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Application of Fourier transform infrared (FT-IR) spectroscopy combined with chemometrics for authentication of cod-liver oil

Abdul Rohman[a,b], Yaakob B. Che Man[a,c,*]

[a] Laboratory of Analysis and Authentication, Halal Products Research Institute, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia
[b] Laboratory of Analytical Chemistry, Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Gadjah Mada University, Yogyakarta 55281, Indonesia
[c] Department of Food Technology, Faculty of Food Science and Technology, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia

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ABSTRACT

Some vegetable oils such as canola (CaO), corn (CO), soybean (SO), and walnut (WO) oils have similar color with cod liver oil (CLO), therefore, the presence of these oils was difficult to detect using naked eye. For this reason, Fourier transform infrared (FTIR) spectroscopy using horizontal attenuated total reflectance (HATR) as sampling accessory and in the combination with chemometrics was developed for detection and quantification of these vegetable oils as adulterants in CLO. The quantification of vegetable oils was carried out by using multivariate calibrations of partial least squares (PLS) and principle component regression (PCR), while the classification between pure CLO and CLOs adulterated with CaO, CO, SO, and WO was performed using discriminant analysis (DA). PLS with FTIR normal spectra was more suitable compared with PCR for quantification purposes with coefficient of determination (R^2) higher than 0.99 and root mean square error of calibration (RMSEC) in the range of 0.04–0.82% (v/v). The PLS model was further used to predict the levels of these vegetable oils in independent samples for validation/prediction purpose. The root mean square error of prediction (RMSEP) values obtained were of 1.75% (v/v) (CaO), 1.39% (v/v) (CO), 1.35% (v/v) (SO), and 1.37% (v/v) (WO), respectively. The classification using DA revealed that the developed method can classify CLO and that mixed with these vegetable oils using 9 principal components.

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1. Introduction

In the last decades, cod-liver oil (CLO) has received great interest because of its nutritional supplements and has long been marketed as a source of vitamins A, D, and long-chain omega-3 fatty acids of *cis*-5,8,11,14,17-eicosapentaenoic (EPA) and *cis*-4,7,10,13,16,19-docosahexaenoic (DHA) acids [1–3]. The epidemiological studies revealed that there is an inverse relationship between high fish oil consumption and low mortality following coronary heart disease or breast cancer [4]. Animals fed with CLO demonstrated reduced body weights [5]. The daily use of CLO was also associated with reduced risk of death in patients with solid tumor and lung cancer [6]. Due to its high price value in the market, CLO can be a target of adulteration with the low price oils like some vegetable oils in order to gain economical profit.

The adulteration is a serious problem in trade of fats and oils for a long time, because there is a great difference in price for different oil products. The adulteration is increasingly more difficult to detect when the oil adulterant has similar chemical composition to the authentic oil [7,8]. Because of its ability to serve as a "fingerprint technique", IR spectroscopy can be taken into account as an ideal instrumental method for the authenticity studies of edible fats and oils. The presence of various spectroscopic sampling techniques such as attenuated total reflectance (ATR) and chemometric data evaluation software allows fast and reliable technique for authentication study of CLO [9,10].

FTIR spectroscopy was typically combined with multivariate calibration approaches to analyze the level of adulterants [11]. The two most common multivariate calibrations used for quantitative analysis are partial least squares (PLS) and principal component regression (PCR). PLS calibration works with the information obtained from the whole spectra to develop the regression equation between FTIR spectra (independent variables) and concentration of analytes of interest (dependent variable). Meanwhile, PCR performs multiple inverse regressions of the predictor variables against the scores rather than the original data [12,13].

We have developed an FTIR spectroscopy method combined with PLS and discriminant analysis (DA) to analyze the presence of lard as adulterant in CLO [14]. The present study highlights the application of FTIR spectroscopy for quantification of selected veg-

* Corresponding author at: Laboratory of Analysis and Authentication, Halal Products Research Institute, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia.
E-mail address: yaakobcm@gmail.com (Y.B. Che Man).

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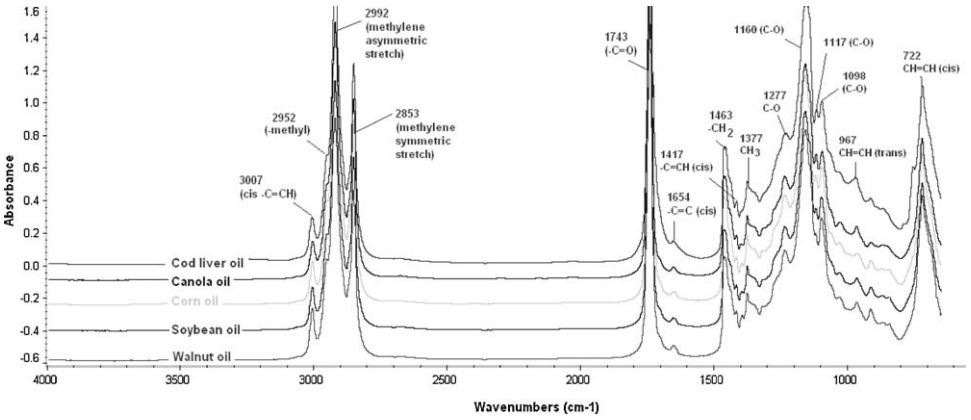

Fig. 1. FTIR spectra of cod-liver oil and some vegetable oils at wavenumber 4000–650 cm^{-1}.

etable oils as oil adulterants in CLO using multivariate calibration (PLS and PCR). Further analysis is carried out to distinguish CLO and that adulterated with these vegetable oils using DA based on Mahalanobis distance.

2. Materials and methods

Cod-liver oil (CLO) and selected vegetable oils, namely canola oil (CaO), corn oil (CO), soybean oil (SO), and walnut oil (WO) were purchased from the local market in Jogjakarta, Indonesia. The composition of fatty acids of the studied oils was determined according to Marina et al. [15]. The standard of fatty acid methyl esters (FAME) obtained from Sigma Chemicals, St. Louis (Deisenhofen, Germany) was used to calculate the percentage of fatty acids based on its band area. Quantification of FAME was performed using internal normalization technique.

2.1. Preparation of calibration and validation samples

Twenty-one calibration samples consisting of CLO and vegetable oils (CaO, CO, SO, and WO) were prepared by mixing of both at concentrations of 1–50% (v/v). For validation or prediction samples, 20 independent samples were constructed. Pure CLO and vegetable oils as well as their blends were analyzed using FTIR spectroscopy.

2.2. Discriminant analysis (DA)

DA was performed by preparing CLO and CLO mixed with vegetable oils in order to obtain a series of training sets or standard samples of both classes (pure CLO in chloroform and CLO adulterated samples, containing 1–50%, v/v of vegetable oils). The samples containing vegetable oils were assigned as "adulterated", while a series of pure CLO was assigned as "cod liver oil" and classified using their FTIR spectra.

2.3. FTIR instrumental analysis

An FTIR spectrometer (Nicolet 6700 from Thermo Nicolet Corp., Madison, WI) was used to scan the oil samples. The instrument was equipped with a deuterated triglycine sulphate (DTGS) detector and was controlled by the OMNIC software system (Version 7.0 Thermo Nicolet). The procedure of FTIR spectral acquisition was similar to that in our previous paper [14].

2.4. Data analysis

The software TQ Analyst™ from Thermo electron Corporation was used to construct data analysis, including PLS and PCR for quantification and DA for classification. FTIR spectral regions offering the highest values of coefficient of determination (R^2) and the lowest values of root mean square error of calibration (RMSEC) were selected for developing PLS and PCR calibration models. The calibration model was cross-validated using the "leave-one-out" technique. The calibration models were further used to predict the level of oil adulterants in the prediction samples. The values of R^2 and root mean square error of prediction (RMSEP) were used for prediction criteria.

3. Results and discussion

3.1. FTIR spectral analysis and fatty acid composition

Fig. 1 shows FTIR spectra of CLO and some vegetable oils (CaO, CO, SO, and WO) at mid-infrared regions (4000–650 cm^{-1}) presenting the characteristic bands of edible oil spectra as described by Guillen and Cabo [16]. The fatty acid (FA) composition of CLO and selected vegetable oils is compiled in Table 1. FTIR spectra of the studied oils can be used as a potential means which allows one to make the first differentiation between CLO and these vegetable oils.

Upon the detailed investigation, these spectra reveal slight differences in terms of band intensities and the exact frequencies at which the maximum absorbance is generated in each oils due to the different FA composition, the number of chain length, the degree and the position of double bonds in triglyceride [16]. These spectral differences can be seen at frequency regions of 3007 (attributed to the stretching vibration of *cis*-vinylic), 2922 and 2852 cm^{-1} due to asymmetrical and symmetrical stretching vibrations of $-CH_2-$ as well as at 1237, 1117 and 1098 cm^{-1} which are corresponding to C–O stretching vibrations [17]. For this reason, these frequency regions in which the spectral variation was observed between CLO and vegetable oils (CaO, CO, SO, and WO) were optimized to be exploited for quantification and classification of those in CLO.

3.2. Quantification of vegetable oils in CLO

Multivariate calibration of PLS and PCR models was developed for quantifying those vegetable oils in concentration range of 0–50% (v/v). Fig. 2 is an example of FTIR normal spectra of CO in CLO used in the calibration model. PLS and PCR models were optimized in terms of FTIR spectral regions and spectral treatments (normal, first derivative, and second derivative). The first derivative removes the common intensity effect of FTIR spectral and can simplify the baseline selection. Furthermore, the second derivative can eliminate the slope effect. However, derivation treatments can strongly affect the sensitivity of measurements. For this reason, the use of derivative

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