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Original Article

AUTHENTICATION OF GRAPE SEED FACE OIL USING FTIR SPECTROSCOPY COMBINED WITH CHEMOMETRICS TECHNIQUES

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ABSTRACT

Objective: This research aims to authenticate grape seed oil products using FTIR spectroscopy combined with chemometric methods.

Methods: In the initial stage, exploratory data analysis was carried out by applying the main components with the Principal Component Analysis (PCA) model. Second derivative spectra resulting from preprocessing of the original spectra are used to create multivariate Principal Component Regression (PCR) and Partial Least Squares (PLS) calibration models. The second derivative spectra of Grape Seed Oil (GO), Olive Oil (OO), and the binary mixture GO+OO are utilized to generate a sparse partial least squares-discriminant analysis (SPLS-DA) model.

Results: The PCA model was successfully obtained with visualization that depicted a total of 93.8% in the first and second dimensions. Multivariate calibration produced the best model in PLS with second derivative spectra for both GO and OO. PLS model for GO resulted the value of R_{cal}^2, R_{CV}^2, R_{val}^2, RMSEC, RMSECV, and RMSEP of 0.998, 0.992, 0.982, 0.700, 1.557, and 2.331, respectively. The SPLS-DA model was successfully built and discriminated with AUC-ROC values of 1.000, 1.000, and 0.994 for GO, OO, and GO+OO, respectively.

Conclusion: Authentication of grape seed face oil can be undertaken using FTIR spectroscopic methods and chemometric techniques, which can produce high sensitivity and specificity values.

Keywords: Grape seed oil, Face oil, Adulteration, FTIR spectroscopy, Chemometrics

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INTRODUCTION

The high demand for cosmetic products for both men and women provides opportunities for the cosmetic industry in Indonesia [1–3]. Modern cosmetics are reported to contain harmful chemicals and have ecological impacts on the environment [4]. With growing awareness, consumers tend to prefer natural products [5–8]. One of the most needed cosmetic products for both teenagers and adults is skincare, especially facial skincare [9]. One type of facial skincare is face oil, aimed at moisturizing and smoothing. One widely used type of face oil is grape seed oil.

Grape seed oil contains antioxidants that are beneficial for skin care. The antioxidants contained in it are vitamin E and Oligomeric Proanthocyanidins (OPC) [10]. In the previous research, grape seeds were reported to contain 8-20% oil in the dry state [11]. Grape seed oil has a high vitamin E content, ranging from 1 to 53 mg per 100 g of oil, which is higher than olive oil [10]. Even though grape seed oil has greater economic value than other oils, they appear to share many similar physical characteristics. Currently, research on grape seed oil to detect whether the grape seed extract is adulterated or not is still lacking. Therefore, it is very significant to develop a simple and fast method for the detection of grape seed oil adulteration [12].

In previous related research, analysis of sunflower oil in a ternary mixture with grape seed oil and candlenut oil in a mixed system using FTIR spectroscopy and chemometrics was successfully carried out [13]. However, research that applies the FTIR spectroscopy method combined with chemometric techniques on grape seed face oil has never been carried out. This research aims to authenticate grape seed oil products using FTIR spectroscopy combined with chemometric methods. The undertaken chemometric techniques include Principal Components Analysis (PCA), Partial Least Squares (PLS), and Partial Least Squares Discriminant Analysis (PLS-DA).

MATERIALS AND METHODS

Materials

Grape Seed Oil (GO) and Olive Oil (OO) are obtained from distributors in Indonesia, with a Certificate of Analysis to verify and prove their authenticity.

Tools and software

In this research, a complete instrument was used with Thermo Nicolet iS10 Thermo Scientific FT-IR spectrophotometer, Socorex® Micropipette with sizes of 20-200 µl and 100-1000 µl and a Globolab measuring cup, the results of the FTIR spectrum data were exported to Excel 2019 software (Microsoft Inc., USA) and saved as a. csv file before being analyzed using statistical software R Version 4.3.2.

Methods

Methods used in this study were developed according to the previous study from Riswanto *et al.* (2023) [14] with several modifications. In this research, chemometrics techniques were implemented to authenticate grape seed face oil from olive oil as adulterant.

Calibration and validation sample preparation

Calibration and validation solution test samples containing grape seed oil and olive oil were made from a mixture of the two ingredients with a concentration range of 0-100% (v/v) to obtain 15 variations of the concentration of the calibration solution and 30 variations of the concentration of the validation solution.

Sample preparation for discrimination

The solution for PLS-DA analysis is available in three different samples, namely grape seed oil, olive oil, and a binary mixture that contains grape seed oil and olive oil with a range of concentration 0-100% (v/v). Eight pure grape seed oil solutions, eight pure olive oil solutions, and forty-three solutions containing grape seed oil and olive oil were obtained and labelled to create a discrimination analysis model.

FTIR spectra acquisition

FTIR spectra acquisition was carried out using an FTIR spectrophotometer in which samples of pure grape seed oil, pure olive oil, and the binary mixed of grape seed oil were placed on the ATR crystal and then measured in the mid-infrared area (4000-600 cm^{-1}). FTIR spectra used absorbance mode on the resolution of 8 cm^{-1} with a number of scans of 32. Air (blank) spectra measurements were applied before each sample measurement as the background spectra. Each sample was measured using three replications. The cleaning of ATR crystals was done using ethanol after each sample measurement.

Exploratory data analysis using the PCA method

The FTIR spectra obtained from the data acquisition stage were then evaluated [15]. The dominant peaks of the analysis, namely grape seed oil, olive oil, and a mixture of samples containing grape seed oil and olive oil, were used to construct the PCA model. Scree plots, variable plots and individual plots are displayed to visualize the constructed model.

Multivariate calibration analysis

The PLS multivariate calibration model produced predictive models for the two oils. The performance of the multivariate calibration model was examined by evaluating statistical parameters, including coefficients of determination for calibration (R_{cal}^2), cross-validation (R_{CV}^2), validation (R_{val}^2), root mean square error of calibration (RMSEC), root mean square error of cross-validation (RMSECV) and root mean square error of prediction (RMSEP). The cross-validation process, as an internal validation, applies the leave-one-out technique. The selected multivariate calibration model for each oil was determined by evaluating R_{cal}^2, R_{CV}^2, R_{val}^2, RMSEC, RMSECV, and RMSEP [16].

Construction of the PLS-DA model

The PLS-DA model utilized the FTIR spectrum of grape seed oil, olive oil, and a mixture of samples containing grape seed oil and olive oil. Background prediction and 3D individual plots visualized the discrimination model. Evaluation of model performance applied Area Under Curve-Receiver Operating Characteristics (AUC-ROC). Optimization of this model was further carried out by selecting output variables until the final result was obtained considering the error rate in classification and feature selection.

RESULTS

This research develops a rapid detection technique for counterfeiting grape seed face oil using the Fourier Transform Infrared (FTIR) spectroscopy method combined with chemometric techniques. The FTIR spectroscopy method combined with chemometrics was chosen in this research because this analysis requires minimal material preparation, is easy, and fast [17, 18].

The infrared spectrum characteristics of samples in the range of 4000-600 cm^{-1} area produce 12 dominant peaks for grape seed oil, olive oil and mixtures, namely at 2970, 2947, 2922, 2912, 1743, 1653, 1462, 1376, 1238, 1160, 1099, and 718 cm^{-1} (fig. 1).

Exploratory data analysis using PCA

Principal Component Analysis (PCA) is a data processing technique to construct linear multivariate models from complex data sets [19]. PCA facilitates visualization of data groupings, initial evaluation of similarities between groups or classes, and finding factors or reasons behind observed patterns through correlation by considering chemical or chemical-physics properties [20]. The processing of data from an analytical instrument using an FTIR spectrophotometer with a range of 4000-600 cm^{-1} with a resolution of 8 cm^{-1} produces the absorbance of twelve main peaks; this data then produces a PCA model (fig. 2).

Multivariate calibration analysis

In this research, a multivariate calibration is developed using PCR and PLS techniques; these two techniques are used to predict GO and OO content and to obtain the best prediction model in various spectral modes (table 1). Absorption data at each wave number in the range of 4000-600 cm^{-1} is further processed through a preprocessing stage in order to produce the original spectrum, first derivative, second derivative, standard normal variate (SNV), and savitzky golay (SG). Plot of grape seed oil and olive oil predictions resulting from the best calibration model were presented in fig. 3.

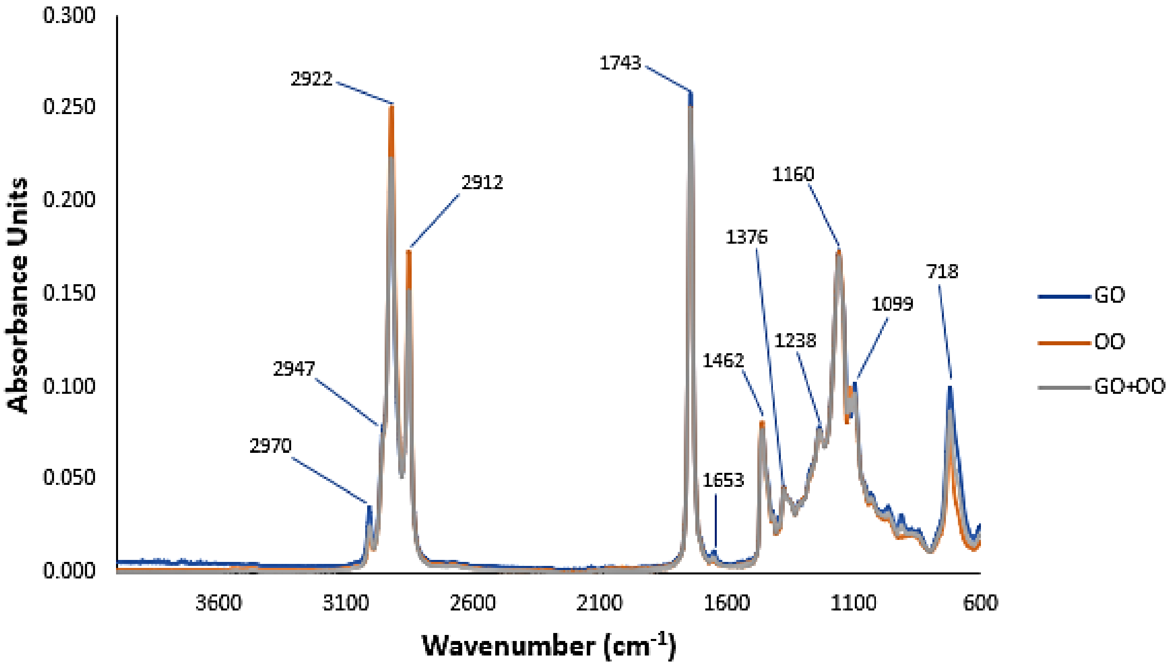

Fig. 1: FTIR spectra of GO (Grape seed Oil), OO (Olive Oil), and GO+OO (Grape seed Oil+Olive Oil)

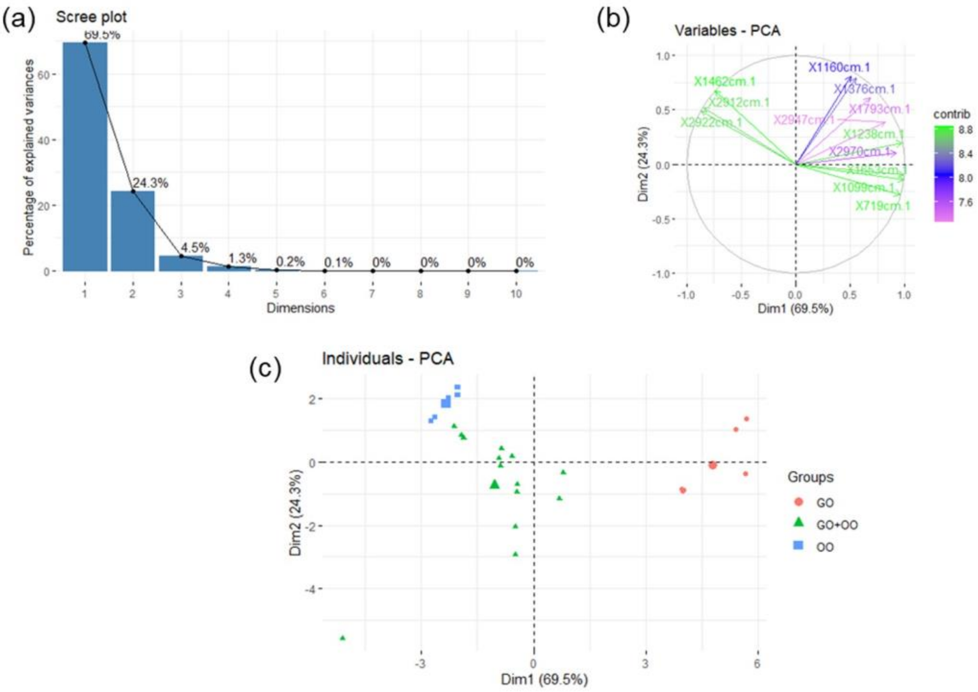

Fig. 2: Results of principal component analysis of the original spectra with 12 selected wavenumbers in the form of scree plot (a), variable plot (b), and individual plot (c)

Table 1: PCR and PLS models to predict the content of mixtures containing grape seed oil and olive oil

Oils	Multivariate calibration	Type of spectra	Number of components	R_{cal}^2	RMSEC	R_{CV}^2	RMSECV	R_{val}^2	RMSEP
Grape seed oil	PCR	Original	8	0.995	1.175	0.990	1.762	0.984	2.169
		First derivative	5	0.995	1.197	0.993	1.410	0.982	2.311
		Second derivative	7	0.995	1.178	0.992	1.559	0.976	2.660
		SNV	2	0.993	1.431	0.991	1.657	0.966	3.191
		SG	8	0.995	1.180	0.989	1.771	0.984	2.159
	PLS	Original	4	0.994	1.317	0.989	1.785	0.977	2.603
		First derivative	3	0.996	1.088	0.994	1.383	0.982	2.342
		Second derivative	**5**	**0.998**	**0.700**	**0.992**	**1.557**	**0.982**	**2.331**
		SNV	2	0.994	1.397	0.991	1.644	0.967	3.127
		SG	4	0.994	1.320	0.989	1.788	0.978	2.591
Olive oil	PCR	Original	8	0.995	1.175	0.990	1.762	0.984	2.169
		First derivative	5	0.995	1.197	0.993	1.410	0.982	2.311
		Second derivative	7	0.995	1.178	0.992	1.559	0.976	2.660
		SNV	2	0.993	1.431	0.991	1.657	0.966	3.191
		SG	8	0.995	1.180	0.989	1.771	0.984	2.159
	PLS	Original	4	0.994	1.317	0.989	1.785	0.977	2.603
		First derivative	3	0.996	1.088	0.994	1.383	0.982	2.341
		Second derivative	**5**	**0.998**	**0.700**	**0.992**	**1.557**	**0.982**	**2.331**
		SNV	2	0.994	1.397	0.991	1.644	0.967	3.127
		SG	4	0.994	1.320	0.989	1.788	0.978	2.591

Note: Selected model of calibration for each material were marked with bold. PCR: Principal Component Regression; PLS: Partial Least Squares; SNV: Standard Normal Variate; SG: Savitzky-Golay smoothing with polynomial order of 3 and window width of 11 points.

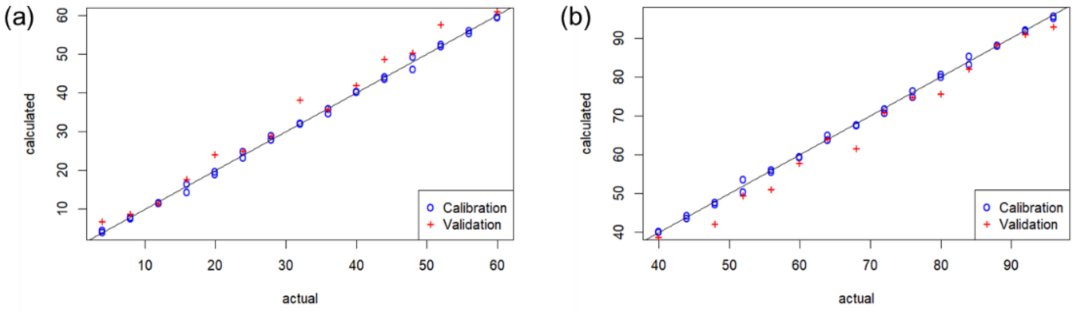

Fig. 3: Plot of grape seed oil (a) and olive oil (b) predictions resulting from the best calibration model

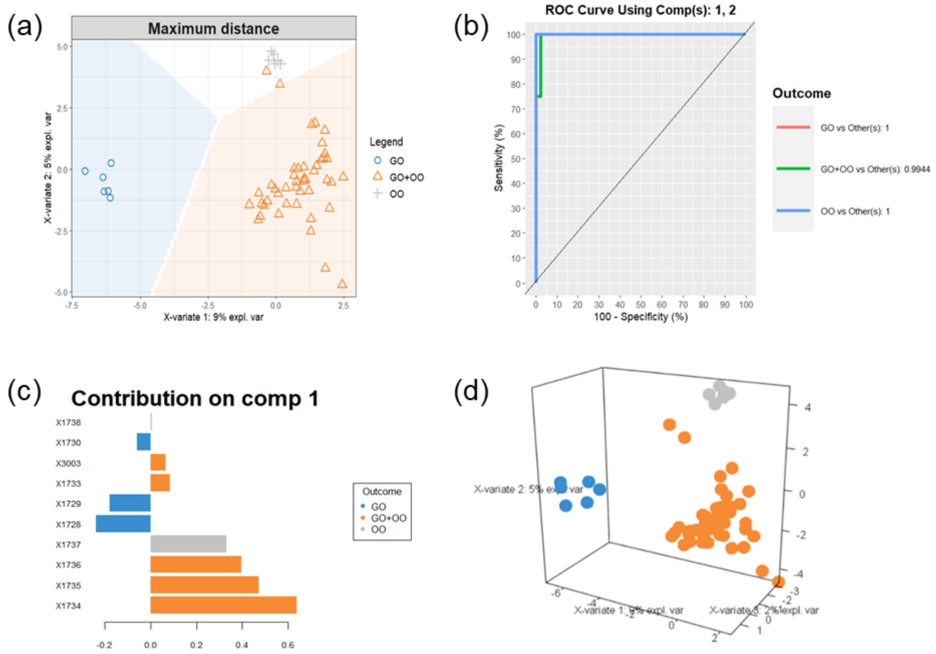

Fig. 4: Output of sPLS-DA processing for grape seed oil authentication, including background prediction plot (a), AUC-ROC plot (b), contribution plot (c), and 3D individual plot (d)

Sample discrimination using sPLS-DA

Sparse Partial Least Squares Discriminant Analysis (sPLS-DA) is a development of Sparse Partial Least Squares (sPLS) regression, which is applied for classification and discrimination purposes [21]. sPLS-DA, which is developed for second derivative spectra accompanied by graphical visualization (fig. 4), is stated to be more effective for the authentication technique in this research [14].

DISCUSSION

The FTIR spectrum of the three oils appears quite similar. However, careful examination of the FTIR spectrum of the sample shows several differences in the peak profile in the area 1743-718 cm^{-1}: OO has a dominant peak at 1160 cm^{-1} while GO has a dominant peak at 1743 cm^{-1}, which marks pulling vibration (stretching vibration) of the carbonyl group (C=O) [22]. The absorption intensity at 2922 and 1743 cm^{-1} is related to the presence of ester groups and aliphatic chains found in triglycerides [10]. Other areas at 1376, 1160, and 1099 cm^{-1} are related to bending and stretching vibrations by the –C-H,-C-O,-CH$_2$-, and-CH$_3$ functional groups in fatty acids [23]. This frequency area was further optimized to measure GO levels in OO with the help of multivariate calibration [24].

The main component analysis (fig. 2) used from the original spectrum is presented in the data Scree Plot, Variable Plot, and Individual Plot of the PCA model. Scree plots are used in visual assessments that show how much variation each component or dimension has; variable plots are useful in evaluating the constructing variables of the main components through the angles formed between vectors, while individual plots show individual positioning of data on a two-dimensional display for the first two components [9].

In the fig. 2, the individual plot produces the separation of pure GO, OO, and GO+OO oils. The total variance generated to create a two-dimensional PCA model is 93.8%, which is obtained from Dim1 (69.5%) and Dim2 (24.3%). Since the spectral data were obtained from twelve main peaks to construct the PCA, it is interesting to evaluate the contribution of each original variable. The variable plot shows the load of each variable, as well as its contribution profile. The absorbance numbers at 1743, 1653, 1238, 1099 and 718 cm^{-1} are the main contributors in the construction of the PCA model. In conclusion, the vibrational bands in these areas provide specific fingerprint properties for GO and OO. The vibration bands close to 1653 and 1099 cm^{-1} are generated from the GO content. Meanwhile, the OO content contributes to the existence of bands close to 1099 and 718 cm^{-1}.

The selected spectrum type is the second derivative spectrum in the PLS model for both GO and OO. In table 1, it can be seen that for R_{cal2}, the value is high, while for RMSEC, the value is low; this indicates that FTIR spectroscopy combined with the PLS method is precise and accurate for GO and OO quantities [25].

The prediction model generated from a training data set refers to the calibration model in chemometrics. R_{cal2} and RMSEC values are determined to evaluate this model. The performance of cross-validation as internal validation of the training data set is reviewed using the leave-one-out technique. The R_{CV}^2 and RMSECV values indicate the quality of the model developed when the internal validation model is applied. Considering that the construction of the external validation model comes from an independent data set or test data set, the model's predictive ability is verified quantitatively through the R_{val}^2 and RMSEP values (fig. 3).

The sPLS-DA model on the background prediction plot provides visualization and discrimination markers for each group. The sample categorization classification is developed using the maximum distance approach model [26]. For the GO, OO, and GO+OO samples, the AUC-ROC plot provides an illustration of the ability of the sPLS-DA model to discriminate. The AUC curve represents the degree of model separation, while the ROC curve represents the probability of discrimination model. GO and OO are separated into another class because the model results show a value of 1 or 100%, while the value for GO+OO is 0.994. These results indicate that the chance of the sPLS-DA model to differentiate GO+OO from the others is 99.4%. The contribution plot presents the contribution of each real variable to constructing the components of the discrimination model. The constructor of the sPLS-DA model with the highest contribution values for GO, OO and GO+OO were 1728, 1737 and 1734 cm^{-1}, respectively. The variable with the highest contribution is produced from a narrow band above 1700 cm^{-1}; in other words, the stretching vibration of the carbonyl group can be characterized in this area [27].

CONCLUSION

This research developed a rapid detection technique for counterfeiting grape seed face oil using the Fourier Transform Infrared (FTIR) spectroscopy method combined with chemometric techniques. Exploratory data analysis was carried out using the PCA technique, followed by constructing a multivariate calibration model using PLS and PCR, as well as the discrimination using sPLS-DA. The best multivariate calibration model was obtained from second derivative spectra processed using PLS for both GO and OO. The SPLS-DA model was successfully constructed and discriminated with AUC-ROC values of 1.000, 1.000, and 0.994 for GO, OO, and GO+OO, respectively.

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AUTHORS CONTRIBUTIONS

A. P. conducted all sample preparation, chemometrics techniques development, data interpretation and initiated the original draft of the manuscript. W. A. and A. W. carried out the data acquisition using FTIR spectroscopy. E. P. I. and F. D. O. R conceptualized the research project. F. D. O. R reviewed and edited the manuscript. All authors have approved the final version of the manuscript.

CONFLICTS OF INTERESTS

All authors have none to declare

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