the next 3 weeks the fluorescence emission goes through a “drop – rise – drop” cycle with a typical variation of 15 % of its magnitude. The intensity of the emission continues to drop in weeks 7 and 8 with a similar rate. By the end of Week 8, the intensity has dropped to 12 % of that of cuvette 6.1 (Week 1) at 490 nm and 7 % at 442 nm. Clearly emission at 442 nm is more affected by the thermal ageing process. The ratio of intensity at 442 nm to that at 490 nm changes from 1.19 at the end of Week 1 to 0.92 at the end of Week 3, 0.79 at the end of Week 6, and 0.6 at the end of Week 8.

Figure 6.4 Intensity of fluorescence emission of Diala S2-ZUI in arbitrary unit from 400 nm to 700 nm with cuvette label given in Table 6.1 as keys to the curves, obtained from System A with an excitation wavelength of 404 nm. The colour patches from the top are in same order as the legend.
Results from System B under similar conditions are given in Figure 6.5 can be seen that there are now 3 peaks at 408 nm, 430 nm and 490 nm. This may be due to the change of the excitation wavelength of the LED light source (365 nm). However looking closely at the two peaks of 408 nm and 430 nm, they may be originally the 432 nm peak which has split into two. The intensity of the spectra, in arbitrary units, is 24000 at 430 nm. The excitation source is different in the two systems. System A uses a more powerful laser source (5 mW) while System B uses a LED diode (1 mW). To improve the signal to noise ratio the integration time for Figure 6.5 is set to 10 seconds, which is much longer than the integration time used in System A (100 ms).

It is possible to have an analysis of the relevant largeness of the magnitude of the output from the two systems. Taking the value of Week 2 cuvette samples (Curves 6.2 and 3.2) at 490 nm as an example, System B’s reading is 12500/2500 = 5 times that of System A. The probe configuration, the spectrometer and optical detector have nearly identical characteristics. The integration time ratio of System B to System A is 100. Therefore, the product of useful exciting power and quantum yield of System A is 20 times that of System B.

Similar to Figure 6.4, the fluorescence emission intensity in Figure 6.5 at wavelength shorter than 470 nm changes more rapidly in the ageing process and there is also a reversal in emission intensity in Week 4. Different from Figure 6.4, the most obvious change in emission
intensity is observed in the short wavelength range around the two peaks of 408 nm and 430 nm. The intensity ratio of 408 nm to 490 nm is 1.92 in Week 1, 1.78 by Week 2, 1.33 by Week 3, 1.0 by Week 3, 1.0 by Week 7, and 0.6 by Week 8. All 3 peaks become undistinguishable by the end of Week 8.

6.3.2 Analysis of Results for DIALA S2-ZUI

There are several features for these experiments. Firstly, the intensity changes at the peaks will be studied to characterise the overall change. Assuming the intensities of the fluorescence light at the two wavelengths are \( I_1 \) and \( I_2 \) with arbitrary unit and they change with time, they are normalised by

\[
I_i^* = \frac{I_i}{I_{1r} + I_{2r}}
\]

where \( i = 1 \) or \( 2, \) \( I^* \) is the normalised intensity, and \( I_{1r} \) and \( I_{2r} \) are the reference values which are taken as the intensity of the two peaks at the end of Week 1.

To demonstrate their relationship with different levels of ageing, they are normalised first for comparison with other tests. Ideally, the intensity of fresh oil should be used. However, the fluorescence light intensity of the fresh oil is so strong that the intensity at a later stage becomes very small. For convenience, the intensities at the end of Week 1 are used for normalisation. The intensity at the end of Week 1 was reasonable and convenient to be used as a reference. In practice this means after a short time of operation of the transformer the oil settles down in the transformer and a sample will then be assessed and taken as the reference.

In Figure 6.6 the intensity changes as a function of time at 442 nm and 490 nm are shown together with their ratio and sum. Unfortunately measurement of the colour index has not been done due to a lack of suitable equipment. The colour patches are therefore shown in the diagram for reference purposes. It is clear that the four curves all reflect the change in colour in general, but the sum of intensities provide a resolution between Week 2 and Week 3 while still maintaining a relatively high sensitivity.
Figure 6.6 Change of normalised fluorescence light emission of Diala S2-ZUI at 442 nm and 490 nm from System A as a function of ageing time. For comparison the colour patches of the aged oil are also given. This figure corresponds to the original results shown in Figure 6.4.

A similar diagram as given in Figure 6.7 is produced for results from System B with an excitation wavelength of 365 nm. It has rather similar features as Figure 6.6 except the ratio of the two lines starts with a much higher value of 1.9.

Figure 6.7 Change of fluorescence light emission of Diala S2-ZUI from System B at 408 nm and 490 nm as a function of ageing time. This figure corresponds to the original results shown in Figure 6.5.

Since the intensity of different spectral peaks change with a different rate with the ageing time, the change of the sum of the intensities at two peaks was studied. The results from both systems were given in Figure 6.8. Because of the normalisation process (Equation 18) applied to the spectral results with Week 1 intensities as reference values, it is possible to compare
the relative change of the quantities, as shown in Figure 6.8. It has been found that despite the large differences in the intensities at different wavelengths (two of the peaks in this case) for the two systems, the sum of the dimensionless intensities are rather close to each other with a maximum difference of 0.1. If an average is taken of the two sums, the difference of the two systems from the average curve is 0.05. As discussed in Section 6.2, the system repeatability is better than 2.5 %. Taking the dimensionless value of 0.6 in Week 5 (Figure 6.7) as a typical value, the repeatability of 2.5 % leads to a scattering of 0.015 for the dimensionless intensity values, which is sufficiently small in comparison with possible dimensionless quantities in the analysis.

Another approach has been tested to explore its effectiveness in differentiate the oil ageing states. It involves the scaling of the original intensity curves presented in Figure 6.4 and Figure 6.5 so that the intensity values at a particular wavelength are made the same for all aged cuvette samples. For the System A results, the wavelength is chosen to be 490 nm, which is the second peak. The choice of this wavelength is based on the following consideration. Results in Figure 6.4 and Figure 6.5 clearly show that the most significant change of the fluorescence spectra takes place in the wavelength range of 400 nm to 500 nm. 490 nm is not only close to the upper limit of the above wavelength range but also a peak in the spectra. Taking this wavelength point to normalize the spectral curves, the relative change
in the range below 500 nm, including the short wavelength peaks, will be made more apparent.

Figure 6.9 Showing Diala S2-ZUI results in Figure 6.6 (System A) scaled at 490 nm.

The fluorescence spectra from System A and System B after scaling are given in Figure 6.9 and Figure 6.10. It is not expected that the ratio of 442 nm to 490 nm in results from System A will change as a result of scaling. However the scaled intensities will follow a different trend with respect to time. Plotting the intensities and their ratio after scaling, it is found that the variation of the 442 nm peak now is in the range of 0.26 to 0.56 (Figure 6.11), which is smaller than the range of 0.04 to 0.56 obtained from the same set of results without the application of scaling (Figure 6.6), leading to a loss of resolution. The ratio of the two peaks is now in the range of 0.57 to 1.25 in comparison with the range of 0.5 to 1.15 without scaling, giving no advantage in differentiating the changes in oil samples. This is also true for results from System B whose results are also shown in Figure 6.11 after scaling. Another important observation from Figure 6.11 is that the difference between the two intensity sums (one for System A and one for System B) increases with ageing time, which is very different from the trend exhibited in Figure 6.8.
One of the focuses in the present work is to assess the applicability of the Principal Component Analysis (PCA) method in monitoring the ageing of transformer oils. In preparing the input data for PCA, the discrete intensity counts at each wavelength is regarded as a variable (dimension) and the fluorescence spectra of oil aged for different number of weeks is regarded as samples. Applying PCA to results in Figure 6.4 and Figure 6.5, the following component plot in rotated space (after applying the Varimax transformation explained in Section 5.1.1 of Chapter V) were obtained as shown in Figure 6.12 and Figure
Component 1 and Component 2 are the two dominant principle components with highest value of eigenvalues.

It is clear that the general trend of ageing of the oil is clearly shown by the change in location of the points in both figures (Figure 6.12 and Figure 6.13). The distance between two adjacent weeks matches well with the space between the curves in Figure 6.4 and Figure 6.5. Curves placed close to each other in Figure 6.4 and Figure 6.5 cannot be well distinguished in the component plot of Figure 6.12 and Figure 6.13.

From the component plot, it is possible to define a degradation angle for each oil sample. The degradation angle of a sample is defined as the angle that is made by two lines, one passing through the sample point and the origin of the plot and the horizontal axis. It is interesting to calculate the change in degradation angle with respect to that at the end of Week 1 and compare it with the intensity sum derived in Figure 6.8. The comparison is given in Figure 6.14 where the change of angle with respect to sample W1 (Week 1 sample) is converted into a negative value for comparison. It can be seen that the intensity sum curve and the degradation angle have similar trends but differ in details. The difference between the points is well beyond the 2.5 % uncertainty.

Figure 6.14 allows a direct comparison of the performance of the two systems and the two algorithms (sum of normalised intensity and PCA degradation angle) in terms of their resolution of the samples at different aged periods. The errors in the results are less than 2.5 %. The uncertainty in the component plot has a similar uncertainty level observed in sensitivity studies by changing the magnitude in the raw data.

It has been found that PCA is most efficient in resolving the difference between two profiles. A typical example is the spectral profiles between Week 2 and Week 3 where the peak at 440 nm experiences a large relative change in comparison with the peak at 490 nm. When two profiles are similar and only differs in their magnitude, PCA does not differentiate them. This can be seen from the PCA degradation angle change from Week 6 to Week 7 where the magnitude changes between 400 nm to 600 nm while the profiles are similar. Therefore care has to be taken in concluding on its suitability for an application, i.e. it is necessary to calibrate the aged oil samples against their fluorescence spectra profiles using PCA. This only needs to be done once to determine the suitability of PCA on a type of oil.
Figure 6.14 clearly shows that the sum of normalised intensity method is a good method in differentiating the aged oil samples of Diala S2-ZUI. The algorithm is simple and quick and offers sufficient resolution of the aged samples. On the other hand, PCA has experienced drawbacks since some of the spectral profiles are similar. In this sense the first method is better than the PCA method.

Given the 2.5 % error bars in the results, it can be firmly concluded that System B’s performance is at least not worse than that of System A, judged from the sum of intensity method and the PCA method. In fact it provides better resolution between Week 1 and Week 2, and between Week 6 and Week 7. Therefore System B is preferred.

Figure 6.12 PCA Component plot in rotated space for results from System A (Figure 6.4), i.e. ageing results for Shell Diala S2-ZUI.
6.4 THERMALLY AGED NYTRO LIBRA

6.4.1 Experimental Results

Nytro Libra is also an uninhibited mineral oil. It is non-corrosive to copper with a density of 875 kg m\(^{-3}\) at 20 °C. For information the total acidity is 0.55 mg KOH g\(^{-1}\). It is a good
dielectric medium with a higher breakdown voltage (40 to 60 kV rms value for a 2.5 mm electrode gap) than required by industry standard (30 kV for used oils). It has good oxidation stability (induction time of 164 hours per 120 °C) and is efficient in heat transfer. It also has excellent low temperature properties (pour point of -51 °C, kinematic viscosity of 1100 mm² s⁻¹ compared with industrial standard of 1800 mm² s⁻¹ at -30 °C.

In the present work it is thermally aged under the same conditions (130 °C) as the Diala S2-ZUI. The length of ageing in this case is 7 weeks, as given in Table 6.2. Cuvette 5.1 and Cuvette 2.3 were both taken from the same bottle which was aged for one week. Cuvette 5.1 was used in System A test and Cuvette 2.3 used in System B test. This practice also applies to other tests in Table 6.2.

Table 6.2 Ageing duration and cuvette labels for Nytro Libra

<table>
<thead>
<tr>
<th>Ageing time (Weeks)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuvette No. (System A)</td>
<td>5.1</td>
<td>5.2</td>
<td>5.3</td>
<td>5.4</td>
<td>5.5</td>
<td>5.6</td>
<td>5.7</td>
</tr>
<tr>
<td>Cuvette No. (System B)</td>
<td>2.3</td>
<td>2.4</td>
<td>2.5</td>
<td>2.6</td>
<td>2.7</td>
<td>2.8</td>
<td>2.9</td>
</tr>
</tbody>
</table>

The original experimental data are shown in Figure 6.15 and Figure 6.16. Different from Diala S2-ZUI, the degradation of the Nytro Libra oil is well resolved by both systems before the oil becomes very dark (indicating an extreme case). Consistent with the results for Diala S2-ZUI, the two peaks in Figure 6.15 for System A are also at 442 nm and 490 nm. However the case with System B is not so straightforward since the peak at 408 nm disappeared although a distinct change of the rate of rise of the intensity with respect to wavelength is recognisable. Another important feature is that the reversal of intensity and colour as discussed in Section 6.3 does not occur with Nytro Libra.

Another important observation from Figure 6.15 and Figure 6.16 is that the emission of fluorescence light from Nytro Libra decays at a variable rate with respect to time. In the second week (difference between Curves 5.1 and 5.3, and between Curves 2.3 and 2.4) the fluorescence emission drops by 10 % of the starting value (end of Week 1 value). In Week 3 the density drop accelerated, resulting in a drop of 39 % of the week starting value. The rate of decrease is slowed down in Week 4 with a decrease rate of 18 %, then in Weeks 5 and 6 an equal magnitude drop of 50 % of the value at the beginning of Week 5. The change in Week 7 is small without much meaningful information.
It is also interesting to note that the colour of Nytro Libra becomes so dark, compared with Diala S2-ZUI, at the end of Week 6 and the intensity is already low (100 counts at 490 nm).

Figure 6.15 Intensity of fluorescence emission for Nytro Libra in arbitrary unit from 400 nm to 700 nm with cuvette labels given in Table 6.2 as keys to the curves, obtained from System A with an excitation wavelength of 404 nm. The samples were sealed. The colour patches from the top are in same order as the legend.

Figure 6.16 Intensity of fluorescence emission for Nytro Libra in arbitrary unit from 400 nm to 700 nm with cuvette labels given in Table 6.2 as keys to the curves, obtained from System B with an excitation wavelength of 365 nm. The samples were sealed. The colour patches from the top are in same order as the legend.
6.4.2 Analysis of results for thermally aged Nytro Libra

Following a similar approach that has been adopted in Section 6.3, Figure 6.17 is generated to help characterise the ageing test. The agreement between System A and System B is surprisingly close. The dimensionless intensity at 430 nm after applying the normalisation as described in Equation (18) using 430 nm and 490 nm from System B almost overlaps on the intensity curve at 442 nm from System A (the two solid lines in Figure 6.17). In this case the reference value for normalisation is taken again as the value at the end of Week 1. The individual intensities vary between 0.04 and 0.5. The reason is that their magnitudes are more or less the same and thus have an equal share. The value at the end of Week 7 does not contain much information since at the end of Week 6 the cuvette sample had become so dark and the fluorescence light emission was negligibly weak. The variation in the intensity sum is naturally doubled, giving more reliable indication of the oil degradation.

In view of the small experimental uncertainty of 2.5 % as analysed in Section 6.2, a firm conclusion can be drawn here that the portable System B using a shorter wavelength LED (365 nm) gives equally good performance as the expensive and bulky System A in monitoring the ageing of Nytro Libra.

![Figure 6.17 Change of normalized fluorescence light emission intensity at 430/442 nm and 490 nm as a function of ageing time. For comparison the colour patches of the aged oil are also given. The error bar is 2.5 % in either direction.](image)

The intensity values for Nytro Libra are also scaled towards a common intensity value at 485 nm which is a point very close to the second peak. The results are shown in Figure 6.18.
and Figure 6.19. As a result of the scaling process, the relation among the profiles changed. The change is mainly in the wavelength range longer than 490 nm. This is because in the original record the intensity at wavelength longer than 490 nm drops less rapidly in the short wavelength range. Because of the low intensity, strong noise is present in the Week 6 and Week 7 spectra.

Applying the same normalisation algorithm as that used in Figure 6.17 to the scaled results in Figure 6.18 and Figure 6.19, the normalised intensity and intensity sum are shown in Figure
It is clear that the scaling process compresses the variation range of the intensity at 430 and 442 nm. The variation range is compressed from 0.96 to 0.24, by a factor of 75%. Thus in terms of characterisation of the intensity profiles changes with different thermal ageing period, scaling is not recommended.

PCA is also applied to the raw data given in Figure 6.15 and Figure 6.16. The component plots are given in Figure 6.21. Because Figure 6.15 and Figure 6.16 show similar patterns in the decay of fluorescence light, the PCA results are also similar. A large distance between the points of two adjacent weeks indicates a higher decay rate. The largest distance between the end of Week 5 and end of Week 6 is caused by the disappearance of the first peak, rendering cuvette sample at the end of Week 6 more associated with PC 2. It is evident that PCA can reliably distinguish any reasonably large change in the fluorescence emission. The small distance between Week 1 and Week 2, and Week 3 and Week 4 is a result of the similarities in the concerned spectral profile. Despite the differences in the magnitude, it can be said that PCA is most effective in identifying the change in the shape of the profiles, not the magnitude.

Figure 6.20 Scaled intensity at 430/442 nm and 490 nm as a function of ageing time for results from System A in Figure 6.15 and System B in Figure 6.16. The ratio and sum of the two peaks is also shown.
Figure 6.21 Component plot in rotated space for (a) results from System A (Figure 6.15), and (b) System B (Figure 6.16), i.e. ageing results for Nytro Libra.

6.5 THERMALLY AGED 10 GBN

10 GBN is also an uninhibited oil used for electrical insulation and cooling, with specifications which fulfil the requirements of IEC 60296. It is manufactured from napthenic type mineral oil with the aim to provide good resistance to oil degradation. This is mainly due to its natural inhibitors, which react instead of the oil in the process of oxidation (see Chapter II). At 20 °C the oil has a density of 886 kg m⁻³. For information, the acidity of the oil is 0.01 mg KOH g⁻¹; sludge has a measure of 0.18 % (weight) and the aromatic content is approximately 14 %. It has a high breakdown voltage at 60 kV rms for a 2.5 mm electrode gap test. 10 GBN was used for two different experiments. This is separated into Section I and II. The experiments in each section involved different parameters which are mentioned in detail in each of their individual sections.

6.5.1 Section I: 10 GBN Experimentation

The 10 GBN oils in this section are oils aged at 115 °C for 7 weeks. The test was designed to see the influence of acid and moisture on the fluorescence spectra. The different parameters in which the oils were tested are shown in Table 6.3. LMA and HMA are commonly used organic acids which are added to the oil to test its influence on fluorescence emission. The procedure has been described in Chapter IV. For this experiment measurements were only taken using System A because at the time of performing these tests System B was not available. Therefore the objective of the work in this section is to study the ageing behaviour.
of 10 GBN, not for the feasibility study of System B. The fluorescence spectra are shown in Figure 6.22 to Figure 6.27 in the wavelength range of 400 to 700 nm.

Table 6.3 Showing the different parameters and the period in which the oils were aged under

<table>
<thead>
<tr>
<th>Ageing parameters</th>
<th>1 week</th>
<th>2 weeks</th>
<th>4 weeks</th>
<th>5 weeks</th>
<th>7 weeks</th>
<th>Related figure no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sealed, dry, no copper, no acid</td>
<td>A1</td>
<td>A2</td>
<td>A3</td>
<td>A4</td>
<td>A5</td>
<td>Figure 6.22</td>
</tr>
<tr>
<td>Sealed, dry, no copper, LMA</td>
<td>A6</td>
<td>A7</td>
<td>A8</td>
<td>A9</td>
<td>A10</td>
<td>Figure 6.23</td>
</tr>
<tr>
<td>Sealed, dry, no copper, HMA</td>
<td>A11</td>
<td>A12</td>
<td>A13</td>
<td>A14</td>
<td>A15</td>
<td>Figure 6.24</td>
</tr>
<tr>
<td>Sealed, wet, no copper, no acid</td>
<td>B1</td>
<td>B2</td>
<td>B3</td>
<td>B4</td>
<td>B5</td>
<td>Figure 6.25</td>
</tr>
<tr>
<td>Sealed, wet, no copper, LMA</td>
<td>B6</td>
<td>B7</td>
<td>B8</td>
<td>B9</td>
<td>B10</td>
<td>Figure 6.26</td>
</tr>
<tr>
<td>Sealed, wet, no copper, HMA</td>
<td>B11</td>
<td>B12</td>
<td>B13</td>
<td>B14</td>
<td>B15</td>
<td>Figure 6.27</td>
</tr>
</tbody>
</table>

The fluorescence spectra in each figure represent the different stages of ageing for each set of parameters mentioned in Table 6.3. For example, A1 to A5 will together form as a set of data in Figure 6.22 for oils that have been aged without acid and are dried. There is no copper present and the sample was sealed.

It is also very apparent from these figures that there are two distinctive peaks, one at 442 nm and the other around 490 nm. The spectral intensity that has a steep negative slope at 404 nm is due to the excitation source; mainly from strong backscattering of the excitation light due to the front surface geometry. This is also the reason for the intensity being off the range. In Figure 6.22 (A1-A5, no acid, dry), Figure 6.25 (B1-B5, no acid, wet) and Figure 6.26 (B6-B10, LMA, wet), there are drops in the arbitrary intensity of the oils aged for 2 weeks approximately in the range of 438 to 445 nm.

Whilst in Figure 6.23 (A6-A10, LMA, dry), Figure 6.24 (A11-A15, HMA, dry) and Figure 6.27 (B11-B15, HMA, wet), there are practically no changes in the intensity in the second week (440 nm). There is, in general, a decrease in the spectra of the fluorescence as the oils become more aged for up to 7 weeks; the exception being in Figure 6.23. In Figure 6.23, the peaks at 440 nm have negligible change (with only a change in the spectra in the range of 460 to 600 nm) for 1 week to 4 weeks aged oil. The drop in intensity can be seen to be around 5 week aged oil where there is suddenly an approximately drop of 64.3 % in the peak at 440 nm (from 7000 to 4500 counts).
The spectrum of 7 weeks aged oil is similar to the 5 weeks aged oil. There is a slight difference in spectra in the range of 460 to 620 nm between 5 and 7 weeks aged oil, in which both start with an initial rise and then drop in the spectrum. For 5 weeks aged oil, the intensity changes from 3200 (460 nm) to 3500 at 487 nm then to 0 arbitrary units at 620 nm. The corresponding intensity change for 7 weeks aged oil follows the pattern of 3200 at 460 nm, rising to 4100 at 487 nm then dropping to 0 at 620 nm.
Figure 6.22 Fluorescence spectra from 400 nm to 700 nm of cuvette samples A1-A5, no acid, dry; obtained from System A with an excitation wavelength of 404 nm. The colour patches from the top are in same order as the legend showing change in their colour as the oil samples become aged.

Figure 6.23 Fluorescence spectra from 400 nm to 700 nm of cuvette samples A6-A10, LMA, dry; obtained from System A with an excitation wavelength of 404 nm.

Figure 6.24 Fluorescence spectra from 400 nm to 700 nm of cuvette samples A11-A15, HMA, dry; obtained from System A with an excitation wavelength of 404 nm.
Figure 6.25 Fluorescence spectra from 400 nm to 700 nm of cuvette samples B1-B5, no acid, wet; obtained from System A with an excitation wavelength of 404 nm. The colour patches from the top are in same order as the legend showing change in their colour as the oil samples become aged.

Figure 6.26 Fluorescence spectra from 400 nm to 700 nm of cuvette samples B6-B10, LMA, wet; obtained from System A with an excitation wavelength of 404 nm.

Figure 6.27 Fluorescence spectra from 400 nm to 700 nm of cuvette samples B6-B10, HMA, wet; obtained from System A with an excitation wavelength of 404 nm.
6.5.2 Analysis of results of 10 GBN with LMA and HMA

The changes in the peaks can be easily visualised by studying Figure 6.28 to Figure 6.33. These graphs are generated by manipulating the raw spectral data in Figure 6.22 to Figure 6.27 using the normalisation method given in Equation (18).

In Figure 6.28 (dry with no acid case) there is a drop in the dimensionless intensity at 442 nm from 0.68 for 1 week aged oil to 0.66 for 2 week aged oil, then to 0.62 for 4 week aged oil, 0.56 for 5 week aged oil and 0.31 for 7 week aged oil. Overall there is a 54 % decrease in the intensity at 442 nm over the 7 weeks as the oil deteriorates. The second peak, which is at 490 nm, responds alternatively as there is a gradual increase in the intensity over the 7 weeks from 0.32 to 0.38 in terms of the dimensionless intensity. The graph for the sum of the dimensionless intensities, which is the sum of the intensity for the peak at 442 nm and 490 nm for System A, also shows a similar trend to the intensity of the peak at 442 nm. The dimensionless intensity ratio of the peak at 442 nm and 490 nm also shows a similar trend but has a much sharper gradient. This is a result of increasing intensity at 490 nm as the denominator and decreasing intensity at 442 nm.

Figure 6.29 corresponds to Figure 6.23. It can be seen that in the intensity of the peak at 442 nm has a dimensionless intensity of 0.68, which does not change for the oils which have been aged up to 4 weeks. There is then a drop in the intensity to 0.44 for oils that have been aged for 5 weeks. The intensity then remains constant for oils aged up to 7 weeks. The intensity of the peak at 490 nm increases from 0.32 to 0.4 for 1 week to 7 week aged oil. The sum of the intensity for this graph reflects both the spectra for the 442 and 490 nm peaks. The peak ratio has a continuous drop from 2.1 to 1.1. From the above analysis it can be concluded that LMA dry does not have significant ageing effect up to 4 weeks at a temperature of 115 °C.

Figure 6.31, Figure 6.32 and Figure 6.33 have similar spectra behaviour to that of Figure 6.30. There is an initial increase in the spectra for 1 to 2 week aged oil. The peak at 442 nm in Figure 6.32 has an initial increase in the intensity from 0.64 to 0.7 and then goes through a mild drop-rise-drop cycle to 0.4. The intensity of the peak at 490 nm has a rise in the intensity for 1 to 7 week aged oil. The peak ratio drops from 1.8 to 0.85.
Figure 6.28 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples A1-A5, no acid, dry. For comparison the colour patches of the aged oil are also given.

Figure 6.29 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples A6-A10, LMA, dry.

Figure 6.30 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples A11-A15, HMA, dry.
Figure 6.31 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples B1-B5, no acid, wet.

Figure 6.32 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples B6-B10, LMA, wet.

Figure 6.33 Change of fluorescence light emission at 442 nm and 490 nm as a function of ageing time for cuvette samples B11-B15, HMA, wet.
The PCA results are shown in Figure 6.34 to Figure 6.40 and the comparison between the degradation angle changes in the PCA graphs with the sum of the intensity are shown in Figure 6.41 to Figure 6.46.

The fluorescence spectra of the oils in Figure 6.22 to Figure 6.27 show an overall decrease in the intensity spectra as the oil aged. However there are points that are not reflected accurately. PCA gives a more robust presentation of the features in the data. For example, in Figure 6.23 although the oils are aged for 3 weeks the fluorescence spectrum is very similar except in the range of 460 to 640 nm. The manipulated data in Figure 6.29 shows an overall trend of the ageing, however it does not give an accurate representation of the data because it does not reflect the trend of the ageing. The PCA results shown in shows that there is actually a difference between 1 week, 2 week and 4 week aged oil. Therefore PCA can catch up the difference in the overall spectrum. The distance in between the points on the PCA graph (Figure 6.35) indicate the degree of ageing.

As the gap between spectral curves in the original fluorescence curves becomes bigger there is an indication that the oil has aged significantly, changing in association with the two Principal Components (PC). This can be linked with the angle of the points by taking (0,0) as the centre (degradation angle as defined in Section 6.3.2). Using W1 as a starting point the other angles of the cuvette samples can be measured and the slope of the degradation can be plotted which is shown in Figure 6.41 to Figure 6.46.

An analysis of the change in degradation angle will provide quantitative information on the performance of the PCA method. In Figure 6.34 the angle of W1 is 20.8 ° from the horizontal axes. W2, W4, W5 and W7 are 22.4 °, 24 °, 36.6 ° and 68.2 ° respectively. Taking W1 as the reference the other angles can be calculated with respect to W1. This can be seen in Table 6.4.
Table 6.4 Angles in PC plot for different cuvette samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>W1</th>
<th>W2</th>
<th>W4</th>
<th>W5</th>
<th>W7</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1-A5</td>
<td>20.8</td>
<td>22.4</td>
<td>24.0</td>
<td>36.6</td>
<td>68.2</td>
</tr>
<tr>
<td>A6-A10</td>
<td>27.4</td>
<td>32.0</td>
<td>37.0</td>
<td>55.8</td>
<td>61.9</td>
</tr>
<tr>
<td>A11-A15</td>
<td>20.7</td>
<td>24.0</td>
<td>33.4</td>
<td>51.7</td>
<td>70.2</td>
</tr>
<tr>
<td>B1-B5</td>
<td>25.1</td>
<td>27.5</td>
<td>38.5</td>
<td>45.4</td>
<td>65.1</td>
</tr>
<tr>
<td>B6-B10</td>
<td>25.2</td>
<td>27.9</td>
<td>42.2</td>
<td>43.4</td>
<td>65.2</td>
</tr>
<tr>
<td>B11-B15</td>
<td>28.0</td>
<td>28.4</td>
<td>44.6</td>
<td>55.1</td>
<td>64.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Samples</th>
<th>W1</th>
<th>W2</th>
<th>W4</th>
<th>W5</th>
<th>W7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degradation angle relative to W1 (degree)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1-A5</td>
<td>0.0</td>
<td>1.6</td>
<td>3.2</td>
<td>15.8</td>
<td>47.4</td>
</tr>
<tr>
<td>A6-A10</td>
<td>0.0</td>
<td>4.7</td>
<td>9.7</td>
<td>28.5</td>
<td>34.5</td>
</tr>
<tr>
<td>A11-A15</td>
<td>0.0</td>
<td>3.4</td>
<td>12.7</td>
<td>31.1</td>
<td>49.5</td>
</tr>
<tr>
<td>B1-B5</td>
<td>0.0</td>
<td>2.5</td>
<td>13.5</td>
<td>20.3</td>
<td>40.1</td>
</tr>
<tr>
<td>B6-B10</td>
<td>0.0</td>
<td>2.7</td>
<td>17.1</td>
<td>18.2</td>
<td>40.0</td>
</tr>
<tr>
<td>B11-B15</td>
<td>0.0</td>
<td>0.4</td>
<td>16.6</td>
<td>27.1</td>
<td>36.9</td>
</tr>
</tbody>
</table>

In Figure 6.40 all the cuvette samples are collectively analysed using PCA and then rotated using a varimax rotation. Samples which have been aged for the same period have been circled using different colours; 1 and 2 weeks (green), 4 weeks (blue), 5 weeks (orange) and 7 weeks (red). Although there is some overlap it can be clearly seen that as the oil ages the degradation angle increases. Table 6.5 shows the degradation angle and correlated degradation angle using A1 as the reference. Observing the colour of the oil for 1 and 2 week aged oil it can be seen that for all the cuvette samples the difference in colour is negligible. This may be the cause for the clustering of the samples.

Since the samples are aged under dry and wet conditions, it would be interesting to make a comparison of the ageing patterns using the PC1 results. The overall behaviour is qualified using the angle change between Week 1 and Week 7.

For the no acid case, the angle difference between dry and wet (dry angle to wet angle) is $47.27 - 42.16 = 5.11\, ^\circ$. For the LMA case, the angle change is $34.87 - 45.60 = -10.73\, ^\circ$. For the HMA case, the angle difference is $50.7 - 40.37 = 10.33\, ^\circ$. It seems that that for no acid and HMA cases, the existence of moisture may lead to less drop in fluorescence emission intensity whilst for the LMA case, the trend is opposite.
Table 6.5 Angles in PC plots for each cuvette sample listed according to types of sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degradation angle (degree)</th>
<th>Correlated degradation angle (degree)</th>
<th>Ageing parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>22.25</td>
<td>0.00</td>
<td>No acid, dry</td>
</tr>
<tr>
<td>A2</td>
<td>24.02</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>25.19</td>
<td>2.95</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>38.53</td>
<td>16.29</td>
<td></td>
</tr>
<tr>
<td>A5</td>
<td>69.51</td>
<td>47.27</td>
<td></td>
</tr>
<tr>
<td>A6</td>
<td>22.65</td>
<td>0.40</td>
<td>LMA, dry</td>
</tr>
<tr>
<td>A7</td>
<td>27.15</td>
<td>4.91</td>
<td></td>
</tr>
<tr>
<td>A8</td>
<td>32.10</td>
<td>9.86</td>
<td></td>
</tr>
<tr>
<td>A9</td>
<td>50.68</td>
<td>28.44</td>
<td></td>
</tr>
<tr>
<td>A10</td>
<td>57.11</td>
<td>34.87</td>
<td></td>
</tr>
<tr>
<td>A11</td>
<td>24.18</td>
<td>1.93</td>
<td>HMA, dry</td>
</tr>
<tr>
<td>A12</td>
<td>27.83</td>
<td>5.58</td>
<td></td>
</tr>
<tr>
<td>A13</td>
<td>37.81</td>
<td>15.56</td>
<td></td>
</tr>
<tr>
<td>A14</td>
<td>55.95</td>
<td>33.71</td>
<td></td>
</tr>
<tr>
<td>A15</td>
<td>72.94</td>
<td>50.70</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>24.47</td>
<td>2.23</td>
<td>No acid, wet</td>
</tr>
<tr>
<td>B2</td>
<td>26.91</td>
<td>4.67</td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>38.14</td>
<td>15.89</td>
<td></td>
</tr>
<tr>
<td>B4</td>
<td>44.99</td>
<td>22.74</td>
<td></td>
</tr>
<tr>
<td>B5</td>
<td>64.37</td>
<td>42.12</td>
<td></td>
</tr>
<tr>
<td>B6</td>
<td>28.17</td>
<td>5.92</td>
<td>LMA, wet</td>
</tr>
<tr>
<td>B7</td>
<td>30.94</td>
<td>8.70</td>
<td></td>
</tr>
<tr>
<td>B8</td>
<td>45.64</td>
<td>23.39</td>
<td></td>
</tr>
<tr>
<td>B9</td>
<td>46.68</td>
<td>24.43</td>
<td></td>
</tr>
<tr>
<td>B10</td>
<td>67.85</td>
<td>45.60</td>
<td></td>
</tr>
<tr>
<td>B11</td>
<td>25.77</td>
<td>3.52</td>
<td>HMA, wet</td>
</tr>
<tr>
<td>B12</td>
<td>26.14</td>
<td>3.90</td>
<td></td>
</tr>
<tr>
<td>B13</td>
<td>42.41</td>
<td>20.16</td>
<td></td>
</tr>
<tr>
<td>B14</td>
<td>52.82</td>
<td>30.58</td>
<td></td>
</tr>
<tr>
<td>B15</td>
<td>62.62</td>
<td>40.37</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.34 Component plot in rotated space for results from System A of 10 GBN samples A1-A5, no acid, dry.

Figure 6.35 Component plot in rotated space for results from System A of 10 GBN samples A6-A10, LMA, dry.

Figure 6.36 Component plot in rotated space for results from System A of 10 GBN samples A11-A15, HMA, dry.
Figure 6.37 Component plot in rotated space for results from System A of 10 GBN samples B1-B5, no acid, wet.

Figure 6.38 Component plot in rotated space for results from System A of 10 GBN samples B6-B10, LMA, wet.

Figure 6.39 Component plot in rotated space for results from System A of 10 GBN samples B11-B15, HMA, wet.
Figure 6.40 PCA Component plot in rotated space of A1 - A15 and B1 - B15 using System A with the different aged samples circled in their various colours.

Figure 6.41 Angle of degradation for 10 GBN as a function of ageing time for samples A1-A5. The sum of the intensity is also displayed for comparison.
Figure 6.42 Angle of degradation for 10 GBN as a function of ageing time A6-A10.

Figure 6.43 Angle of degradation for 10 GBN as a function of ageing time A11-A15.

Figure 6.44 Angle of degradation for 10 GBN as a function of ageing time B1-B5. The sum of the intensity is also displayed for comparison.
Figure 6.45 Angle of degradation for 10 GBN as a function of ageing time B6-B10.

Figure 6.46 Angle of degradation for 10 GBN as a function of ageing time B11-B15.
6.5.3 Section II: Performance of System A and B on 10 GBN Samples

The objective of this section is to provide further assessment of the capability of System B, the portable system, in identifying the differences among aged samples. The samples measured are 10 GBN oil with and without copper aged under unsealed and sealed conditions at 115 °C. Both System A of 404 nm and System B of 365 nm were used to analyse the samples.

The fluorescence emission spectra for the samples without copper are given in Figure 6.47 for unsealed and Figure 6.49 for sealed. It is to be noted that the intent is not to compare the ageing behaviour for unsealed and sealed oil samples because it has already been carried out previously. In fact the ageing conditions were different, invalidating for a direct comparison. The interest lies in the comparison of measurement between System A and System B of the same sample.

The intensity reading from System B is much higher because of its much longer integration time. On appearance System B better resolves the difference between 3 day and 7 day cuvette samples (red and blue curves). However from Figure 6.49 it is evident that PCA is able to resolve the difference between 3 day and 7 day cuvette samples for both systems. The locational patterns of all points in the two PC plots are similar.

Another point is to be made here based on observation of the PC plots and the original spectral graphs. When there is a change in the shape of the profile, there will be a distinctive difference between two points in the PC plot. A change of shape can be caused by

- A change in the peak intensity
- A change in the ratio of integrated intensity of the two parts divided by the 490 nm wavelength.

PC 1 is associated with the shorter wave length portion (shorter than 490 nm) and PC 2 with the portion of longer wavelength. This is because the variance of PC1 is approximately 90 % which matches the fact that the change in the fluorescence spectra is mainly in the shorter wavelength range up to 490 nm for oil samples aged for different weeks. The change in this spectra longer than 490 nm is less than that in the short wavelength and the first two PCs account for nearly 99% of all the variance in the original emission spectra.
The second sample is sealed 10 GBN without copper (Figure 6.49). In this case the emission profiles for 3 day and 7 day cuvette samples are less resolved by System B. It is however rather surprising that the PCA from System B (Figure 6.50) gives a larger separation (distance between the two points in the component plot) in comparison with that from System A. The reason is that the 3 day and 7 day curves on (b) in Figure 6.49 are more different than the corresponding curves in the (a). PCA for System B does not well resolve the 36 day and 45 day cuvette samples because they are rather similar in their profiles in Figure 6.50. However there is certainly change in the overall intensity between the two profiles, which is not picked up by PC 1.
Comparative measurements were also conducted when copper is added. The ageing conditions are the same as those for the no copper case. Results are given in Figures 6.49 and 6.50. Despite the large visual separation in the intensity profiles from System A, PCA produces confusing results. The 14 day point and the 21 day point are close to each other. This raises a serious issue of the capability of PCA in distinguishing similar profiles. In comparison PCA well resolves the difference among the cuvette samples, especially the 20 day and 21 day cuvette samples. A further insight into the details reveals that the two curves corresponding to 20 day and 21 day have only subtle differences. Because of the fact that the samples were severely aged at later stage and the complexity involved in PCA transformation
it is not possible to give a clear explanation on the rotation reversal in Figure 6.52 and Figure 6.54.

Figure 6.51 Fluorescence spectra from unsealed 10 GBN with copper, obtained from System A (404 nm laser, left) and System B (365 nm LED, right).

For the case of sealed 10 GBN with copper, there are only three cuvette samples (Figure 6.53). PCA from both systems (Figure 6.54) gives a small separation in the component plot between the 21 day and 36 day cuvette samples despite the large visual difference in the profiles. Whereas the separation between the 36 day and 45 day is large. Again in this case the 45 day cuvette sample no longer shows any identity of the emission peaks while the other two profiles have clear and similar peaks.
Figure 6.53 Fluorescence spectra from sealed 10 GBN with copper, obtained from System A (404nm laser, left) and System B (365 nm LED, right).

Figure 6.54 PCA plot of fluorescence spectra from sealed 10 GBN with copper, obtained from System A (404 nm laser, left) and System B (365 nm LED, right).

6.6 SUMMARY

The fluorescence emission results from System A and System B are presented and analysed for three samples, Diala S2-ZUI, Nytro Libra, and 10 GBN. The features in the spectral profiles are discussed in detail. Different methods have been tried to differentiate the oil conditions with different ageing times.

The experimental errors were first estimated and it was found that 2.5 % of relative error can be used in the analysis of the results. There is an offset of the system when there is no excitation light in the sample. This offset has been subtracted in all results presented in this chapter.
The first observation is with Diala S2-ZUI, whose fluorescence emission profiles in terms of intensity magnitude reverses from Week 4 to Week 5. This will need further confirmation in future.

Results show that fluorescence emission from the samples have different rate of degradation as a function of time. Diala S2-ZUI and Nytro Libra have the largest emission attenuation in Week 3. For 10 GBN this happens near Week 4 and in Week 7. The emission peaks in all cases are clearly seen at the beginning of the ageing process. However they quickly attenuate with time and eventually disappeared.

Two methods have been used to study the ageing process. The first one is normalised intensity at the peaks. The most effective method for monitoring the degradation process is to use the sum of the normalised intensity at the two chosen peaks. PCA was also applied, which shows very promising results in resolving the differences between the samples. The only exception is when the emission profiles are linearly correlated, i.e. they have very similar profiles, PCA is not able to resolve their difference despite there is apparent difference in the overall intensity.
CHAPTER VII: CONCLUSION AND FUTURE WORK

7.1 SUMMARY AND CONCLUSION

The use of two different optical systems with different excitation wavelengths (365 and 404 nm) as potential technologies for monitoring the condition of aged transformer oils was assessed in this project in terms of their ability to resolve the differences between the aged oil samples. Three types of transformer oils were used. To this end, an existing method, the Principal Component Analysis method, and a new method based on the normalised fluorescence emission peaks were applied to analyse the data obtained from the two optical systems. The main work and findings are given below.

7.1.1 Baseline data for different types of transformer oils

Effort has been made to have a good understanding of the principles involved in the operation of the two optical systems, System A and System B.

System A, which uses a 404 nm Gallium Nitride semiconductor laser diode as an excitation source, used a more traditional setup for collecting fluorescence signals. The optical instruments were separate, bulky and require a PC for data acquisition. System B, which can be considered to have an opposite setup, uses a 365 nm LED excitation source with a much more compact setup. It has individual modules that are connected together without the need for any exterior wires and an on-board DPU system and allows data acquisition without a PC.

The characteristics of the two systems were studied in chapter IV. The two systems use very similar probe arrangement and optical detection devices. The main difference is with the excitation source. The choice of the shorter wavelength light source was based on previous study on the optimum excitation wavelength of fluorescence emission from transformer oils and the need to reduce interference to the emission in the visible light wavelength range.

The experimental errors including systematic error (15260 counts), fluctuation in output signals (300 counts) and repeatability (2.5%) were discussed under defined conditions and
typical test results analysed in Chapter VI. It was found that a relative error of 2.5 % is a comfortable value to be used in result analysis. The systematic error has been deducted from all data before presented and analysed in Chapter VI.

It was found that the excitation range of the fluorescence is in the visible spectrum range of 400 to 700 nm. For the molecules excited by System A there were strong intensity signals around 442 and 490 nm. These fluorescence peaks are thought to be from the larger aromatic hydrocarbons such as PAHs although the actual molecules are unknown. For System B the strong intensity signals were about 432 and 490 nm. A common problem found with using System B was that it had a much lower intensity signal than that of System A. System B required a much longer integration time than System A. This is because the power of System B was much lower than the power injected into the laser in System A, resulting in a lower light emission. The advantage of using a shorter excitation wavelength is that there is less backscattering in the visible light wavelength range and the fluorescence light collected from the sample is not affected by the backscattering of the excitation source.

7.1.2 Performance of the sum of normalised peak intensity method

This method was developed based on a study of the fluorescence emission spectra of the transformer oil from both systems. It was found that during the ageing process there is a large difference in the rate of change of the peak intensities of the spectra, which provides very useful information in classifying the state of the aged oil samples (Section 6.3). Results show that this method is able to well differentiate the aged oil samples since the change in the intensity sum from samples aged for different weeks is significantly larger than the experimental uncertainty in the case of Diala S2-ZUI (Figure 6.14). This is also true for Nytro Libra (Figure 6.17). It can therefore be concluded that this method is valid in the long term monitoring of aged transformer oils.

7.1.3 Principal component analysis method

From PCA analysis it can be seen that the degradation angle as defined in Section 6.3 is a good indication of the condition of the oil. Oils that are more aged will have a larger degradation angle than the less aged oils. The difference in the gap between the points on the PCA rotated graph can potentially indicate the ageing stage of the oil. If a database of fresh and aged oils is assembled for a specific type of oil, new test results can then be added onto
the database to deduce the current condition of the oil. Additionally this will also create a historical record of the condition of the oil during operation. This may be useful for future analysis or maintenance operations.

This method has been applied to all three types of oils. It has been found that the method is most effective in differentiating fluorescence spectra that have very different profiles. It is less effective for spectra with similar profiles but only differing in their overall magnitude (Figure 6.14 and its associated original spectra). Thus care has to be taken when this method is applied to monitor the condition of a certain type of oil. It is essential to characterise the fluorescence emission profiles of oil samples with different ageing period to ensure that there is sufficient difference in the profiles of the spectra and the method is effective.

The method of intensity sum after normalisation is advantageous over the PCA method for Shell Diala S2-ZUI since the former provides higher resolution in the spectral profiles (Figure 6.14).

### 7.1.4 Scaling of spectral profiles at a chosen wavelength

This method is based on the idea that spectral profiles with different overall intensity can be scaled to make their values comparable in favour of PCA analysis. However results show that this approach generally compresses the range of variation of both the intensity sum and the degradation angle as defined in Section 6.3. Therefore it is not recommended in the processing of fluorescence spectra profiles in relation to transformer oil condition monitoring.

### 7.2 FEASIBILITY OF PORTABLE FLUORESCENCE PROBES BASED ON SYSTEM B

System B is a representation of a “shoulder strap” fluorescence probe setup for portable analysis. The results and analyses have indicated that the use of portable and online system monitoring technology is feasible. Ideally, this portable system will allow simple and quick measurements to be accomplished without the need of bulky and expensive instrumentation employing traditional methods, such as DGA.
System B is very compact with a total weight of approximately 0.53 kg. This is very ideal for portable or in-situ measurements as it is light compared to other equipment such as System A, which may be much more bulky and heavy. The cost of System B is also comparably cheaper compared to the equipment required by other methods. A DGA system may cost around £20-30k compared with System B, which only costs about £2500 (mainly due to spectrometer and optical detector). Although these values are estimates with the rapid rate at which technology is advancing and the discovery of new materials System B (mainly costs of spectrometer and optical detector) may be much cheaper in future. Due to its simple and straightforward design and based on the fluorescence spectrum data the possibility of using cheap LEDs to excite the peaks at around 432 nm and 490 nm could be constructed.

Using System B will also solve current issues with existing monitoring methods. Existing methods often require many different tests to be done before a conclusion can be made about the condition of the oil. The tests are often slow and repetitive and require the use of large and expensive equipment which are normally stored in laboratories that are far away from most of the transformers in question. The time required for a test to be taken using System B only takes a maximum of 2 to 5 minutes. This is much faster than tests using other equipment, such as DGA, which may take up to 45 minutes for a test. System B also has the ability to instantly store all the files on SD cards in order to store the data. If System A was used the data can only be stored on the PC first. Therefore System B has a much more flexible transfer of data.

Due to the small size, compactness and light weight of this system, its use is very flexible. Instead of storing data on the SD cards or on PCs the system can also potentially use wireless networks and General Packet Radio Services (GPRS). GPRS is essentially data transfer technology used in the 2G or 3G cellular communication networks to transfer data. This is only applicable because the size of the data which is saved using System B is only 31 kB. For one complete measurement 6 text files will need to be saved which amount to 186 kB. This will mean the data can be uploaded or downloaded with speed. This will allow the data to be directly sent to the command centre where a program can be used to analyse and compute the data. This will reduce transportation time and costs in transferring data.

Remotely controlled monitoring technology will also allow the idea of online systems. This would mean samples are not required to be removed from the transformer because the Jaz™
(Ocean Optics Inc.) system can be left on site with the probe directly inserted into the transformer. This is a much complicated task as there are many health and safety issues and design criteria that must be considered before this can be done. One major issue might be the high voltage and current levels in the transformer which may influence the system. Another idea may be data processing while offline. The system does not need to be on for the data to be processed. It does not require much power and can therefore be monitored conveniently. A fully embedded system based on microprocessor resources can be used for the PCA. By doing this a warning signal can be sent out when appropriate.

Another suggestion for remotely controlled monitoring technology is that it can be used in conjunctly with portable monitoring. For transformers closer to a command centre the condition of the transformer oils in the transformer can be manually measured using System B. The cost for this is relatively cheap as only a few portable systems are required. For transformers that are located very remotely (for example in mountainous areas) an online monitoring system based on System B can be installed directly onto the transformers. This will reduce the costs of maintenance and travel and reduce the potential risk of human hazards.

7.3 FUTURE WORK

In order to improve the performance of the system and the analysis of the results it is crucial to understand the pillars supporting this method. The design of the system is very fundamental. Depending on the setup the ability of the system to excite, collect and acquire data may be influenced.

Firstly, there is a need to improve stability and efficiency of the system to collect fluorescence. By creating a more stable platform for the experimental method the analysis of the results will be more reliable and accurate for analysis. An improvement in the efficiency of the probe to excite and collect fluorescence will allow better signal to noise ratio. Another important consideration in the design is the applicability of either portable or online monitoring systems. Portable measurements will need a standard routine in which all tests should follow so that the results are comparable to results taken from other locations. Online tests would require the close analysis on system setup and safety issues. Existing equipment
may cause unpredicted faults or interference with data collection therefore special care is required when implementing the system.

The second area for future work would be correlation of the results with existing methods for testing the condition of transformer oils. This has not been done due to limit in time for this research. The PCA results and those form the sum of normalised intensity should be correlated with colour and acidity in particular as they are common methods used for testing. The experimentation should be continued to include transformer oils in operation and other various oils other than mineral oils, such as vegetable oils, to experiment the range of applicability. Potential correlations can then be made to more accurately contrast the condition with parameters that already well known.

Lastly, the “drop-rise-drop” behaviour observed in Section 6.2.1 cannot be explained. The effect of temperature gradient in the oven was not able to cause this pattern since the rotation cycle took only 3 days. Therefore further work will be needed to establish the cause for this behaviour.
References


17. ASTM D 1816-84a, "Test method for dielectric breakdown voltage of insulating oils of petroleum origin using VDE electrodes", 1990
22. T. B. S. Institute, "BS148 - Specification for unused mineral oils for transformers and switchgear", United Kingdom, 1998
34. C. Karlsson and D. P. Wikland, "Measuring peroxides in oil", 2010


[60] A. Tan Kim Liang, "Design of a portable fibre optic based sensor system for in-situ measurements of fluorescence emission from gasoline, transformer and engine oils", MSc, Department of electrical engineering and electronics, University of Manchester, 2002


