# Fluorescence Spectroscopy and Silica Gel Applied as a Tool for Capture and Detection of Compressor Lubricant Oils

Claudio Yamamoto Morassuti* [ID] [a], Sandro Marcio Lima [ID] [b], and Luis Humberto da Cunha Andrade [ID] [b]

Here, we report the use of fluorescence spectroscopy for the identification of lubricant oils used in reciprocating compressors, and the use of silica gel as an adsorbent to capture lubricant oil vapors. The silica gel was tested for adsorption of lubricant oil vapors, by heating the samples at 200°C, the emission spectrum of the lubricant oils is observed on the silica gel layer, over 20 min of heating. The spectrum of the lubricant oils over the silica gel layer presents a redshift, an indication of the degradation effect. In order to investigate this effect on the optical properties, we conducted an experiment by heating the samples at (130 ± 4) °C, and collected at different times. The MID-infrared absorption of the samples presents bands of oxygen-containing groups at 1010 and 1050 cm^{-1}, and NIR infrared absorption measurements at 3444 cm^{-1} show an increase in the hydroperoxide band during the degradation time. These two results indicate that the oxidation process is associated with the observed redshift of the absorption and emission bands in lubricant oils and over the adsorbent layer.

Graphical abstract
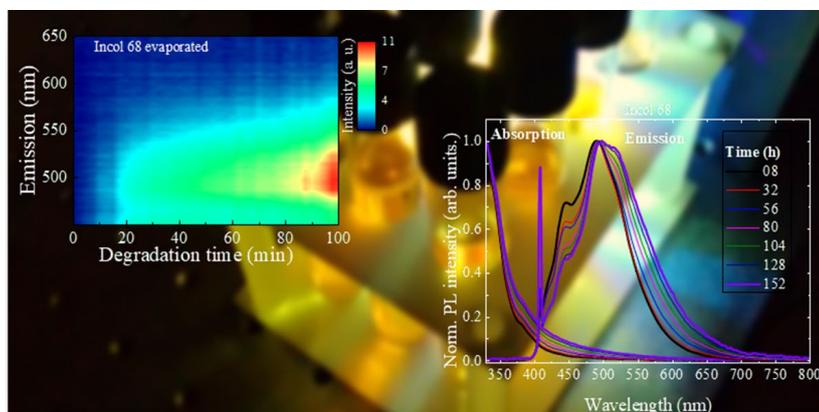
1. Introduction

Petroleum hydrocarbons are widely used around the world as fuels (diesel, gasoline, kerosene) and lubricant oils. Frequently, these refined petroleum-derived products can cause some accidents involving spillages and leakages. In some cases, lubricant oils are responsible for 40% of the petroleum hydrocarbons found in rivers and land [1]. It is known that these oil products have some PAHs (polycyclic aromatic hydrocarbons) [2, 3]. These PAHs are potentially toxic to natural environments, which represents a risk for living organisms as some of them are highly carcinogenic [4, 5].

Lubricant oil leakages are associated with issues in the lubrication system due to inadequate maintenance and mechanical failures [6]. Compressors are widely used as vacuum pumps, power plants, refrigeration systems, and natural gas stations [7, 8].

Lubricant leakages in the compressors are present as lubricant aerosols, which can cause serious damage in the mechanical systems by accumulation over inlet and outlet valves, decreasing the compression rate and increasing the power consumed in the compression process [10]. In this

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[a] Instituto de Física, Universidade Federal de Mato Grosso do Sul (UFMS). Av. Costa e Silva - Pioneiros, zip code 79070-900, Campo Grande, Mato Grosso do Sul, Brazil. [b] Centro de Estudos em Recursos Naturais, Universidade Estadual de Mato Grosso do Sul (UEMS). Rod. Dourados/Itahum km 12 - Universitário, zip code 79804-970, Dourados, Mato Grosso do Sul, Brazil. *Corresponding author. E-mail: **claudiomorassuti@uems.br**

case, it also contaminates the compressed fluid with lubricant oil particles, spreading PAHs in several other systems. Reciprocating (pistons) compressors with low input pressure, typically use mineral-based lubricant oils according to DIN 506 standards, with a viscosity of ISO VG 68 to ISO VG 150 [9].

These PAHs present a high fluorescence intensity when excited with ultraviolet light and their emission can be used for a selective, simple, and direct form of analysis for multi-fluorophore systems [2, 3]. Fluorescence spectroscopy is not only applied to scientific investigations, but also as a tool for the development of lubricant sensors [11, 12], fluorescent thermometers [13, 14], and LED devices [15, 16] with the light emission of these materials. In other words, fluorescence spectroscopy is a powerful tool for the identification of lubricant spillages and leakages. Moreover, when the technique is associated with the use of adsorbent materials it is possible to detect and monitor the spreading of PAHs avoiding damage in the environmental compartments and compression systems.

Recently, we reported the use of fluorescence spectroscopy for the identification of compressor lubricant oils mainly due to the presence of di-aromatic and poly-aromatic compounds in the reciprocating compressors' lubricant [6]. In this study, silica gel was used as a lubricant oil adsorbent material for the adsorption of the oil vapor produced by heating the oil samples at 200 °C, the results demonstrated an increase in lubricant oil emission on the silica gel layer with time. The changes observed mainly in the UV-Vis, NIR, and MIR regions, due to oxidation of samples subjected to high temperatures, showed an increase in NIR absorption bands and changes in MIR absorption bands related to oxygen-containing groups that are associated with the red-shift observed in the UV-VIS absorption and emission spectra.

2. Results and Discussion

In our previous work, we reported the study of lubricant oils having aromatic compounds, in which their emissions were characterized by high fluorescence intensity. Those emissions are useful for the identification of lubricant leakages and spillages [6]. Here, we study the detection of lubricant oil vapors adsorbed over the silica gel layer under 405 nm laser excitation to test simultaneously the adsorption and detection of lubricant emissions by fluorescence technique. Figure 1 shows the online monitoring results of lubricant oil adsorption over a single silica gel layer in each sample (as described in the methodology section). The left column shows the emission spectra for pure lubricant oil samples (bulk), and on the right column are the emission spectra monitored over the macerated silica gel layer, both as a function of degradation time.
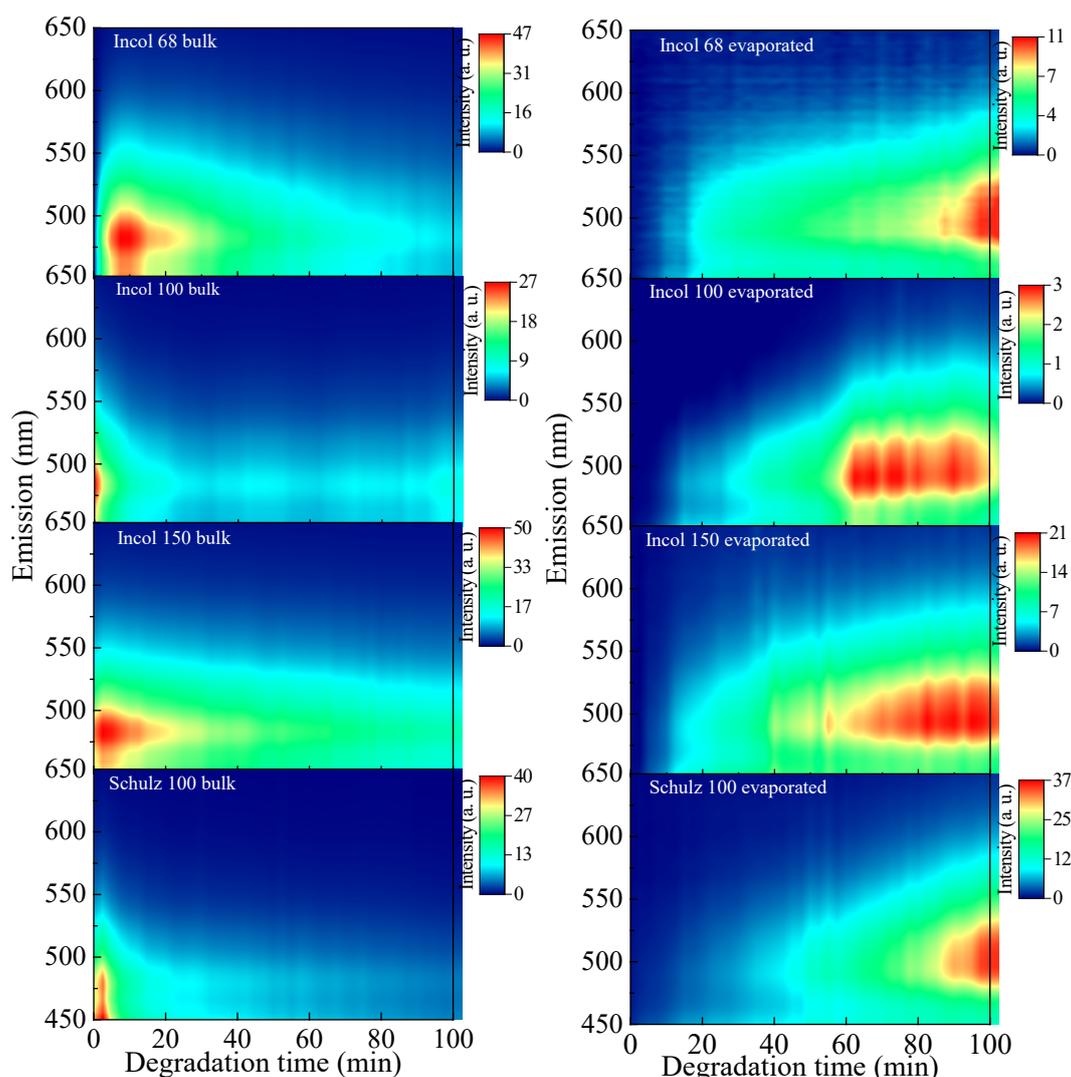

Fig. 1. Evaporation experiment over the silica gel layer. The right column presents the lubricant oil monitored emission, and the left column the adsorbed lubricant emission on the silica gel layer.

Due to the high temperature, there is a degradation of lubricant oil and its fluorescence intensity decreases with degradation time in all samples. It is possible to note that there are differences in intensity decay profiles, characteristic of each lubricant: Incol 100 and Schulz 100 quickly decrease the intensity in the first 60 minutes, while in Incol 68 and Incol 150 the decrease is slower. These results show that the changes in the fluorescence band of samples induced by thermal degradation are different for all samples, making possible the differentiation of each lubricant oil.

In the silica gel, it is possible to observe emission intensity changes due to the low vapor pressure of oil, causing variation in the amount of oil absorbed in the layer as a function of time. A broad emission band around 495 nm is observed over 20 minutes of degradation time, suggesting an increase in the amount of lubricant adsorbed over the silica gel layer.

However, in all spectra of lubricant oils and vapors adsorbed on the silica gel layer, it is observed a shift to the long wavelength region due to the degradation of the samples by the temperature.

When working, lubricant oils may undergo degradation through three most dominant processes: oxidation, nitration, and sulphation [17]. These processes induce changes in the structural composition of samples that also change their optical properties. To investigate these changes, the thermal degradation experiment was carried out where all samples were placed in separate beakers and heated at (130 ± 4) °C and lubricant aliquots were collected as described in the Materials and Methods section. Figure 2 shows the results of the fluorescence under 405 nm laser excitation, and the UV-VIS absorption of all the collected samples.
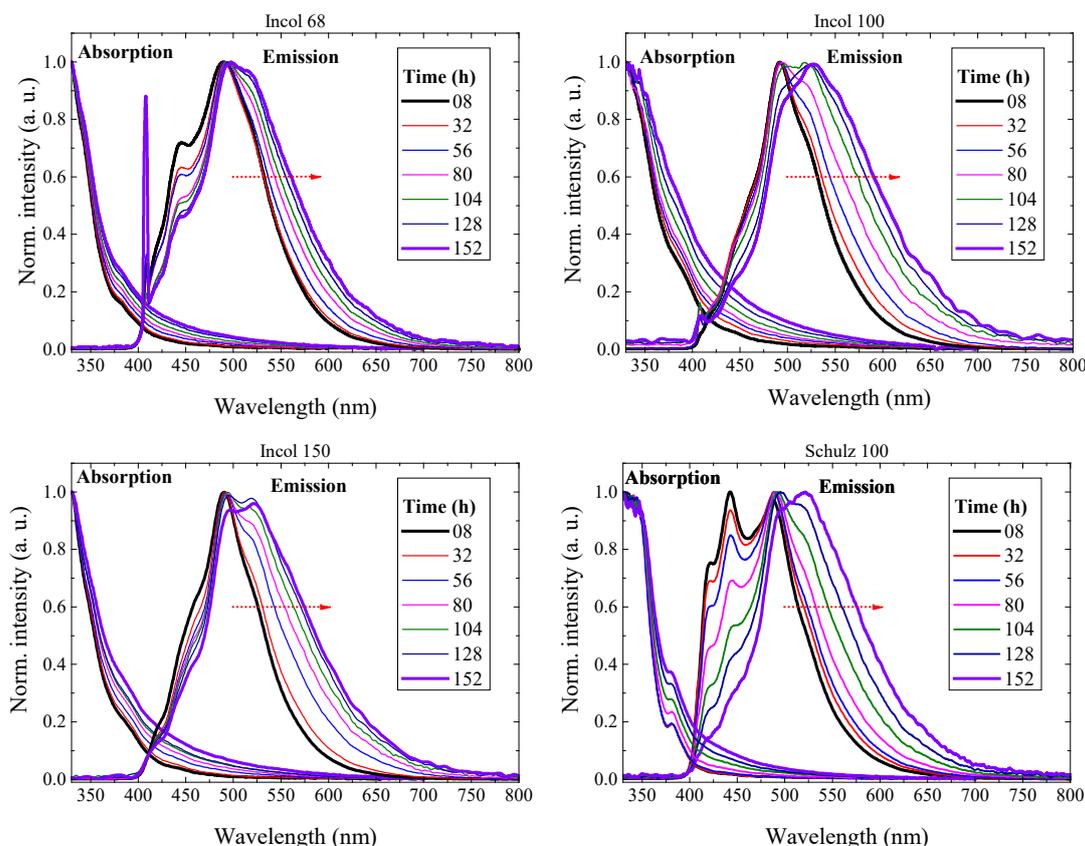

Fig. 2. Fluorescence and UV-Vis absorption of the degraded samples for 152 hours at (132 ± 4) °C. Each sample was collected at intervals of 24 h.

Figure 2 presents an emission band with peak intensity at 490 nm for lubricants of the Incol group, while for the lubricant Schulz 100, fluorescence spectrum shows two peaks around 440 and 490 nm. The absorption spectrum shifts to a longer wavelength region with time, increasing the crossing area between the absorption and emission spectra, this behavior can also increase the reabsorption of the emitted light of the samples. Comparing the wavelength position at the intensity of 0.6 (a. u.) in the fluorescence spectra (dotted red arrow), after 8 and 132 hours of degradation it is observed that Incol 100 sample presents the highest displacement (Δn = 16 nm) to the region of longer wavelengths, followed by Incol 150 (Δn = 8 nm), Schulz 100 (Δn = 6 nm) and Incol 68 (Δn = 4 nm).

This spectral displacement behavior is attributed to the so-called critical temperature (CT) for lubricant oils, which, when heated to a temperature T, where T > CT there is thermal

activation breaking of macromolecules present in the lubricant that may also cause an increase in oil polarity and changes in the dielectric constant of the lubricant oil [18].

Lubricant oil oxidation can cause both rapid changes in unsaturated aromatic molecules with oxygen-containing groups and lead to increased polarity in most cases. Oxidation of aromatic molecules leads to the formation of oxygen bridges, resulting in the relocation of electrons in π orbitals, which leads to an increase of emitting centers in the region of long wavelength, which therefore causes fluorescence shifts towards the region of longer wavelengths [12].

Increasing the number of cycles of aromatic compounds or the length of the double bonds increases the mobility of π electrons, shifting the absorption and emission spectra to longer wavelengths [12]. Oxidation of these lubricants may also cause an increase of C=C bonds, as the base oil

degradation causes the dehydrogenation of paraffinic compounds and form naphthenic compounds, which later can also dehydrogenize and form C=C bonds and aromatic compounds [19].

To investigate all these possible changes in sample composition, (that are correlated to optical changes), MIR infrared absorption measurements are usually a common technique to assess oxidation, nitration, and sulphation [17, 20]. Figure 3 presents MIR measurements of samples with 8, 80, and 156 hours of degradation.
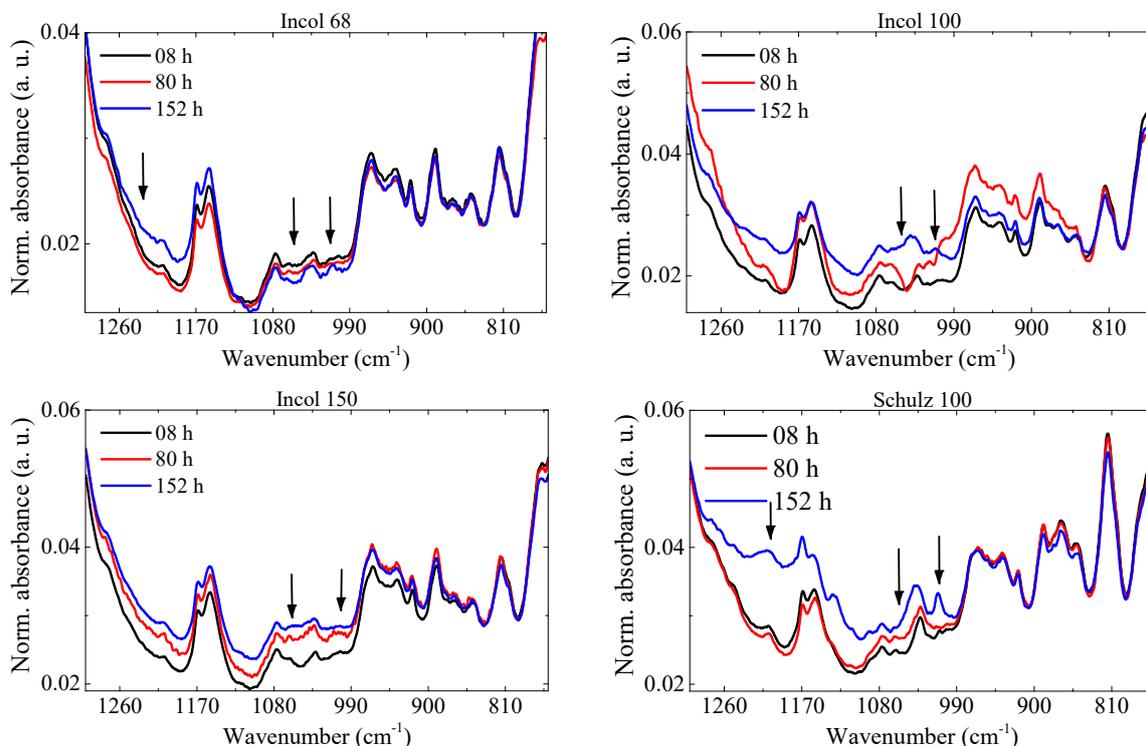

Fig. 3. Infrared spectra of the studied samples with 08, 80, and 132 h of thermal degradation. The arrows indicate the regions of changes due to thermal oxidation.

The spectra of the lubricant samples show slight changes in absorption around 1054 cm^{-1} and it is possible to observe an increase in bandwidth compared with the thermal degradation time for the Incol 100, Incol 150, and Schulz 100. As for the sample Incol 68, the opposite occurs, the bandwidth decreases with oxidation time. Absorptions in the regions 1050 and 1010 cm^{-1} may indicate the presence of Aryl-O-CH$_2$ ether [14]. This fact suggests, as reported by Ref. [12], that the oxidation of aromatic compounds causes a rapid modification of these molecules with oxygen-containing groups, which as a general rule leads to the formation of oxygen bridges (alkyl/aryl ethers). Changes due to nitration (1650–1600 cm^{-1}), NO$_2$ symmetric and asymmetric stretch, according to Ref. [17] and at 1605 cm^{-1} (C=C) were not taken into account due to the interference of water vapor absorption overtones in this region. A slight change at 1180 – 1120 cm^{-1}, observed in the Schulz sample can be attributed to the SO$_2$ or C-SO$_3$ H$_3$O$^+$ symmetric stretch (sulphation), according to Refs. [17, 20].

In order to verify the changes induced by the temperature in this region, we selected a sample of Incol group, and Schulz 100 for the NIR absorption of the samples with 08, 80, and 152 h of degradation at (130 ± 4) °C (Figure 4). Nujol is used here as a paraffinic oil reference due to no antioxidants content in the composition and no aromatic compounds, ideal for fast verification of the oxidation on the paraffinic oil base of the lubricant oils, this sample was degraded at 200 °C for 24h for the analysis.
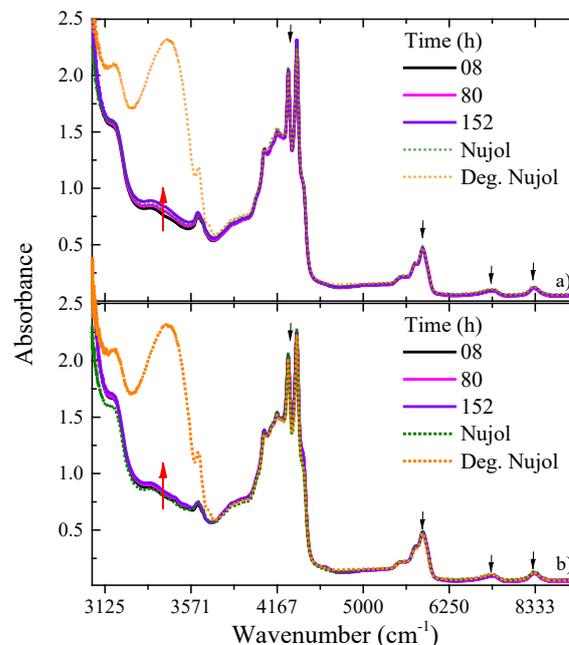

Fig. 4. NIR infrared absorption of a) Incol 68 (08, 80, 152 h), and b) Schulz 100, (08, 80, 152 h) and Nujol.

The bands at 8333, 7184, and 5804 cm^{-1} are, respectively: the first C-H bond overtone, the second C-H bond overtone, and the second and first C-H bond overtones combinations [21]. The bands at 4167 cm^{-1} are also mixing C-H bond overtones [22], confirmed unless non-degraded Nujol samples have only alkenes in the composition, and the bands present the same peak positions in this region.

In the region at 3200 – 3700 cm^{-1}, (In the Nujol the peak band is around 3444 cm^{-1}). An increase is observed in the absorption intensity attributed to the formation of hydroperoxides (OH stretching of hydroperoxides) [23] during the oxidation process by the temperature. These compounds are formed by the oxidation after the formation of alkyl radicals from the breakdown of hydrocarbon bonds by hydrogen abstraction and the dissociation of carbon-carbon bonds. When the alkyl radicals react with oxygen, there is a formation of peroxy radicals, once formed, can randomly abstract hydrogen from another hydrocarbon molecule to form hydroperoxides [24].

The changes observed in the UV-Vis, NIR, and MIR absorption bands suggest that thermal degradation oxides the samples, increasing the oxygen-containing groups in lubricant oil hydrocarbons. Comparing the changes between absorption and fluorescence measurements, it is noticeable that the oxidation induces changes more visible by emission spectra than UV-Vis and infrared absorption bands. Thus useful for the development of sensors that use fluorescence as a detection tool.

3. Material and Methods

To study the fluorescence and spectroscopic characteristics of these types of lubricants, three commercial samples of Incol Lub group (Incol 68, Incol 100, and Incol 150) and one from Icolub Company (Schulz 100) were selected. All these lubricant oils are used in reciprocating compressors, with a viscosity index ISO of VG 68,100,150 according to reports for reciprocating compressors [9].

3.1. Online monitoring of lubricant oil adsorption over silica gel layer

For vapor adsorption, silica gel (Silica Gel Blue, Synth®, 4/8 mm, PA) was used, previously macerated in a ball mill, and then sifted through granulometric sieves (Granutest®, Brazilian industry) of 0.500 and 0.250 mm, respectively. Particles larger than 0.250 mm were macerated again using an agate mortar and sieved to pass through a 0.250 mm sieve. After this stage, the silica gel sieved was dried at 100 °C for 3 hours in a vacuum heater and stored in a glass without atmospheric air contact. Figure 5 illustrates the experimental setup.
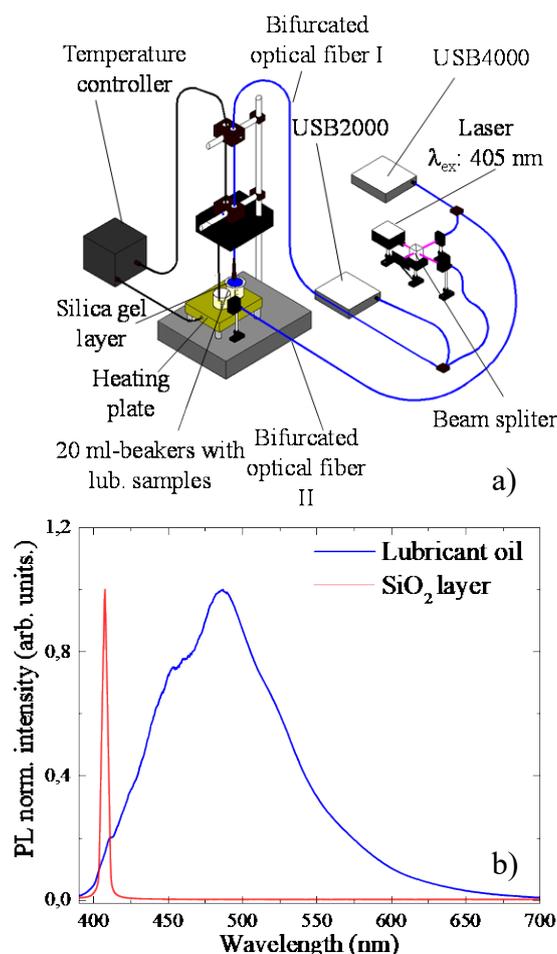

Fig. 5. a) Experimental setup in the lubricant oil emission and b) emission of the lubricant oil adsorbed over the silica gel layer.

For this experiment (Figure 5a and b), (14.010 ± 0.001) g of lubricant was inserted in two 20 ml beakers and inserted on the heating plate. The first beaker was sealed with filter paper and, a circular layer with a thickness of (0.52 ± 0.05) mm, or (0.031 ± 0.002) g of macerated silica gel was added on the surface of the filter. The second beaker was kept in contact with the room air. Samples inside these two beakers were heated at (200 ± 3) °C aiming for evaporation of lubricant oils

in the first beaker to be adsorbed by the silica gel layer and improve degradation in the second one. The temperature was controlled by a PID temperature controller Autonics, model TZN4S.

After the beakers were inserted on the heating plate, a 405 nm laser was turned on, and their light beam was divided by the beam splitter into two beams, each 405 nm beam was conducted by optical fibers (Bifurcated optical fibers I and II) for a simultaneous excitation and collection of the emissions over the silica gel layer and, the lubricant oil samples.

The emissions in both beakers were conducted by optical fibers coupled with two Ocean Optics spectrometers: model USB2000 to collect the fluorescence of lubricant oil adsorbed on the silica gel layer and an Ocean Optics model USB4000, for the lubricant oils of the second beaker. Both data acquisitions were performed with 250 ms of integration time and an average of 5 acquisitions for each registered spectrum. Figure 5b represents the lubricant oil spectrum (Incol 68 - blue line), and the silica gel layer spectrum (red line) at the beginning of the experiment, both excited at 405 nm laser light, at room temperature. In the layer, only the excitation line at 405 nm is observed due to no adsorbed oils on the silica gel.

3.2. Degradation study of lubricant oils by temperature

The degradation study of the lubricants, (98.040 ± 0.001) g of each lubricant was placed in 150 ml-beakers and heated at a temperature around (130 ± 4) °C by a controlled heating system for PID temperature control (Autonics, TZN4S model). Medium aliquots were collected at regular intervals of 24 hours. For each collected sample, (3.000 ± 0.001) g of Lubricant oil were removed from the beakers. The total volume collected from each beaker was calculated not to exceed 55% of the total volume of lubricant subjected to thermal degradation. Samples collected were placed in properly capped amber glass vials and stored at room temperature without exposure to sunlight or artificial light, for further UV-VIS, fluorescence, and infrared absorption measurements.

3.3. UV-VIS and NIR/MIR absorption measurements

The UV-Vis absorption spectra were measured by Ocean Optics spectrometer HR4000 coupled with a deuterium tungsten halogen source, and an optical fiber coupled with an Ocean Optics transmission probe (TP300 UV-VIS). To avoid spectral saturation, a solution of (3.071± 0.001) g of hexane and (0.127± 0.001) g of lubricant oil sample were used for each aliquot. The absorption spectra were collected using an integration time of 500 ms, and 5 measures on average. The NIR absorption measurements were performed by the spectrophotometer Perkin Elmer Lambda 1050 from 1000 – 3000 nm range with 1 nm resolution. The samples were inserted in quartz cuvettes with a 1 mm path length.

3.4. MIR infrared absorption measurements

The vibrational modes of the samples were determined by infrared absorption in the spectral range 4000-650 cm^{-1}, using a Fourier transform infrared spectrophotometer (Nexus 870 - Nicolet) with an attenuated total reflection (ATR) accessory. Samples were deposited using a micropipette, 3 drops of 10 μL each of lubricating oil, on the ZnSe crystal plate of ATR detector. Each spectrum is a result of an average of 64 consecutive spectra of the same sample with a spectral resolution of 0.5 cm^{-1}.

4. Conclusions

In summary, we have characterized different samples of lubricant oil for reciprocating compressors by FTIR, UV-VIS, and NIR absorption, as well as, by fluorescence spectroscopy,

under normal and degradation conditions. In the degradation experiment, NIR, FTIR, and UV-Vis absorption were important to verify the changes in the absorption bands due to the oxidation of the samples under 130 °C. Changes were observed around 1054 cm^{-1} and 1250-1100 cm^{-1}, an indication of Aryl-O-CH_2 ether formation, and in the NIR/MID-infrared measurements, were also observed an increase of absorption on the hydroperoxide band, which confirms the induced oxidation by the thermal degradation. These changes are also observed by the UV-Vis absorption shifts towards the region of longer wavelengths due to the increased delocalization of electrons in π orbitals, causing an increase in the number of emitting centers in the longer wavelength region that also shifts the fluorescence bands to the same region. Fluorescence spectroscopy showed promising results for the identification of lubricant oil. By subjecting the samples to these two conditions (pure and degraded samples), it is possible to differentiate the characteristics of each lubricant sample; the changes induced by thermal degradation as the intensities decay as a function of time and the spectral shift to the region of longer wavelengths. Overall, for the lubricants used, the fluorescence and the changes observed in it are mainly due to the aromatic hydrocarbons. Due to high fluorescence emission, online monitoring of lubricants with portable spectrometers, low-cost lasers, and silica gel as adsorbent material showed a promising method for lubricant detection. The changes induced by thermal degradation in the optical properties are more easily observed by the fluorescence spectrum than by absorption methods. In other words, this setup (fluorescence and silica gel) is useful for the development of low-cost sensors for applications in lubricant oil systems for monitoring the oil leakages, avoiding high PAH's spreading in other systems, and preventing serious damage and power losses in reciprocating compressors.

Author Contributions

Claudio Yamamoto Morassuti: Conceptualization, Formal Analysis, and Investigation. Sandro Marcio Lima: Conceptualization, Formal Analysis, and Investigation. Luis Humberto da Cunha Andrade: Conceptualization, Formal Analysis, and Investigation.

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