Single Component Oil in Edible Oil Blends

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Edible oil blends are composed of two or more edible oils in varying proportions, which can ensure nutritional balance compared to oils comprising a single component oil. In view of their economical and nutritional benefits, quantitative analysis of the component oils in edible oil blends is necessary to ensure the rights and interests of consumers and maintain fairness in the edible oil market. An introduction to the basic concept of single component oil in edible oil blends is provided. The importance of the quantitative analysis of single component oil in edible oil blends and provides several analytical methods used for single component oil quantification is described.

Keywords: edible oil blends ; sample design ; instruments ; chemometrics ; quantitative analysis

1. Introduction

Edible oil is an important ingredient used for cooking and flavoring a wide range of foods. Chemically speaking, edible oil not only provides nutrients, such as unsaturated fatty acids and fat-soluble vitamins, but also offers some essential nutritional requirements that cannot be endogenously produced by humans . However, a single type of edible oil cannot meet the requirements of functional and nutritional balance. Therefore, it is common to mix two or more types of edible oils in different proportions to prepare edible oil blends, which can effectively overcome the nutritional shortcomings of the single oil types. Furthermore, the various fatty acids found in edible oil blends can provide protection against some severe chronic illnesses, such as neurodegenerative, inflammation and cardiovascular diseases [1]. Consequently, the practice of blending edible oils is becoming increasingly common, with sales volumes of edible oil blends continuing to rise in recent years.

Due to the different geographical sources, yields and nutritional values, the prices of different edible oils can vary widely [2]. Conventional edible oils, such as soybean, sunflower, olive, corn, and rapeseed oils, are most commonly utilized as the base oils for edible oil blends as they are relatively cheap and readily available. On the other hand, more unconventional edible oils, such as flaxseed, camellia and peony seed oils, have higher nutritional value and unique flavors, thus are more expensive than conventional edible oils. As a result of these large price variances between edible oils, some businesses market their product with strong emphasis on the presence of the high-grade oil (which is only present in small amounts) and omit the proportion of lower-grade oil [3], which can be seen as misleading consumers. Due to the similar appearance of different oils and the homogeneity of oil blends, the content of each oil cannot be distinguished visually. Therefore, in order to protect the rights and interests of consumers and maintain a fair edible oil market, it is necessary to develop reliable quantitative detection methods for the quantitative authentication of edible oil blends.

Spectroscopic-based techniques have the advantages of non-destructive testing, simple operation, rapid analysis and high sensitivity , and have been widely used for quantifying single component oil in edible oil blends. However, the spectra from different edible oils can be difficult to distinguish due to the similarity in their components, making quantitative analysis difficult to implement. Pairing spectroscopic techniques with chemometrics can help solve this problem. The spectral matrix is processed by chemometric methods, and multivariate calibration models are established between the spectral matrix and target values to determine the content of the single component oil. A range of multivariate calibration methods, including multiple linear regression (MLR), principal component regression (PCR), partial least square (PLS) regression and support vector regression (SVR), may be used [4]. As the spectra matrix for model establishment usually contain some useless information and hundreds of variables, preprocessing and variable selection methods are used to improve model accuracy and robustness.

2. Instrumental Techniques

This section introduces several commonly used instrumental techniques for single component oil quantification in edible oil blends, including infrared, near-infrared, Raman, fluorescence, ultraviolet-visible, nuclear magnetic resonance

spectroscopy and mass spectrometry. Chromatography, a common separation method, is usually used in combination with ultraviolet spectroscopy, diode array detector, nuclear magnetic resonance spectroscopy and mass spectrometry. Chromatography-based techniques use these detectors to determine the content of single component oil in edible oil blends by measuring the ratios of specific compounds, such as fatty acids or triacylglycerol [5][6][7]. Therefore, chromatography is not discussed in this entry.

2.1. Infrared Spectroscopy

Infrared (IR) spectroscopy, also referred to as mid-infrared (MIR) spectroscopy, commonly has a wavenumber range of 4000–400 cm^{-1}. It provides an absorption spectrum of energy level transitions caused by molecular vibrations and rotations, which can provide information regarding molecular functional groups . Fourier transform infrared (FTIR) spectrometer takes the incident light after Fourier transform, providing the advantages of high resolution, high sensitivity and fast scanning speed [8]. However, it is usually difficult to determine the molecular source of each peak due to the complex composition of edible oils [9]. Consequently, multivariate calibration methods combined with FTIR spectroscopy are used to analyze this complex information [10][11][12].

Oil blend samples analyzed by transmission FTIR spectroscopy need pretreatment. The samples should be diluted with solvents, which is a time-consuming process and produces additional solvent waste. However, it does not require any oil pretreatments by attenuated total reflectance FTIR (ATR-FTIR) spectroscopy. The spectra can be collected directly by placing the oil blend samples onto the ATR crystal without dilution [13]. ATR-FTIR spectroscopy obtains the structural information of the organic components through the IR signal reflected from the sample's surface [14].

2.2. Near-Infrared Spectroscopy

Near-infrared (NIR) spectroscopy is a rapid, non-destructive and sensitive technology operating in the wavenumber range of 12,500–4000 cm^{-1}. It has been widely applied for qualitative and quantitative analysis of agricultural products and foods [14]. NIR spectroscopy mainly records hydrogen-containing groups in organic molecules, such as O-H, N-H, C-H and S-H chemical bonds. However, the broad and often-overlapping bands caused by molecular overtones and combination vibrations make NIR spectra quite complex to interpret [15]. Therefore, chemometric methods must be used to extract useful chemical information. The rapid development of chemometrics has promoted the development of NIR technology in quantitative analysis. To date, this technology has been widely used in the quantitative analysis of binary and ternary oil blends [16][17].

2.3. Raman Spectroscopy

Raman spectroscopy is based on the Raman scattering effect. The Raman effect allows the acquisition of vibrational situations inside the molecule, thus allowing the characterization of different functional groups present. Furthermore, quantitative analysis models can be built based on the area or intensity of characteristic peaks [1]. Again, quantitative analysis is made more challenging due to spectral collinearity, and overlapping peaks, as well as the Raman intensity highly depends on the concentrations of the target analytes [18][19]. Therefore, it is necessary to combine advanced chemometric methods with Raman spectroscopy to improve the efficiency and accuracy of quantitative analysis.

2.4. Fluorescence Spectroscopy

Fluorescence (FS) spectroscopy has the advantages of efficient, convenient and sensitive detection. 'Fluorescence' is a cold luminescence phenomenon of photoluminescence. It operates on the principle that after a substance absorbs electromagnetic radiation, the excited atoms or molecules return to their ground state. In this process of transitioning from a higher energy level to a lower energy level, energy is released in the form of electromagnetic radiation. The relationship between the FS energy and the corresponding wavelength is the FS spectrum. The content of a substance can be determined according to the FS intensity [20]. Due to the presence of various common fluorophores in edible oils, the FS spectra can be overlapped when analyzing oil blends [21]. Again, chemometric means are needed to extract and optimize the FS spectra to improve prediction performance [22][23]. Since it has a lower detection limit than other spectroscopic techniques [24], FS spectroscopy is a powerful tool to quantify single component oil in edible oil blends.

2.5. Ultraviolet-Visible Spectroscopy

Ultraviolet-visible (UV-vis) spectroscopy is a very common analytical technique that includes parts of the ultraviolet and visible light regions (200–800 nm). The resultant UV-vis spectrum is the result of electron energy level transitions in molecules or atoms, which absorb the UV-vis light. Different substances often show unique UV-vis spectra owing to their different compositions and spatial structures, although the peaks will often be overlapped due to the presence of common

UV-active moieties. Particularly in complex matrices such as oil blends, it is difficult to directly use the spectra for quantitative analysis [25]. However, with the maturation of chemometrics as a discipline, many researchers have adopted UV-vis spectroscopy combined with chemometric techniques for single component oil quantification. In this way, the contents of specific substances can be quantified using the intensity of their characteristic UV-vis peaks [26].

2.6. Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) is a physical process based on radio frequency radiation absorbed by atomic nuclei subjected to strong magnetic fields. Under a constant external magnetic field, the atomic nuclei with spin is irradiated by radio frequency radiation. When the radio frequency is exactly equal to the precession frequency of the atomic nuclei, it can be absorbed. The resulting resonance absorption spectrum is called a NMR spectrum [27]. NMR spectroscopy can directly provide the numbers of specific atoms in a sample present under different chemical environments, as well as the structural information of their adjacent groups. Consequently, it provides information about the molecular arrangement of organic samples.

2.7. Mass spectrometry

Mass spectrometry (MS) is a technique used to identify unknown compounds in samples by preparing, separating, and detecting gas-phase ions. It separates the gas-phase ions according to their mass-to-charge ratio. MS analyzes the structures of compounds by the position of their mass peaks, and can quantify compounds from the peaks intensities.

3. Chemometric Methods

The obtained datasets shuold be propossed by chemometric methods for signal pretreatment and quantitative model establishment. Chemometrics is used to extract pertinent information from spectra and reduce background interference. It mainly includes preprocessing, variable selection and multivariate calibration. This section introduces some popular chemometric methods used for single component oil quantification in edible oil blends.

3.1. Preprocessing Methods

In addition to possessing useful chemical information of samples, the measured matrix also contains some useless information and noise, which can affect the accuracy of quantitative analysis. Therefore, signal pretreatment is necessary to eliminate the influence of useless information and noise before constructing quantitative models. The commoly used preprocessing methods include mean centering (MC), normalization, smoothing, derivative, standard normal variate (SNV) transformation and multiplicative scatter correction (MSC).

3.2. Variable selection methods

The measured matrix usually contains hundreds of variables due to the complex composition of edible oil blends. Each of these variables may be informative, uninformative or just represent inter-correlated variables. Additionally, using a large number of variables and small number of samples may cause overfitting problems [28][29]. Thus, it is necessary to select the most informative variables before constructing quantitative models. The process of variable selection aims to choose a small number of variables which relate to the properties of interest to improve the prediction performance of the models. Competitive adaptive reweighted sampling (CARS) and bootstrapping soft shrinkage (BOSS) are the two most commonly used variable selection methods.

3.3. Multivariate calibration methods

Multivariate calibration methods, including linear and nonlinear calibration methods, are often used for model development in the quantitative analysis of single component oil in edible oil blends. The premise of linear calibration methods is that the spectral matrix has linear additivity, that is, it obeys the Lambert-Beer law. It mainly includes MLR, PCR, and PLS models. However, in practice, there is not always a linear relationship between the spectral matrix and the target values due to instrument noise, baseline drift and other issues. In this case, nonlinear calibration models need to be established. The most commonly used nonlinear calibration methods include ANN, SVR and extreme learning machine (ELM).

References

1. Rifna, E.J.; Pandiselvam, R.; Kothakota, A.; Rao, K.V.S.; Dwivedi, M.; Kumar, M.; Thirumdas, R.; Ramesh, S.V. Advanced process analytical tools for identification of adulterants in edible oils-A review. Food Chem. 2022, 369, 130898.
2. Hu, R.; He, T.; Zhang, Z.W.; Yang, Y.H.; Liu, M.L. Safety analysis of edible oil products via Raman spectroscopy. Talanta 2019, 191, 324–332.
3. Zhang, J.H.; Bian, J.M.; Liu, W.; Shang, X.B.; Yang, X.L. Research progress on detection technology of single component content in edible vegetable oil. Hunan Agric. Sci. 2017, 3, 109–112.
4. Nunes, C.A. Vibrational spectroscopy and chemometrics to assess authenticity, adulteration and intrinsic quality parameters of edible oils and fats. Food Res. Int. 2014, 60, 255–261.
5. Xing, C.R.; Yuan, X.Y.; Wu, X.Y.; Shao, X.L.; Yuan, J.; Yan, W.J. Chemometric classification and quantification of sesame oil adulterated with other vegetable oils based on fatty acids composition by gas chromatography. Lwt-Food Sci. Technol. 2019, 108, 437–445.
6. Yang, H.; Tong, P.J.; Jiang, Y.R.; Cao, W.M.; Wang, X.C.; Wei, T.T.; Li, T.; Zhong, C.; Zhang, Y.M.; Zhou, C.; et al. A new strategy for quantitative proportions in complex systems of blended oils by triacyglycerols and chemometrics tools. J. Am. Oil Chem. Soc. 2017, 94, 631–642.
7. Salghi, R.; Armbruster, W.; Schwack, W. Detection of argan oil adulteration with vegetable oils by high-performance liquid chromatography-evaporative light scattering detection. Food Chem. 2014, 153, 387–392.
8. Rohman, A.; Ghazali, M.A.B.; Windarsih, A.; Irnawati; Riyanto, S.; Yusof, F.M.; Mustafa, S. Comprehensive review on application of FTIR spectroscopy coupled with chemometrics for authentication analysis of fats and oils in the food products. Molecules 2020, 25, 5485.
9. Jimenez-Sotelo, P.; Hernandez-Martinez, M.; Osorio-Revilla, G.; Meza-Marquez, O.G.; Garcia-Ochoa, F.; Gallardo-Velazquez, T. Use of ATR-FTIR spectroscopy coupled with chemometrics for the authentication of avocado oil in ternary mixtures with sunflower and soybean oils. Food Addit. Contam. A 2016, 33, 1105–1115.
10. Amit; Jamwal, R.; Kumari, S.; Kelly, S.; Cannavan, A.; Singh, D.K. Rapid detection of pure coconut oil adulteration with fried coconut oil using ATR-FTIR spectroscopy coupled with multivariate regression modelling. Lwt-Food Sci. Technol. 2020, 125, 109250.
11. Jamwal, R.; Kumari, S.; Dhaulaniya, A.S.; Balan, B.; Singh, D.K. Application of ATR-FTIR spectroscopy along with regression modelling for the detection of adulteration of virgin coconut oil with paraffin oil. Lwt-Food Sci. Technol. 2020, 118, 108754.
12. Sun, X.D.; Lin, W.Q.; Li, X.H.; Shen, Q.; Luo, H.Y. Detection and quantification of extra virgin olive oil adulteration with edible oils by FT-IR spectroscopy and chemometrics. Anal. Methods 2015, 7, 3939–3945.
13. Arslan, F.N.; Caglar, F. Attenuated total Reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy combined with chemometrics for rapid determination of cold-pressed wheat germ oil adulteration. Food Anal. Method 2019, 12, 355–370.
14. Rodriguez-Saona, L.E.; Allendorf, M.E. Use of FTIR for rapid authentication and detection of adulteration of food. Annu. Rev. Food Sci. Technol. 2011, 2, 467–483.
15. Jiang, H.; Chen, Q.S. Determination of adulteration content in extra virgin olive oil using FT-NIR spectroscopy combined with the BOSS-PLS algorithm. Molecules 2019, 24, 2134.
16. Zhuang, X.L.; Xiang, Y.H.; Qiang, H.; Zhang, Z.Y.; Zou, M.Q.; Zhang, X.F. Quality analysis of olive oil and quantification detection of adulteration in olive oil by near-infrared spectrometry and chemometrics. Spectrosc. Spect. Anal. 2010, 30, 933–936.
17. Peng, X.X.; Chen, W.M.; Qiao, X.H.; Gao, R.X.; Yin, Z.R.; Xu, H.D. Quantitative determination of walnut oil adulteration with rapeseed oil, soybean oil and corn oil by near infrared spectroscopy. J. Chin. Cereal. Oil Ass. 2015, 30, 106–113.
18. Huang, F.R.; Li, Y.P.; Guo, H.X.; Xu, J.; Chen, Z.; Zhang, J.; Wang, Y. Identification of waste cooking oil and vegetable oil via Raman spectroscopy. J. Raman Spectrosc. 2016, 47, 860–864.
19. Omar, J.; Sarmiento, A.; Olivares, M.; Alonso, I.; Etxebarria, N. Quantitative analysis of essential oils from rosemary in virgin olive oil using Raman spectroscopy and chemometrics. J. Raman Spectrosc. 2012, 43, 1151–1156.
20. Shi, X.; Luo, Y.K.; Zhang, J.R.; Shi, C.; Zhao, Z.Y. Research progress of fluorescence spectrum analysis technology in food detection. Sci. Technol. Food Ind. 2022, 43, 406–414.
21. Xu, J.; Liu, X.F.; Wang, Y.T. A detection method of vegetable oils in edible blended oil based on three-dimensional fluorescence spectroscopy technique. Food Chem. 2016, 212, 72–77.

22. Li, B.N.; Wang, H.X.; Zhao, Q.J.; Ouyang, J.; Wu, Y.W. Rapid detection of authenticity and adulteration of walnut oil by FTIR and fluorescence spectroscopy: A comparative study. Food Chem. 2015, 181, 25–30.
23. Chen, H.; Geng, D.C.; Chen, T.; Lu, D.L.; Chen, B. Second-derivative laser-induced fluorescence spectroscopy combined with chemometrics for authentication of the adulteration of camellia oil. CYTA-J. Food 2018, 16, 747–754.
24. Uncu, O.; Ozen, B. A comparative study of mid-infrared, UV-visible and fluorescence spectroscopy in combination with chemometrics for the detection of adulteration of fresh olive oils with old olive oils. Food Control 2019, 105, 209–218.
25. Wu, X.Y.; Bian, X.H.; Lin, E.; Wang, H.T.; Guo, Y.G.; Tan, X.Y. Weighted multiscale support vector regression for fast quantification of vegetable oils in edible blend oil by ultraviolet-visible spectroscopy. Food Chem. 2021, 342, 128245.
26. Wu, W.M. Application of UV-VIS recording spectrophotometer. Life Sci. Instrum. 2009, 7, 61–63.
27. Zhao, C.X.; Chen, S.M.; Zhang, H.D.; Jia, M.; Sun, Y.Y.; Chen, G. Application of nuclear magnetic resonance spectroscopy in food quality and safety. Quality and Safety of Agro-products 2021, 18-24.
28. Zheng, K.Y.; Feng, T.; Zhang, W.; Huang, X.W.; Li, Z.H.; Zhang, D.; Yao, Y.; Zou, X.B. Variable selection by double competitive adaptive reweighted sampling for calibration transfer of near infrared spectra. Chemometr. Intell. Lab. 2019, 191, 109-117.
29. Wang, K.Y.; Yang, S.; Guo, C.Y.; Bian, X.H. Spectral variable selection methods based on LASSO algorithm. Journal of Instrumental Analysis 2022, 41, 398-402.