Food Chemistry 129 (2011) 583–588

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

The use of Fourier transform mid infrared (FT-MIR) spectroscopy for detection and quantification of adulteration in virgin coconut oil

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ARTICLE INFO

Article history:
Received 2 March 2010
Received in revised form 27 February 2011
Accepted 22 April 2011
Available online 29 April 2011

Keywords:
FT-MIR spectroscopy
Virgin coconut oil
Corn oil
Sunflower oil
Adulteration

ABSTRACT

Currently, the authentication of virgin coconut oil (VCO) has become very important due to the possible adulteration of VCO with cheaper plant oils such as corn (CO) and sunflower (SFO) oils. Methods involving Fourier transform mid infrared (FT-MIR) spectroscopy combined with chemometrics techniques (partial least square (PLS) and discriminant analysis (DA)) were developed for quantification and classification of CO and SFO in VCO. MIR spectra of oil samples were recorded at frequency regions of 4000–650 cm^{-1} on horizontal attenuated total reflectance (HATR) attachment of FTIR. DA can successfully classify VCO and that adulterated with CO and SFO using 10 principal components. Furthermore, PLS model correlates the actual and FTIR estimated values of oil adulterants (CO and SFO) with coefficient of determination (R^2) of 0.999.

1. Introduction

Since very early time, fats and oils have been liable to adulteration, either intentionally or accidentally (Rossell, King, & Downes, 1983). The detection of adulteration is an attractive issue for researchers, because food producers do not wish to be subjected to unfair competition from devious processors who would get economical profit (Gallardo-Velázquez, Osorio-Revilla, Zuñiga-de Loa, & Rivera-Espinoza, 2009). The detection of adulteration is more difficult, especially when the adulterant has similar chemical composition to that of the original oil (Anklam & Bantaglia, 2001).

Virgin coconut oil (VCO) is obtained from the flesh coconut in which the oil extraction does not involve the use of thermal or chemical treatments (Nik Norulaini et al., 2009). VCO is an emerging functional food oils due to its ability to posses several biological activities such as antiviral and antimicrobial (Marina, Che Man, & Ismail, 2009). In the market, it is estimated that the price of VCO is approximately 10–20 times higher than that of common plant oils like corn, palm, and sunflower oils. Therefore, VCO is a target to adulteration practise with the low price plant oils.

Several analytical methods have been developed for detection and quantification of adulterants in fats and oils such as differential scanning calorimetry (DSC) (Chiavaro, Vittadini, Rodriguez-Estrada, Cerretani, & Bendini, 2008); spectroscopic based-methods (Lerma-García, Ramis-Ramos, Herrero-Martínez, & Simó-Alfonso, 2010), and wet chemical methods. Quantification of adulterants in fats and oils by chromatographic method was reviewed by Cserhati, Forgacs, Deyl, and Miksik (2005) and by Aparicio and Aparicio-Ruiz (2000). For the analysis of VCO adulteration, Marina, Che Man, and Amin (2010) have developed electronic nose based on surface acoustic wave in combination with the chemometrics of principal component analysis to monitor the adulteration of VCO with palm kernel oil. Another technique used was DSC for monitoring the presence of palm kernel oil and soybean oil (Marina, Che Man, Nazimah, & Amin, 2009). Some of these methods are impractical and too laborious. Therefore, rapid and accurate analytical methods must be developed in order to detect and to quantify the oil adulterants.

Over the last 3 decades, mid infrared (MIR) spectroscopy combined with chemometric methods have been used in numerous analytical applications (Sinelli, Cerretani, Di Egidio, Bendini, & Casiraghi, 2009). MIR spectroscopy has been identified as an ideal analytical method for authenticity studies of edible fats and oils (Reid, O'Donnell, & Downey, 2006) due to its capability to serve as "fingerprint" technique, meaning that there are no two samples with the same FTIR spectra, either in the number of peaks or in the maximum peak intensities (Pavia, Lampman, & Kriz, 2001). The methods allow sensitive, fast, and reliable technique, ease in sample presentation, and can be used for monitoring the quality

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doi:10.1016/j.foodchem.2011.04.070

aspects of fats and oils at spectral region of 4000–650 cm^{-1} (Roggo et al., 2007; Wilson & Tapp, 1999).

FT-MIR spectroscopic methods were developed for detection and quantification of oil adulterants such as sunflower, corn, soybean and hazelnut oils in extra virgin olive oil (EVOO) using chemometrics of multiple linear regression and linear discriminant analysis (Lerma-García et al., 2010), sunflower and corn oils in EVOO with aid of principal component analysis and PLS-discriminant analysis (Gurdeniz & Ozen, 2009), soybean oil in camellia oil (Wang, Lee, Wang, & He, 2006), hazelmut oil in refined olive oil (Baeten et al., 2005) and animal fats in cod-liver oil (Rohman & Che Man, 2009a). Our group has used FT-MIR spectroscopy combined with chemometrics of PLS and DA for quantification and classification of palm kernel oil (Manaf, Che Man, Hamid, Ismail, & Syahariza, 2007) and palm oil (Rohman & Che Man, 2009b) as oil adulterants in VCO. The present study highlights the application of FT-MIR spectroscopy for detecting and quantifying corn oil (CO) and sunflower oil (SFO) as oil adulterants in VCO.

2. Materials and methods

The samples of virgin coconut oil (VCO), sunflower oil (SFO), and corn oil (CO) were purchased from the local market in Jogjakarta, Indonesia. The used plant oils were coming from the mixture of three different brands with similar fatty acid (FA) composition. The FA profiles of these oils are in accordance with those listed in Codex Alimentarius (2003). Some factors contributed to the slight FTIR spectral variation of VCO, such as origin of plants, year of coconut plantation, maturity, etc. For this reason, the samples of VCO were mixed to compensate this variation.

2.1. Classification

The classification of VCO and VCO blended with adulterants (CO and SFO) was carried out using discriminant analysis (DA). DA is one of the supervised pattern recognition techniques which start with a number of samples whose group membership is known. These samples are sometimes called the learning or training samples (Miller & Miller, 2005). VCO and adulterants were blended in order to obtain a series of training sets of pure VCO (50% VCO in chloroform) and VCO containing 1–50% of adulterants in chloroform. VCO samples mixed with adulterants were marked as “adulterated”, while a series of pure VCO was assigned with “VCO”. Both classes were classified using DA based on their FT-MIR spectra.

2.2. Quantification

For quantitative analysis, CO and SFO were mixed as binary mixture with VCO (each comprises 20 samples for calibration and 20 samples for validation). The concentration of each oils used in both calibration and validation is presented in Table 1. Each sample was subjected for FT-MIR analysis.

Table 1
The composition percentage for calibration and validation sets used in the binary mixtures of CO and SFO with VCO.

Samples	CO in VCO				SFO in VCO			
	Calibration		Validation		Calibration		Validation	
	CO	VCO	CO	VCO	SFO	VCO	SFO	VCO
1	2.0	98.0	0.0	100.0	0.0	100.0	0.0	100.0
2	3.0	97.0	1.5	98.5	1.5	98.5	2.0	98.0
3	5.0	95.0	2.5	97.5	3.0	97.0	3.0	97.0
4	6.0	94.0	7.5	92.5	4.0	96.0	4.0	96.0
5	8.0	92.0	8.0	92.0	5.0	95.0	5.0	95.0
6	9.0	91.0	10.0	90.0	6.0	94.0	6.0	94.0
7	10.0	90.0	14.0	86.0	7.5	92.5	7.5	92.5
8	12.5	87.5	15.0	85.0	10.0	90.0	10.0	90.0
9	15.0	85.0	20.0	80.0	12.5	87.5	12.5	87.5
10	17.5	82.5	22.5	77.5	15.0	85.0	15.0	85.0
11	22.5	77.5	25.0	75.0	17.5	82.5	17.5	82.5
12	25.0	75.0	30.0	70.0	20.0	80.0	20.0	80.0
13	27.5	72.5	32.5	67.5	22.5	77.5	22.5	77.5
14	30.0	70.0	37.5	62.5	25.0	75.0	25.0	75.0
15	32.5	67.5	47.5	52.5	30.0	70.0	30.0	70.0
16	35.0	65.0	50.0	50.0	35.0	65.0	35.0	65.0
17	50.0	50.0	55.0	45.0	40.0	60.0	37.5	62.5
18	60.0	40.0	60.0	40.0	50.0	50.0	40.0	60.0
19	70.0	30.0	65.0	35.0	75.0	25.0	45.0	55.0
20	100.0	0.0	80.0	20.0	100.0	0.0	50.0	50.0

2.3. FT-MIR analysis

FT-MIR spectra of samples were obtained using Nicolet 6700 FTIR spectrometer (Thermo Nicolet Corp., Madison, WI) with HATR crystal of ZnSe 45° equipped with deuterated triglycine sulphate (DTGS) as detector, potassium bromide (KBr) as beam splitter and controlled with the Omnic Software (Version 7.0 Thermo Nicolet). The measurements were directly carried out by putting oil samples on HATR surface at controlled room temperature (20 °C) in MIR region of 4000–650 cm^{-1}, by accumulating 32 scans with the resolution of 4 cm^{-1}. These spectra were subtracted from reference spectrum of air, acquired by collecting a spectrum from the cleaned blank HATR crystal before the measurement of each oil sample replication. The sample spectra were collected in triplicate and displayed as the average spectra. At the end of every scan, the surface of HATR crystal was cleaned with hexane twice and dried with special soft tissue, cleaned with acetone, and finally dried with soft tissue following the collection of each spectrum.

2.4. Chemometrics

The chemometrics analyses were performed using the software TQ Analyst™ version 6 (Thermo electron Corporation, Madison, WI). Classification and quantification of adulterants (CO and SFO) in VCO were carried out using discriminant analysis (DA) and partial least square (PLS), respectively. Frequency regions for PLS and DA were automatically selected by the software and were confirmed by investigating peaks where variations were observed. PLS calibration model was cross-validated using “leave-one-out” technique. This model was further used to predict the level of CO and SFO in independent samples in order to evaluate its predictive capability.

3. Results and discussion

Chemically, fats and oils are glycerol esterified with fatty acids. Some of the fats and oils might have quite similar composition; consequently, it is often difficult to detect adulteration of fats and oils physically (Christy, Kasemsumran, Du, & Ozaki, 2004). However, because of its capability as a fingerprint technique, MIR spectroscopy allows one to differentiate authentic oils and those adulterated with others by observing the spectra changes due to the adulteration (Yap, Chan, & Lim, 2007).

Fig. 1 exhibits MIR spectra of VCO, CO, and SFO at frequency region of 4000–650 cm^{-1}. The assignment of functional groups responsible for IR absorption is as follows: 3008 cm^{-1} (*trans* =C–H stretch), 2954 (–CH$_3$ asymmetrical stretch), 2922 and 2853 (symmetrical and asymmetrical stretching of –CH$_2$), 1743 (–C=O stretch), 1654 (*cis* –C=C stretch), 1463 (–CH$_2$ bending), 1417 (*cis* =C–H bending), 1377 (–CH$_3$ bending), 1237 (–C–O stretch), 1160 (–C–O stretch; –CH$_2$ bending), 1120 (–C–O stretch), 1098 (–C–O stretch), 1032 (–C–O stretch), 965 (*trans*-CH=CH– bending