Food Chemistry 217 (2017) 274–280

Contents lists available at ScienceDirect

Food Chemistry

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

Synchronous front-face fluorescence spectroscopy for authentication of the adulteration of edible vegetable oil with refined used frying oil

Jin Tan, Rong Li, Zi-Tao Jiang *, Shu-Hua Tang, Ying Wang, Meng Shi, Yi-Qian Xiao, Bin Jia, Tian-Xiang Lu, Hao Wang

Tianjin Key Laboratory of Food Biotechnology, College of Biotechnology and Food Science, Tianjin University of Commerce, Tianjin 300134, People's Republic of China

ARTICLE INFO

Article history:
Received 2 May 2016
Received in revised form 13 July 2016
Accepted 18 August 2016
Available online 20 August 2016

Keywords:
Synchronous front-face fluorescence
Edible vegetable oil
Used frying oil
Adulteration
Partial least squares regression

ABSTRACT

Synchronous front-face fluorescence spectroscopy has been developed for the discrimination of used frying oil (UFO) from edible vegetable oil (EVO), the estimation of the using time of UFO, and the determination of the adulteration of EVO with UFO. Both the heating time of laboratory prepared UFO and the adulteration of EVO with UFO could be determined by partial least squares regression (PLSR). To simulate the EVO adulteration with UFO, for each kind of oil, fifty adulterated samples at the adulterant amounts range of 1–50% were prepared. PLSR was then adopted to build the model and both full (*leave-one-out*) cross-validation and external validation were performed to evaluate the predictive ability. Under the optimum condition, the plots of observed versus predicted values exhibited high linearity ($R^2 > 0.96$). The root mean square error of cross-validation (RMSECV) and root mean square error of prediction (RMSEP) were both lower than 3%.

1. Introduction

The so-called "gutter oil", or namely, "recycled cooking oil", is currently a food safety topic of wide public concern (Lu & Wu, 2014). It is a term to describe illicit cooking oil which has been recycled from waste oil collected from restaurant fryers, grease traps, slaughterhouse waste and etc (Lu & Wu, 2014). The longtime and recycled use of frying oil and the adulteration of fresh edible vegetable oil (EVO) with used frying oil (UFO) are important aspects of "gutter oil", considering that frying may be one of the most traditional and popular cooking methods throughout the world. It has been reported that almost half the orders in canteens and restaurants incorporate at least one fried item (Hein, Henning, & Isengard, 1998). However, during the frying process, several nutritional components in EVO such as tocopherols (Vitamin E), amino acids, fatty acids and chlorophylls are deteriorated, and hydrolyzation, oxidation and thermal reactions yield oxidized and polymerized products that are undesirable from a healthy point of view (Brenes, García, Dobarganes, Velasco, & Romero, 2002; Choe & Min, 2007; Quaglia, Comendador, & Finotti, 1998). Actually, more than 400 kinds of heat-induced compounds have been found in UFO (Sebastian, Ghazani, & Marangoni, 2014). Among them, many can be absorbed into the fried items and have been shown to be harmful to health after intake. For instance, the *cis-trans* isomerization may be caused during heating and the intake of extensive amounts of isolated *trans*-fatty acids has been associated with arteriosclerosis and heart disease (Dréau, Dupuy, Artaud, Ollivier, & Kister, 2009).

After longtime high temperature treatment contacted with various foods, several kinds of toxic compounds may be yielded and introduced into UFO, such as acrylamide, polyaromatic hydrocarbons, heavy metals, aldehydes and ketones. Therefore the physical and chemical properties of UFO including acid value, peroxide value, iodine value and conductivity would significantly change. However, after conventional refining process including filtering, degumming, neutralizing, bleaching and deodorization, the above-mentioned compounds could be removed from UFO and it is not easy to distinguish between EVO and refined UFO solely based on the traditional physical–chemical indicators (Lu & Wu, 2014). Actually in real-world, the illegal merchants sometimes do not change fresh EVO with the UFO completely but just add the UFO to fresh EVO at uncertain ratios (He et al., 2013), which makes the differentiation between fresh and adulterated EVO and the further quantification of the adulteration even more challenging.

* Corresponding author.
E-mail addresses: tanjin@tjcu.edu.cn (J. Tan), lirong@tjcu.edu.cn (R. Li), ztjiang@tjcu.edu.cn, ztjiang@yahoo.com (Z.-T. Jiang), shtang103@tjcu.edu.cn (S.-H. Tang), yingwang@tjcu.edu.cn (Y. Wang), 767370235@qq.com (M. Shi), 495637806@qq.com (Y.-Q. Xiao), 451992732@qq.com (B. Jia), 2350914998@qq.com (T.-X. Lu), 609910716@qq.com (H. Wang).

http://dx.doi.org/10.1016/j.foodchem.2016.08.053
0308-8146/

Considerable efforts have been paid to the quality assessment of EVO after thermal treatment, based on chromatography (Tu, Li, Wu, Zhao, & Li, 2014) and various spectroscopies including UV–visible (UV–vis) (Gonçalves, Março, & Valderrama, 2014; Hamed, abo El-Wafa, El-Ghorab, & Shibamoto, 2011; Liu et al., 2013; Zhang et al., 2015), nuclear magnetic resonance (NMR) (Zhang, Saleh, & Shen, 2013), near-infrared (NIR) (Engelsen, 1997; Zhou, Liu, & Li, 2015), Fourier transform infrared (FT-IR) (Engelsen, 1997), FT-Raman (Engelsen, 1997) and fluorescence (Mas, Bouveresse, & Birlouez-Aragon, 2004; Poulli, Chantzos, Mousdis, & Georgiou, 2009). Among these spectroscopies, fluorescence spectroscopy owning the advantage of high sensitivity and selectivity has been demonstrated to be highly effective for food authentication (Dankowska & Małecka, 2009; Dankowska, Małecka, & Kowalewski, 2013; Karoui & Blecker, 2011; Kunz, Ottaway, Kalivas, Georgiou, & Mousdis, 2011; Poulli, Mousdis, & Georgiou, 2006, 2007; Sikorska, Górecki, Khmelinskii, Sikorski, & Kozioł, 2005; Sádecká & Tóthová, 2007; Wójcicki et al., 2015). Although the monitoring of the deterioration of EVO, especially extra virgin olive oil during heating via fluorescence spectroscopy has been well-documented (Cheikhousman et al., 2005; Guzmán, Baeten, Pierna, & García-Mesa, 2015; Kongbonga, Ghalila, Majdi, Feudjio, & Lakhdar, 2015; Poulli, Mousdis, & Georgiou, 2009; Tena, García-González, & Aparicio, 2009; Valderrama, Março, Locquet, Ammari, & Rutledge, 2011), the application of fluorescence to the qualification and quantification of UFO was few. Engelsen (1997) compared several spectroscopies for determining the deterioration of UFO and fluorescence was proved to be the best model for anisidine value, oligomers, iodine value and Vitamin E. Poulli, Chantzos et al. (2009) monitored the quality change of several kinds of EVO during thermal stress by total synchronous fluorescence. In the above two studies, traditional right-angle geometry was adopted. Compared with the conventional right-angle geometry, the front-face strategy can reduce the primary and secondary inner filter effects occurring in strongly absorbing samples. It can reflect the intrinsic fluorescence property of bulk food samples and can be used for the rapid and non-destructive detection (Karoui & Blecker, 2011). However, to the best of our knowledge, the utilization of front-face fluorescence spectroscopy for the detection of UFO has not been reported.

Herein, we report the discrimination of UFO from EVO, the rough estimation of the frying time of UFO and the determination of EVO adulteration with UFO based on synchronous front-face fluorescence spectroscopy. The object of this work is to develop a simple, rapid and non-destructive method for the qualification and quantification of the adulteration with UFO, providing a novel solution for the detection of "gutter oil".

2. Materials and methods

2.1. Oil samples

The most frequently used EVO for frying foods in China including colza oil (CO), palm oil (PO) and soybean oil (SO) samples were purchased from online or local supermarkets (Table 1). The botanical origin and quality of all the samples were guaranteed by the manufacturers. All the samples were produced in 2015 and stored in the dark at room temperature prior to analysis. As there were only several brands for each botanical origin commercially available in local and online markets whose quality could be guaranteed, only three to five renowned brands per botanical origin were studied. The numbers of CO, PO and SO samples were four, three and five, respectively. Two real-world UFO samples were collected from local twisted cruller and fried chicken sellers in college canteens (Table 1). Simulated UFO samples were prepared from fresh EVO by thermal treatment. Specifically, 30.0 ± 0.1 mL fresh oils were added to 40 mL cylindrical porcelain crucibles (the inner diameter of its cross section was 4.0 cm) and then transferred into a drying oven previously heated at 180 ± 1 °C. The area of the upper surface of the oil which was in direct contact with the air was 12.6 cm^2, and the ratio of such area and the volume was 0.42 cm^{-1} (12.6 cm^2/30 cm^3). While the surface area/volume ratio for thermal treatment of oils was 1.84 cm^{-1} (55.2 cm^2/30 cm^3). Samples were heated in air at 180 ± 1 °C for 0.5, 1, 2, 3, 5, 6, 8, 12, 16, 24, 32, 40 and 48 h, respectively. The crucibles were left open during heating. The samples were only heated at daytime (9:00–17:00, 8 h). Hence the samples heated no more than 8 h were obtained within one day by continuous heating and those heated more than 8 h were prepared on several successive days. Each day after thermal treatment, the oils were left in the porcelain crucibles and naturally cooled to room temperature. During the nights without heating, the samples were stored in the dark at room temperature.

Due to the deep color after longtime use, the raw real-world UFO samples were processed by bleaching with activated clay (Zhang et al., 2013). During the heating of UFO at 85–90 °C, 10% activated clay was introduced. The mixture was stirred for 30 min, cooled to room temperature and filtered by gauze. The filtrate was centrifuged at 4000 r/min for 10 min and the supernatant was collected. The obtained discolored UFOs were stored in the dark at room temperature and were analyzed within three days.

The adulterated edible oil samples were prepared by adding an adulterant to the corresponding fresh oil at amount range of 1.0–50 mL/100 mL with 1.0 mL interval. Thus, for each adulterant, fifty adulterated oil samples were obtained (n = 50). The adulterant was the corresponding oil which had been heated at 180 ± 1 °C for 24 h.

Table 1
Edible vegetable oil (EVO) and used frying oil (UFO) samples investigated in this study.

Classification	Sample code	Botanical origin	Brand	Geographical origin	Source
EVO	C1	Colza	Luhua	China	Online retailer
	C2	Colza	Youyihua	China	Online retailer
	C3	Colza	Xiancan	China	Online retailer
	C4	Colza	Evergrande	China	Online retailer
	P1	Palm	Weini	Malaysia	Online retailer
	P2	Palm	Gaysorn	Thailand	Online retailer
	P3	Palm	Textron	Spain	Online retailer
	S1	Soybean	Fulinmen	China	Local supermarket
	S2	Soybean	Jinlongyu	China	Local supermarket
	S3	Soybean	Yuanbao	China	Online retailer
	S4	Soybean	Jiusan	China	Online retailer
	S5	Soybean	Evergrande	China	Online retailer
UFO	UFO1	Soybean	Yuanbao	China	Twisted cruller fryer
	UFO2	Soybean	Unknown	China	Fried chicken fryer

Simulated UFOs and real-world UFOs after bleaching were both selected as the adulterant for the corresponding fresh oil from the same botanical origin. Besides, the adulteration of the mixture of five SO samples S1–S5 was also tested to demonstrate the practical applicability of the method. The five SO samples were mixed in the same proportion and the mixed oil that had been heated at 180 ± 1 °C for 24 h was added to the mixture at amount range of 1.0–50 mL/100 mL with 1.0 mL interval.

2.2. Synchronous front-face fluorescence spectroscopy

Fluorescence spectra were obtained with an F-4600 spectrofluorometer with a 950 W xenon lamp source (Hitachi, Japan). The slit widths for excitation and emission were both 2.5 nm. The front-face geometry of neat oils was used for the spectra acquisition with a 5 × 10 mm fused-quartz cuvette. The incidence angle of the excitation radiation was 22.5°. The excitation and emission in the 250–500 nm range with a wavelength resolution of 1 nm were scanned simultaneously with a constant wavelength interval (Δλ) between them. Spectra were recorded at Δλ values of 20, 40, 60, 80 and 100 nm for each sample. Fluorescence intensities were plotted as a function of the excitation wavelength. For each sample three spectra were measured successively and the average of the three replicates was used for further analysis.

2.3. Statistical analysis

Prior to statistical analysis, the standard normal variate (SNV) pretreatment was adopted to correct for possible baseline shift and global intensity changes in the fluorescence data. Principal component analysis (PCA) and partial least squares regression (PLSR) were performed using Unscrambler 9.7 (CAMO, Norway). PCA was applied to the fluorescence data obtained after different thermal treatment time. The differentiation of fresh EVOs from the three botanical origins and the corresponding UFOs was then achieved by linear discriminant analysis (LDA) based on the first five PCs with eigenvalues higher than one by using IBM SPSS 19.0 (IBM, USA). PLSR was executed to estimate the thermal treatment time and the full (*leave-one-out*) cross-validation was used to assess the predictive ability of the model. Root mean square error of calibration (RMSEC), coefficient of determination for calibration (R_c^2), root mean square error of cross-validation (RMSECV) and coefficient of determination for cross-validation (R_{cv}^2) were calculated. The optimal number of PLSR components was decided by plotting the RMSECV versus the number of components and determining the minimum of the plot.

For the adulteration determination, both full cross-validation and external validation were employed. For each adulterant, fifty adulterated EVO samples were sorted by the adulterant concentration and every five sample was injected into the test set ($n = 10$). The remaining samples composed the training set ($n = 40$). The training set was used to build PLSR models and was validated by full cross-validation. RMSECV and R_{cv}^2 were obtained. The optimal number of PLSR components was decided by plotting the RMSECV versus the number of components and determining the minimum of the plot. The test set was then used to evaluate the predictive ability of the built models. RMSEC, root mean square error of prediction (RMSEP) and the corresponding coefficient of determination for prediction (R_p^2) were determined.

3. Results and discussion

3.1. The preparation of simulated UFO samples by thermal treatment and the selection of real-world UFO samples

As the extrinsic compounds yielded and introduced into UFO during frying process can be removed by conventional refining process including filtering, degumming, neutralizing, bleaching and deodorization, the simulated UFO samples were obtained by heating the neat EVO at 180 °C without frying any food. However, due to the high complexity and uncertainty of the real-world UFOs, the complete simulation by heating oil at laboratory is impossible. Thus in this study the laboratory heated oil samples were prepared to represent the real-world UFOs to some extent. We primarily focused on the intrinsic change of EVO after thermal treatment.

Two real-world UFO samples were obtained from local twisted cruller and fried chicken sellers in college canteens. Twisted cruller and fried chicken may be the most popular frying foods in China. The frying oils used here were both SO as told by the fryers. The brand of UFO1 was Yuanbao which was the same as sample S3, however, the brand of UFO2 was not announced. UFO1 had been used for about one week and the color of the oil was still yellow but became a little darker. UFO2 had been used for at least two weeks and its color had already changed to deep brown. After the bleaching with activated clay, the color of UFO1 recovered to normal and can hardly be discriminated from the fresh EVO by naked-eye. The color of UFO2 became much lighter but was still darker than the fresh EVO. However, it was still not easy to discern the adulteration of EVO with UFO2 at low ratios.

3.2. Synchronous front-face fluorescence spectra of EVO and UFO

The fresh EVO samples showed relatively stronger fluorescence at Δλ = 60 and 80 nm, followed by Δλ = 40 and 100 nm, and much weaker fluorescence could be observed at Δλ = 20 nm (Fig. 1a). The fluorescence maxima shifted from 365 to 335 nm with increasing Δλ from 20 to 100 nm, which is normally observed in synchronous fluorescence. The major compounds responsible for the

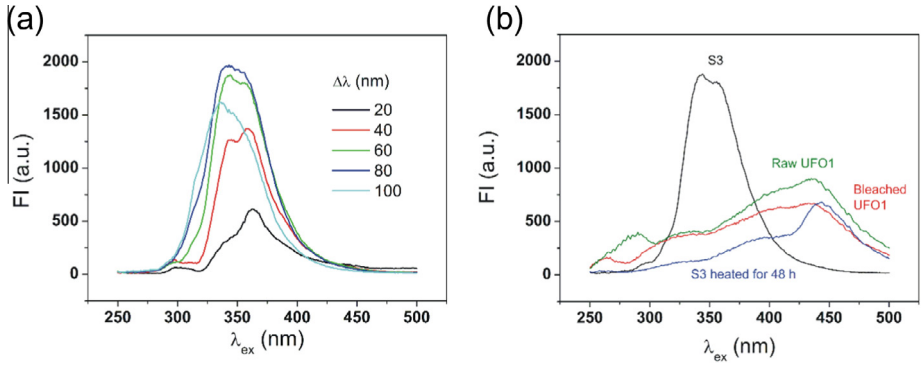

Fig. 1. (a) Synchronous fluorescence spectra of sample S3 at different Δλ. (b) Synchronous fluorescence spectra at Δλ = 60 nm of sample S3, a simulated UFO made from S3 by heating at 180 °C for 48 h and a real-world sample UFO1 before and after bleaching.

fluorescence in this range are phenolic antioxidants and other intrinsic fluorophores in oils (Poulli, Chantzos et al., 2009). The weak band around 300 nm is the characteristic of Vitamin E, which was verified by the comparison of the fluorescence of Vitamin E standard and Vitamin E spiked EVO. After thermal treatment at 180 °C, the fluorescence of the EVO changed dramatically. For example, as can be seen from Fig. 1b, the fluorescence maxima of the sample S3 heated at 180 °C for 48 h becomes much weaker. The original fluorescence from 300 to 400 nm almost disappears. A new band centered at 440 nm arises, along with a weaker should peak at 395 nm. These emerging fluorescence bands can be ascribed to the oxidation products (Poulli, Chantzos et al., 2009). The fluorescence of the raw real-world UFO1 before pretreatment displayed distinct pattern compared with the fresh EVO. The bands belonging to the oxidation products are significantly strong, suggesting the high degree of lipid oxidation after longtime frying. While after bleaching, these bands become a little weaker, indicating the partial removing of the oxidation products by the adsorption of activated clay. The real-world UFO1 showed similar fluorescence to the simulated UFO heated for 48 h. Interestingly, UFO1 had been actually used for about one week. Such coincidence demonstrates that the rough estimation of the frying time of UFO by the observation of synchronous fluorescence changes of the oil is feasible. The remarkable changes in fluorescence are mainly attributed to the deterioration of Vitamin E, phenolic antioxidants and other intrinsic fluorophores in oils and the lipid oxidation after longtime thermal treatment.

The time response of the simulated UFO was carefully examined. The typical time-dependent fluorescence changes of sample S3 toward thermal treatment is depicted in Fig. 2. Within 2 h of thermal treatment, the oils present similar synchronous fluorescence, and along with the further thermal treatment, the fluorescence at 300 nm belonging to Vitamin E and the bands related to the phenolic antioxidants and other intrinsic fluorophores both gradually reduce, indicating the continuing deterioration of these compounds. After heated for 5 h, the EVO intrinsic fluorescence diminishes to only no more than half of the initial, and after 8 h, such fluorescence nearly disappears, showing the almost completely deterioration of the intrinsic fluorophores in EVO. On the other hand, a new peak at 440 nm appears at 8 h and then increases dramatically, which demonstrates that the lipid oxidation largely occurs after 8 h heating and then strengthens with the further thermal treatment. This result is in good agreement with the observation of Poulli, Chantzos et al., 2009 that the fluorescence of several EVOs in the region of 400–450 nm increased after 8 h at 190 °C due to the formation of secondary oxidation products. The time response of the simulated UFO reveals that dramatic changes take place after 2–8 h of thermal treatment at 180 °C which may be used as the critical point to differentiate UFO and EVO. The frying oils used for no more than 2 h can be regarded as fresh oils or oils in-use and those used for at least 8 h should be treated as wasted UFO and had better be discarded.

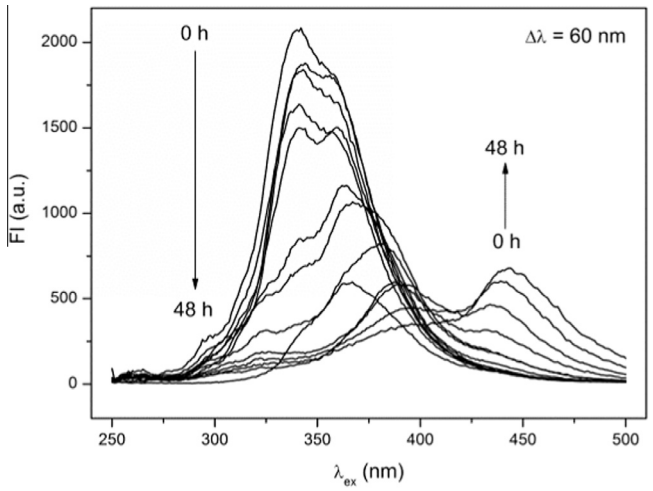

Fig. 2. Time-dependent changes of synchronous fluorescence spectra at Δλ = 60 nm of sample S3 with thermal treatment at 180 °C for 0–48 h.

3.3. Discrimination of UFO from EVO

To reduce the data dimensionality, to reveal the underlying variables, and to present the fingerprints more clearly, PCA was executed to the raw data from the synchronous fluorescence spectra of the EVOs and UFOs. Fig. 3 shows the obtained PCA scores and loading plot. In general, the EVO and UFO can be roughly differentiated using the first two PCs. The fresh POs (heated for 0–2 h) mainly locate in the first quadrant and the brands from different countries are scattered, which can be explained by the varied composition of fluorescent species related to the geographical origins. Compared with the fresh POs, the used POs (heated for 5–48 h) obtain lower scores in the first PC. The fresh COs and SOs are tightly clustered in the fourth quadrant while the used ones mainly shift to the second and third quadrants. The PCA result is in agreement with the observation in the time response of the fluorescence of the simulated UFO.

The loading plot shows the dominating factors responsible for the discrimination. The first PC is highly related to the fluorescence in 300–400 nm which is mainly attributed to Vitamin E, phenolic antioxidants and other intrinsic fluorophores. The second PC largely corresponds to the fluorescence in 400–450 nm, and this range belongs to the secondary oxidation products. Such result proves that the intrinsic fluorophores in EVO is the critical component that mostly helps distinguishing the UFO and EVO, while the amount of oxidation products plays a secondary role for the discrimination. Currently Europe is the only region that owns regulations on UFO based on the test of total polar compound (TPC)

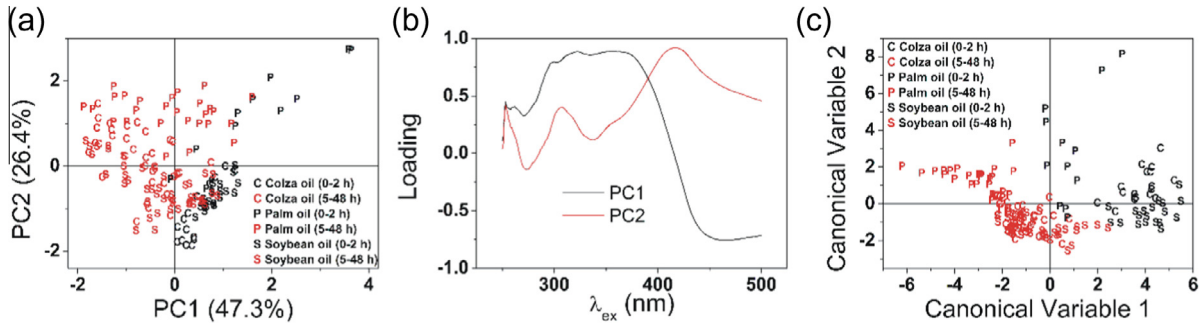

Fig. 3. PCA score (a), loading (b) and LDA score (c) plots from synchronous fluorescence spectra at Δλ = 60 nm for discrimination of the EVOs with thermal treatment at 180 °C for different times.

(Sebastian et al., 2014). TPC is highly related to the oxidation products. Here we show that the intrinsic fluorophores in EVO can also be used as an indicator for the frying oil quality. However, as the content of Vitamin E and phenolic antioxidants in EVO is largely reliant on the botanical origin and the loss of Vitamin E may also occur after package depending on various storage conditions such as exposure to radiation, oxygen and high temperature (Gonçalves et al., 2014), the real applicability of using Vitamin E and phenolic antioxidants to characterize UFO needs further investigation using large number of oil samples.

LDA was then performed to distinguish the fresh EVOs (heated for 0–2 h) and UFOs (heated for 5–48 h). The obtained LDA score plot shown in Fig. 3c exhibits a preliminary isolation of the fresh EVOs and UFOs, which mainly locate in the upper right half and lower left half of the plot, respectively. However, the used CO and SO samples are still severely overlapped with each other.

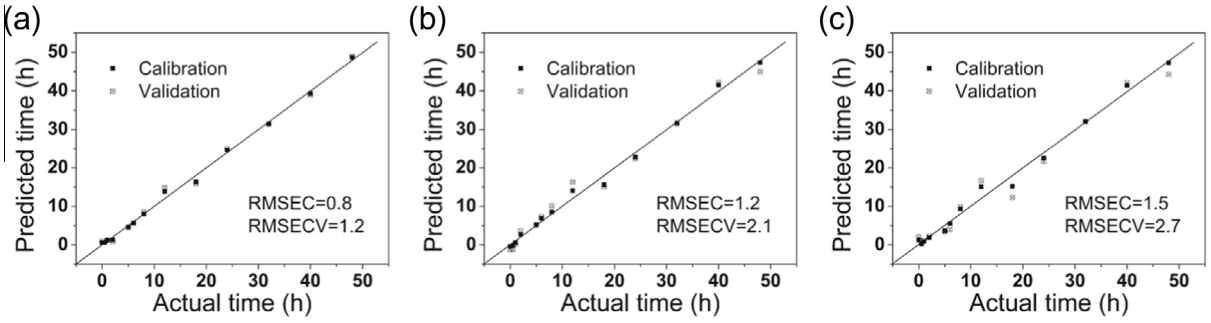

Fig. 4. Predicted versus actual thermal treatment time at 180 °C of samples C2 (a), P2 (b) and S3 (c) based on the synchronous front-face fluorescence spectra under optimum conditions (see Table S1).

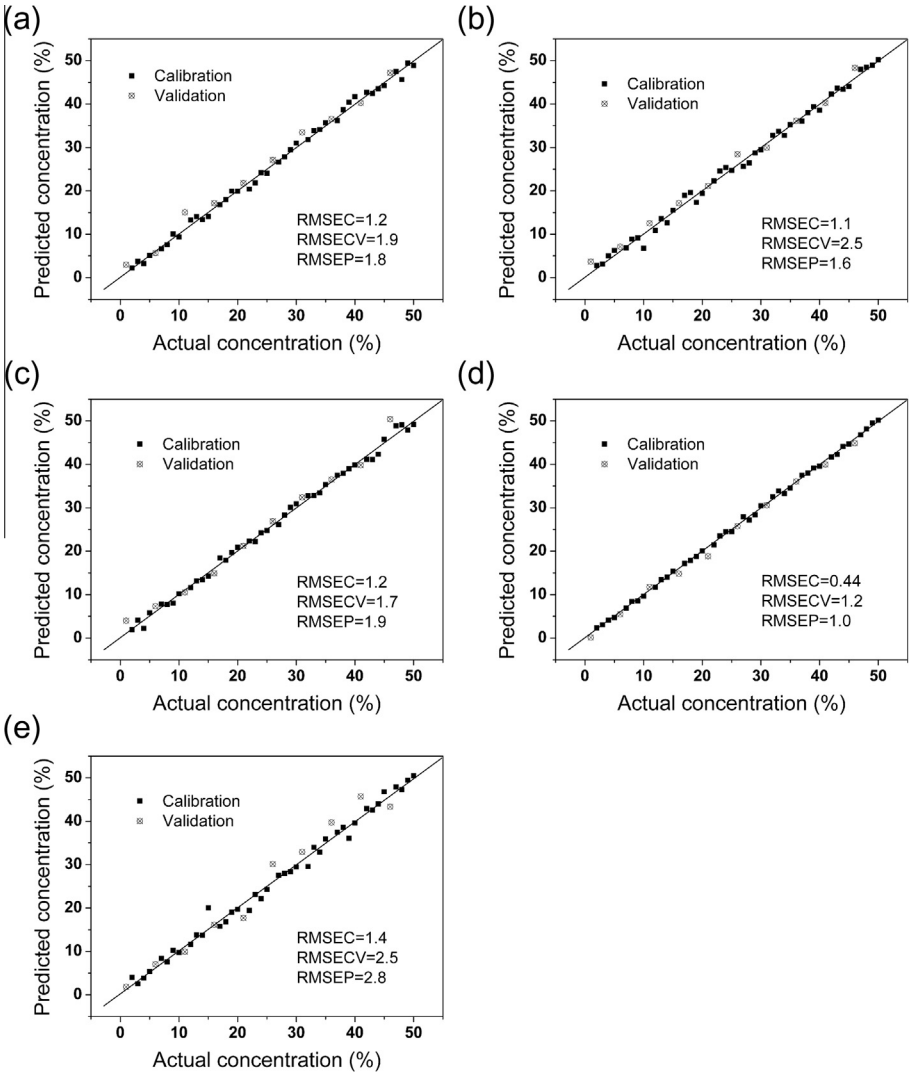

Fig. 5. Predicted versus actual concentration of UFO samples C2 (a), P2 (b), S3 (c), a real-world sample UFO1 (d) and the mixture of five SO samples S1–S5 (e) in the same proportion in the corresponding EVO based on the synchronous front-face fluorescence spectra under optimum conditions. The adulterant was the corresponding oil which had been heated at 180 ± 1 °C for 24 h. (see Table S2).

Although the fresh CO and SO samples can be separated by fluorescence based on their different intrinsic fluorophore profiles, the differentiation of the used CO and SO samples solely by fluorescence is hard to achieve, possibly due to the deterioration of the intrinsic fluorophores and the formation of similar oxidation products. Nevertheless, it does not influence the discrimination of UFOs from EVOs.

3.4. Determination of the using time of UFO

By using PLSR, the thermal treatment time of the simulated UFOs can be estimated (Fig. 4). All the EVO samples were tested and the optimum conditions for regression and the regression results are listed in Table S1 (Supplementary Data). Most of the optimal $\Delta\lambda$ for regression locate in 60–100 nm, which is in accordance with the Stokes shift of Vitamin E and the secondary oxidation products (Poulli, Chantzos et al., 2009). Under these conditions, the plots of observed versus predicted values exhibit good linearity. The R^2_{cv} values are all higher than 0.9. The RMSECV range from 0.8 to 5.2 h and most of them are no more than 3 h.

To verify the applicability of this method to predict the frying time of real-world UFO samples, UFO1 was set as the testing sample based on the built model using the simulated UFO made from S3 as the calibration set. The frying time of UFO1 was calculated to be 51 h, which was not largely deviated from the fact that UFO1 had been actually used for about one week. The above results suggest that the PLSR model based on synchronous fluorescence is competent for the rough estimation of the frying time of UFO.

3.5. Quantification of the EVO adulteration with UFO

To simulate the adulteration of EVO with UFO, each one sample from each botanical origin of EVO after thermal treatment at 180 °C for 24 h and two real-world UFO samples were selected as the adulterants. Besides, the mixture of all the SO samples was also tested. The fresh EVO was mixed with the corresponding UFO at different ratios of 1–50% (v/v). The determination of EVO adulteration with UFO based on the synchronous front-face fluorescence was attempted by PLSR. The optimum conditions obtained after the rational selection of $\Delta\lambda$ are listed in Table S2 (Supplementary Data). As shown in Fig. 5, high linearity is presented in the plots of observed versus predicted values, for laboratory prepared UFOs, real-world UFOs and even mixed oil. The slopes and intercepts are close to 1 and 0, respectively. The R^2_{cv} and R^2_{p} values are at least 0.96. The RMSECV and RMSEP are all lower than 3%. These results demonstrate that the built model is effective for the detection of EVO adulteration with UFO at low adulteration levels.

4. Conclusion

In conclusion, this study achieved the discrimination of UFO from fresh EVO, the estimation of the frying time of UFO and the determination of EVO adulteration with UFO. The simple, fast and non-destructive qualification and quantification were based on the combination of synchronous front-face fluorescence spectroscopy and multivariate analysis. The largest difference between UFO and fresh EVO was pointed out to be the content of Vitamin E, phenolic antioxidants, other intrinsic fluorophores in EVO and lipid oxidation products. The rough frying time can be predicted via monitoring the time response in fluorescence of the UFO. The adulteration of EVO with UFO can be determined by PLSR. Under the optimum condition, the model presented high linearity and the method could detect lower to 3% UFO adulterated in EVO. The high convenience, rapidity and sensitivity of the proposed method demonstrate that the synchronous front-face fluorescence spectroscopy can be a promising measure for the detection of "gutter oil".

Acknowledgements

The present research was financially supported by the National Natural Science Foundation of China (21405111), the Natural Science Foundation of Tianjin (12JCZDJC34100 and 13JCYBJC18700), and National Training Programs for Innovation and Entrepreneurship of Undergraduates (201510069044).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2016.08.053.

References

Brenes, M., García, A., Dobarganes, M. C., Velasco, J., & Romero, C. (2002). Influence of thermal treatments simulating cooking processes on the polyphenol content in virgin olive oil. *Journal of Agricultural and Food Chemistry, 50*, 5962–5967.

Cheikhousman, R., Zude, M., Bouveresse, D. J.-R., Léger, C. L., Rutledge, D. N., & Birlouez-Aragon, I. (2005). Fluorescence spectroscopy for monitoring deterioration of extra virgin olive oil during heating. *Analytical and Bioanalytical Chemistry, 382*, 1438–1443.

Choe, E., & Min, D. B. (2007). Chemistry of deep-fat frying oils. *Journal of Food Science, 72*, 77–86.

Dankowska, A., & Małecka, M. (2009). Application of synchronous fluorescence spectroscopy for determination of extra virgin olive oil adulteration. *European Journal of Lipid Science and Technology, 111*, 1233–1239.

Dankowska, A., Małecka, M., & Kowalewski, W. (2013). Discrimination of edible olive oils by means of synchronous fluorescence spectroscopy with multivariate data analysis. *Grasas y Aceites, 64*, 425–431.

Dréau, Y. L., Dupuy, N., Artaud, J., Ollivier, D., & Kister, J. (2009). Infrared study of aging of edible oils by oxidative spectroscopy index and MCR-ALS chemometric method. *Talanta, 77*, 1748–1756.

Engelsen, S. B. (1997). Explorative spectrometric evaluations of frying oil deterioration. *Journal of the American Oil Chemists Society, 74*, 1495–1508.

Gonçalves, R. P., Março, P. H., & Valderrama, P. (2014). Thermal edible oil evaluation by UV–Vis spectroscopy and chemometrics. *Food Chemistry, 163*, 83–86.

Guzmán, E., Baeten, V., Pierna, J. A. F., & García-Mesa, J. A. (2015). Evaluation of the overall quality of olive oil using fluorescence spectroscopy. *Food Chemistry, 173*, 927–934.

Hamed, S. F., abo El-Wafa, G. A., El-Ghorab, A., & Shibamoto, T. (2011). Quality assessment of heated cooking oil, Agab, using a simple newly-developed spectrophotometric method. *Journal of the American Oil Chemists Society, 88*, 1851–1855.

He, J., Xu, W., Shang, Y., Zhu, P., Mei, X., Tian, W., & Huang, K. (2013). Development and optimization of an efficient method to detect the authenticity of edible oils. *Food Control, 31*, 71–79.

Hein, M., Henning, H., & Isengard, H. (1998). Determination of total polar parts with new methods for the quality survey of frying fats and oils. *Talanta, 47*, 447–454.

Karoui, R., & Blecker, C. (2011). Fluorescence spectroscopy measurement for quality assessment of food systems—A review. *Food Technology and Biotechnology, 4*, 364–386.

Kongbonga, Y. M., Ghalila, H., Majdi, Y., Feudjio, W. M., & Lakhdar, Z. B. (2015). Investigation of heat-induced degradation of virgin olive oil using front face fluorescence spectroscopy and chemometric analysis. *Journal of the American Oil Chemists Society, 92*, 1399–1404.

Kunz, M. R., Ottaway, J., Kalivas, J. H., Georgiou, C. A., & Mousdis, G. A. (2011). Updating a synchronous fluorescence spectroscopic virgin olive oil adulteration calibration to a new geographical region. *Journal of Agricultural and Food Chemistry, 59*, 1051–1057.

Liu, T.-B., Zhou, Y., Lv, J., Chen, Z.-W., Li, B.-B., & Shi, Y. (2013). Authentication of edible vegetable oil and refined recycled cooking oil using a micro-UV spectrophotometer based on chemometrics. *Journal of the American Oil Chemists Society, 90*, 1599–1606.

Lu, F., & Wu, X. (2014). China food safety hits the "gutter". *Food Control, 41*, 134–138.

Mas, P. A., Bouveresse, D. J. R., & Birlouez-Aragon, I. (2004). Fluorescence spectroscopy for monitoring rapeseed oil upon heating. *Czech Journal of Food Science, 22*, 127–129.

Poulli, K. I., Chantzos, N. V., Mousdis, G. A., & Georgiou, C. A. (2009). Synchronous fluorescence spectroscopy tool for monitoring thermally stressed edible oils. *Journal of Agricultural and Food Chemistry, 57*, 8194–8201.

Poulli, K. I., Mousdis, G. A., & Georgiou, C. A. (2006). Synchronous fluorescence spectroscopy for quantitative determination of virgin olive oil adulteration with sunflower oil. *Analytical and Bioanalytical Chemistry, 386*, 1571–1575.

Poulli, K. I., Mousdis, G. A., & Georgiou, C. A. (2007). Rapid synchronous fluorescence method for virgin olive oil adulteration assessment. *Food Chemistry, 105*, 369–375.

Poulli, K. I., Mousdis, G. A., & Georgiou, C. A. (2009). Monitoring olive oil oxidation under thermal and UV stress through synchronous fluorescence spectroscopy and classical assays. *Food Chemistry, 117*, 499–503.

Quaglia, G., Comendador, J., & Finotti, E. (1998). Optimization of frying process in food safety. *Grasas y Aceites, 49*, 275–281.

Sádecká, J., & Tóthová, J. (2007). Fluorescence spectroscopy and chemometrics in the food classification – A review. *Czech Journal of Food Science, 25*, 159–173.

Sebastian, A., Ghazani, S. M., & Marangoni, A. G. (2014). Quality and safety of frying oils used in restaurants. *Food Research International, 64*, 420–423.

Sikorska, E., Górecki, T., Khmelinskii, I. V., Sikorski, M., & Kozioł, J. (2005). Classification of edible oils using synchronous scanning fluorescence spectroscopy. *Food Chemistry, 89*, 217–225.

Tena, N., García-González, D. L., & Aparicio, R. (2009). Evaluation of virgin olive oil thermal deterioration by fluorescence spectroscopy. *Journal of Agricultural and Food Chemistry, 57*, 10505–10511.

Tu, D., Li, H., Wu, Z., Zhao, B., & Li, Y. (2014). Application of headspace solid-phase microextraction and multivariate analysis for the differentiation between edible oils and waste cooking oil. *Food Analytical Methods, 7*, 1263–1270.

Valderrama, P., Março, P. H., Locquet, N., Ammari, F., & Rutledge, D. N. (2011). A procedure to facilitate the choice of the number of factors in multi-way data analysis applied to the natural samples: Application to monitoring the thermal degradation of oils using front-face fluorescence spectroscopy. *Chemometrics and Intelligent Laboratory Systems, 106*, 166–172.

Wójcicki, K., Khmelinskii, I., Sikorski, M., Caponio, F., Paradiso, V. M., Summo, C., Pasqualone, A., & Sikorska, E. (2015). Spectroscopic techniques and chemometrics in analysis of blends of extra virgin with refined and mild deodorized olive oils. *European Journal of Lipid Science and Technology, 117*, 92–102.

Zhang, W., Li, N., Feng, Y., Su, S., Li, T., & Liang, B. (2015). A unique quantitative method of acid value of edible oils and studying the impact of heating on edible oils by UV–Vis spectrometry. *Food Chemistry, 185*, 326–332.

Zhang, Q., Saleh, A. S. M., & Shen, Q. (2013). Discrimination of edible vegetable oil adulteration with used frying oil by low field nuclear magnetic resonance. *Food and Bioprocess Technology, 6*, 2562–2570.

Zhou, Y., Liu, T., & Li, J. (2015). Rapid identification between edible oil and swill-cooked dirty oil by using a semi-supervised support vector machine based on graph and near-infrared spectroscopy. *Chemometrics and Intelligent Laboratory Systems, 143*, 1–6.