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# DESIGN AND INSTRUMENTATION OF A LOW-COST RAMAN SPECTROMETER FOR IN-SITU TRIBOLOGICAL ANALYSIS

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### **Abstract.**

*When used in conjunction with microscopic characterizations, Raman spectroscopy gives good information about wear in lubrication of tribological systems. This technique of vibrational spectroscopy does not require initial sample preparation. There are even cases where using the method has become viable in evaluating sliding surfaces in real-time. In lubricated tribological contacts, film formation occurs through mechanisms that need to be identified, reinforcing the use of this equipment for in-situ evaluations in sliding systems. This work proposes the design and instrumentation of a low-cost Raman spectrometer to assess tribological systems in real-time. In this project, the efficient assembly of all the components necessary for tribology applications was considered. The prototype was all modeled in CAD software, using the primary parts indicated in the literature and the fixing and alignment needed accessories for the alignment of the system. Due to the smaller number of components, the mounting configuration used was 180 ° (backscatter), the laser used was the DPSS type with a wavelength of 532 nm, with a reflectance probe and an objective microscope lens. The spectrometer was assembled in a pin-on-disk tribometer, and lubricated tests were carried out with epoxidized soybean oil. AISI 1045 steel disc and AISI 52100 steel ball were used as test specimens, the lubricant used as epoxidized soybean oil, and the load tested was 100 N. The results show that the project is feasible and can be used. Spectra, according to the literature, were obtained for the intended application. The spectrometer acquired the same characteristic spectrum as epoxidized soybean oil during the test, with decreasing intensity over time. This fact was expected due to the dynamics of the test and the non-renewal of the lubricant in the wear track.*

**Keywords:** Tribology, Raman Spectroscopy, Boundary lubrication

## 1. INTRODUCTION

The constant growth and modernization in industrial development have caused the demand for energy to increase significantly, and it is estimated that from 2010 to 2030, energy consumption will increase by about 33.5% (Saidur et al. 2011). In this context, considering the current global energy matrix, more petroleum-based products, including fuels and lubricants, are required to supply this demand. However, petroleum-based products are made from resources that cause significant environmental impact, due to the toxicity of the elements that make them up, around 30 to 40 million tons of lubricants are produced annually, and 55% of this production is discarded in the environment (Mang and Dressel, 2007).

As an alternative, vegetable-based oils have become a very viable option for replacing mineral and synthetic bases and the use of low toxicity additives. As an example of this, Souza et al. (2014) analyzed the behavior of epoxidized soybean oil as a base lubricant in steel/steel contact, which showed a positive result in reducing wear on surfaces without surface treatment.

The tribological study of lubricated mechanical systems is carried out by evaluating friction and wear through surface characterization techniques, where in general, are performed after the process. However, the tribological phenomena that occur during the process happen by mechanisms that also need to be explained. Given this need, some authors used Raman spectroscopy as an alternative to explain these phenomena. In some cases, it was possible to identify the tribological mechanisms acting in each system.

Several recent works, such as Khaemba et al. (2015) and Okubo and Sasaki (2017), used Raman spectroscopy in conjunction with tribological analyses, mainly in the characterization of wear mechanisms in steel/steel contact. These studies showed positive results in the use of Raman spectroscopy for the evaluation of friction and wear.

Conventional bench spectrometers have several limitations, not only concerning assembly but also to high costs. In this sense, this study aims to develop a low-cost Raman spectrometer for use in tribological tests lubricated with vegetable oil. In this study, a portable spectrometer Raman was built, and tribological tests were carried out in a pin-on-disk tribometer, which uses a load cell to acquire the coefficient of friction; Raman analyzes were carried out on the wear track during the test with epoxidized soybean oil in the boundary lubrication regime, the worn region was also analyzed by Raman spectroscopy (*in situ*) and profilometry.

## 2. MATERIALS AND METHODS

This work was carried out in two stages; initially, the modeling, assembly, and instrumentation of the pin-on-disk tribometer was performed with the Raman spectrometer, initial tests, and all adjustments for the entire operation. The second stage consisted of a tribological test. The steps of the methodology are described in the diagram in Figure 1

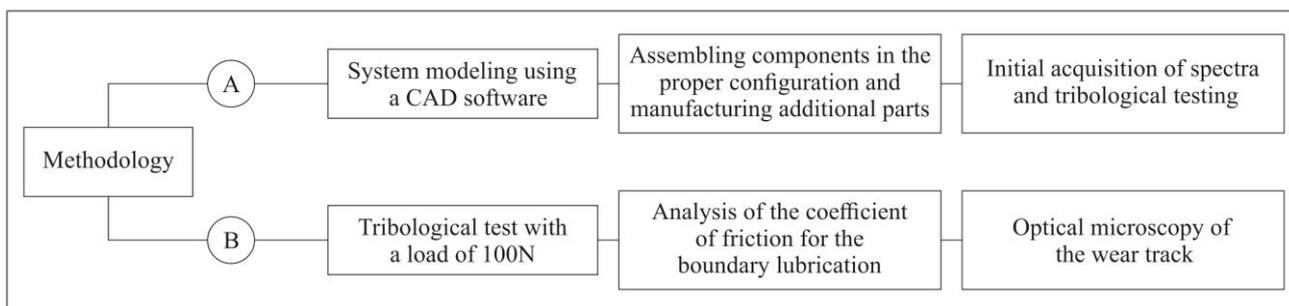


Figure 1 – Flowchart of methodology steps.

### 2.1 Assembly and instrumentation of the Raman spectrometer.

The spectrometer was drawn in Solid Works 2016 © software. The assembly followed the pattern described in the schematic diagram as shown in figure 2, a diagram that was elaborated according to the model presented in work by Mohr et al. (2010). The selection of components was carried out in order to assemble a portable spectrometer with *in situ* probes, and the parts were acquired through ThorLabs ©, RGB photonics ©, Laser Line ©, and Nikon ©. The assembly was carried out considering the schematic diagram in Figure 2, following the manufacturer's recommendations to obtain the best possible performance. After assembly, the spectrum of pure epoxidized soybean oil was acquired and compared with the literature.

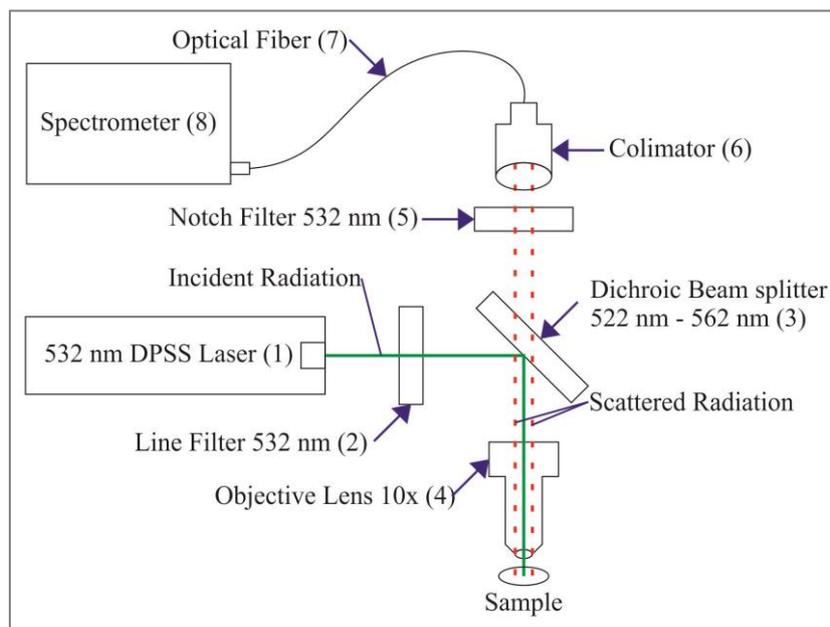


Figure 2 – Assembly diagram of a Raman spectrometer for in situ evaluation, based on the model by Mohr *et al.* (2010).

## 2.2 Tribological tests

In this study, the tribological test used was the pin-on-disk test; the working principle of a schematic diagram was previously described in the literature. The model TE-165 LE - 131/2014 tribometer was used with non-conformal contact (ball-disk) to simulate the slippage of steel bodies within the boundary lubrication regime. An amount of 5ml of lubricant was added in the region of contact between the bodies. Figure 3 is the diagram that describes the main components of the tribometer and the positioning of the objective spectrometer lens.

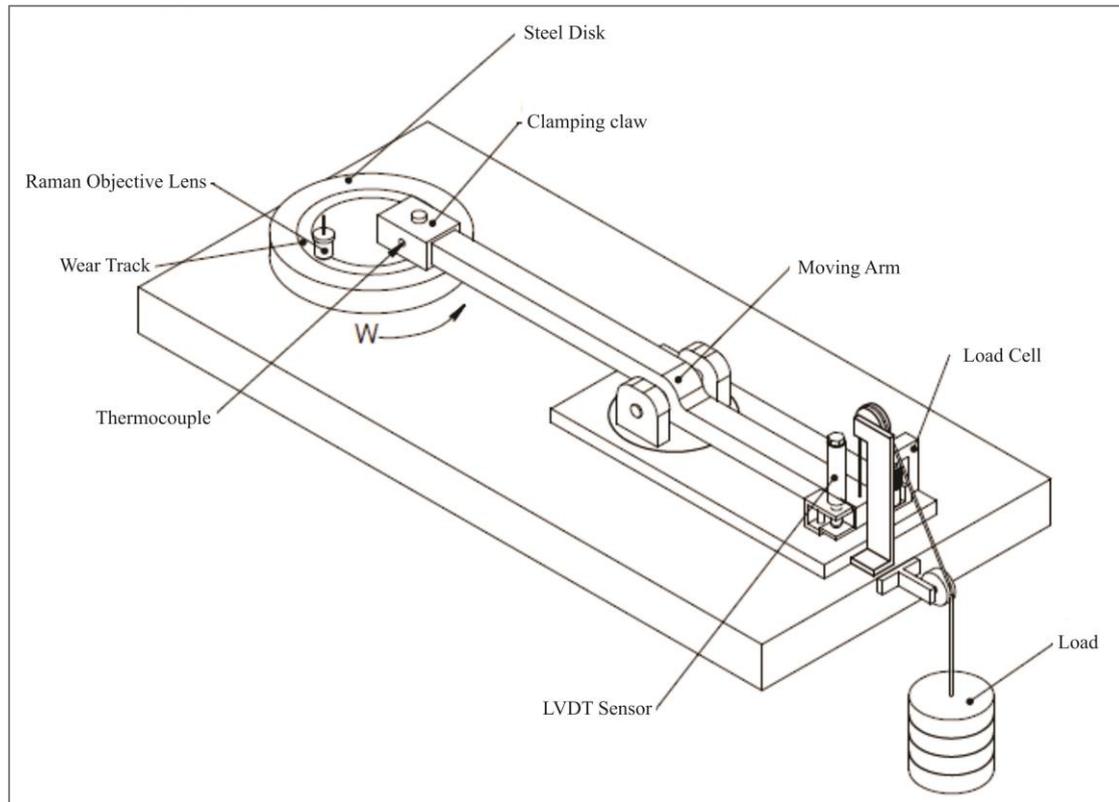


Figure 3 – Schematic diagram of pin-on-disk tribometer with Raman spectroscopy.

The parameters used in the test are described in Table 1; the parameters were adopted to reach boundary lubrication, which is characterized by having low sliding speeds and high load. An AISI 1045 steel disc 80 mm in diameter and an AISI 52100 steel ball 8 mm in diameter are used as body and counter body. A Poisson modulus of 0.3 was assumed for steel.

Table 1 - Parameters used in carrying out pin-on-disk test.

<b>Load</b>	100 N
<b>Contact Pressure</b>	1,6 GPa
<b>Sliding Speed</b>	0,314 m/s (100 RPM)
<b>Sliding distance</b>	1130 m
<b>Wear Track Radius</b>	30 mm
<b>Time</b>	60 min

The Hertz contact pressure was calculated according to Equations 1, 2, and 3, proposed by Hutchings and Shipway (2017).

The Elasticity modulus (E) in the contact depends on the modulus of elasticity's modulus ( $E_1$  and  $E_2$ ) and the Poisson coefficients ( $\nu_1$  and  $\nu_2$ ), calculated by Equation 1.

$$\frac{1}{E} = \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2}, \quad (1)$$

The load applied ( $\omega$ ) to a sphere of radius ( $r$ ) under a plane produces a spherical-shaped contact area, where the radius of this area ( $a$ ) is obtained by Equation 2.

$$\alpha = \left(\frac{3\omega r}{4E}\right)^{1/3}, \quad (2)$$

The contact pressure (PC) at the nonconforming contact is then defined by the applied load ( $\omega$ ) divided by the contact area as per Equation 3.

$$PC \approx \frac{\omega}{\pi a^2}, \quad (3)$$

Epoxidized soybean oil, supplied by Inbra Indústrias Quimica Ltda (São Paulo, Brazil), was used as a base lubricant, the physical-chemical properties of epoxidized soybean oil are described in Table 2. For comparative purposes, it was also performed a dry test.

Table 2 - Physicochemical properties of epoxidized soybean oil.

Property	Especificacion
Density	0,990 g/ml
Acidity level	0.70 mg KOH/g max.
Iodine index	3.50g I/100g MÁX.
Epoxy index	6.50g O/100 g min.
Viscosity a 25°C	380 cP
Flash point	280° C
Volatiles	0.20% max.

### 2.3 Analysis of worn surfaces

The wear track depth was measured according to ISO 4288:1996 (Rules and procedures for the assessment of surface texture) in a Taylor Hobson Precision model Surtronic 25 profilometer, the cut-off used was 8 mm. Measurements were taken in the region of the wear track, between the radius of 28 mm and 32 mm, the area analyzed. The probe positioning can be seen in Figure 4.

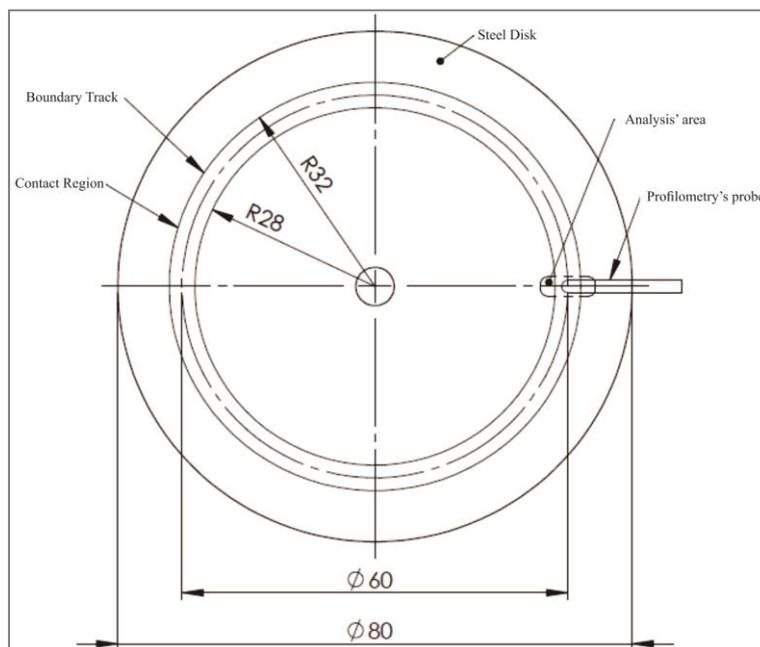


Figure 4 - Profilometry analysis methodology.

The worn material volume was calculated using the equation provided by ASTM G99:17 (Standard test method for wear testing with a Pin-on-disk apparatus) from profilometry results. The volume calculation equation is described according to Equation 4, where (R) the radius of the track, (r) the radius of the sphere, and (d) the width of the worn track.

$$\text{Disk volume loss} = 2\pi R[(r^2 \sin^{-1}(d/2r) - (d/4)(4r^2 - d^2)^{1/3}], \quad (4)$$

### 3. RESULTS

#### 3.1 Assembly and equipment setup

The assembly of the spectrometer was carried out according to the components described in Table 3. From Figure 5 can be seen the initial modeling performed in the Solid Works 2016 © software.

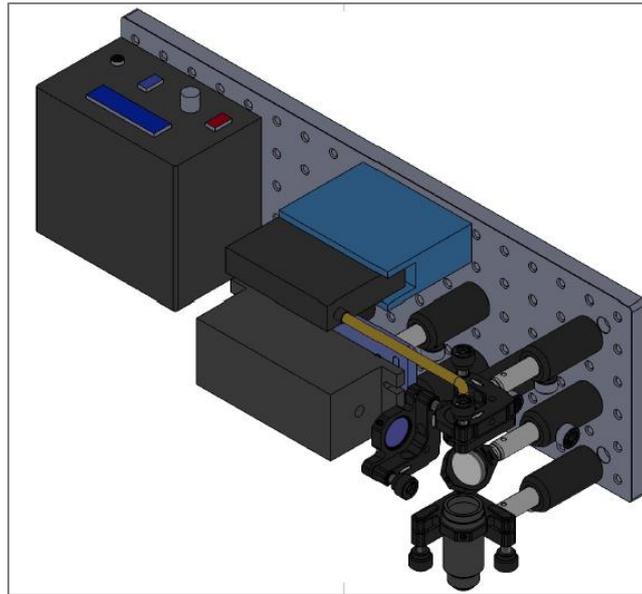


Figure 5 - Raman spectrometer's assembly in *SolidWorks 2016*© software.

In the initial project, support parts for the laser and the spectrometer were added, manufactured in ABS plastic by 3D printing. Figure 6 shows the top view in the section of the assembled equipment and the main components of the system listed in Table 3.

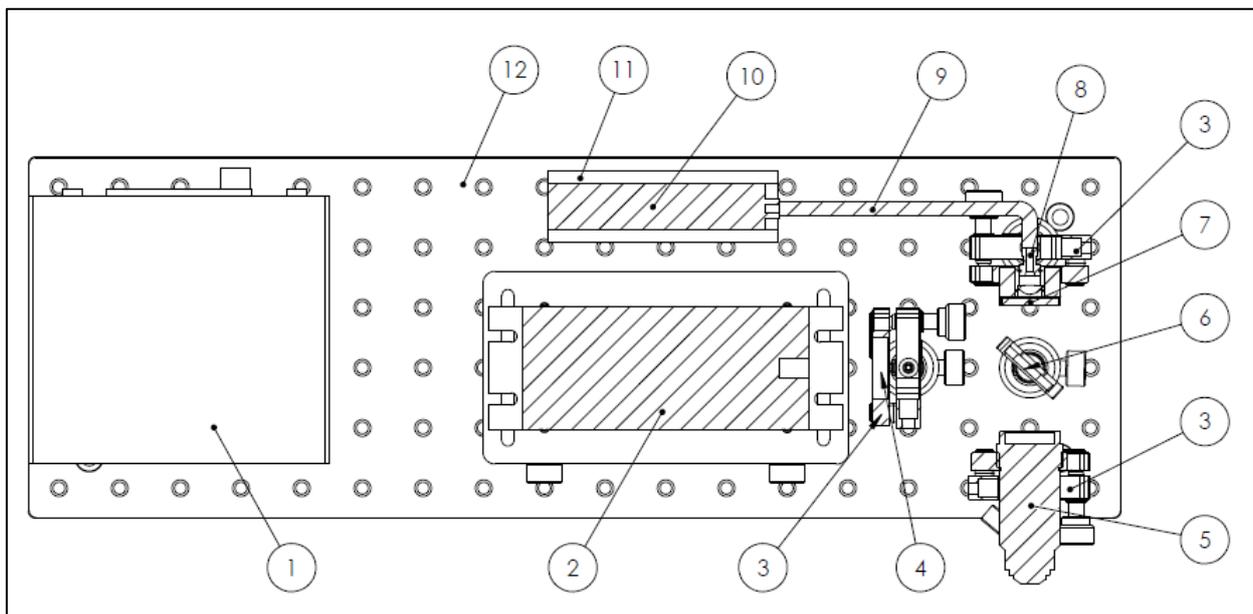


Figure 6 - Top sectional view in *SolidWorks 2016*© software with a description of the main components.

Table 3 - List of main components described in the schematic diagram in Figure 6

Reference	Q	Supplier	Description	Part Number
IZI 532 nm	1	Laser Line	DPSS Laaser, 532nm / 100 mw	1
Power source	1	Laser Line	Power supply 220v	2
FL 532-1	1	ThorLabs	Line Filter 532 nm	4
DMLP-550	1	ThorLabs	Dichroic Beam Splitter 522 - 564 nm	6
NF 533-17	1	ThorLabs	Notch Filter 532 nm	7
F240 SMA	1	ThorLabs	SMA Light Colimator	8
M25 L01	1	ThorLabs	Optic fiber cable SMA / SMA	9
PH2 - P5	5	ThorLabs	Assembly Bracket	3
MB 1545 / M	1	ThorLabs	Aluminium base (450 mm x 150 mm)	12
Q WAVE - Mini (VIS)	1	RGB photonics	Mini Spectrometer (370 nm -750 nm)	10
Objective Lens	1	Nikon	Objective Lens 10x Ampliation	5

### 3.2 Initial spectra acquisition

The initial spectrum acquisition carried out in epoxidized soybean oil can be seen in Figure 7. A very intense photoluminescence band stands out in this spectrum, which starts around 900  $\text{cm}^{-1}$  and decreases at longer wavelengths.

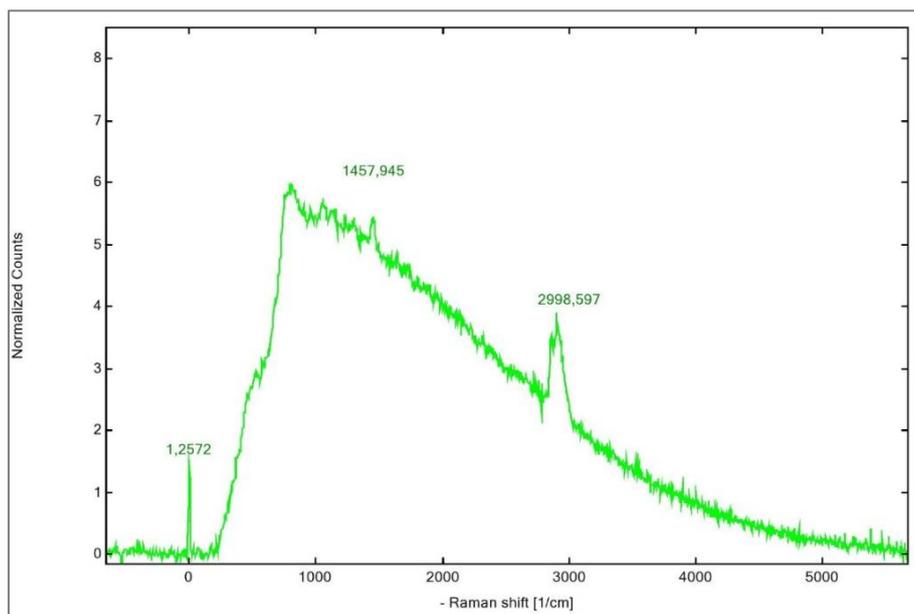


Figure 7 - Raman spectrum of epoxidized soybean oil

This photoluminescent effect is due to the energy package (photon) provided by the laser and the electronic transition of the excited electrons, resulting in the sample's light emission. This same effect was also observed in work by Khaemba *et al.* (2015). In more expensive commercial spectrometers, the photoluminescent effect is reduced using different types of lasers.

Despite the high photoluminescence, peaks at 450  $\text{cm}^{-1}$  and 1950 – 3250  $\text{cm}^{-1}$  stand out in the spectrum related to saturated hydrocarbons. According to Cooney *et al.* (1982), the Raman spectrum of saturated hydrocarbons is highlighted by the intense modes of the C – H elongation (2800 to 2900  $\text{cm}^{-1}$ ), as well as the deformation modes  $\text{CH}_2$  and  $\text{CH}_3$  (1420  $\text{cm}^{-1}$ ), which suggests that this spectrum belongs to epoxidized soybean oil.

### 3.3 Tribological tests

#### 3.3.1 *In situ* Raman Spectroscopy

Figure 8 shows the spectra obtained for the oil with a charge of 100N, the region analyzed was from 0 to 5000  $\text{cm}^{-1}$ . These spectra were obtained during the test (in situ), and without pauses, with acquisition every 10 minutes

Also, from Figure 8, it can be seen that the intensity of the spectra decreases with test time; however, it is still possible to visualize low-intensity peaks in the regions of identification of the epoxidized soybean oil (1450  $\text{cm}^{-1}$  and 2900  $\text{cm}^{-1}$ ). Test dynamics can explain this behavior; with disk rotation, the oil is spilled for disk border, accumulating on the surface outside the track.

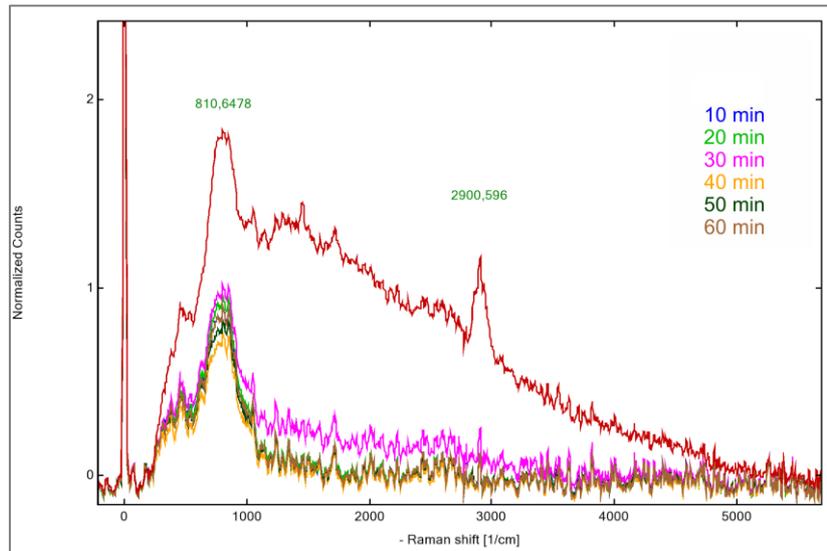


Figure 8 - In situ Raman spectra for 1-hour test.

An unsaturated chain of triglycerides forms vegetable soybean oil. According to Gupta and Harsha (2018), the oil epoxidation reaction inserts an epoxy ring in its molecular chain (eliminating the double bond between carbons and forming single bonds with an oxygen molecule). This characteristic influences the oil's absorption during film formation, increasing kinematic viscosity and improving the oil viscosity index. All these characteristics influence wear reduction and improve the oil-metal interaction.

#### 3.3.2 Wear and friction

In Figure 9, it is observed that the formation of bows occurred at the edges of the contact. This behavior occurs due to the plastic deformation suffered by the base metal during the accommodation of the material surfaces. In the region of the bottom of the trails, the presence of irregular peaks is verified, which indicates that the application of load in these places forms peaks and roughness continuously at each cycle, favoring abrasive wear, the worn volume was  $5,82 \times 10^{-6} \text{ mm}^3$ .

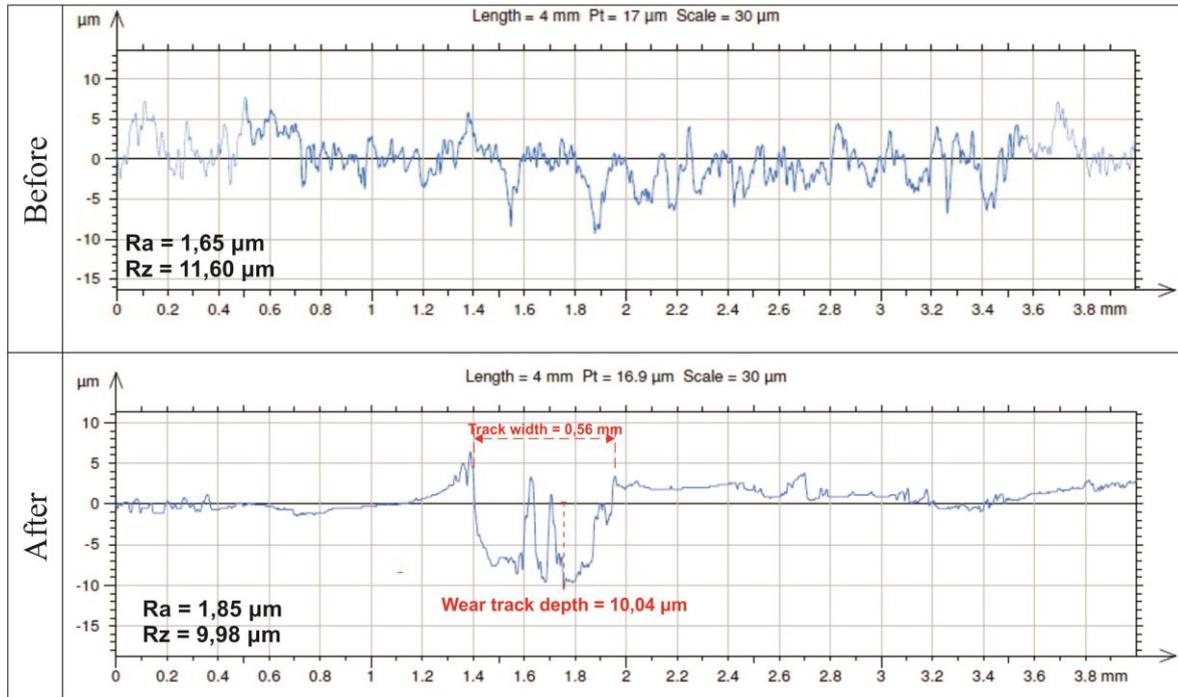


Figure 9 – Roughness profile performed before and after the test.

Figure 10 displays the coefficient of friction (COF) during the tribological test, even a small volume of lubricant (5 ml). The COF kept in low values and stable, and few changes occurred due to lubrication fault because of high loads and boundary lubrication regime.

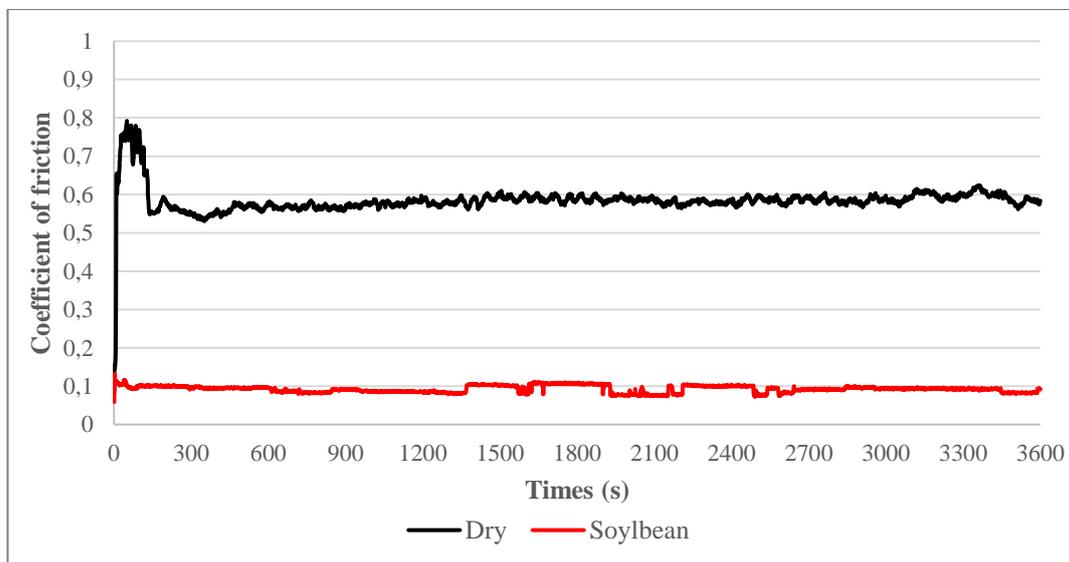


Figure 10 - Coefficient of friction for dry and lubricated testing.

The friction behavior (Fig. 10) reveals small jumps in the friction coefficient during the tests (sigmoidal curves); this behavior occurs due to the "stick-slip" phenomenon, with the curve's ascending the stick and the descending the slip, according to Hutchings and Shipway (2017). This behavior can occur due to the adhesion of a fixed body that rubs against another body in motion, causing a self-excited vibration based on the difference between the dynamic and static friction coefficients. This behavior was also observed by Souza (2015) in the study of composite materials tested in a pin-on-disk tribometer.

#### 4. CONCLUSIONS

The prototype spectrometer developed in this study showed good operation in conjunction with the pin-on-disc tribometer. Despite the photoluminescent effect from the samples, it was possible to identify the characteristic spectra of the epoxidized soybean oil before and after the tests. The epoxidized soybean oil showed excellent tribological performance for the adopted condition, considering the boundary regime condition and the limited amount of 5 ml used in the lubrication of the contacts.

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