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Rapid detection of peanut oil adulteration using low-field nuclear magnetic resonance and chemometrics

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ABSTRACT

^{1}H low-field nuclear magnetic resonance (LF-NMR) and chemometrics were employed to screen the quality changes of peanut oil (PEO) adulterated with soybean oil (SO), rapeseed oil (RO), or palm oil (PAO) in ratios ranging from 0% to 100%. Significant differences in the LF-NMR parameters, single component relaxation time (T_{2W}), and peak area proportion (S_{21} and S_{22}), were detected between pure and adulterated peanut oil samples. As the ratio of adulteration increased, the T_{2W}, S_{21}, and S_{22} changed linearly; however, the multicomponent relaxation times (T_{21} and T_{22}) changed slightly. The established principal component analysis or discriminant analysis models can correctly differentiate authentic PEO from fake and adulterated samples with at least 10% of SO, RO, or PAO. The binary blends of oils can be clearly classified by discriminant analysis when the adulteration ratio is above 30%, illustrating possible applications in screening the oil species in peanut oil blends.

1. Introduction

Edible vegetable oils are widely used in cooking at home and in the food industry (Zhang et al., 2014). Owing to its pleasant flavor and the presence of compounds such as resveratrol (Xie, Liu, Yu, Song, & Hu, 2013), peanut oil is one of the major edible oils in China, besides soybean oil and rapeseed oil. However, peanut oil is more expensive than the other two, making it prone to adulteration by the unscrupulous dealers. For example, oils such as soybean oil, sunflower oil, canola oil, and palm oil are blended into peanut oil in varying proportions (Fang, Goh, Tay, Lau, & Li, 2013), or worse, cheaper oils are used to make fake peanut oil by adding peanut oil flavor. The authentication of vegetable oils and the detection of adulteration are important issues, and a lot of studies have focused on detecting adulteration of oil (Agiomyrgianaki, Petrakis, & Dais, 2010; Apetrei & Apetrei, 2014; Lerma-García, Ramis-Ramos, Herrero-Martínez, & Simó-Alfonso, 2010). However, to the best of our knowledge, no technique is available for the authentication and detection of adulteration in peanut oil in particular. The adulteration of oils not only infringes upon the rights and interests of consumers, food processors and industries, but also leads to potential health risks, such as the threat known as Spanish toxic oil syndrome and the resale of "recycled oil" in China (Garcia de Aguinaga et al., 2008; Lu & Wu, 2014). Therefore, establishing a simple and rapid method to detect adulteration in peanut oil is important.

Several analytical methods have been developed to determine the adulteration of oils on the basis of their physical or chemical properties. Traditional analytical methods such as gas chromatography (GC) (Hajimahmoodi et al., 2005; Hilali, Charrouf, Soulhi, Hachimi, & Guillaume, 2007), high-performance liquid chromatography (HPLC) (Cunha & Oliveira, 2006; Marikkar, Ghazali, Che Man, Peiris, & Lai, 2005), or gas chromatography–mass spectrometry (GC–MS) (Aparicio & Aparicio-Ruız, 2000; Chandratilleke, Nadim, & Narayanaswamy, 2012; Park, Chang, & Lee, 2010) have been used extensively and are proven to be excellent tools. However, these methods have several drawbacks; most significantly, they are time consuming, often involve complicated sample pretreatments, and require expensive instruments, hazardous chemicals, and highly skilled personnel. The development and integration of rapid methods for accurately evaluating the quality of fats and oils is of significant importance in ensuring their safety and quality. Thus, several rapid and non-destructive novel instrumental methods such as differential scanning calorimetry (DSC) (Chiavaro et al., 2008), near infrared spectroscopy (NIR) (Casale, Casolino, Ferrari, & Forina, 2008; Woodcock, Downey, & O'Donnell, 2008), Raman spectroscopy (Baeten, Meurens, Morales, & Aparicio, 1996), electronic nose (Bougrini et al., 2014), headspace-mass spectrometry (Marcos Lorenzo, Perez Pavon, Fernandez Laespada, Garcia Pinto,

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& Moreno Cordero, 2002), and stable carbon isotope technology (Guo, Xu, Yuan, Wu, & Wang, 2010; Seo et al., 2010) have been proposed to overcome these hurdles. Unfortunately, in many cases, these methods are not adequate to screen more sophisticated adulteration. Therefore, more effective detection methods of adulteration in oils is needed.

^{1}H low-field nuclear magnetic resonance (LF-NMR) has been suggested as a rapid, simple and effective tool to be widely used in food quality control and material property measurements (Micklander, Peshlov, Purslow, & Engelsen, 2002; Todt et al., 2001). Spin-lattice relaxation (T_1) and spin–spin relaxation (T_2) are two important LF-NMR parameters that represent two features of proton relaxation. Nowadays, T_2 is being used more frequently because it is more sensitive and can provide more information about the relaxation time. Based on the mobility and distribution of water and fatty-acid hydrogen protons (Todt, Guthausen, Burk, Schmalbein, & Kamlowski, 2008), different kinds of protons such as those bound in free water or in bound water, or protons attached to carbohydrates, lipids, and proteins (Bluemich, Casanova, & Appelt, 2009) can be distinguished. This method has also been used to study water mobility in acidified milk drinks (Salomonsen, Sejersen, Viereck, Ipsen, & Engelsen, 2007; Saragusty & Arav, 2011), hake muscle after different freezing and storage conditions (Miklos, Cheong, Xu, Lametsch, & Larsen, 2015), and the drying degree and quality of chicken jerky (Sanchez-Alonso, Moreno, & Careche, 2014). Moreover, LF-NMR provides a powerful tool to evaluate the quality of deep-frying oil, and there is good correlation between total polar compounds (TPCs), viscosity, and LF-NMR parameters (Shen et al., 2013). However, there have been very few reports on the measurement of edible oil adulteration by using LF-NMR relaxation measurements. To date, only one study by Zhang, Saleh, and Shen (2012) has demonstrated that LF-NMR can be a useful tool to detect the adulteration of edible oils with used frying oil. They found that the T_2 distributions between the qualified oil and used frying oil are different, and this could be assigned to polymer products produced during the deep-fat frying process.

The main aim of this study was to detect the adulteration of peanut oil with less expensive vegetable oils and fake peanut oils by using LF-NMR. In addition, multivariate statistical analysis was used for the qualitative analysis of peanut oil adulterated with inexpensive vegetable oils.

2. Materials and methods

2.1. Sourcing of authentic refined vegetable oils

Four types of commercially available refined vegetable oils of different brands were purchased from a local supermarket in Shanghai, China. The vegetable oils included peanut oil (PEO), soybean oil (SO), rapeseed oil (RO), and palm oil (PAO). All samples were preserved in a refrigerator at 4 °C until analysis.

2.2. Preparation of oil blends

Ninety-nine binary blend samples were prepared by adding either SO, RO, or PAO into PEO at percentages ranging from 10% to 90% by volume. Forty-five fake peanut oil samples were prepared by adding 0.2% (v/v) peanut oil flavor into SO, RO, PAO, or a mixture of two of the vegetable oils. Peanut oil flavor (oil soluble) was purchased from HangZhou Mingyuan food additive company.

All the adulterated oil samples were kept in a refrigerator at 4 °C until analysis.

2.3. Instrumentation and working conditions

An LF-NMR analyzer NMI20-Analyst (Niumag Electric Corporation, Shanghai, China) combined with a Windows analysis platform, and an inversion of a multiexponential fitting analysis (T-invfit) program was employed for the NMR measurements. The strength of the magnetic field was 0.53 T, which corresponded to a proton resonance frequency of 22 MHz.

The prepared oil mixture was transferred to a thermostatic water bath and equilibrated to 32 °C, after which it was introduced to the NMR probe by filling 2.6 mL of the sample into the LF-NMR glass tube (18 mm in diameter). Transverse relaxation (T_2) was measured using the Carr-Purcell-Meiboom-Gill pulse sequence (CPMG). Data were acquired from 6000 echoes over four scans at 31.99–32.00 °C. The repetition time between scans was 2000 ms, and the time between the 90° and 180° pulses was 250 μs. The T-invfit software was used to invert the CPMG sequence into a spin–spin relaxation time (T_2) distribution. The samples were analyzed in triplicate and each reported value is the average of a minimum of nine measurements.

2.4. GC–MS analysis of the edible vegetable oils (PEO, SO, RO, and PAO)

All chemicals and reagents were of ACS reagent grade and purchased from Sinoreagent (Shanghai). The FAME standards were purchased from Sigma-Aldrich. Transmethylation of fats and oils was carried out in triplicate according to GB/T 17376—2008, which is equal to IS0 5509:2000. FAME standards were analyzed on a 7890N-5975C GC–MS equipped with a flame ionization detector and a capillary column DB-5 (50 m × 0.25 mm × 0.25 μm). Helium (99.999% purity) was used as the carrier gas at a constant flow rate of 3.0 mL/min. The column temperature was first set to 60 °C, subsequently increased to 180 °C at a rate of 10 °C/min, then maintained at 180 °C for 10 min, followed by an increase to 270 °C at a rate of 5 °C/min, where it was held for an additional 5 min. The temperatures of the injector, ion-source, and detector were set to 260 °C, 230 °C, and 150 °C, respectively. A 1.0-μL sample of each oil was injected. The full scans were acquired from 50 to 650 amu with the electron ionization (EI) mode set to 70 eV.

2.5. Statistical analysis

2.5.1. One-way analysis of variance (ANOVA)

One-way ANOVA was performed on the three data sets (PEO + SO, PEO + RO, and PEO + PAO) to determine if there was any significant difference between the adulterated oil samples and pure peanut oil as the adulteration ratio increased.

TQ Analyst software (Copyright (C) 1989-2011 Agilent Technologies, Inc) was used for spectral analyses. The retention time of FAME standards in MS was used to determine the specific kind of fatty acids present in the samples, and their relative contents were determined using the peak area normalization method. Thus, the relative content of a specific fatty acid was calculated, and the percentage contents of SFA, MUFA, DUFA, and TUFA were calculated from the specific fatty acid contents. Data were processed in Microsoft Excel 2010, and figures were prepared in Origin 8.0.

2.5.2. Principal component analysis (PCA)

PCA was used to classify the fake peanut oil samples and the adulterated oil samples. PCA was also used to classify the four types of oils used in the study. Separate PCA models were used for each of the three groups of adulterated oils (PEO + SO, PEO + RO, and PEO + PAO) to classify the binary blend samples at