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Communication

Detection of Elemental Composition of Lubricating Grease Using Laser Induced Breakdown Spectroscopy

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Abstract: The elemental composition of lubricating soft grease used in rail engines are studied using laser induced breakdown spectroscopy (LIBS) technique. LIBS spectra of fresh, partially used and fully used grease samples are recorded using time-gated ICCD spectrometer for verification of compositional degradation of the used grease. LIBS spectra of grease samples are analyzed by comparing with emission spectra of elements published by NIST standard database. Many spectral lines of impurity elements like Fe, Cu, Ba, Mg, Mn, Ni, S, Zn, Si, Pb, Ti, Ca and Al present in the grease in ppm or ppb level in trace level concentrations are observed in excess in the used grease mainly due to wear and tear. On the other hand in fresh grease, spectral lines of Ca, Al and Na are observed predominantly.

Keywords: laser induced breakdown spectroscopy; ICCD detector; lubricating grease

1. Introduction

Any machinery with rolling elements or ball bearings requires lubrication to prevent the wear and tear of the machinery parts. In general, engine oils and grease are used as lubricants in all heavy machinery. Grease is a semisolid material which is highly useful for the heavily loaded components of the machinery where pressures are extremely high on the point of contact of metallic surfaces. The viscosity behavior of grease follows the Newtonian fluid equation for shear stress and shear strain at low pressure contacts between metal surfaces. Barus (1893) also presented the pressures and temperature dependent viscosity equation but the properties of lubricating grease shows its non-Newtonian behavior [1,2]. Grease was first tested as a lubricant in 1913 by Westcott, by performing some characteristic tests [3]. The performance of grease lubrication is primarily studied under two conditions as fully flooded and starvation [4]. The performance of grease as a lubricant for rolling bearings is widely studied by Wada and Hayashi [5–8].

The gel-type structure of grease is composed of base fluids, thickener and additives. Minerals or vegetable oils are used as the base fluid between 65%–80%. Fatty acids such as stearic, oleic, linoleic and linolenic are generally used in the grease compositions [9]. The thickener which is stearates of metal soaps like lithium, calcium, sodium, aluminum and titanium forms the fiber structures which immobilize the base oil. It is generally used in proportion of 15%–25% in the grease. Additives like Mo, S and Cu in 5% are used in the grease as anti-oxidant, anti-rust, anti-wear and corrosive agents [10]. Detailed studies of the interactions of the additives, friction and adsorption were presented by Jahanmir and Beltzer (1986) but the tribological behavior of the grease is not very well studied [11]. The fiber structure in grease thus formed gives the estimation of its wear and tear [12]. In fact, the degradation of grease occurs mainly due to mechanical and thermal stresses which results in physical and chemical changes of grease [13]. The oxidation of thickener and base oil and loss of low molecular weight also contributes to the degradation of grease [14,15].

Lubricating grease is generally evaluated by conventional laboratory tests like the gear wear test, the 4-ball wear test, Ash, by its acidity, or by using spectrographic techniques, in order to determine the degradation of the material. More sophisticated tests like SEM and TEM tests can also provide information on the structural stability to large extent [16]. In the present work, laser induced breakdown spectroscopy (LIBS), a laser based analytical technique is employed to verify the compositional degradation of grease by elemental analysis of soft fresh, partially used and fully used grease samples. LIBS technique is one of the very sensitive laser spectroscopic techniques for the elemental analysis of solids and liquids *in situ* without touching the samples of investigation. With a single laser pulse of a few nanoseconds duration impinged on the material of investigation, LIBS set-up can acquire all the information of elemental composition of the material as emission spectral lines of the constituent elements. This technique can be particularly useful for on-line evaluation of elemental composition of lubricating grease that is used in Rail and other locomotive engines to account for degradation of grease and likely failure of any machinery parts for want of lubrication.

In the present study on grease, the LIBS technique is applied for the elemental analysis of the semisolid grease samples which are used in the wheel bearings of the rail train. Based on the comparison between three forms of grease, the detection of toxicants can be studied in three different samples.

2. Theoretical Section

For the plasma temperature, the total spectrally integrated line intensity corresponding to the transition between the upper level *i* and the lower level *j* is given by [17]:

$$I_{ij} = n_i^s A_{ij} = \frac{A_{ij} g_i}{U^s(T)} n^s e^{\frac{-E_i}{kT}} \tag{1}$$

On considering the two lines λ_{ij} and λ_{mn} of the same sample, the characterized by two different values of energy levels ($E_i \neq E_m$), the relative intensity can be used to calculate the plasma temperature given as:

$$T = \frac{E_i - E_m}{k ln(\frac{I_{mn} g_i A_{ji}}{I_{ij} g_m A_{mn}})} \tag{2}$$

Under local thermodynamics equilibrium and optically thin conditions, Saha-Boltzmann expression for the line emissivities, ε^z (Wm^{-3}) for an element and different ionic species is given by [18]:

$$\ln\left(\frac{\varepsilon^z \lambda}{A g_j}\right)^* = -\frac{1}{kT} E_j^{z^*} + \ln(\frac{hc\mathrm{N}^{\circ}}{Q^{\circ}(T)}) \tag{3}$$

Equation (1) includes emissivities of lines from different ionic species of the same element. Ionization ratio given by Saha is N^1/N^0 is different for each element due to the partition function and ionization energy. Further, Saha-Boltzman equation is written for the line emissivities from different elements as

$$\ln\left(\frac{\varepsilon_\alpha^z \lambda}{A g_j}\right)^* = -\frac{1}{kT} E_{j,\alpha^*}^z + \ln(hc\mathrm{N}) \tag{4}$$

where,

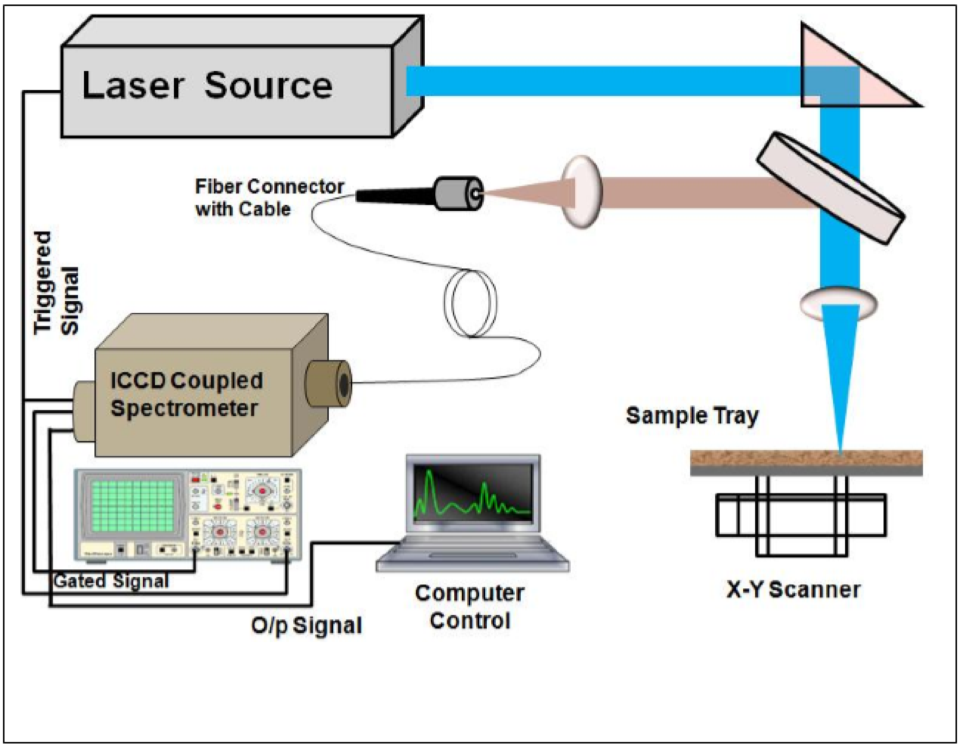
$$\ln\left(\frac{\varepsilon_\alpha^z \lambda}{A g_j}\right)^* = \ln\left(\frac{\varepsilon_\alpha^z \lambda}{A g_j}\right)^* - B^z(T, \mathrm{N_e}) - D_\alpha(T, N_e) \tag{5}$$

$$D_\alpha(T, \mathrm{N_e}) = \ln\left(\frac{C_\alpha}{100} \frac{1}{Q_\alpha^o(T)(1 + S_\alpha^{10})}\right) \tag{6}$$

3. Experimental Details

Fresh, partially used and fully used soft grease samples are collected from a railway diesel shed belonging to the Indian Railway on a glass Petra dish and a grease sample on glass plates are prepared for LIBS study. The grease sample is taken by a clean glass rod and pasted on a glass slide with uniform thickness of 6 mm. The sample plate is firmly attached on an X-Y scanner platform as shown in Figure 1. Three separate sample plates are prepared with fresh, partially used and used grease samples.

Figure 1. Schematic of laser induced breakdown spectroscopy for grease analysis.

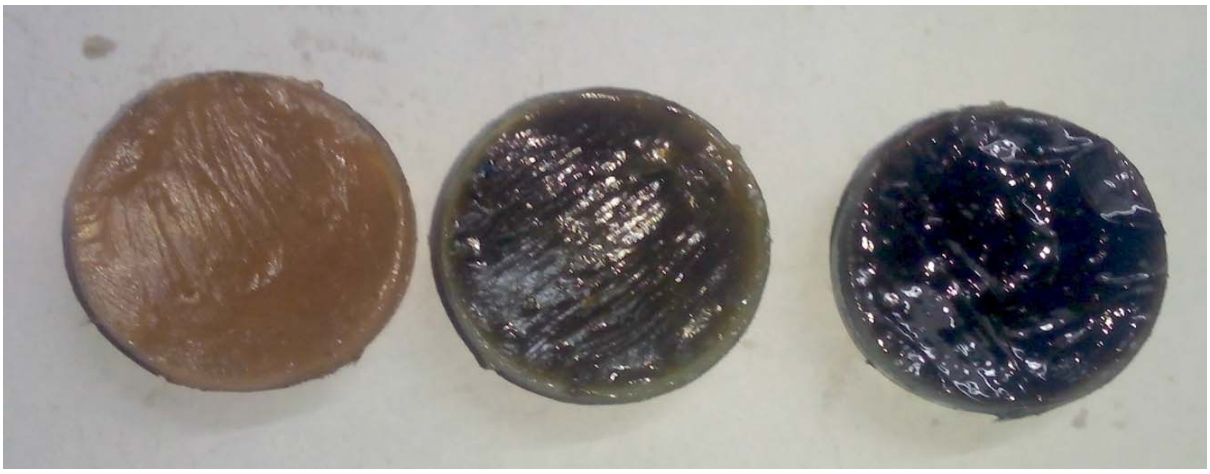


The experimental arrangement of the LIBS schematic is shown as in Figure 1. An Nd:YAG laser from Quantel, operating at 1064 nm having pulse width of 6 ns is used in the experiment. The laser is operated with fixed pulse energy of 50 mJ at repetition rate of 1 Hz. The intense pulses of laser were focused on the grease sample using a 2 inch diameter fused silica plano convex lens of focal length 30 cm making a focal spot size of about 72 µm and power density of 2×10^{11} W/cm^2. Laser induced plasma was generated on the grease sample and the emission signal was collected using a broadband (200–850 nm) dichroic mirror in 45° angle in the optical axis of the excitation laser. The collected emission signal was focused by a 1 inch diameter fused silica plano convex lens of focal length 10 mm into an optical fiber of core diameter 400 µm which was coupled to the spectrograph (ANDOR, Model: SR303i and ICCD detector from Andor (Model No. iStar720-25-U). The ICCD was triggered by the Q-switch output of the laser pulse which precedes the laser pulse but synchronized using laser control. The LIBS signals were acquired by the ICCD spectrometer by employing a delay of 1 µs and gate width of 20 µs so that the continuum emission from the plasma is filtered. The LIBS spectra of grease sample are captured with single shot excitation by operating the laser at 1 Hz repetition rate. A single shot also enables us to move the position of the sample with focus spot during the laser firing. The final recording of the LIBS spectra was taken by averaging 20 single pulse spectra to increase the signal to noise ratio of the LIBS spectra. The grating having 1800 lines/mm was used to obtain the LIBS spectrum between 200–700 nm. The recorded data files of the LIBS spectra are stored in computer for offline analysis. LIBS spectra of both fresh and used grease samples were analyzed offline using Plasus-Specline software by comparing with the NIST database provided by the software. The judicious identification of the emission spectral lines of elemental and molecular species of grease sample was carried out by NIST and other published data on the elemental analysis.

4. Results and Discussions

Grease is employed in ball bearings where the shaft connecting the two wheels rotates. The lubrication performance of grease depends on its physical properties that are based on its structure which is related to the holding capacity of base oil. Shear degradation of soap thickener releases its base oil which damages the quality of grease. As the machinery parts rotate, it damages the quality of the grease which results into the addition of various elemental impurities within the grease samples. Most of the properties of grease are dependent on their shear stability, viscosity, dripping, spattering, *etc.* The dependability of lubricating grease depends on their physical properties that are structurally related which are obtained by the proper selection of ingredients and processing. The physical and chemical behavior of grease is largely controlled by the hardness which is dependent upon the microstructure of soap fibers. Between the surfaces of metals and grease, two types of interactions take place. The adhesive interactions which are sensitive to number of functional grease and lateral interactions are sensitive to structural properties. The dispersive interactions are between the hydrocarbons chain. TEM studies can describe the chain length of fatty acid in soap base. The fibers structure can then defined the quality of the grease. The three grease samples were collected from the wheel bearing box of rail train. Some conventional test to check the lubricating properties of grease are friction, viscosity and color changes. The three samples under investigation were selected on the basis of their color, which is given in Figure 2. The fresh sample is selected as the brown sample. The partially used grease sample appears to be greyish green and the fully used grease sample appears as completely dark green in color.

Figure 2. Fresh grease, partially grease and fully grease samples collected from wheel bearings of train.



In routine test of grease of Indian Railways follows the Fe contamination tests for its degradation analysis. The instrument used by the researchers in Indian railway for the detection of Fe content in the grease is from Kitiwake company model: Analex fd M Plus. In order to check the degradation of three grease samples, the iron detection test was conducted. From the test, it was observed that the fresh grease sample has zero level of iron (Fe) content, the partially used grease sample has Fe in 404 ppm and the third sample is treated as the fully used grease as it contains Fe in 1565 ppm concentration level. On the basis of the iron test results, the three samples were classified into three different forms and studied for the elemental analysis from LIBS technique. Time-gated LIBS spectra of fresh, partially used and fully used grease samples were recorded between the spectral ranges of 200–700 nm to evaluate the degradation of grease used in wheel bearings of Rail engines by elemental analysis.

The study of the detection of toxicants or impurities in the sample has a great significance as the presence of impurities in the sample indicates the wear and tear of the machinery parts. The analytical measurement systems with any matrix condition can extract the toxicants in any samples which are present in low trace level concentrations down to ppm or ppb level. The direct exposure to the toxicants can lead to the many activities like intentional ingestion, poisoning, occupational and environmental exposures. This can affect the tissues of organs; the chronic results might lead to the mutation in genes. The listed elemental impurities in the partially and fully used grease samples are Fe, Si, Mg, Pb, Ca, Al, Mo, Ba, Na, Cu, Mn, Mo, Ni, Ba, S, Zn, Ti.

In the LIBS study, various elemental impurities like Fe, Si, Mg, Pb, Ca, Al, Na, Ba, Zn and Ti were observed. The LIBS spectra of three grease samples for the investigation of elemental composition are given in Figure 3. The maximum number of impurity lines is present in the fully used grease sample. The recorded spectral lines are carefully assigned to the corresponding elements as per the NIST standard database. As the grease is composed of metal soaps, so the strong lines of elements like calcium, sodium, and aluminum are observed in the fresh, partially used and fully used samples of grease. Table 1 shows the elemental composition of fresh grease sample consisting of Ca, Na and Al which shows the presence of metal soaps. The spectrum of fresh grease sample shows the prominent lines of Na, Al and Ca which constitutes the basic composition of grease. The elemental lines obtained in the used grease spectra are authentically verified by comparing with the NIST standards as well as the LIBS analysis made by several groups in their studies on other type of samples [19–24]. Tables 2 and 3 shows the list of the emission lines observed in the LIBS spectra of partially used and fresh grease sample in expanded scale between the range 200–700 nm. Figures 4 to 8 represent the precisely elaborative form of the LIBS spectra of grease sample in the small region between 200 to 700 nm. The prominent impurities found in the fully used grease are Si, Mn, Mg, Ni, Al, Ca, Cu, Pb, Ba, S, Ti and Zn [25–27]. In general, the bearing surfaces have the composition of C-Si-Mn with iron and the iron used in the crankshafts and camshafts have Mn, Ni, Mg, P elements present in its composition. On comparing the elements present in both the two grease samples, it has been noticed that the partially used grease samples have impurities like Fe, Si Mg, Pb, Ca, Al and Ba which comes from wear and tear of the wheel box and bearing components. However, the additional transition lines of Mn, Ni, Zn and Ti have also been found in the fully used grease sample. Presence of lead comes from the wear of either connecting rod or turbocharger bearing wear. On the other hand, Al comes from the inefficient filtration. The presence of Cu and Fe could be of bushing shaft wear. The presence of Si is an indicator of air-born dirt in the grease sample. Sulfur (S) and copper (Cu) are the minor contributors in the composition of the cast iron and also present in grease as additive.

Figure 3. LIBS spectra of fresh, partially used and fully used grease samples using nanosecond pulsed laser and time-gated ICCD spectrograph.

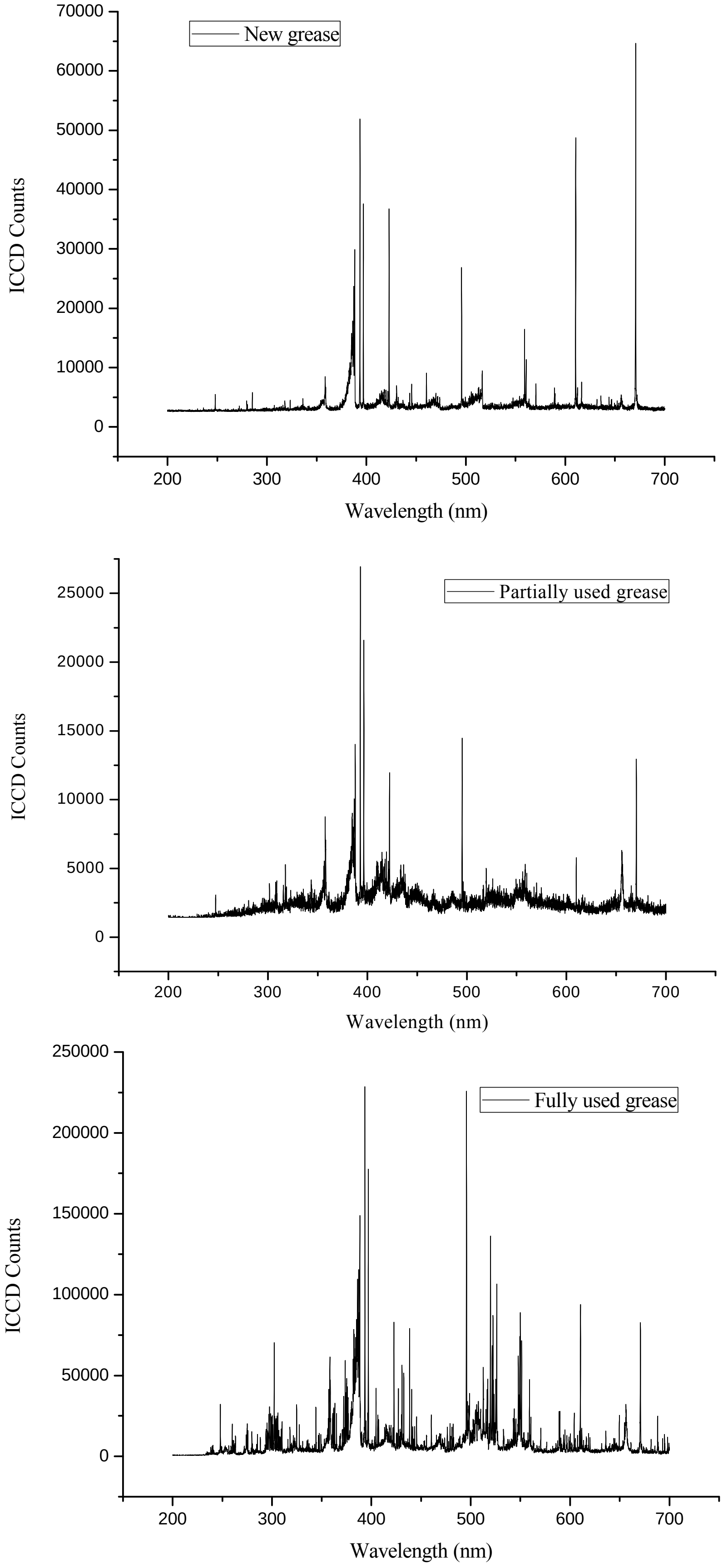


Table 1. Elemental composition of some major identifying wavelengths (nm) of fresh grease sample.

Elements	Major Identifying Wavelengths Observed at (nm)
C	247.89
Na	279.6, 589.11, 589.734
Al	336.104
Ca	393.496, 397.011, 422.77, 430.419, 432.002, 443.589, 445.46, 480.07, 610.474, 612.367, 616.345, 644.037
C2	358.543, 473.714, 516.507
CN	385.192, 385.54, 386.274, 387.162, 388.398, 418.137, 421.651
S	594.25

Table 2. Elemental composition of some major identifying wavelengths (nm) of partially grease sample.

Elements	Major Identifying Elements Lines (nm)
Fe	273.509, 298.136, 300.247, 341.205, 342.292, 343.649, 346.019, 348.611, 356.055, 358.018, 361.98, 367.572, 375.608, 381.089, 383.792, 404.975, 407.049, 412.381, 414.825
Si	251.882
Mg	279.361, 516.628, 518.294
Pb	364.054
Ca	318.504, 370.349, 392.939, 397.383, 408.493, 409.826, 411.455, 422.269, 424.824, 431.379, 432.675, 436.934, 493.075, 558.696, 560.141, 616.282, 647.056, 649.241, 665.128, 666.424
Al	309.172
Mo	427.824, 429.453, 570.028
Ba	449.562, 467.263
Na	330.058, 498.222
Cu	324.244

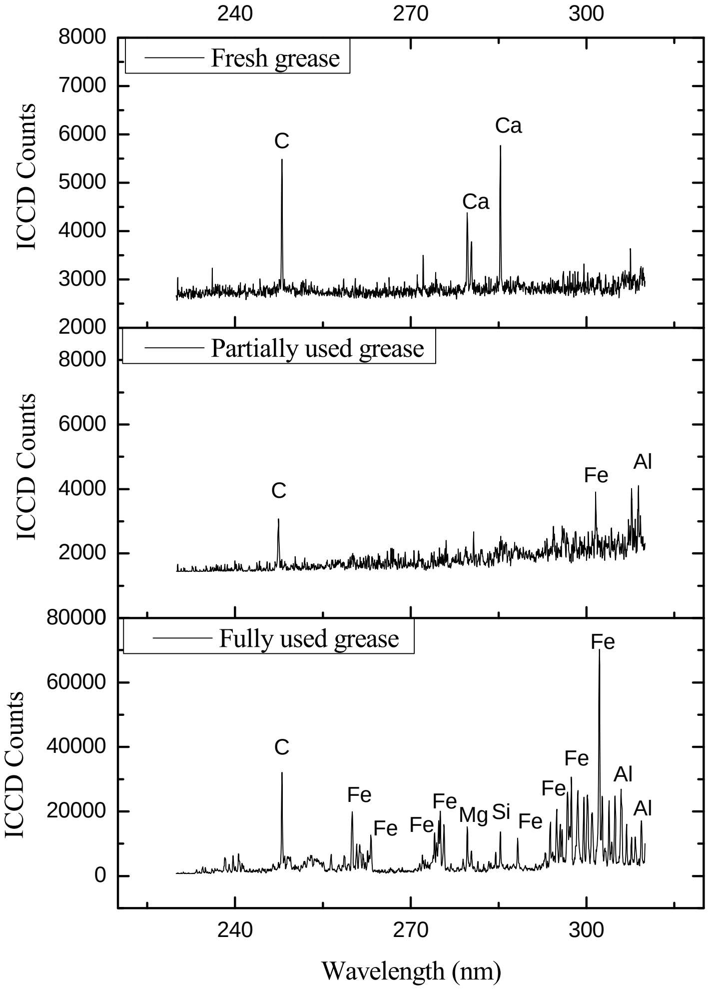
Table 3. Elemental composition of some major identifying wavelengths (nm) of used grease sample (Si, Mg, Ca, Ba, Zn, Fe, Pb, S).

Elements	Major Identifying
Si	288.251
Fe	238.274, 239.665, 248.007, 258.628, 260.01, 274.077, 275.042, 293.851, 299.567, 300.147, 303.854, 306.867, 322.702, 356.689, 358.234, 361.015, 363.294, 364.916, 372.138, 373.644, 375.073, 375.962, 376.541, 381.716, 382.18, 383.57, 385.115, 385.54, 386.158, 387.201, 388.398, 392.453, 404.735, 407.323, 413.386, 414.545
Mn	293.851, 294.933, 322.702, 441.658, 443.627, 476.533
Mg	279.66, 279.638, 516.584, 517.27, 518.708
Mo	414.545, 438.164, 549.954, 570.501
Ni	303.854, 305.901, 336.142

Table 3. *Cont.*

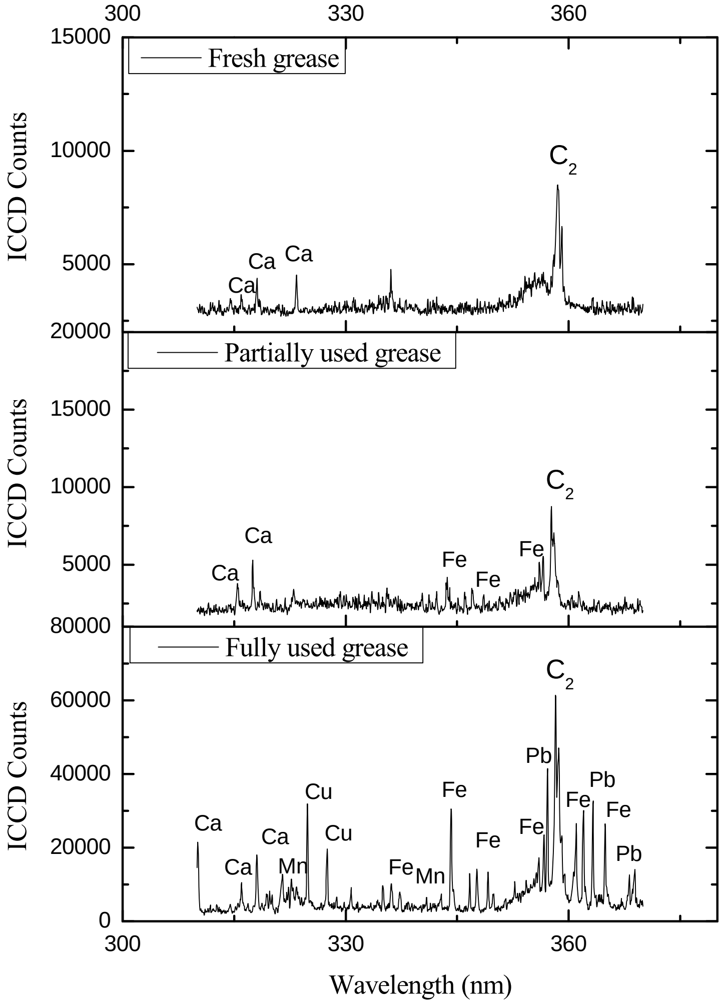
Elements	Major Identifying
Al	256.427, 306.867, 308.335, 309.377
Ca	315.982, 318.067, 371.057, 422.81, 428.449, 430.28, 430.921, 442.662, 443.627, 445.597, 488.043, 526.317, 527.089, 551.267, 557.713, 559.223, 560.691, 610.474, 613.525, 616.345, 670.879
Cu	324.865, 327.53, 509.98, 521.489
Pb	357.153, 363.294, 368.16
Ba	455.484, 553.661
S	501.483, 502.294, 543.89, 545.589, 593.481, 594.755, 604.256 605.26, 607.578, 609.663, 695.211, 698.223
Zn	481.091
Ti	263.186, 460.428, 498.123, 523.613

Figure 4. LIBS spectra of three grease samples between 230–310 nm.



The strong elemental lines of impurities like Fe, Mg, Si and Al have been observed in the fully used grease sample in the region 230–310 nm. Though, the impurity elements like Fe and Al are present in the partially used grease sample which is shown in Figure 4. The impurity elements like Cu and Pb are also observed in fully used shown in Figure 5. The impurities like Ba and Zn are observed in the region 370–490 nm in fully degraded sample of grease along with few impurity lines of Fe, Si and Ca represented in Figure 6. Apart from elemental lines, the emission lines due to CN bands have also been observed in this region in all three samples of grease. The lines of Na, Mo and Ca are observed in all three samples of grease between 540–590 nm shown in Figure 7. A few lines of S and Ba are also observed in this region with an impurity of Fe and Figure 8 shows the region between 590–700 nm in which few transition lines of sulfur are observed. Along with the elemental lines, lines of carbon (C), CN, C2 were also observed which can also be studied further to quantify the degradation of grease.

Figure 5. LIBS spectra of grease between 310–370 nm.



The toxicity of the metals on the human organs depends on the route of exposure. It has been reported the literature that metals such as Zn and Mn can be very toxic when inhaled. The exposure of Mn results in a serious nervous system disease that resembles the movement disorders of Parkinson's disease and Zn metals can cause fever, weakness and sweating. The presence of Pb as impurity in sample is hazardous to the human sample is hazardous to the human health as even the few traces of Pb could lead to the permanent brain damage and reduce intelligence, possibly resulting in death. The presence of Ni can be in the lungs a carcinogen, which can cause cancer. The intake of aluminum in blood by any means can cause dialysis dementia and the higher levels of which can result in Alzheimer's disease. The presence of Fe contents in grease makes it green in color [28].

Figure 6. LIBS spectra of three grease samples between 370–490 nm.

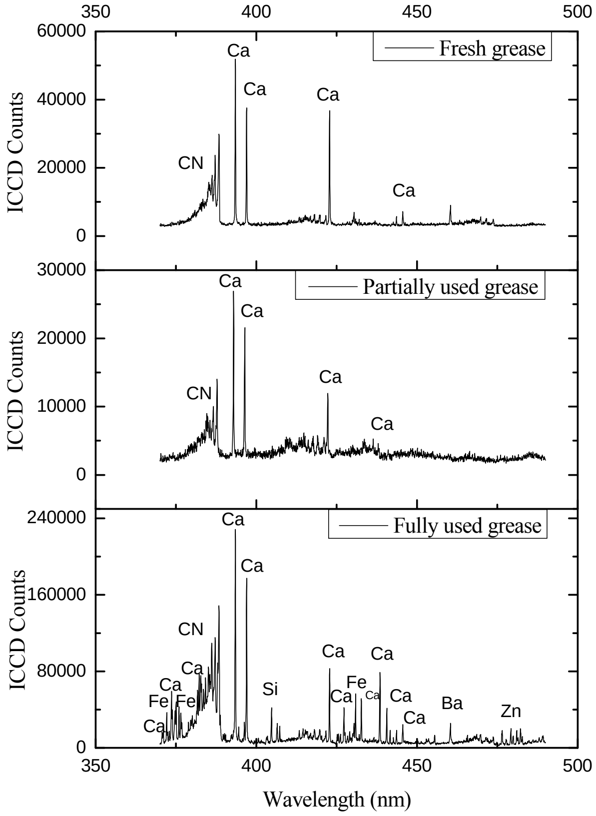


Figure 7. LIBS spectra of three grease samples between 540–590 nm.

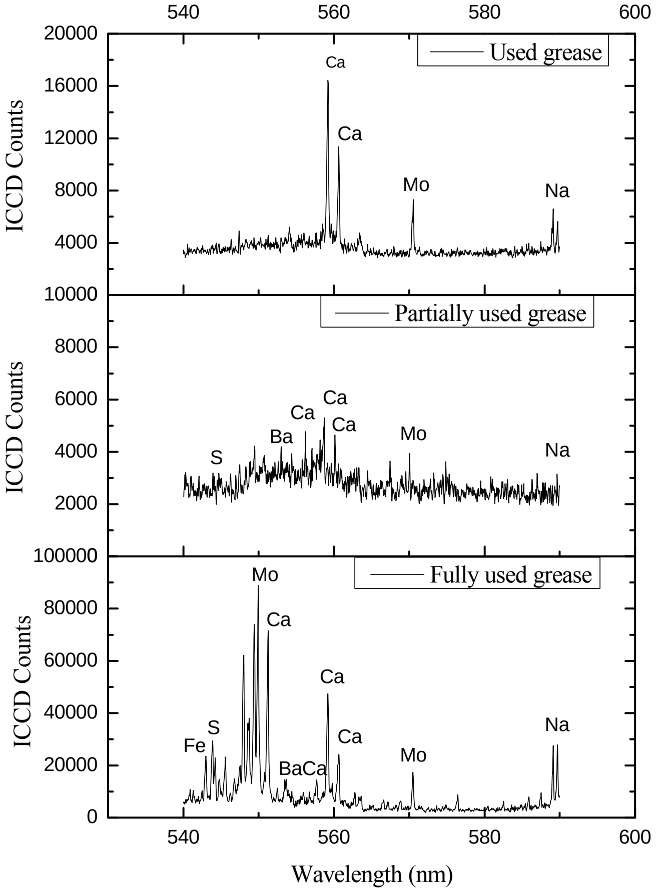
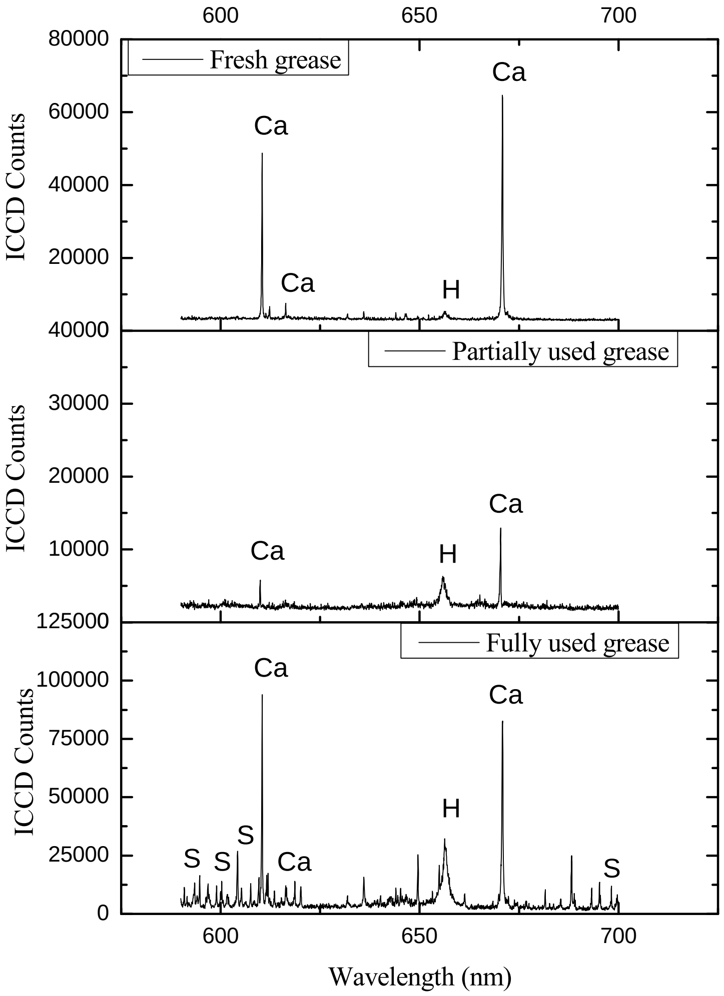


Figure 8. LIBS spectra of three grease samples between 590–700 nm.



5. Conclusions

LIBS spectra of fresh, partially used and fully used grease samples were recorded in the spectral region between 200–700 nm and analyzed by assigning the emission lines to elements present in the grease samples. In the fully used grease sample, many impurity elements such as Si, Fe, Mn, Mg, Ni, Al, Ca, Cu, Pb, S and Zn have been found in excess quantities which suggest the degradation of performance of the grease to the critical level. LIBS is an alternative to the conventional laboratory techniques that can be implemented to detect toxicants present in the sample matrix in trace level concentration. LIBS technique can further be improved to implement for the stand-off detection of toxicants in the grease present in the wheel bearings of trains. The small portable system based on LIBS technique can be designed to monitor the grease quality in the bearings, which would be remarked on as a great achievement for the *in situ* analysis of the grease samples.

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Author Contributions

Cherry Dhiman designed and performed the LIBS experiment and was involved in the analysis of the data and also prepared the manuscript. Kamal Gulati gave experimental support and participated in analysis of the data. Martha N. Reddy was involved in conceptualization of the study, gave experimental support. Mohd. Shahid Khan reviewed the results and gave critical inputs. All authors discussed the results and implications and commented on the manuscript at all stages.

Conflicts of Interest

The authors declare no conflict of interest.

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