



Analytical Methods

Detection and quantification of adulteration of sesame oils with vegetable oils using gas chromatography and multivariate data analysis



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ABSTRACT

This study was performed to develop a hierarchical approach for detection and quantification of adulteration of sesame oil with vegetable oils using gas chromatography (GC). At first, a model was constructed to discriminate the difference between authentic sesame oils and adulterated sesame oils using support vector machine (SVM) algorithm. Then, another SVM-based model is developed to identify the type of adulterant in the mixed oil. At last, prediction models for sesame oil were built for each kind of oil using partial least square method. To validate this approach, 746 samples were prepared by mixing authentic sesame oils with five types of vegetable oil. The prediction results show that the detection limit for authentication is as low as 5% in mixing ratio and the root-mean-square errors for prediction range from 1.19% to 4.29%, meaning that this approach is a valuable tool to detect and quantify the adulteration of sesame oil.

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1. Introduction

Sesame oil, which is an edible vegetable oil derived from sesame seeds, is often used as a flavor enhancer and a popular source of food oil in China and many other Asian countries. In many markets, sesame oil is widely available, however, adulteration in sesame oil is a problem that has existed for a long time due to economic reasons (Seo et al., 2010). For example, adulteration of sesame oil products aim at maximizing profit by adding other cheaper or low-quality oils. In China, the adulteration of sesame oil is potential a great commercial problem because sesame oil is much more expensive (8–30 times) than other vegetable oils. The most common adulterants found in sesame oil include soybean oil, rapeseed oil, cottonseed oil and so on (Dong-Sun, Eun-Sung, Hyun-Jung, Shin-Ok, & Kun, 2001). Although in most cases the adulteration is not such a serious problem (Ulberth & Buchgraber, 2000), a potential threat to public health still exists such as ‘Spanish Toxic Syndrome’, an outbreak of food poisoning attributed to consumption of low-quality olive oil adulterated with rapeseed oil (Ortega-Benito, 1992). Thus, excellent analytical techniques are needed to control the purity and authenticity of sesame oil product.

Various techniques existing which can be used to detect adulteration of sesame oil by other vegetable oils, such as UV spectrophotometry, Raman spectroscopy, NMR analyses and IR spectrometry (Aued-Pimentel, Takemoto, Antoniassi, & Badolato, 2006; Baeten & Aparicio, 2000; Kim, 1996; Li-Chan, 1994; Michelangelo, Caterina, & Nelson, 2013; Segal et al., 2010; Vlachos et al., 2006) have been used for many years. However, these techniques have limitations as detection methods since the spectral differences of most vegetable oils, which contain the same fatty acids, are quite small. Recently, the electronic nose was reported to be applied in the detection of adulteration of sesame oil (Hai & Wang, 2006; Martin, Pavon, Cordero, & Pinto, 1999). Unfortunately, in many cases, these methods are not adequate to detect more elaborated frauds. Usually, each vegetable oil has its own characteristic fatty acid composition (Spencer, Herb, & Gormisky, 1976). Therefore, determining the levels of fatty acid compositions by chromatographic methods can provide useful information about the authenticity or possible adulteration of sesame oil. The fatty acid determination can be carried out by liquid chromatography (LC) or gas chromatography (GC). Because most LC methods require derivatization to enhance detectability of fatty acids, GC is now widely used for the compositional determination of fatty acids. On the other hand, the chromatographic data is often a multidimensional set, and it has to be reasonably interpreted to discriminate the authentic and adulterated sesame oil by chemometric methods, especially the multivariate analysis such as principal component analyses (PCA) (Yang & Wang, 1999,

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discriminant analyses (Xiaobo, Jian, David, & Jun, 2013), partial least square (PLS) Geladi & Kowalski, 1986 and so on. However, the discrimination of adulteration of sesame oil is not easy because vegetable oils have narrow triacylglycerols compositional spectra (Dong-Sun et al., 2001). Especially, it is very difficult to predict a mixing ratio of adulterants. Until now, it seems that there is no a single model which can detect all kinds of adulterants in adulterated sesame oil (Shukla & Singh, 2005). Thus, a suitable detection and quantification method of the adulterant is needed.

The aim of this paper is to design a hierarchical approach, which could firstly get the type of adulterant prior to predict what level it is mixed with the pure sesame oil by exploring chromatographic datasets using multivariate analysis. The results can be used to control the authenticity of sesame oil. In the present work, six sets of binary mixture of oils are prepared. Then a two-step support vector machine-based classification in combination with PLS is evaluated to determine the level of sesame oil in the mixture of oils.

2. Materials and methods

2.1. Materials

All reagents used were of analytical grade. The analyzed samples, sesame oil (6 samples, pure degree, various districts including Henan, Shandong, Jilin, Hunan and Hubei) from various geographical origins, rapeseed oil (3 samples, pure degree, various districts including Henan, Shandong and Shanxi), soybean oil (5 samples, pure degree, various districts including Henan, Shandong, Liaoning and Hubei), sunflower seed oil (4 samples, pure degree, various districts including Gansu, Shandong, Xijiang and Jilin), cottonseed oil (4 samples, pure degree, various districts including Henan, Shandong, Xinjiang and Hebei) and palm oil (4 samples, pure degree, various districts including Guangdong, Yunnan, Malaysia and Indonesia), were purchased from the local market. The shelf life of these samples is at least six months. To avoid any changes in the chemical composition, samples were analyzed immediately after unpacking in the laboratory. Fatty acid methyl esters used as standards were procured from Sigma Chemical Co., Ltd. Other reagents including methanol, sodium, hexane were analytical grade and purchased from local sources.

For the investigation of detection and quantification of adulteration of the sesame oil with other vegetable oils, mixtures of the pure sesame oils with each one of the above pure vegetable oils were prepared. The mixed proportions of vegetable oils range from 5% to 50%. For each vegetable oil, six mixtures were prepared with percentages 5%, 10%, 15%, 20%, 30% and 50% of the respective oil in the adulterated sesame oil samples. Totally, 720 oil mixture samples and 26 pure oil samples were prepared. These samples were kept in a cold room with constant temperature before and during analysis.

2.2. Methods

For the determination of FAs composition, the methyl esters were prepared according to the IUPAC method (IUPAC, 1987). The analysis of fatty acid methyl esters (FAME) was performed on a gas chromatograph (Agilent 6890N) equipped with a flame ionization detector (FID) and a BPX-70 capillary column (30 m × 0.32 mm, 0.25 μm of film thickness) (Agilent Technologies Co., Ltd.). Analysis conditions were: column, injector and detector temperatures at 180 °C, 230 °C and 230 °C, respectively. The flow rate of carrier gas N₂ with split ratio of 1:20 is at 1.5 mL/min. Provided that the sum of the areas of the peaks

corresponding to the various FAMES were equal to 100%, the relative percentage of each FAME was calculated.

2.3. Chemometric analyses

The 746 samples of vegetable oils are characterized by the compositions of ten fatty acids, namely myristic (C14:0), palmitic (C16:0), palmitoleic (C16:1), stearic (C18:0), oleic (C18:1), linoleic (C18:2), linolenic (C18:3), eicosenoic (C20:1), behenic (C22:0) and erucic (C22:1). The percentage levels of these ten fatty acids represent ten variables, and the 1 × 10 variable vector represents the corresponding sample, further used in data analysis. The PCA and self-organizing map (SOM) were applied to investigate the similarity and dissimilarity between sample groups. Then, the support vector machine (SVM) was used as a modeling method to detect the adulteration and classify the mixture sample. The parameter optimization of SVM is accomplished by particle swarm optimization (PSO) technique Schutte & Groenwold, 2005. Based on the classification result, PLS model is developed to predict the level of sesame oil. All the programs in the following sections were done using Matlab 2006a (MathWorks, USA). The SOM and SVM were implemented with the help of SOM Toolbox 2.0 (Laboratory of Computer and Information Science, 2010) and LIBSVM toolbox (National Taiwan University, 2010), respectively.

3. Results and discussion

3.1. Fatty acid composition of samples

The percentage levels (maximum value and minimum value) of fatty acid compositions of six kinds of authentic vegetable oils are shown in Fig. 1. The major fatty acids are palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid, and these experimental fatty acid composition levels are in compliance with Codex Alimentarius ranges (FAO/WHO, 1999). As shown in Fig. 1, cottonseed oil and palm oil compared to other oils have a higher percentage of palmitic acid and myristic acid. Linolenic acid is rich in rapeseed oil and soybean oil, and oleic acid is a predominant fatty acid in sesame oil and palm oil, whereas the oils, sesame, soybean, sunflower seed and cottonseed have considerably high linoleic acid content. Soybean oil and sunflower seed oil show similar fatty acid compositions, however, palmitic acid content of the former is much higher than the latter. Additionally, the erucic acid content of rapeseed oils is much higher than other oils. We can afford from the Fig. 1 that fatty acids can be influenced not only by species, but also by regions, climate and processing conditions, etc. (Dong-Sun, Bong-Soo, Sun-Yong, & Kun, 1998). Based on fatty acid content comparison, these experimental results of the compositional determination are useful for fingerprinting oils, detecting adulteration and evaluating product quality.

3.2. Principal component analysis

Principal component analysis is utilized to provide an overview of the capacity to characterize vegetable oils based on gas chromatography data. By choosing the first three principal components (PC), 98.47% of the total variability is explained (PC1 = 54.76%, PC2 = 30.55%, PC3 = 13.16%) indicating that we do not lose a considerable amount of information by keeping only the first three PCs. The scores for the first three PC are plotted as a scatter diagram in Fig. 2. Generally, the stereochemical distribution of the mixtures depends on the nature of the oils. It is clear that several clusters are formed, corresponding to the five different kinds of mixture. In each cluster, the samples are dispersed from the center (six pure sesame oils) to the rim (the five kinds of pure non-sesame

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