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Raman spectroscopic analysis to detect olive oil mixtures in argan oil

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Abstract

Adulteration of argan oil with some other cheaper oils with similar chemical compositions has resulted in increasing demands for authenticity assurance and quality control. Fast and simple analytical techniques are thus needed for authenticity analysis of high-priced argan oil. Raman spectroscopy is a potent technique and has been extensively used for quality control and safety determination for food products In this study, Raman spectroscopy in combination with a net analyte signal (NAS)-based methodology, i.e., hybrid linear analysis method developed by Goicoechea and Olivieri in 1999 (HLA/GO), was used to predict the different concentrations of olive oil (0 - 20%) added to argan oil. Raman spectra of 90 samples were collected in a spectral range of 400 - 1400 cm^{-1}, and calibration and validation sets were designed to evaluate the performance of the multivariate method. The results revealed a high coefficient of determination (R^2) value of 0.98 and a low root-mean-square error (RMSE) value of 0.41% for the calibration set, and an R^2 of 0.97 and RMSE of 0.36% for the validation set. Additionally, the figures of merit such as sensitivity, selectivity, limit of detection, and limit of quantification were used for further validation. The high R^2 and low RMSE values validate the detection ability and accuracy of the developed method and demonstrate its potential for quantitative determination of oil adulteration.

Keywords: argan oil, food adulteration, olive oil, Raman spectroscopy, spectral analysis

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Introduction

Argan oil is produced from the nuts of the argan tree which only grown in Southwestern Morocco. This tree belongs to Sapotaceae family which have eight varieties (Khallouki et al., 2005) and has successfully adapted itself to the drought and other harsh environmental conditions and has been

protected by UNESCO since 2007. Argan oil is used for many purposes such as cooking, cosmetics, and medicinal use. Edible argan oil is obtained from slightly roasted kernels, whereas cosmetic grade oil is obtained from unroasted kernels. Generally, argan oil composed of unsaturated fatty acids, particularly oleic and linoleic acids, and also rich in antioxidants such as tocopherols twice in concentration as compare to antioxidant concentration in olive oil. The presence of unique plant sterols such as spinasterol and schottenol make this oil unique; in fact, no other vegetable oils with a comparable phytosterol composition have yet been reported (Charrouf and Guillaume, 1999).

As the oil is a relatively new product to the international market that nowadays being exported only by Morocco, although different companies in Europe and North America distribute it around the globe. The unique properties of the oil create a possibility that the demand of such a product will increase globally in the near future (Cherki et al., 2006). In addition, because of the low yield production and the time-consuming and tedious oil extraction method makes it costlier than other vegetable oils (Oussama et al., 2012). Thus, considering the high-price, high demand, and low production, argan oil is susceptible to get adulterated with a range of vegetable oils (i.e., olive oil, sunflower oil, soybean oil, and some other oils) for economic gain. Thus, the quality assurance and authenticity screening of argan oil have become important for food industry and regulatory organizations.

The adulteration of high-quality oils with cheap quality is a commonly found problem either for the regulatory agencies, for the oil suppliers and mostly to the consumers. Several analytical methods such as high-performance liquid chromatography (HPLC) (El-Hamdy and El-Fizga, 1995), gas chromatography (Hilali et al., 2007), and nuclear magnetic resonance spectroscopy (Fragaki et al., 2005) have been proposed for the adulteration detection in oils. A few studies have also focused on argan oil adulteration detection using electronic nose and voltammetric electronic tongue (Bougrini et al., 2014), inductively coupled plasma optical emission spectrometry (Gonzálvez et al., 2010), and HPLC (Salghi et al., 2014). However, these methods are very sensitive and have low detection limits, but they are time-consuming, destructive and require expertise in handling instruments (Yang et al., 2015; Hong et al., 2018). Therefore, there is a need to develop a technique which will overcome all aforementioned drawbacks and provides an alternative tool for quality control and authenticity analysis of high-priced argan oil.

Spectroscopic methods that do not require such sample preparation steps and expensive chemicals have been utilized as a rapid and non-destructive method for detection of various kinds of adulterants in different varieties of oil samples (Lohumi et al., 2015). Raman spectroscopy is a form of analytical vibrational spectroscopy, which arises due to inelastic scattering of the light photons, gained a lot of attention because of its useful analytical applications (Qin et al., 2017). On the other side, near-infrared (NIR) spectroscopy is also a widely used technique for authenticity analysis of oils; however, the presence of overtones and combination bands and large numbers of possible vibrations makes NIR spectra very complex (Lim et al., 2017; Mo et al., 2017; Ning et al., 2018). In addition, the overlapping peaks which result in broadness of spectra reduces its applicability. Compared with infrared spectra, Raman spectra generally contain fewer sharper and more discrete bands that are significantly stronger and much informative. This afford Raman spectroscopy several advantages over infrared absorptions.

Owing to unique properties of Raman spectroscopy and its advantages over infrared spectroscopy, this technique in combination with chemometric methods has been widely used for quality screening and authenticity analysis of a range of oil samples. A previous study combined Raman spectroscopy with principal component analysis for the olive oil authentication from different types of oils (soybean oil, rapeseed oil, sunflower seed oil, and corn oil) (Zhang et al., 2011). In another study, quantitative adulteration of extra virgin olive oil had been done using Raman spectroscopy in combination with Bayesian framework least squares support vector machines (Dong et al., 2012). However, to the best of our knowledge, no study has

employed hybrid linear analysis (HLA) for Raman spectroscopic data analysis in particular for authenticity analysis of (oil) food products. Since the raw (unprocessed) Raman spectra typically contain irrelevant noise and therefore do not provide sufficient information about the analyte, integrating them with a multivariate data analysis method can aid the extraction of meaningful information from the resultant spectra. For this study, the net analyte signal (NAS)-based HLA methodology (Goicoechea and Olivieri, 1999) (hereby abbreviated as HLA/GO) has been used. This method combines the explicit-modeling advantage of knowing a pure spectrum with the implicit-modeling advantage of ignoring all other species, and has been found to improved prediction results as compared to partial least-squares (PLS) (Goicoechea and Olivieri, 1999; Muñoz de la Peña et al., 2002; Marsili et al., 2003; Rahman et al., 2018). Many spectroscopic studies have utilized the NAS based multivariate data analysis for determining analytes concentration in agro-food and pharmaceutical samples (Short et al., 2007; Lohumi et al., 2016).

This study aims to evaluate the potential of Raman spectroscopy for the quantitative determination of different adulteration levels of olive oil in argan oil. Spectral analysis of eight different concentrations of olive oil in argan oil (0, 1, 2, 3, 4, 5, 10, 15, and 20%) was conducted. Hence, the overall objective of this study was to use Raman spectroscopy integrated with NAS-based HLA/GO method as a rapid, non-destructive, and high-throughput technique for predicting olive oil concentration in argan oil.

Materials and Methods

Sample collection and preparation

Because of the several health benefits and medicinal properties of argan oil it attracts a relatively high price in comparison with other (vegetable) edible oils and thus susceptible for being adulterated with cheaper oils. Since argan oil is identical in color with olive oil, thus difficult to visually recognize the purity of argan oil (Rueda et al., 2014). Therefore, in order to demonstrate the potential of Raman spectroscopic technique for authenticity analysis of the argan oil, both argan oil and olive oil with ~ 100% purity were purchased from a supermarket in South Korea. Argan oil samples were spiked with olive oil to achieve the target sample concentrations 1, 2, 3, 4, 5, 10, 15, and 20% (v/v) based on previous study (Addou et al., 2016). All the samples were prepared in a total volume of 20 mL and filled in the glass vials. In order to mix the samples properly, each sample was subjected to Vortex mixing (Scientific Industries, Inc., USA) for 40 s. In addition to 8 adulterated groups, one group of pure argan oil (10 samples) was also prepared. Therefore, 10 samples from each of 9 groups, i.e., 90 samples were tested.

Raman spectroscopy

Raman spectra collection was performed using portable i-Raman spectrometer (BWTEK Inc., USA) configured with charge-coupled device (CCD) detector. For reducing the background and sample fluorescence, 785 nm was selected as the standard excitation laser. The spectra were collected separately for each sample at a wavelength range between 400 - 1500 cm^{-1} at the spectral resolution of 4 cm^{-1}. A total of 90 samples were analyzed under this study from which 50 samples used for calibration set while the remaining 40 samples used for the validation set. In order to acquire a high quality Raman spectrum, each sample underwent four successive scans and an integration time 1,000 ms was used for each scan. The averaged spectra of each sample were saved for further analysis.

Data analysis

In general, spectral data contains random noise and spectral variations generated by the instrument and sample itself, thus the appropriate data preprocessing is required before subjecting it to multivariate analysis. Data pre-processing thus plays a very important role to mitigate the unwanted effects, such as light scattering, instrumental drift etc. in order to provide good prediction accuracy (Rinnan et al., 2009). In this study, standard normal variate (SNV) pre-processing method was utilized for the spectral analysis of samples. This method is widely used for scattering correction in a way by removing slope variation from the spectra caused by scattering and change in the particle size. The general formula used for carrying out SNV transformation is given below.

$$x_{\mathrm{corr}} = \frac{\mathrm{x_{org}} - \mathrm{a_0}}{\mathrm{a_1}} \quad (1)$$

Here, a_0 indicates the average value of the sample spectrum to be corrected, a_1 is the standard deviation of the sample spectrum (Rinnan et al., 2009).

The preprocessed spectral data were then subjected to multivariate analysis method of HLA/GO to predict the added olive oil concentrations in argan oil. The general concept of NAS bases HLA/GO method put forth by Lorber (1986), defined as the part of the spectrum which is orthogonal to the spectra of other components. In this work, we adopted the method described by Goicoechea and Olivieri (1999) and Marsili et al. (2003) in order to calculate the NAS vector of each sample. Fig. 1 emphasize the NAS concept through the vector projection. In order to understand the procedure, a pure target analyte spectrum and background spectra is collected which consist of all sorts of variances except the target analyte (Bai, 2010). NAS concept allows the calculation of various figures of merits (FOMs) of the multivariate calibration method, and the resulted values of FOMs are generally used to express the effectiveness of the developed technique, and to compare the performance of two different models. Hence, under multivariate calibration, various FOMs namely selectivity (SEL), sensitivity (SEN), limit of detection (LOD), and limit of quantification (LOQ) were calculated (Lorber, 1986; Lorber et al., 1997).

SEL evaluates the degree of overlap between the analyte signal and interferences, thus indicating the part of the signal which was lost in the overlap. An SEL value of 0 implies complete overlap, whereas an SEL value of 1 indicates no overlap. In NAS

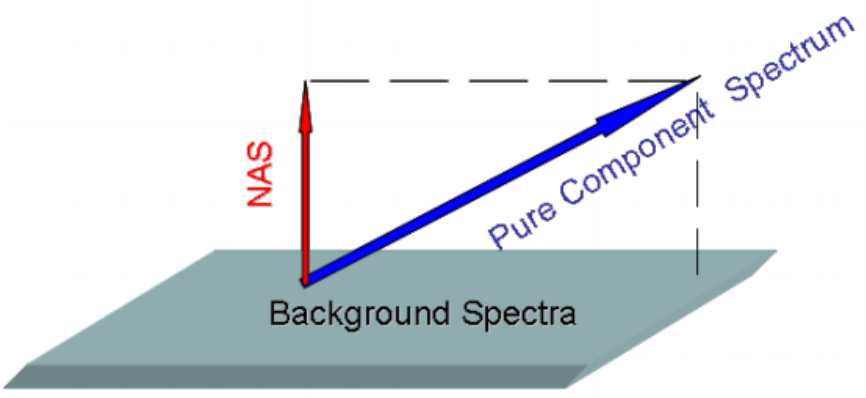

Fig. 1. A depiction of net analyte signal (NAS) projection in a 3 dimensional space (Bai, 2010).

algorithm, the selectivity of a NAS calibration model is estimated from equation (2):

$$SEL = \frac{\| r^* \|}{\| r \|} \tag{2}$$

Here, r^* is the NAS vector and r is the sample spectrum. While SEN value is helpful for estimating the extent of variation in the signal caused due to a change in analyte concentration (Lorber, 1986). In multivariate calibration, SEN can be estimated from equation (3):

$$SEN = \frac{1}{\| b_k \|} \tag{3}$$

Here, b_k is the vector of the final regression coefficients appropriate for component k. Further, LOD can be defined as the lowest analyte concentration that can be distinguished from a sample without analyte and is a useful indicator of model availability, while LOQ is the point at which the difference between two concentration values can be calculated (Lohumi et al., 2017). In the NAS algorithm, LOD and LOQ can be estimated from equation (4) and (5):

$$LOD = 3\| \epsilon \| \| b_k \| \tag{4}$$

$$LOD = 10\| \epsilon \| \| b_k \| \tag{5}$$

Here, $\| \epsilon \|$ is a measure of instrumental noise. $\| \epsilon \|$ can be calculated by collecting several spectra for blank samples and calculating the NAS norm and corresponding standard deviation for each sample.

In addition to the FOMs, various other parameters important for the evaluation of model performance, viz. the coefficients of determination for calibration (R_C^2), cross- validation (R_{CV}^2) and prediction (R_P^2), root- mean- square errors of calibration (RMSEC) and prediction (RMSEP), ratio of standard error of performance to standard deviation (RPD), and range error ration (RER) were used. The R^2 value is important for evaluating the proportion of variability explained by the developed model. The value of R^2 generally ranges from 0 to 1, and a value close to 1 indicates a good fit of the model. RMSE, another frequently used parameter is a measure of the difference between values predicted by a model and the values actually observed from the environment being modelled. It plays a key role in evaluating the model performance in regression analysis. The RPD and RER are generally used to evaluate the performance of each model and further measure the goodness of fit. The values of statistical parameters mentioned above in the text were determined by the following equations mentioned below:

$$R^2 = 1 - \frac{\sum_{i=1}^{Z} (y_i - \hat{y}_i)^2}{\sum_{i=1}^{Z} (y_i - \bar{y}_i)^2} \tag{6}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{Z} (y_i - \hat{y}_i)^2}{z}} \tag{7}$$

$$RER = \frac{y_{max} - y_{min}}{RMSEP} \tag{8}$$

$$RPD = \frac{SD}{RMSEP} \tag{9}$$

In the above equations, z indicates the number of samples, y_i and $\hat{y}_i$ are the true and the predicted values for the i^{th} sample, respectively, y_{max} and y_{min} correspond to the maximum and minimum reference values for data in the validation set, and SD represents the standard deviation of values obtained in reference analysis. All calculations and data analysis were carried out using MATLAB version 7.0.4 (Math Works, Inc., MA, USA).

Results and Discussions

Spectral Interpretation

The SNV preprocessed Raman spectra of pure and olive oil adulterated argan oil sample shown in Fig. 2. SNV preprocessing was applied for extracting spectral information through the spectra. The spectral region from 400 - 1500 cm^{-1} is only selected f or developing the model due to the presence of the peaks related to olive oil concentration in argan oil, while rest of region from 1504 - 1800 cm^{-1} was not considered in this study due to no relevant information in this spectral region. The peak obtained in the region at 1380 cm^{-1} is related to CH_3 group while region from 1400 - 1470 cm^{-1} is sensitive to CH_3 asymmetric vibration. As evident in Fig. 2, the minor differences between the Raman spectra of the two oils only occur in certain spectral regions which makes it difficult to differentiate the pure and adulterated spectra by merely looking at the specific peaks. Hence, the use of multivariate calibration methods is necessary to achieve superior analytical performance and make a clear quantitative analysis.

Therefore, the HLA/GO multivariate calibration method was then used to model the additional mixing of olive oil concentration in argan oil from the SNV preprocessed Raman spectra within the spectral range of 400 - 1500 cm^{-1} In order to avoid over-fitting problems by selecting optimum number of factors, a leave-one-out cross validation method was used and thus a total number of four factors were selected based on the lowest RMSE cross validation.

Fig. 3a shows the Raman spectra of pure olive oil and mean of calculated NAS vector for each group of concentration in the validation data set are shown in Fig. 3b. As seen, the NAS vector for the pure argan oil is almost flat with no spectral peaks observed. However, NAS vector for 1% adulterated argan oil shows minor peaks in the spectral regions where the pure olive oil (Fig. 3a) shows more extreme peaks. Moreover, at higher concentrations (20%), there change in intensity of the NAS vector

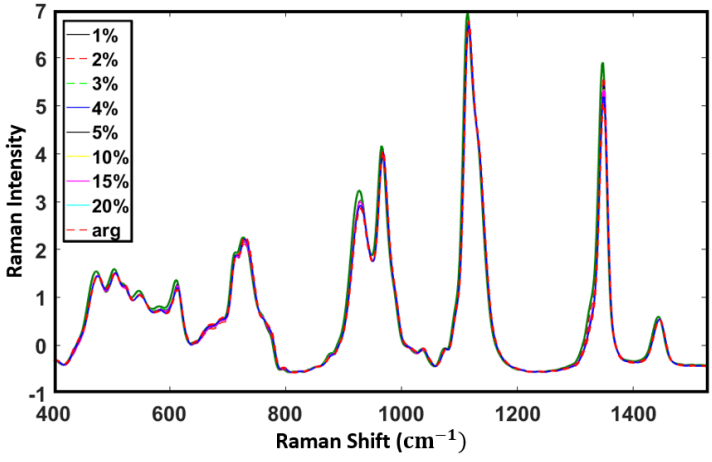

Fig. 2. Raman preprocessed spectra using standard normal variate (SNV) preprocessing method within spectral range of 400 - 1500 cm^{-1} for eight different concentrations of olive oil in argan oil.

is proportional to the concentration of the analyte. The NAS regression plot shown in Fig. 3c was constructed by plotting the elements of r* (NAS spectrum) as a function of elements of s* (sensitivity vector) and the NAS regression plot illustrates a linear behavior for this following dataset.

The performance of the developed model was further assessed using the coefficient of determination (R^2) and root mean square error (RMSE). Fig. 4 shows the original olive oil concentrations and the values predicted by the HLA/GO model for the argan oil samples, showing excellent agreement between original and predicted values. This is a measure of how close the data

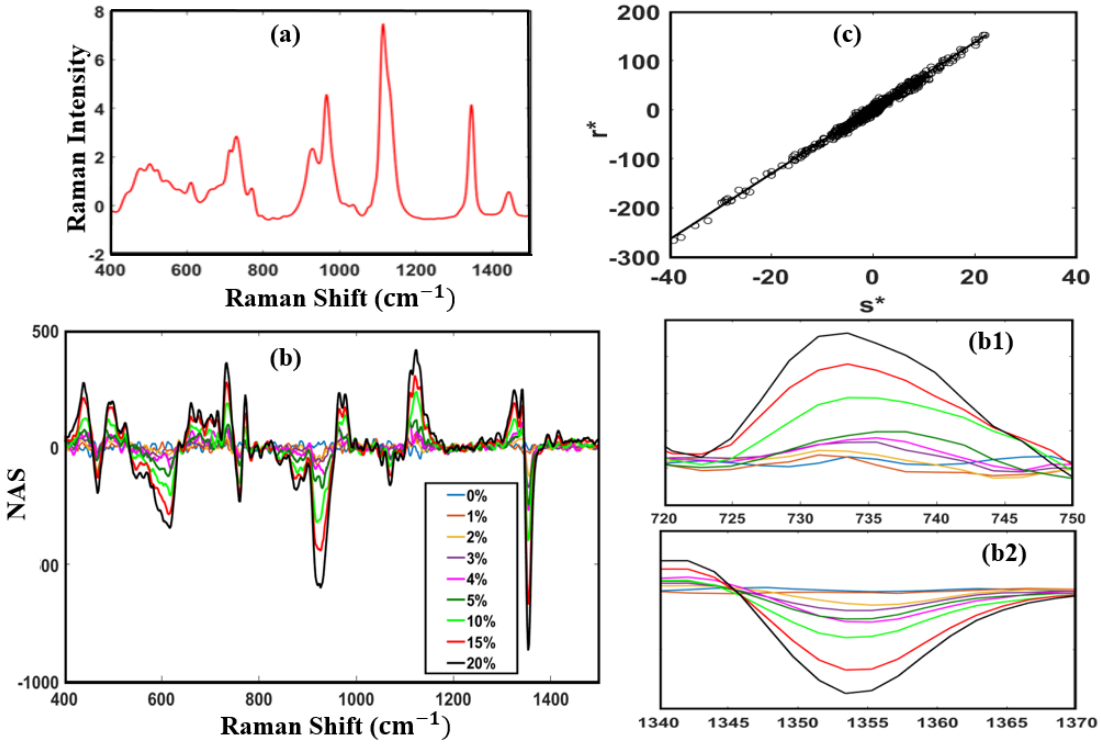

Fig. 3. Raman spectra of pure olive oil (a), mean of calculated net analyte signal (NAS) vectors for each olive oil concentration in validation set (b), and NAS regression plot (c). Here (b1) and (b2) are the expanded spectral regions of (b).

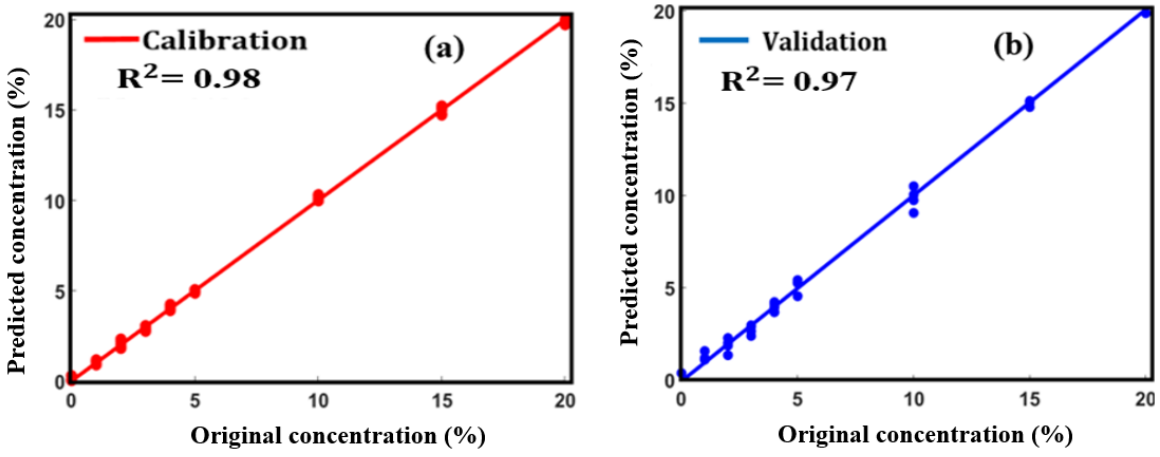

Fig. 4. HLA/GO based regression plots for actual versus predicted concentrations of olive oil in argan oil for the calibration (a) and validation sets (b).

points are to the regression line. If the value of coefficient of determination (R^2) is 1, it is a perfect fit and the line accurately describes the data. If the value obtain for R^2 is 0, indicates no linear correlation, and the straight line does not describe the data at all. In this study, a total of 50 samples were used for calibration set, while 40 samples were used for the validation set to e valuate the performance of developed model. Fig. 4a and 4b shows the obtained regression plots for calibration and validation sets, respectively. The calibration model gave a very good R^2 value of 0.98 with a low value of root mean square error of calibration (RMSEC) of 0.41%, whereas R^2 and root mean square error of validation (RMSEV) values for the validation set were 0.97 and 0.36%, respectively. The obtained results demonstrated that the combination of Raman spectroscopy with HLA/GO-based multivariate calibration model is a strong analytical tool for determining olive oil concentration in adulterated argan oil.

Fig. 5 presents the beta-coefficient plot from the HLA/GO model. The plot is generally useful for locating wavebands that contain valuable information about chemical features. In a simple linear regression, this is the slope of the regression line,

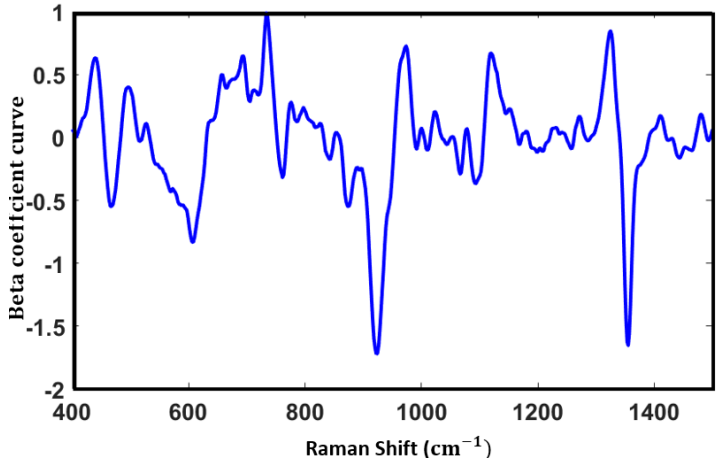

Fig. 5. Beta coefficient plot derived from HLA/GO model developed for prediction of olive oil concentration in argan oil.

Table 1. Statistical parameters and FOM obtained using the HLA/GO model.

Multivariate calibration model	
Parameters	Values
R_C^2	0.98
R_V^2	0.97
RMSEC	0.41%
RMSEV	0.36%
RER	21.08
RPD	7.84
SEN	0.04
SEL	0.01
LOD	0.354%
LOQ	1.181%

FOM, figures of merit; HLA/GO, hybrid linear analysis methodology developed by Goicoechea and Olivieri in 1999; R_C^2, coefficients of determination for calibration; R_V^2, coefficients of determination for validation; RMSEC, root- mean- square errors of calibration; RMSEV, root- mean- square errors of validation; RER, range error ration; RPD, ration of standard error of performance to standard deviation; SEN, selectivity; SEL, sensitivity; LOD, limit of detection; LOQ, limit of quantification.

whereas, in a multiple linear regression, this is the slope of the (hyper) plane in the direction of the predictor. This means that the value of the beta coefficient indicates the extent of change in the predicted value when the corresponding predictor is increased by 1 unit, keeping all other predictors constant. The higher the beta value, the greater is the difference between the groups (Okparanma and Mouazen, 2013). As the plot shows similar peaks in the spectral range which is sensitive to olive as shown in Fig. 3a. Thus, the beta coefficient obtained from the HLA/GO method is attributable to the variation of olive oil concentration in argan oil samples.

The FOM are important parameters to evaluate the model performance. Thus, the calculated FOM, includes SEL, SEN, LOD, and LOQ, for the HLA/GO method for the olive oil concentration in argan oil samples are summarized in Table 1. Further, the values obtained for RER and the RPD which were considered as key factors for measuring the precision and accuracy of the prediction, were used to evaluate the performance of the model. Values for RER below 3 indicates that a model has a practical utility while values above 3 for RER are limited to good practical utility (Williams and Norris, 2001). The value for the RPD considered for prediction accuracy. If the value is above 3, the prediction is classified as excellent. Thus, the calculated RER of 21.08 and RPD value of 7.84 shows that the model was well developed for determining olive oil concentration in argan oil samples. Moreover, the present research demonstrated a lower RMSEV of 0.36% compared with previous study done using fluorescence spectroscopy with an error of 1.15% for the detection of argan oil adulteration (Addou et al., 2016). In addition, the LOD and LOQ values of 0.354% and 1.181% are reasonable which suggested that the technique used in this study can be further adopted for the detection of low adulterant concentration present in the oils. Hence the present work provides an assurance for quality control and authenticity analysis of argan oil than the other previously mentioned conventional methods which are time consuming and destructive in nature.

Conclusion

Raman spectroscopy was combined with the HLA/GO multivariate analysis method to develop a powerful analytical t echnique for monitoring argan oil purity by quantitatively determining olive oil adulterants. All the datasets were pretreated within the spectral ranges from 400 - 1500 cm^{-1} using SNV preprocessing method. The calibration and validation models developed through the HLA/GO analysis showed an excellent accuracy of $R_C^2 = 0.98$ and $R_V^2 = 0.97$ and low RMSEC of 0.41% and RMSEV of 0.36% for eight different concentrations of olive oil in argan oil. Compared to other aforementioned techniques, the proposed method which requires minimum sample preparation, provides a fast, accurate and convenient alternative for the quantitative determination of olive oil concentration in argan oil. Thus, the prediction results demonstrate that it is feasible to build a HLA/GO model for predicting adulteration in argan oil. In future work, this study will be expanded to other varieties of oils and their mixtures and it is likely that the developed method will give acceptable results and also we will try to determine the lowest concentration of adulterant oil that can be detected using this study.

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