



## Diagnosis of lubricating oil by evaluating cyanide and carbon molecular emission lines in laser induced breakdown spectra

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### ABSTRACT

To prevent engine failure it is essential to change lubricating oil regularly before it loses its protective properties. It is also necessary to monitor the physical and chemical conditions of the oil to reliably determine the optimum oil-change intervals. The present work focuses on studying evolution of the cyanide (CN) and carbon (C<sub>2</sub>) molecular spectral emission lines in the laser induced breakdown spectra of lubricating oil as a function of its consumption. The intensities of these molecular bands have been taken as indicator of engine oil degradation at certain mileage. Furthermore, the percentage of decay of CN and C<sub>2</sub> integral intensity values at the corresponding mileage was calculated in order to relate it to the degree of consumption of the motor oil. Such percentage decay of the CN and C<sub>2</sub> integral intensities have been found to increase gradually with increasing mileage which is accompanied with increasing depletion of engine oil. The results of using LIBS technique in the present measurements proved that it is possible to have a direct, straightforward and easy method for prediction of lubricating oil degree of consumption. This may facilitate scheduling the proper time and/or mileage intervals for changing the oil to avoid any possibility of engine failure.

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### 1. Introduction

The basic keystone of motor lubricating oil is to reduce friction and wear under all extreme operation conditions by interposing a film of material between rubbing surfaces to prevent corrosion of internal engine components and facilitate cooling *via* heat transfer. In an internal combustion engine the lubricating oil undergoes high shear forces. The oil is normally sandwiched between two rotating or sliding metallic parts under load and heat. The molecular structure may essentially tear apart due to these mechanical shear forces. As engine heat and shear forces continue and increase, oil molecules break away from the base structure and provide less and less resistance to wear. If this shearing and excessive heat continues over an extended period of time engine damage can occur [1].

The two basic categories of lube oil are mineral and synthetic. These are hydrocarbon-based polyglycols or dibasic acids esters, polyol esters, and dewaxed waxy raffinate oils and glycerol mono-oleate and at least one additional polyhydric alcohol as well as one or more nitrile compounds. The preferred nitrile compounds may be saturated and unsaturated hydrocarbon compounds containing one or more cyano groups (–C≡N), such compounds preferably do not comprise any additional functional group substituent [2].

The principal source of contamination during oil use is the chemical breakdown of additives and the subsequent interaction among the resultant components to produce corrosive acids and other undesired substances [3]. As these additives are consumed, lubricant performance for the specific application is reduced and equipment failure may result under continued use. In conclusion, oil monitoring programs should be implemented to periodically test oils and verify that the essential additives have not been depleted to unacceptable levels [1].

In principle, the composition of typical waste lubricating oil is a stable dispersion of undegraded base oil and additives coming from the overlay of bearing surfaces and chemical degradation of the fresh lubricant components. For example, hydrocarbon molecules will react to incorporate oxygen atoms into their structure over time. This reaction produces acids, sludge, and varnish that foul or damage metallic parts [4].

There are wide variety of byproducts that may be produced during the combustion process such as ketones, esters, aldehydes, carbonates and carboxylic acids. The exact distribution and composition of these products is complex, however it contribute effectively in depletion of the basic lubricating properties of the oil [5].

Used motor oil may contain minute quantities of gasoline, additives (detergents, dispersants, oxidation inhibitors, rust inhibitors, and viscosity improvers), nitrogen and sulfur compounds, and a broad range of aromatic and aliphatic hydrocarbons with chain lengths ranging from C 15 to C 50, in addition to metals such as lead (Pb), zinc (Zn), calcium (Ca), barium (Ba) and magnesium (Mg).

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These contaminants arise from normal wear of engine components and from heating and oxidation of lubricating oil during engine operation. Used oil may contain higher percentages of polycyclic aromatic hydrocarbons (PAHs) and additives compared to fresh oil [6–8]. As mentioned above, engine oil degradation is a chemical deterioration process. It is caused by the combination of base oil with oxygen, sulfur, and nitrogen to form harmful compounds. It can be also caused by additive depletion due to reactions with contaminants such as heat, air, metal particles, soot, fuel, and glycol [9]. Because of the changes that occur during use, engine oils tend to differ in chemical and physical compositions from fresh oil so the determination of metals and some other elements in lubricating oils has found wide application in industry, e.g. in the preventive care of mechanical failure of oil-wetted mechanisms (analysis of wear metals), in the control of various lubricant additives in oils, and for checking of toxic elements during liquidation of consumed oils [10]. As the oil degrades, a sequence of events occur, each of which can be measured with an oil analysis [11].

Sensitive techniques are required for analysis of used lubricating oils since the capability of monitoring small concentration changes in the key elements is needed. The complexity of the oil matrix, its viscosity and the high organic load impose serious difficulties for analysis adopting conventional analytical techniques [12,13]. Conventional methods, e.g. ICP-MS, ICP-OES, AAS etc., are mainly used in laboratories and are not appropriate for field measurements, in addition the lack of standard samples for calibration represents a real obstacle for quantitative analysis using such techniques.

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique that has been extensively used for analysis of solid and liquid samples. The analysis of solid samples has always been the primary application; however, the analysis of liquids has also received a great deal of attention. It has been demonstrated that LIBS provides a reproducible and easy means for the analysis of a variety of liquid solutions in the form of liquid jets [14–16], static liquid surfaces [17,18], liquids on paper substrates [19] and aerosols [20]. From the analytical point of view, LIBS is well known as an elemental analysis technique, however, it can be also exploited efficiently in detection of molecular species such as CN and C<sub>2</sub> in the spectra of organic and biological samples.

Fortes et al. [21] presented detailed LIBS analysis of crude oil and fuel residues using the intensity ratio of the spectral lines as well as CN and C<sub>2</sub> molecular band emissions in the original fuel and in the aged residues. In their work, field and lab LIBS measurements provided very useful information for the samples characterization and demonstrated the advantages of using information derived from the organic fraction of the samples for discrimination purposes.

LIBS is a very promising technique capable of analyzing elements indicative of wear such as Al, Cu, Ca, Fe, Mg, Mn, Na, and Zn in used engine oils. A comparison of detection limits obtained for several elements in liquid laminar jets and at the surface of static liquids has been reported [16]. A comparison of LIBS analysis of lubricants, using both static liquid surfaces and liquid jets versus analysis using a paper substrate, suggests that the latter is the preferred method because of the use of paper substrates prevents splashing, which means that the plasma emission imaging lens can be located closer to the ablation point. It has been also shown that improved limit of detection, of most relevant elements, by a factor of two is attainable using paper substrate and single pulse LIBS. The additional advantage of using absorbent papers is that no modifications are needed to an experimental LIBS system initially designed to analyze solids [19]. A tradeoff is usually made between the detection limits and increasing the time of analysis by increasing the number of laser shots in order to average a large number of spectra [22,23].

In view of the above given background about the byproducts of the chemical degradation and combustion of engine oil, studying the evolution of CN and C<sub>2</sub> molecular bands in LIBS spectra of lubricating

oil is expected to provide important information about the oil status. In the present work we report on the spectroscopic investigation of the variation of the characteristic cyanide (CN) and carbon (C<sub>2</sub>) molecular emission lines in laser induced breakdown spectra of lubricating oil. The used oil samples were collected from commercial cars of the same type, model, and specifications at different mileage intervals. Identification and explanation of changes of CN to C<sub>2</sub> spectral lines intensity ratios will be investigated. In other words, the ratios of the integrated emission intensity of CN to C<sub>2</sub> will be calculated for collected oil samples in order to assess the combustion process and consumption of motor oil during normal engine operation.

## 2. Experimental

### 2.1. Sample preparation

Pure synthetic engine oil sample was obtained from a local market while the used samples were provided by an authorized car-service center from the same type of cars having the same motor capacity and mechanical specifications. Used engine oils were collected from cars after different ascending mileage intervals, namely 10,000, 30,000, 40,000, 90,000, 160,000 km in addition to the virgin oil sample (zero mileage). The samples were from the 10,000 km regular oil change service in each case. This means that the 160,000 km sample for example is collected from a car that has changed oil 16 times before. About 50 ml of each oil sample was collected in a dark bottle. For LIBS analysis each oil sample was added drop wise onto a substrate of high quality ashless filter paper (50 mm diameter). Samples were left to spread on the filter paper and dry partially for 15 min where they were still wet before analysis. Filter paper was then mounted on an X–Y micrometer translation stage to move the sample during the measurements to ensure that a fresh surface location is available for each laser shot.

### 2.2. Instrumentation

A typical LIBS experimental setup has been used throughout the present measurements. The used laser source is a Q-switched Nd:YAG laser (BRIO, Quantel, France), operating at its fundamental wavelength ( $\lambda = 1064$  nm), with a pulse duration of 5 ns (FWHM) in single pulse regime. The pulse energy was set to 100 mJ and the repetition rate to 1 Hz. The laser beam was focused onto the sample using a 10 cm focal length planoconvex quartz lens. The target was mounted on an X–Y micrometric translation stage. The plasma optical emission was collected by a fused-silica optical fiber with a diameter of 600  $\mu\text{m}$  held at a distance of 2 cm above the plasma at an angle of 30° with respect to the target surface. The collected plasma emission is then fed via the optical fiber to the entrance slit of an echelle spectrometer (Mechelle 7500, Multichannel, Sweden) with a focal length of 17 cm and *f*-number of 5.2. It provides a constant spectral resolution of 7500 corresponding to 4 pixels FWHM, over a wavelength range 200–1000 nm, displayable in a single spectrum. Gateable ICCD camera, (DiCAM-Pro (PCO, computer optics-Germany), with a high-resolution sensor with 1280 × 1024 pixels (9 × 9 mm<sup>2</sup>) coupled to the spectrometer, was used for the detection of the dispersed light. The 25 mm microchannel plate is from DiCAM with a UV-enhanced photocathode. The overall linear dispersion of the echelle spectrometer-camera system ranges from 0.0078 (at 200 nm) to 0.032 nm pixel<sup>-1</sup> (at 700 nm). The ICCD camera control was performed via special multichannel instrument software. To avoid electronic interference and jitters, the CCD intensifier high voltage was triggered optically. Spectra display, processing and analysis were done using 2D- and 3D-Gram/32 software programs (National Instruments, USA). In addition to the atomic data base used by the mentioned software, further spectral lines identification was accomplished using LIPS<sup>++</sup> software

[24]. To optimize the signal-to-noise ratio and guarantee results reproducibility LIBS spectra were collected from five fresh spots where ten consecutive shots were recorded for each spot. The average of the 50 spectra for each sample was analyzed.

### 3. Results and discussion

#### 3.1. Optimization of the experimental parameters

As it is well known in LIBS measurements, it is essential to delay the detection time with respect to the laser firing time to avoid the strong continuum at the early times of the laser induced plasma evolution [25]. In order to obtain an optimum value of the emission intensity with respect to the background, i.e. to maximize the signal to noise ratio (SNR) in the emission spectrum, a proper choice of the delay time was required. Accordingly, the emission spectrum was recorded at different delay times ( $\tau_d$ ) and gate widths ( $\Delta t$ ) in order to select an optimal SNR. To perform such optimization procedure, LIBS analysis was done on standard sample (virgin oil) where the delay time was changed in the time interval between 1  $\mu$ s and 5  $\mu$ s at constant gate width (2  $\mu$ s). Fig. 1 demonstrates the optimization process of the delay time, revealing an optimum value  $\tau_d = 1.5 \mu$ s for both molecular  $C_2$  and CN emission lines at 516.5 and 419.7 nm, respectively (well resolved peaks). Therefore a delay time of 1.5  $\mu$ s and gate width of 2  $\mu$ s have been chosen throughout the spectroscopic measurements.

#### 3.2. Normalization of the spectra

As mentioned before LIBS spectra were acquired from oil samples by averaging 50 LIBS spectra for each sample, taken as 10 spectra at 5 different locations on the filter paper substrate. Normalization of the maximum line intensities was performed to avoid any unwanted experimental fluctuations through dividing each spectrum by the intensity of a well resolved spectral line of one of the major elements in the measured sample. Consequently, all the measured spectra in this work have been normalized against the intensity of Ca (I) spectral line at 428.9 nm. The choice of this calcium line is mainly because it is a well resolved spectral line and nearly free of self absorption with a relatively very low partial self absorption coefficient  $K_R(\lambda) = 5.0078E - 7 \text{ m}^2 \text{ s}^{-1}$  [26]. On the other hand the carbon atomic line at 247.856 nm has been avoided since it suffers from a strong interference with the two iron lines FeII at 247.857 and FeI at 247.948 nm. Fortunately, the used echelle spectrometer facilitates recording of emission lines in the spectral region extending from 200 nm up to 700 nm, which includes

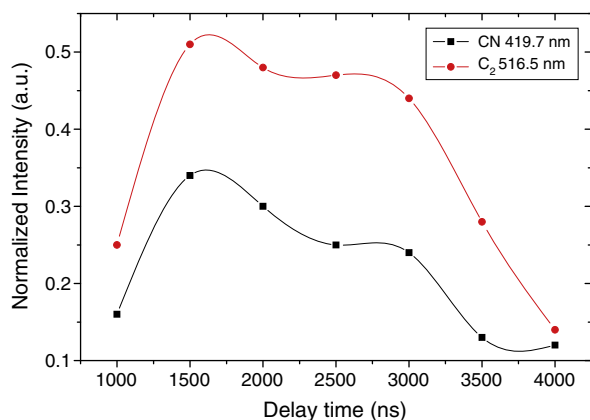


Fig. 1. Optimization of the delay time ( $\tau_d$ ) using one of the molecular cyanide (CN) lines and one of the molecular carbon ( $C_2$ ) lines at constant gate width of 2  $\mu$ s.

simultaneously all the molecular emission bands of  $C_2$  and CN under study.

#### 3.3. Manifestation of lubricating oil consumption

According to the above mentioned information, the engine oil composition includes hydrocarbons and one or more nitrile compounds that contain more cyano groups ( $-C\equiv N$ ). Under normal operation conditions of the engine, such compounds are subjected to chemical deterioration and byproducts are produced during degradation and combustion process of engine oil. Figs. 2 and 3 show the gradual depletion in the cyanide (CN) and molecular carbon ( $C_2$ ) levels respectively given by the decrease in the intensities of the relevant spectral emission lines in the analyzed oil samples at different mileage. The spectral line intensity behavior of the  $C_2$  line at 516.5 nm (not shown) has the same trend of the other shown lines. The intensities of CN and  $C_2$  spectral lines were the highest for virgin oil then it decrease with increasing mileage as shown in the presented spectra.

To minimize the background effect in calculating the spectral line intensity of CN and  $C_2$  emission lines, the line integral (the area under the peak) has been determined in each case. The mileage–signal

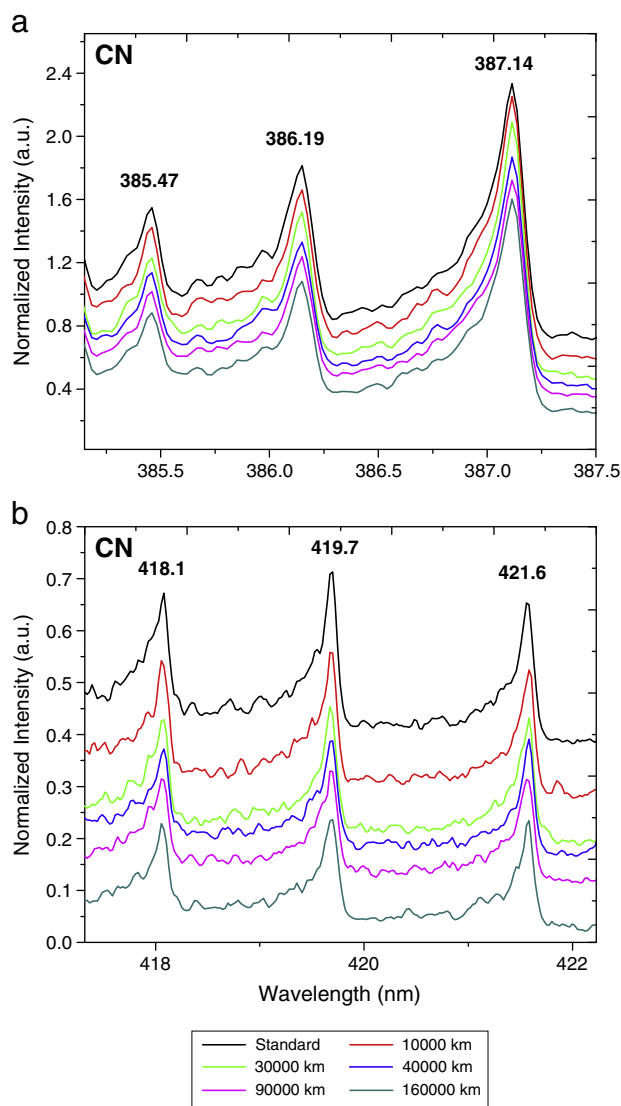


Fig. 2. LIBS spectra for engine oil samples showing CN peaks in UV spectral region (a) and in the visible region (b) at different mileage.

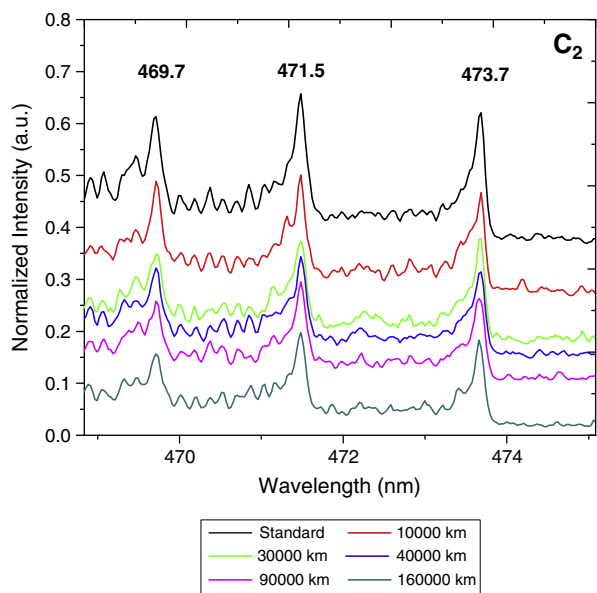


Fig. 3. LIBS spectra for engine oil samples for C<sub>2</sub> peaks in the visible region at different mileage.

behavior for CN and C<sub>2</sub> of the selected spectral emission lines of different oil samples is depicted in Figs. 4–6. The error bars represent the standard deviation of the experimental data. The exponential decay fitting curves of the experimental points in Figs. 4 and 5 describe the dissociation behavior of the cyanide molecules in the oil as a result of different operation conditions under friction and high temperature in the corresponding engine. Similarly the exponential fitting curves of the experimental data in Fig. 6 express the rate of dissociation of molecular carbon (C<sub>2</sub>) in the analyzed oil samples as given by the integrated intensities of C<sub>2</sub> spectral peaks.

In general, it is clear that the trend of the dissociation behavior of both CN and C<sub>2</sub> molecules is similar and can be described theoretically by an exponentially decaying curve equation in both cases. Therefore, we considered to plot the sum of the CN experimental points of different spectral lines versus the corresponding mileage and to do the same for the C<sub>2</sub> lines. The results are displayed in Fig. 7(a). The trend of the data reveals very good exponentially decaying fitting curves that can be used as a standard curve to predict the status of the lubricating oil of the same

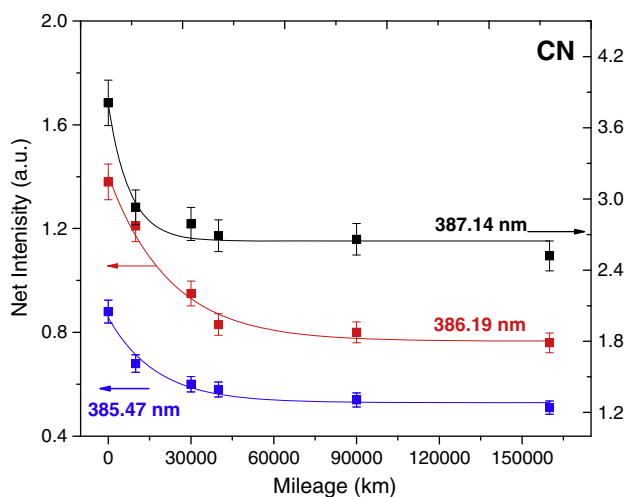


Fig. 4. Trends for integrated intensity values for CN emission lines in the UV at different mileage.

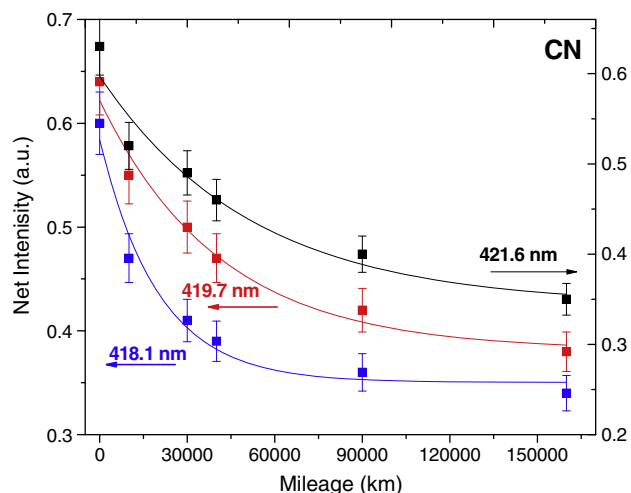


Fig. 5. Trends for integrated intensity values for CN emission lines in the visible region at different mileage.

type used in the same engine type too. The summation of CN and C<sub>2</sub> integrated line intensities can be considered to represent the cyanide and carbon molecular contents of the measured oil. Consequently, the obtained data shown in Fig. 7(a) indicate that, during normal degradation or consumption of engine oil (i.e. oxygen exposure, heating, chemical breakdown and contamination), the number of CN and C<sub>2</sub> molecules that decay after certain mileage is proportional to the number of undecayed molecules that were present in the unused virgin oil. The total decay of the sample decreases with further consumption of the oil because there are fewer and fewer undecayed CN and C<sub>2</sub> molecules with increasing mileage. Hence, to illustrate the depletion that occurred for CN and C<sub>2</sub> molecules through the consumption process of engine oil, the percentage decay of the molecules total intensity values at different mileage intervals can be evaluated as follows:

$$\text{Percentage decay} = \frac{\text{Virgin oil intensity value} - \text{Used sample intensity value}}{\text{Virgin oil intensity value}} \times 100.$$

Table 1 lists the calculated values of the CN and C<sub>2</sub> percentage decay according to the above formula. Inspection of the data in Table 1

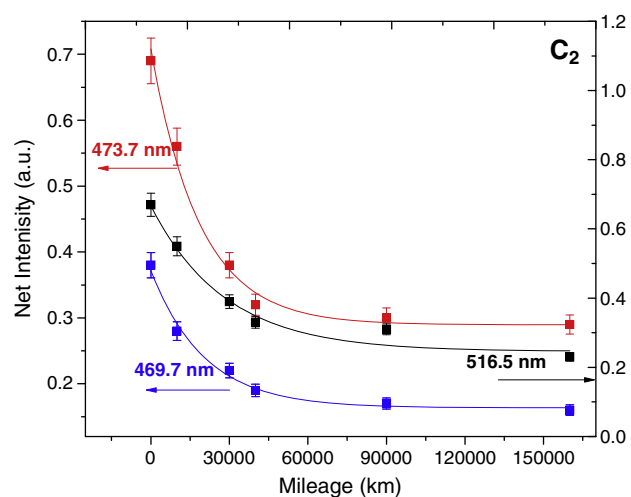


Fig. 6. Trends for integrated intensity values for three C<sub>2</sub> emission lines at different mileage.

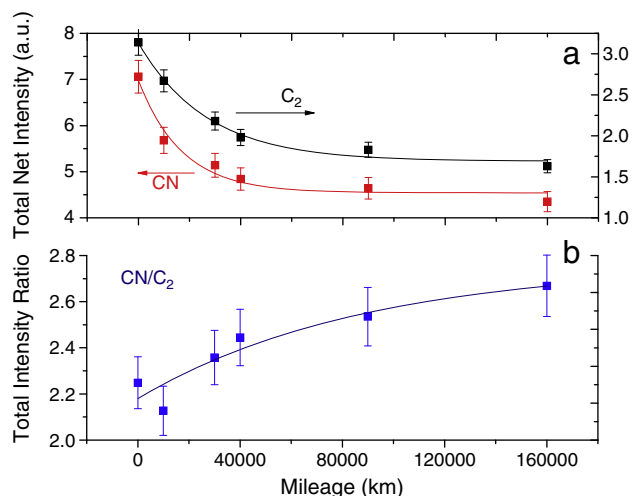


Fig. 7. Trends of summation of integrated line intensities for CN and  $C_2$  peaks (a) and that of CN/ $C_2$  ratio (b) at different mileage.

elucidates that the depletion of CN and  $C_2$  integrated intensity values increases gradually with increasing mileage. The values given by the decay of the cyanide molecules may be considered more reliable in reflecting the oil status due to the higher dissociation sensitivity of CN molecules in nitrile compounds under extreme conditions.

Furthermore, these data display a unique behavioral change in the decay percentages for CN and  $C_2$  values at different mileage. In other words, the decay percentages for these two molecules increased by moving from zero (for pure oil) to 38.39% and 48.09% after 160,000 km for CN and  $C_2$  respectively. Indeed, these values simulate the real oil burning off stages during normal operation conditions of the engine where combustion and/or consumption of the oil increase as the distance intervals done by the car increase. This is also clear from the previous analysis for oil samples that were taken at the regular periods for oil changing. So these results can be taken into account as indicator of normal combustion of engine oil through consecutive distance intervals ranging from 10,000 up to 160,000 km.

### 3.4. Prognostic approach

Predictive maintenance may be similar to preventive maintenance in the sense that its goal is to prevent production of abnormality in advance before abnormality occurs. However, the approach of predictive maintenance is different from the time oriented approach of preventive maintenance. It focuses on the prediction of degradation process, which is based on the assumption that most abnormalities do not occur instantaneously, and usually there are some kinds of

Table 1

Calculated decay percentages for the summation of CN and  $C_2$  integrated intensity values at different mileage.

Species	Mileage (km)	Integrated intensity value (a.u.)	Decay (%)
CN	0 <sup>a</sup>	7.06	0
	10,000	5.68	19.55
	30,000	5.14	27.2
	40,000	4.84	31.44
	90,000	4.64	34.28
	160,000	4.35	38.39
$C_2$	0 <sup>a</sup>	3.14	0
	10,000	2.67	14.97
	30,000	2.18	30.57
	40,000	1.98	36.94
	90,000	1.83	41.72
	160,000	1.63	48.09

<sup>a</sup> Virgin oil sample.

degradation processes from normal state to abnormalities [27]. Hence, unlike breakdown maintenance and preventive maintenance that concentrates on fault detection and diagnostics of components, predictive maintenance focuses on degradation monitoring and prognostics. This enables us to identify and solve latent problems in advance before vehicle damage occurs. In particular, under the new environment where we can easily access and receive vehicle status information in a ubiquitous way, we can make a prognosis of vehicle status, predict vehicle's abnormality, and execute proactive maintenance, i.e. do predictive maintenance [9].

The degree of consumption and combustion of oil should be anticipated in all engines in which increasing in burning motor oil is a prelude to engine failure. Thus, one of the key points for implementing predictive maintenance is to develop relations between the most common structured molecules that degraded and exhausted significantly with normal combustion of engine oil then relate these relations to degradation status and the engine combustion efficiency as well as consumption of oil.

Given these facts, CN/ $C_2$  integral line intensity ratio was calculated for increasing mileage. Such ratios exhibit an exponentially increasing behavior that is depicted in Fig. 7(b) where it grows up with increasing mileage. The larger CN/ $C_2$  intensity ratio exhibited by the consumed oil indicates a lower aromatic content in comparison with the virgin oil [21]. Such results indicate the possibility of using this relation as a monitor for consumption and combustion of motor oil that would be a simpler and fast sensing tool and can be considered as an Oil Condition Analysis (OCA) that is similar to Wear Rate Analysis (WRA) but it evaluates chemical compounds and molecules in the oil [2]. If for example the CN/ $C_2$  line intensity ratio for an oil sample under investigation fluctuates up or down of the ratio value given for unused oil, this can be an indication of burning of the oil sample in the engine.

## 4. Conclusions

In the present study, it has been shown that it is feasible to make use of LIBS with its advantages as a simple, straightforward and possibly *in situ* technique for the estimation of consumption and/or combustion of motor oil during routine engine operation. This has been performed by following up the intensities of molecular emission lines relevant to the main compounds of oil in its LIBS spectra, while the oil undergoes a range of chemical and physical transformations during consumption. Accordingly, we studied the variation of the characteristic cyanide (CN) and carbon ( $C_2$ ) molecular spectral lines at different wavelengths in the LIBS spectra of the lube oil after different mileage. The results show that the trend of integral intensity values of CN and  $C_2$  emission lines versus the mileage at all selected wavelengths is similar and can be described by an exponentially decaying curve. The rates of dissociation for CN and  $C_2$  contents in oil samples were calculated to be taken as indicator for consequent depletion of engine oil. Additionally, the ratios for the integrated emission intensity of CN to  $C_2$  have been calculated and found to be proportional to the corresponding mileage. Furthermore, the obtained trend can be used as prognostic approach for normal degradation of engine oil.

## References

- [1] N.I. Grigor'eva, E.B. Ivankina, S.A. Chesnokov, G.S. Kirichenko, S.M. Smirnova, N.I. Kolobov, Lubricating oil for fluid-friction bearings and high-speed rolling mill reducing gears, Chem. Technol. Fuels Oils 27 (1991) 182–183.
- [2] S.V. Kotov, Manufacture of bases and components of oils and additives from lower olefins, Chem. Technol. Fuels Oils 39 (2003) 136–140.
- [3] Chemistry and Technology of Lubricants, in: R.M. Mortier, S.T. Orszulik (Eds.), second ed, Blackie Academic and Professional, UK, 1997.
- [4] R. Jesusa, C. Pablo, T.G. Maria, Regeneration of used lubricant oil by ethane extraction, J. Supercrit. Fluids 39 (2007) 315–332.
- [5] M.A. Al-Ghouti, L. Al-Atoum, Virgin and recycled engine oil differentiation: a spectroscopic study, J. Environ. Manage. 90 (2009) 187–195.

- [6] R.K. Hewstone, Safety and environmental aspects of used crankcase lubricating oils, *Sci. Total. Environ.* 156 (1994) 255–268.
- [7] R. Vazquez-Duhalt, Environmental impact of used motor oil, *Sci. Total. Environ.* 79 (1989) 1–23.
- [8] F.O. Cotton, M.L. Whisman, S.W. Gowtzing, J.W. Reynolds, Analysis of 30 used motor oils, *Hydrocarb. Process.* (1977) 131–140.
- [9] Jun Hong-Bae, D. Kiritsis, M. Gambera, P. Xirouchakis, Predictive algorithm to determine the suitable time to change automotive engine oil, *Comput. Ind. Eng.* 51 (2006) 671–683.
- [10] M. Pouzar, T. Černohorský, A. Krejčová, Determination of metals in lubricating oils by X-ray fluorescence spectrometry, *Talanta* 54 (2001) 829–835.
- [11] Z.-P. Janina, Examination of used motor oils by flame AAS for criminalistic purposes: a diagnostic study, *Forensic Sci. Int.* 91 (1998) 171–179.
- [12] V. Sychra, I. Lang, G. Sebor, Analysis of petroleum and petroleum products by atomic absorption spectroscopy and related techniques, *Prog. Anal. At. Spectrosc.* 4 (1981) 341–426.
- [13] K.J. Eisentraut, R.W. Newman, C.S. Saba, R.E. Kauffman, W.E. Rhine, Spectrometric oil analysis: detecting engine failures before they occur, *Anal. Chem.* 56 (1984) 1086A–1094A.
- [14] W.F. Ho, C.W. Ng, N.H. Cheung, Spectrochemical analysis of liquids using laser-induced plasma emissions: effects of laser wavelength, *Appl. Spectrosc.* 51 (1997) 87–91.
- [15] P. Yaroshchik, R.J.S. Morrison, D. Body, B.L. Chadwick, A dual beam spectrometer using laser-induced breakdown spectroscopy, *Rev. Sci. Instrum.* 75 (2004) 5050–5052.
- [16] P. Yaroshchik, R.J.S. Morrison, D. Body, B.L. Chadwick, Quantitative determination of wear metals in engine oils using laser-induced breakdown spectroscopy: a comparison between liquid jets and static liquids, *Spectrochim. Acta Part B* 60 (2005) 986–992.
- [17] B. Charfi, M.A. Harith, Panoramic laser-induced breakdown spectrometry of water, *Spectrochim. Acta Part B* 57 (2002) 1141–1153.
- [18] P. Fichet, P. Mauchien, J.-F. Wagner, C. Moulin, Quantitative elemental determination in water and oil by laser induced breakdown spectroscopy, *Anal. Chim. Acta* 429 (2001) 269–278.
- [19] P. Yaroshchik, R.J.S. Morrison, D. Body, B.L. Chadwick, Quantitative determination of wear metals in engine oils using LIBS: the use of paper substrates and a comparison between single- and double-pulse LIBS, *Spectrochim. Acta Part B* 60 (2005) 1482–1485.
- [20] D.E. Poulain, D.R. Alexander, Influences on concentration measurements of liquid aerosols by laser-induced breakdown spectroscopy, *Appl. Spectrosc.* 49 (1995) 569–579.
- [21] F.J. Fortes, T. Ctvrtníčková, M.P. Mateo, L.M. Cabalín, G. Nicolas, J.J. Laserna, Spectrochemical study for the in situ detection of oil spill residues using laser-induced breakdown spectroscopy, *Anal. Chim. Acta* 683 (2010) 52–57.
- [22] R.L. Vander Wal, T.M. Ticich, H.R. West Jr., P.A. Householder, Trace metal detection by Laser-Induced Breakdown Spectroscopy, *Appl. Spectrosc.* 53 (1999) 1226–1236.
- [23] D. Alamelu, A. Sarkar, S.K. Aggarwal, Laser-induced breakdown spectroscopy for simultaneous determination of Sm, Eu and Gd in aqueous solution, *Talanta* 77 (2008) 256–261.
- [24] M. Corsi, G. Cristoforetti, V. Palleschi, A. Salvetti, E. Tognoni, A fast and accurate method for the determination of precious alloys caratage by Laser Induced Plasma Spectroscopy, *Eur. Phys. J. D* 13 (2001) 373–377.
- [25] A.H. Galmed, M.A. Harith, Temporal follow up of the LTE conditions in aluminum laser induced plasma at different laser energies, *Appl. Phys. B* 91 (2008) 651–660.
- [26] Z.A. Abdel-Salam, A.H. Galmed, E. Tognoni, M.A. Harith, Estimation of calcified tissues hardness via calcium and magnesium ionic to atomic line intensity ratio in laser induced breakdown spectra, *Spectrochim. Acta Part B* 62 (2007) 1343–1347.
- [27] C. Fu, L. Ye, Y. Liu, R. Yu, B. Jung, Y. Cheng, Y. Zeng, Predictive maintenance in intelligent-control-maintenance-management system for hydroelectric generating unit, *IEEE Trans. Energy Convers.* 19 (2004) 179–186.