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Research Paper

Facile Detection of Oil Adulteration using UV-Visible Spectroscopy Coupled with Chemometric Analysis

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Abstract

Engine and machine oils, better known as lubricant, is a fast-moving part within the motorcycle and automobile industries. Due to its high demand, these oils are often counterfeited by irresponsible people to get more profit. The thing most often done to adulterate oil is by mixing it with other low-quality or used oil. Here, we propose a simple analytical method to identify oil adulteration by using UV-Visible spectroscopy coupled with chemometric analysis. A number of 425 genuine and adulterated oils were used as samples. After appropriate dilution using n-hexane, the samples were analyzed by UV-Visible spectrophotometer followed by Principle Component Analysis (PCA) and Principle Component Regression (PCR) as part of the chemometric analysis. The results show that prediction samples were accurately classified into their corresponding groups with PCA scores of 49% and 27% for principal component 1 and 2, respectively. PLS model achieved a good prediction to detect lubricant oil adulteration, with R-square of predicted and reference samples were 0.9257 and 0.9204, respectively. The proposed method shows a promising alternative to the conventional chemical method using a more sophisticated instruments such as GC-MS and HPLC for oil or other organic compound identification.

Keywords

Lubricant oil, adulteration, UV-Visible spectroscopy, chemometrics, multivariate analysis

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1. INTRODUCTION

Lubricant, generally, contains 90% base oil and less than 10% additives. Base oil may derive from petroleum fractions, mineral oils, vegetable oils or synthetic liquids such as hydrogenated polyolefins, esters, silicones, fluorocarbons and many others (Iłowska et al. (2018); Liu et al. (2019a)). Synthetic oil is a man-made lubricant that consists of chemically modified materials such as petroleum components (Liu et al., 2019b). Oil is used as lubricant due to it reduces friction; the lubricant is more slippery than the components it is applied to. A reduction in friction generate easier movement, less wear on components, and reduced energy needs of the system (Díaz Tovar et al., 2018). Currently, renewable lubricants with tailored molecular architecture are also introduced to the market (Liu et al., 2019a). High population growth followed by the increase of purchasing power has resulted in more vehicles being produced and used worldwide. Engine (lubricant or machine) oil is one of the fast-moving items in a vehicle whose production is increasing due to the high demand. This results in increasing oil price, accompanied by the oil adulteration that is becoming more widespread. Therefore, it is necessary to develop an analytical method to detect oil adulteration. Up to today, the qualitative and quantitative analysis of oil have been conducted using one or combination of HPLC, GC-MS and FT-IR (Escandar et al. (2006); Mobaraki and Hemmateenejad (2011); Wiberg (2006)). Chemometrics technique were often embedded to the analysis of organic compounds for a more comprehensive and present additional insight on the analysis (Hanrahan (2008); Miller and Miller (2018)). In this paper, we report the development of UV-Vis spectrometry coupled with chemometrics technique to discriminate lubricant-oil adulteration that provide a robust and low-cost alternative to the conventional chemical method.

2. EXPERIMENTAL SECTION

2.1 Materials

Dilution of oil samples were conducted by using n-hexane as a solvent. This n-hexane and other chemicals were purchased from Merck (Darmstadt, Germany). Various lubricant oils were purchased from local market in Bengkulu city, Indonesia. Cheaper and used oils that is often used to adulterate lubricant were obtained from traditional motorbike service and workshop (Figure 1). A Genesys 20 UV-visible Spectrophotometer from Thermo Fisher Scientific (Massachusetts, USA) was used to obtain the


(a) (b) (c)

Figure 1. The photograph of genuine oil X (a), genuine oil Y (b), and adulterated oil (c)

spectra. Quartz and glass cuvettes, beaker glass, erlenmeyer were used for samples preparation and analysis. The chemometrics analysis was done by using The Unscrambler X software from CAMO Analytics (Oslo, Norway).

2.2 Methods

As much as 5 genuine oils from different companies were purchased from the authorized motorcycle workshop. In addition, we purchased various low-quality oils and used oils from traditional motorcycle workshop as samples of mixture and adulterated oils. Before analyzed, oils were filtered and diluted with n-hexane in order to get appropriate absorbance when analyzed by UV-Visible spectrophotometer. Dilution of oil with n-hexane was conducted from 10% (9:1) to 90% (1:9) dilution factors. The prepared samples in cuvettes were scanned from 420 to 920 nm using UV-Visible spectrophotometer. A total number of 425 samples were analyzed in this research, including 5 genuine lubricant oil samples. The csv files from spectrophotometer were converted and processed with MS Excel software (Microsoft, USA) and further analyzed in Unscramble X software using two models, i.e. Principal Components Analysis (PCA) and Partial Least Squares (PLS), as chemometrics analysis (Nunes (2014); Tan et al. (2015); Wold et al. (2001)).

3. RESULTS AND DISCUSSION

3.1 UV-Visible spectroscopy

Figure 2 shows the typical spectra of UV-visible for genuine and adulterated oils at wavelength from 220 to 920 nm. The mixture of oil, including those of adulterated ones, shows distinct absorbance between 350 to 390 nm that we used as the basis to differentiate various lubricant and its mixtures using this simple least square technique. In general, a good separation between each sample were observed from 300 to 420 nm wavelength. Therefore, a good linear correlation between oil impurity and absorbance were noticed, as shown in Figure 2. However, at low wavelength from 220 to 300 nm, the noise of spectra was high and thus it is impossible to differentiate between genuine and adulterated ones using a simple and traditional linear regression. At high wavelength from 520 to 920 nm, the spectra were uniform almost for all samples. In order to obtain a more comprehensive results of adulterated oil identification, a more complex computation of the whole UV-Visible spectra using chemometric technique is necessary. Therefore, we use chemometric as multivariate analysis to elucidate the UV-Visible spectra.

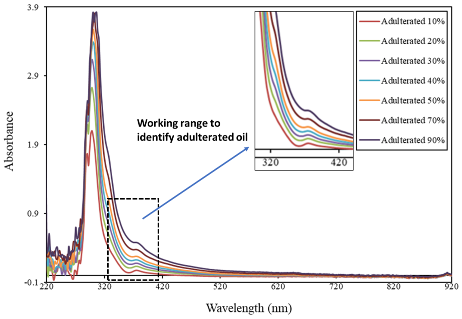

Figure 2. Typical UV-visible spectra of non- and adulterated-oil at wavelength from 220 to 920 nm. The dotted-line box shows the best spectra separation that can be used to draw a simple linear regression

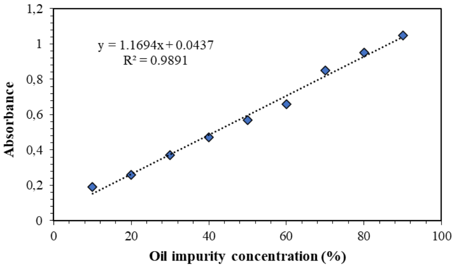

Figure 3. Simple linear regression (SLR) of oil impurity versus absorbance at 380 nm wavelength

A simple linear regression of oil impurity versus absorbance at wavelength of 380 nm is shown in Figure 3. Since the color of diluted oil is pale yellow, it shows a good linearity in ultra violet range with R-square = 0.9891 with linear equation of y = 1.1694x + 0.0437. Genuine oil shows a lower absorbance due to a clearer liquid compared to the adulterated ones. Absorbance ranges from 0.2 to 1.1 that shows a wide dynamic range and in turn it will provides a high sensitivity.

3.2 Chemometrics analysis

Two models of chemometrics, i.e. Principal Components Analysis (PCA) and Partial Least Squares (PLS), were chosen as multivariate techniques to analyze the principal component in oil samples. The PCA technique is well known to predict adulteration of samples with appropriate precision and sensitivity (Herrero-Latorre et al., 2019). Figure 4 shows the PCA plot derived from UV-visible spectra from 220 to 920 nm wavelength of oil using a projection onto the first two principal components. A good separation of genuine and adulterated oils was achieved with percentage of the first principal component (PC-1) and the second principal component (PC-2) were 49% and 27%, respectively. These results show that both PC-1 and PC-2 components represent 76% of the total variability, and successfully capturing the data structures. According to Sugianti et al. (2016), if the number of variants of PC 1 and PC 2 are greater than 70%,

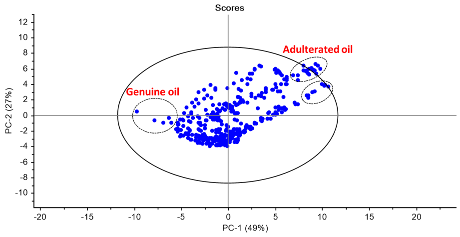

Figure 4. Principal Components Analycsis (PCA) derived from UV-visible spectra of oil using a projection onto the first two principal components

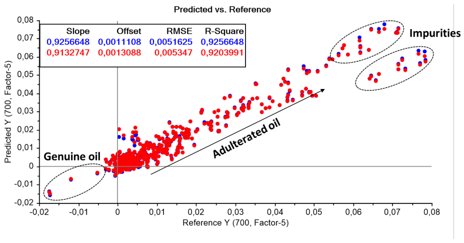

Figure 5. Partial Least Squares (PLS) derived from oil UV-Visible spectra

then the score plot shows a good two-dimensional visualization. Therefore, prediction samples were accurately classified into their corresponding groups of PC-1 and PC-2. Various genuine oils were identified as a cluster between -5 to -10 (PC-1) and -2 to +1 (PC-2), while those of adulterated oils were located between +5 to +10 (PC-1) and +2 to +7 (PC-2).

The second model of chemometrics technique used in this research was Partial Least Squares (PLS), as shown in Figure 5. The UV-Visible spectra from 220 to 920 nm wavelength of 425 samples were applied using a full cross-validation classification model. The R-square of predicted and reference samples were 0.9257 and 0.9204, respectively. The calibration model with R-square greater than 0.91 is treated to be an excellent prediction (Suhandy and Yulia, 2017). These high value of R-square, i.e., close to 1.0, confirm that the PLS model is appropriate to discriminate the genuine lubricant oil and adulterated ones. Furthermore, the value of mean squared error (RMSECV) was low enough for both predicted and reference samples, i.e. 0.0052 and 0.0053, respectively. These low values show that PLS model is not over fitting which is a good result for the purpose of this research (Sirisomboon and Posom, 2019).

Table 1 shows the application of chemometric techniques to analyze various samples that mixed with impurities. Most of the samples are organic compounds and thus HPLC, GC-MS, FT-IR and UV-Vis spectrometry were employed as an initial instrumentation part. Detected samples include pharmaceuticals, food, coffee, wine, and oil. The advantage of UV-Vis spectrometry among other methods is its simple operation procedure. Furthermore, colored samples such as oil can be easily detected using visible spectrometry. Further works will include the digital image colorimetry coupled with chemometric techniques and smartphone applications (Firdaus et al. (2019); Herrero-Latorre et al. (2019)). The most common chemometrics techniques used for organic analysis were PCR and PLS, including those of the present study. The results of present study show that both techniques, i.e., PCR and PLS, can be used as qualitative and quantitative analytical method to identify the adulteration of lubricant oils.

4. CONCLUSIONS

We have successfully discriminated genuine and adulterated oil samples using a simple and rapid method of UV-Vis spectroscopy coupled with chemometrics technique. Both model of PCA and PLS achieved good prediction to detect lubricant oil adulteration, with R-square of predicted and reference samples were 0.9257 and 0.9204, respectively. The results suggest that the proposed method is a promising alternative with a low-cost and less chemicals for assessment of lubricant oil adulteration.

5. ACKNOWLEDGEMENT

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Table 1. Application of chemometric techniques for various samples analysis

Analytical method	Chemometric model	Sample	Reference
HPLC	PCA	Pharmaceutical	(Wiberg, 2006)
	PLS	Pharmaceutical	(Chen et al., 2008)
GC-MS			(Escandar et al., 2006)
	PCA	Pharmaceutical	(Pan et al., 2011)
			(Gröger and Zimmermann, 2011)
	PLS	Metabolomics	
FT-IR	PLS	Carbonyl	(Mobaraki and Hemmateenejad, 2011)
	PCA	Food	(Foca et al., 2011)
UV-Vis spectrometry	PCR	Pharmaceutical	(Hadad et al., 2008)
	PCR	Wine	(Martelo-Vidal and Vázquez, 2014)
	PLS	Pharmaceutical	(Bhaskar et al., 2012)
	PCA, PLS	Coffee	(Souto et al., 2015)
	MLR	Pharmaceutical	(Dinç and Üstündağ, 2003)
	PCA, PLS	Olive oil	(Didham et al., 2020)
	PCA, PLS	Lubricants oil	Present study
Digital image Colorimetry	PLS	Biodiesel	(Costa et al., 2015)
			(Barbosa et al., 2017)
	LDA	Vegetable oil	(Milanez et al., 2017)

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