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Full Paper

Fluorescence Spectroscopy Applied in the Identification of Lubricant Oils

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Abstract: In this work, we report the use of fluorescence spectroscopy to identify lubricant oils. Optical characterization was performed in four commercial lubricant oils that are used in reciprocating compressors. Mid-infrared absorption of samples indicates the presence of aromatic rings showing bands at 1605 cm^{-1} (C=C stretching) and 815 cm^{-1} (C–H stretch out of plane). UV-VIS absorption spectra show bands of di- and polyaromatic rings (around 230 nm and 260 nm, respectively). By exciting the samples at 360 nm, a broad emission band centered at 440 nm is observed, indicating that this excitation is appropriate to be used for the diagnosis of oil presence in the environment.

Keywords: optical spectroscopy; lubricant oil; fluorescence spectroscopy; compressor; infrared absorption

1. INTRODUCTION

Petroleum hydrocarbons are widely used in the world and are present in different commercial products, such as diesel, gasoline, kerosene, and lubricant oils. Frequently, there are accidental oil leakages and spillages that induce their accumulation in soil, which entails serious pollution problem in natural environments [1]. It is known that these products have polycyclic aromatic hydrocarbons (PAHs) in their composition [2–5].

Among the petroleum hydrocarbons, the lubricant oils are the most important to the increase in concentration of hydrocarbons in the environment. Sometimes, they are discharged on land and into rivers, representing about 40% of the total found in these environments [6]. Lubricant oils are used in different machines, as vehicle motors, mechanical parts and in industrial machines as vacuum pumps and compressors. Compressors are often used in industries such as power plants refineries, refrigeration systems and compressed natural gas stations [7]. Generally, these compressors have a lubricant oil system that due to uninterrupted work conditions or inadequate maintenance, may present mechanical failures leading to leakages and consequently, contaminating the environment (e.g. soil, water, air). Due to its toxicity, PAHs represent risks to all living organisms and in some cases they are carcinogens [8].

In reciprocating compressors, the used lubricant oil can be mineral based and can contain some concentration of PAHs in its chemical composition. If the reciprocating compressors have discharge pressure between 2500 and 4000 psi (17 – 28 MPa) the lubricant oil can be mineral or synthetic based according to the compressed gas type (dried, humid, with high CO_2 concentration) [5]. Reciprocating (piston) compressors typically use mineral based lubricants according to DIN 506 standards, with viscosity grades ISO VG 68 to VG 150, whose casings are subjected to low input pressure [9].

The analytical methods for characterization of the base stock oils used in mineral lubricants (aromatic, naphthenic and paraffinic) include the identification of aromatic compounds by ultraviolet absorption from 260 to 350 nm. The HPLC with anthracenes or other aromatics as markers or GC–MS after appropriate

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*Corresponding author. E-mail: luishca@uems.br sample preparation are also used for determination of PAHs [9]. PAHs are highly fluorescents and their emissions can be used for selective, simple and direct analysis in a multi-fluorophore system [10, 11]. In other words, the fluorescence spectroscopy can be used as a quick identification tool for lubricant oil leakages or spillage.

In this paper, four commercial mineral lubricant oils used in reciprocating compressor with different viscosities were selected to evaluate the use of fluorescence spectroscopy for a rapid identification of leakages and spillages of these products. UV-VIS, NIR, and MIR infrared absorption measurements were used to verify the presence of aromatic structures in these samples.

2. MATERIAL AND METHODS

Lubricant oils were acquired in local markets: three from Incol Lub group (Incol 68, Incol 100, Incol 150) and one from Icolub company (Schulz 100). These are the lubricants often used in air compressors.

To determine the optimum wavelengths of excitation and emission for the lubricant samples, a continuum Xenon lamp of 155 W, coupled with a monochromator (Newport Cornerstone 260 ™) was used, operating with a diffraction grating of 246 lines/mm. The fluorescence was collected by a second monochromator (Horiba Jobin Yvon - iHR 320) coupled with a CCD detector (Hamamatsu Sygnature), which was adjusted with an opening of 1 mm slits (input and output) and diffraction grating of 600 grooves/mm. Integration time of 10 seconds. The lubricating oil was inserted into a quartz cuvette of 1mm of path length. Excitations were collected in the spectral range of 360-540 nm with steps of 10 nm and emissions in the spectral range of 360 to 600 nm. The maximum intensity of excitation line normalized each spectrum to generate contour maps.

Vibrational modes of the samples were determined by infrared absorption in the spectral range of 4000-650 cm^{-1}, using a Fourier transform infrared spectrophotometer (Nexus 670 - Nicolet) with an attenuated total reflection (ATR) accessory. The samples were deposited on the ZnSe crystal plate of ATR detector and a spectrum of 64 averages was obtained for the samples with spectral resolution of 0.5 cm^{-1}.

The UV-Vis absorption spectra were collected by an Ocean Optics spectrometer HR4000 coupled with a deuterium-tungsten source. An optical bifurcated fiber (TP300 UV-VIS) was used to conduct the lamp energy to the sample and to propagate the transmitted light from the sample to the spectrometer. The absorption study was performed diluting 0.012 g of sample in 9.280 g of hexane to avoid spectral saturation. The absorption spectra were collected using integration time of 500 ms with an average of 5 spectra.

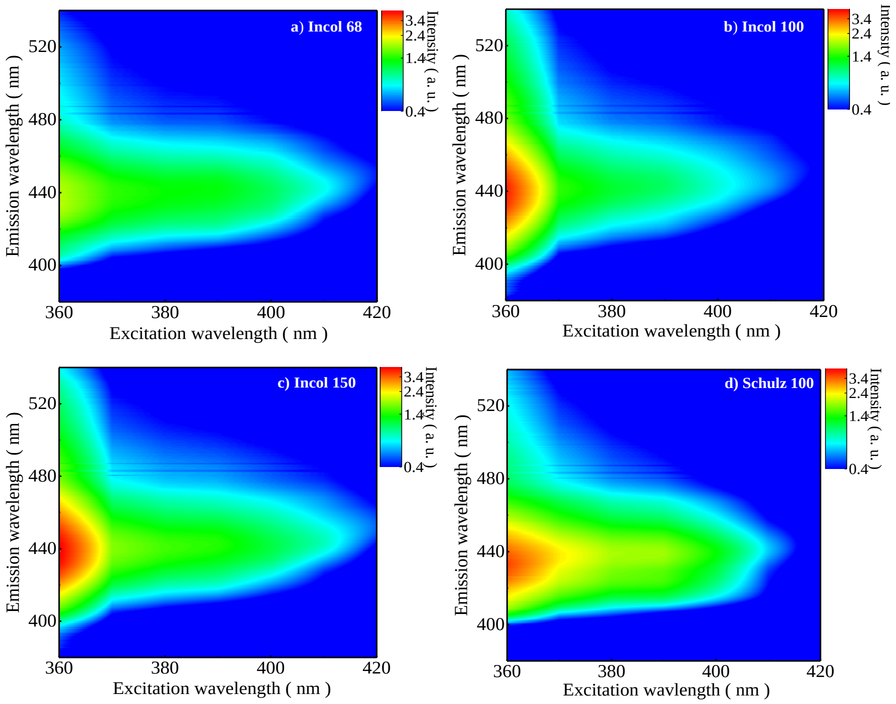

Figure 1. Excitation-emission maps for the Incol 68 (a), 100 (b), 150 (c) and Schulz 100 (d) compressor oils.

3. RESULTS AND DISCUSSION

In order, to identify the best excitation wavelength to excite the compressor oils for a higher emission intensity, excitation spectroscopy was performed varying the excitation from 360 to 420 nm (UV region) and the emission was observed from 380 to 540 nm (UV-Vis region). The obtained excitation-emission maps are plotted in Figure 1 for the Incol 68 (a), 100 (b), 150 (c) and Schulz 100 (d) compressor oils. All maps are in the same intensity log scale for comparison. The compressor oils exhibit a broad emission band with maximum intensity around 440 nm under excitation at 360-370 nm. Among the studied oils, the Incol 68 exhibits lower emission intensity, but the emission shape is like the others. By the maps it is possible to affirm that these four kinds of lubricant oils can be monitored by the fluorescence spectroscopy with UV excitation and probe around blue region.

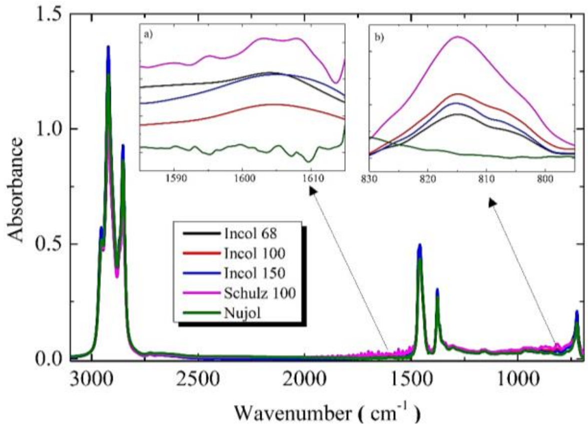

Figure 2. MIR spectra of the studied samples. a) and b) are zoomed two regions from aromatic stretching.

For a complete understanding on the responsible for this emission behavior, absorption spectroscopy was performed since de mid-infrared until the UV region. Figure 2 shows the absorbance spectra obtained for the studied oils, together with the absorbance spectrum for the Nujol. This last one was inserted for comparison, once it is a paraffinic liquid considered as "white oil". It is well known in the literature mainly because it does not exhibit any aromatic compounds in its structure. In the 3100-700 cm^{-1} wavenumber range, all spectra have intense bands at 3000-2840 cm^{-1}, corresponding to the stretching vibration from alkanes (ν C–H), in the fingerprint region at 1460-1350 cm^{-1}, corresponding to the vibrations of bending from alkanes (δ C–H), and 720 cm^{-1} due to rocking vibration (τ C–H) [12, 13]. In the insets (a) and (b) two important regions are zoomed where functional groups from aromatic molecules can be identified: the absorbance around 1605 cm^{-1} is from stretching of C=C and at 815 cm^{-1} is C-H stretch out of plane [14]. By comparing with the Nujol spectrum, the results suggest that the studied lubricant oils are mainly composed of paraffinic base stock and have a little amount of aromatic compounds. These last ones are responsible for the fluorescence observed with UV excitation.

The near infrared (NIR) absorption spectra for the studied oils are shown in Figure 3. There is an intense absorption band between 1650-1800 nm, which is attributed to the overtone of the second harmonic of C-H bond, one absorption band centered at 1200 nm, corresponding to the overtone of the third harmonic of C-H bond, and other absorption band centered at 1400 nm that corresponds to the 2ν(CH) + δ(CH) combination band [15]. The small absorptions due to aromatic compounds are not possible to be observed in this absorption region.

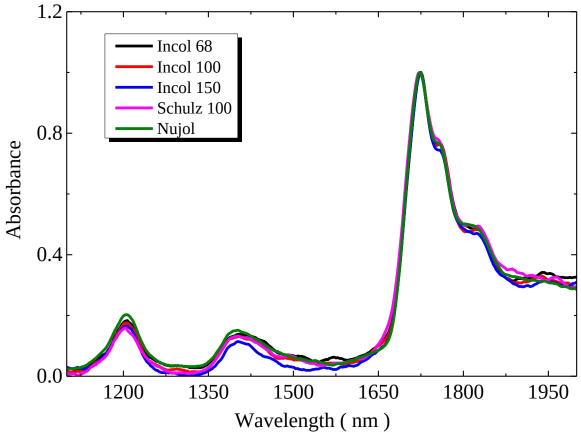

Figure 3. Absorption in the near infrared (NIR) region for all lubricant oils and Nujol.

The possible electronic transitions present into the oil can be seen by the UV-VIS absorption spectroscopy. The spectra obtained for all lubricant oils are shown in Figure 4. According to Totten et al. [16], it is expected that the maximum absorption peak for mono-, di-, and poly-aromatic hydrocarbons is observed at 197, 230, and 260 nm, respectively. Our results reveal two major absorption bands with maximum around 230 and 260 nm, corresponding to di- and poly-aromatic regions, also called polycyclic aromatic hydrocarbons, PAHs. Due to the absence of aromatic compounds in Nujol oil, no ultraviolet absorption bands were observed, in agreement to the mid-infrared spectra discussed before.

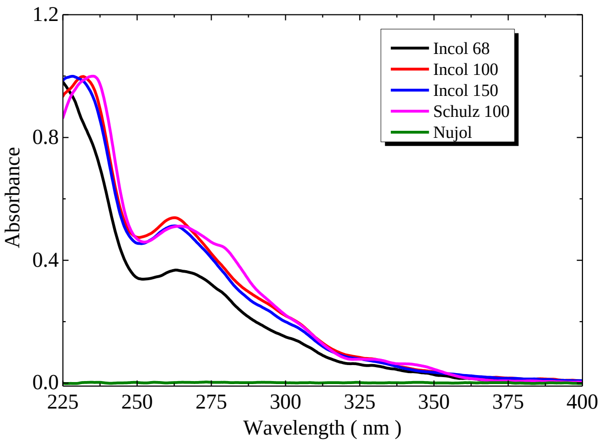

Figure 4. Absorbance in the UV region for all lubricant oils and Nujol.

Finally, emission spectroscopy was performed in the oils by exciting them at 360 nm, which corresponds to the maximum luminescence signal for each kind of oil. The excitation spectroscopy was performed by observing the emission at 440 nm for Incol 68, 100, 150 and Schulz 100, and 433 nm for Incol 68. The emission spectra have maximum emission similar to those reported by Gray and McMillen in crude oils [17]. The maximum intensities are observed around 380/430 nm (excitation/emission) for Incol 68 and Schulz 100, which are due to PAHs with 2, 3 and significant amounts of 4 aromatic rings. Reabsorption process is also possible in the oils because there is an overlap between the absorbance and the emission spectra for each oil, as shown in Figure 5.

It is known that aromatic and polyaromatic compounds are the main sources of fluorescence in organic substances and this fluorescence is due to electronic transition of π orbitals of the C = C bonds in these molecules [18]. Typically, PAHs can emit at higher energy intervals, increasing with the increment in number of aromatic rings, besides, the maximum excitation and emission position is shifted towards longer wavelengths with the increase of these rings [19]. Polycyclic aromatic hydrocarbons are commonly found in lubricants, petroleum, diesel oils, kerosene and 2T oils [2, 4, 20].

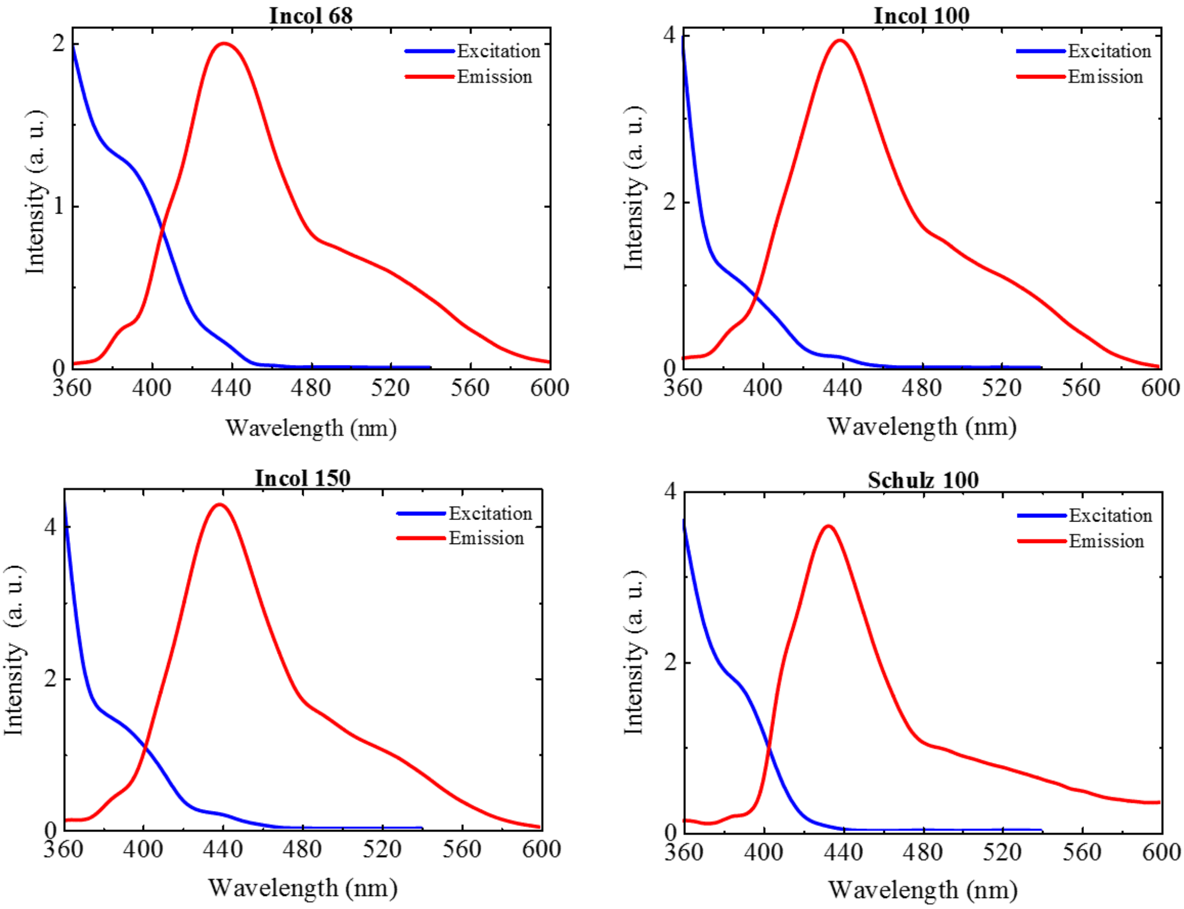

Figure 5. Excitation spectra (blue line) showing the blue emission around 440 nm, and the excitation spectra (red line) with excitation around 380 nm.

4. CONCLUSION

Different lubricant oils used in reciprocating compressors were studied by FTIR, UV-visible and NIR absorption, optical excitation, and fluorescence spectroscopy to investigate whether the fluorescence spectroscopy has potential to identify them in the environment. FTIR, UV-Vis absorption, and NIR proved useful for the detection of aromatic compounds (di-aromatics and poly-aromatics), as well as the identification of paraffinic base oil, since the bands of more intense infrared absorption are alkanes with vibrational modes stretching, bending, and rocking. The fluorescence spectroscopy showed promising results for the identification of lubricant oil.

5. ACKNOWLEDGMENTS

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