Detection of 2FAL Furanic Compound in Transformer Oil Using Optical Spectroscopy Method and Verification Using Morse Oscillation Theory

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ABSTRACT The condition of a power transformer can be predicted based on the contents of the transformer oil. One of the most common parameters that are observed in the transformer oil is 2-Furaldehyde, a compound that is produced due to the aging of Kraft paper. Although the optical characterization of 2-Furaldehyde has been widely reported, the fundamental theories of the observation of the optical absorbance peaks have not been elaborated. This study investigates the optical characteristics of 2-Furaldehyde in the near infrared region. Ten samples with different concentrations of 2-Furaldehyde were prepared and verified using the conventional method. The samples were then characterized using optical spectroscopy method with 50 nm path length cuvettes. Three peaks were observed at 1610 nm – 1640 nm, 1100 nm – 1115 nm and 860 nm – 890 nm wavebands and were correlated to the overtones of the aromatic C-H stretch in 2-Furaldehyde. The appearance of these overtones corresponding to the Morse Oscillation Theory was discussed. This fundamental knowledge is significant in developing a portable optical device that enables the detection of 2-Furaldehyde on site.

INDEX TERMS Furanic compound, insulation paper degradation, Morse oscillation theory, optical spectroscopy, overtones, power transformer, transformer oil, 2FAL.

I. INTRODUCTION

Power transformers are used to transport electrical energy in the transmission and distribution network. The main components of a power transformer are the transformer oil and the insulation paper [1]. The former insulates and cools the transformer as well as provides information on the condition of the transformer [2]. The latter insulates the copper coils in the transformer [3]. Under normal operation, the transformer insulating materials undergo chemical reactions and electrical stresses that result in the production of various chemical compounds. For example, the reactions that occur in the insulation paper produces furanic compounds which can be found dissolved in the transformer oil. Therefore, the condition of the transformer insulation paper can be monitored based on the concentration of furanic compounds in transformer oil.

The types of furanic compounds that are produced by the chemical reaction in the insulation paper are 2-furaldehyde (2FAL), 5-hydroxymethyl-2-furaldehyde (5HMF), 2-furfuryl alcohol (2FOL), 5-methyl-2-furaldehyde (5MEF), and 2-acetyl furan (2ACF) [4]. In comparison to all the furanic compounds, the detection of 2FAL in transformer oil is a major interest amongst researchers due to its good correlation with the degree of polymerization (DP) of the insulation paper [5].

The conventional method of detecting 2FAL in transformer oil is by using high performance liquid chromatography (HPLC) technique based on the International Electrotechnical Commission (IEC) 61198 [6] standard. Although HPLC method is able to accurately determine the
concentration of 2FAL, this measurement technique requires tedious preparation procedures [7]. Therefore, alternative methods were suggested to overcome the limitation of the conventional method [8]–[10].

The utilization of optical method in the detection of 2FAL in transformer oil was proposed by Pahlavanpour and Duffy [11] who studied the absorption spectrum of aniline acetate-2FAL complex. The peak at 526 nm was reported to be the ideal wavelength where aniline acetate-2FAL complex produced a high absorbance. Blue et al. [12] investigated the fluorescence of aniline acetate-2FAL complex. The result of the experiment showed a significant fluorescence peak at 570 nm. Blue et al. [13] also reported the detection of 2FAL in the mid infrared wavelength region (MWIR) at 1730 cm$^{-1}$ wavenumber (corresponds to wavelength of 5780 nm). In 2008, Lai et al. [14] measured different concentrations of furanic compounds using Ultraviolet-Visible (UV-Vis) spectroscopy. The result of the experiment showed the detection of 2FAL at 224 nm waveband.

Though optical detection method has a great potential to be used as an alternative method for 2FAL detection, there are a few areas have been overlooked. For example, the optical detection at the UV-Vis region can be strongly influenced by the color intensity of the transformer oil [15] and the conducting materials present in the transformer oil [16]. Thus, optical measurement at this waveband may not be very accurate.

Apart from that, the detection of 2FAL in the MWIR can be technologically challenging and costly due to the need of utilizing optical source which emits photons at wavelengths $>3000$ nm. In addition, photodetectors operating in the MWIR, which are made of narrow bandgap semiconductor material, possess high dark current that limits the sensitivity of the measurement. Thus, a shorter wavelength such as the near infrared region (NIR) can be explored to detect 2FAL in transformer oil as this region is not affected by the color intensity or the presence of conducting material in transformer oil as well as it is at a lower waveband as compared to MWIR. However, the detection of 2FAL at this region has not been explored. Apart from that, the fundamental study on the peak exhibited by 2FAL samples was also not discussed previously.

Therefore, in this paper, we present a comprehensive study on the optical characterization of 2FAL in transformer oil at the NIR region. The overtones of the aromatic C-H stretch in 2FAL were verified using the Morse Oscillation Theory.

II. EXPERIMENTAL DETAILS

The preparation of different concentrations of 2FAL was done based on dilution method. A stock solution was first prepared based on (1).

$$1000\text{ppm of 2FAL stock solution} = \frac{100000 \ \mu g \text{2FAL}}{100 \text{ ml transformer oil}} \tag{1}$$

A few drops of transformer oil were added into the beaker containing 100000 $\mu$g or 100 mg of 2FAL using a plastic pipette. The solution was mixed by shaking the beaker softly. The solution was then poured into a 100 ml volumetric flask. The process of adding a few drops of transformer oil into the beaker, mixing it with 2FAL and then pouring the solution into the volumetric flask was repeated until there is no residue of 2FAL left on the base of the beaker.

The volumetric flask was then filled with clean transformer oil up to the calibration mark. The mouth of the volumetric mask was closed with a glass cap and was shaken until all of 2FAL had dissolved in the oil. The volumetric flask was then placed in a DAIHAN Scientific Ultrasonic bath for 5 minutes at 28 °C to ensure that 2FAL was completely dissolved in the transformer oil. The prepared 1000 ppm stock solution was used to prepare four (4) concentrations of 2FAL samples based on dilution method as in (2).

$$M_1V_1 = M_2V_2 \tag{2}$$

where $M_1$ is the concentration of 2FAL in the stock solution, $V_1$ is the volume of transformer oil from stock solution, $M_2$ is the required concentration of 2FAL and $V_2$ is the volume of 2FAL in the required concentration of transformer oil.

**TABLE 1. Dilution for 2FAL in transformer oil.**

| 2FAL$\text{nominal}$ (ppm) | Volume of 1000 ppm stock solution (ml) |
|---------------------------|--------------------------------------|
| 10                        | 1                                    |
| 50                        | 5                                    |
| 100                       | 10                                   |
| 500                       | 50                                   |
| 1000                      | -                                    |

The measured stock solution was then poured into a 100 ml volumetric flask. The volumetric flask was then topped up with new, uninhibited transformer oil from Hyrax. The solution was shaken thoroughly and placed in an ultrasonic cleaner for 5 minutes to ensure that 2FAL has dispersed evenly in the oil. The prepared samples were then closed with a lid and wrapped with an aluminum foil paper. The first and second sets of samples were labeled S1 and S2 respectively. Two sets of samples were used in this experiment to analyze the repeatability of the optical measurement. The samples were kept at room temperature before measurement.

A. CONVENTIONAL MEASUREMENT

The diluted 2FAL samples were measured using conventional measurement based on the IEC 61198 standard [17] by an accredited laboratory. It is important to note that the conventional method of measurement is calibrated to measure 2FAL up to 395 ppb only. Therefore, the prepared samples were further diluted to a lower concentration around the calibrated value.
The conventional measurement was carried out to ensure that there were minimum human error or calculation error involved while preparing the samples. The result from the conventional measurement (2FAL_{lab measurement}) and the diluted concentration of 2FAL (2FAL_{N.Diluted}) based on dilution factor (DF) in transformer oil were compared in Table 2.

### TABLE 2. Comparison of conventional measurement and diluted concentration of 2FAL based on DF before and after dilution.

| 2FAL_{nominal} (ppb) | DF | 2FAL_{N.Diluted} (ppb) | 2FAL_{lab measurement} X DF (ppb) |
|----------------------|----|------------------------|---------------------------------|
| 100000              | 286| 350                    | 373                             |
| 500000              | 1667| 300                    | 262                             |
| 1000000             | 3300| 303                    | 226                             |

As can be observed in Table 2, there is a clear difference in the concentration of 2FAL between each sample. The average error between the manually prepared samples and the conventional measurement of samples was 14.8 %. The error increased with increasing concentration of manually prepared 2FAL samples. This could be due to the human error involved during the dilution of the samples. Nevertheless, although there is a difference between the manually prepared samples and the conventional measurement, the increasing trend of 2FAL concentration from 100 ppm to 1000 ppm is clear.

### B. OPTICAL MEASUREMENT

The optical measurements of the two sets of samples (S1 and S2) with different concentrations of 2FAL were measured using Agilent Cary5000 spectrophotometer from 200 nm to 1690 nm. The measurement of the samples was initially done using three different path length cuvettes (10-mm, 20-mm and 50-mm). However, the absorbance peaks for samples measured with 10-mm and 20-mm path length cuvettes were very low and for samples with concentrations <500 ppm, the peaks were not visible. Since the objective of this study is to correlate the absorbance peaks to the functional groups, the analysis was carried out using data obtained from measurements using 50-mm path length cuvette. The result of the measurement showed 3 major absorption peaks.

In Figure 1, a double peak can be observed between 1610 nm – 1640 nm. However, the peaks can only be observed for samples with 500 ppm and 1000 ppm of 2FAL. The samples with concentrations ≤100 ppm of 2FAL have no peaks. The highest optical absorption of 2FAL is 0.0419. The measurement between S1 and S2 is fairly consistent. In Figure 2, a significant peak can be observed between 1100 nm – 1115 nm waveband. However, there is no correlation between the maximum optical absorption and the concentration of 2FAL. As compared to Figure 1 and Figure 2, the spectrum in Figure 3 has more influence of noise and the difference between the S1 and S2 differ greatly. The maximum optical absorption of the spectrum is also lower (0.00261) than that of Figure 1.

In Figure 3, a significant maximum optical absorption can be observed at a waveband of 865 nm to 885 nm. Nevertheless, there is no correlation between the maximum optical absorption and the concentration of 2FAL. As compared to Figure 1 and Figure 2, the spectrum in Figure 3 has more influence of noise and the difference between the S1 and S2 differ greatly. The maximum optical absorption of the spectrum is also lower (0.00105) than those of Figure 1 and Figure 2. It is important to note that a photometric noise test was conducted prior to measurement of samples to determine the minimum detection limit of the spectrophotometer. This test was carried out at 500 nm and 1500 nm. The absorbance of noise measured at these wavelengths was
Figure 3. Optical absorption peak at 860 nm - 890 nm waveband.

≤ 0.0000056 AU, which was below the specification of the instrument at 0.000030 AU. This shows that although there is more noise in Figure 2 and Figure 3, it is still a measurable signal as it has higher absorbance value than that of noise.

III. ASSIGNMENT OF FUNCTIONAL GROUPS

The optical absorbance in Figure 1, Figure 2 and Figure 3 correspond to the first, second and third overtones of aromatic C-H stretch in 2FAL [18]. The overtones are determined based on the equation established by Mizugai et al. [19]. Mizugai calculated the wavenumber of the C-H stretching vibration in 2FAL by associating the data obtained from the conventional spectroscopy measurement and the thermal lens technique [19]. The equation is shown in (3). Table 3 shows the wavenumber, wavelength and energy of photons needed for the first, second and third overtones of the C-H stretch in 2FAL based on (3).

\[
\text{Wavenumber of } x = 3200x - 59x^2 \tag{3}
\]

where, \(x\) is the vibrational quantum number.

As observed in Table 3, the difference in the amount of energy required for the molecules to be promoted from the ground state to a subsequent higher vibrational energy level becomes smaller with increasing overtones. This is because at higher vibrational energy levels, the atoms behave in accordance to the Morse oscillation model which predicts that the difference between the energy levels becomes smaller when approaching the dissociation energy level [20]. At a minimum distance, the atoms repel each other, causing a larger distance between the atoms. This distance becomes greater with increasing vibrational energy levels until the bond between the atoms dissociates [21]. Thus, as shown in Figure 4, the energy gap between two consecutive energy state decreases as it approaches the higher level of energy state.

Figure 4. Anharmonic oscillation model for aromatic C-H stretch in 2FAL, where \(D_o\) is the true energy required for dissociation [32].

Unlike the harmonic oscillation model that does not consider breaking of bonds, the Morse oscillation model considers bond breaking in molecules as well as accounts for the anharmonicity of the real bonds. The equation from Morse oscillation is shown in (4). The various vibrational energy levels in the Morse equation can be seen in Figure 4.

\[
V = D_e \left(1 - e^{-\alpha(R-R_e)}\right)^2 \tag{4}
\]

where, \(V\) is the potential vibrational energy, \(D_e\) dissociation energy, \(R\) is internuclear distance, \(R_e\) is the equilibrium internuclear distance (bond length), \(\alpha\) is an exponent coefficient that can be calculated based on (5).

\[
\alpha = \left(\frac{k}{2D_e}\right)^{1/2} \tag{5}
\]

where, \(k\) is force constant.

There are three C-H bonds in the 2FAL aromatic ring which are involved in this stretching vibration. The three bonds are depicted in Figure 5.

The presence of oxygen in the ring causes the overtone peak to split [20]. As noticed in Figure 1, two peaks are formed in the spectrum. This phenomenon is mainly due to the electronegativity of oxygen and the distance between the

| Table 3. Calculation of overtones of C-H stretch in 2FAL based on Mizugai’s equation. |
|-----------------|----------|---------|----------|
| Fundamental     | 1        | 3141    | 3183     | 0.38     |
| First overtone  | 2        | 6164    | 1623     | 0.76     |
| Second overtone | 3        | 9069    | 1103     | 1.12     |
| Third overtone  | 4        | 11856   | 843      | 1.47     |
carbon atoms in the ring and the oxygen. The lower peak that can be observed at 1615 nm is the C-H stretching vibration at position b (refer to Figure 5) and the higher peak at 1627 nm is the C-H stretching vibration at position a. It is arguable that the effect of C=O in the aldehyde could also contribute to the appearance of double peaks. However, the effect of aldehyde is reduced by the inductive effect of the oxygen in the furan ring as the oxygen is directly attached to the ring compared to aldehyde [22]. Thus, the aldehyde group present in the molecule has negligible effect on the appearance of double peak in the absorbance spectrum.

Theoretically, the second and third overtones of the aromatic C-H stretch in 2FAL should also exhibit double peaks [23]. However, due to the low absorption values of the overtones, the double peaks cannot be observed. The low absorption values of the overtones are due to the lower probability of the absorption of the photons by the molecules at a higher vibrational energy level [24]. Hence, the magnitude of the absorption decreases with increasing overtones. The optical absorbance peak of the three overtones can be observed in Figure 6.

The absorption of the higher overtones can be enhanced by using a cuvette with a longer path length. This is because spectrometry absorption of the molecules obeys the Beer-Lambert Law [25], where the optical absorbance is proportional to the path length and the concentration of compounds in the samples. Therefore, the double peaks in the second and the third overtones can be seen by increasing the path length of the cuvettes.

Alternatively, Mortensen and Xiao [26] suggested the application of liquid-infiltrated photonic crystals to enhance the magnitude of absorption. The slow-light enhancement of the absorption can produce a smaller detection system with increased sensitivity. Nevertheless, this system requires a complex preparation procedure that is tailored to meet the requirement of many parameters such as viscosity, and pressure of the sample. Apart from that, this method is suitable only for samples with the application of shorter path length samples (below 1000 µm). Therefore, in this work, increasing the path length of cuvettes is a better option of increasing the absorption of the overtones of C-H aromatic stretch in 2FAL.

As observed in Figure 1, Figure 2, and Figure 3 the influence of noise becomes more obvious at higher overtones. This is because the optical absorbance decreases with increasing overtones. Therefore, the signal to noise ratio becomes smaller with lower optical absorbance value, resulting in a spectrum with high noise.

IV. CONCLUSION

This study proposes the optical characterization of 2FAL in the NIR region. A total of 10 oil samples with different concentrations of 2FAL were analyzed using the conventional HPLC method and characterized using optical detection technique at the NIR region. Three main optical absorption peaks were observed using the proposed optical technique. Three of the optical absorption peaks at 1610 nm – 1640 nm, 1100 nm – 1115 nm and 860 nm – 890 nm were characterized as the overtones of the aromatic C-H stretching vibrations in 2FAL. The three C-H stretching vibrations were correlated to the Morse Oscillation Theory. The exploration of the NIR region is significant because this waveband is a region that is not affected by the color or the conducting materials in the transformer oil thus, the probability of obtaining a misguided result can be eliminated. However, the measurement conducted using this technique is based on high concentrations of 2FAL in transformer oil. Samples from real transformers contain a very small amount of 2FAL which are measured in ppb based on the standard method. Nevertheless, further improvement in terms of light source and detectors can be customized to give very low concentration detection. The added advantage of this study is the use of clean new transformer oil samples to detect 2FAL.

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