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SHORT COMMUNICATION

Determination of thermally deteriorated sunflower oil re-used as adulterants in different sunflower oils using FTIR spectroscopy

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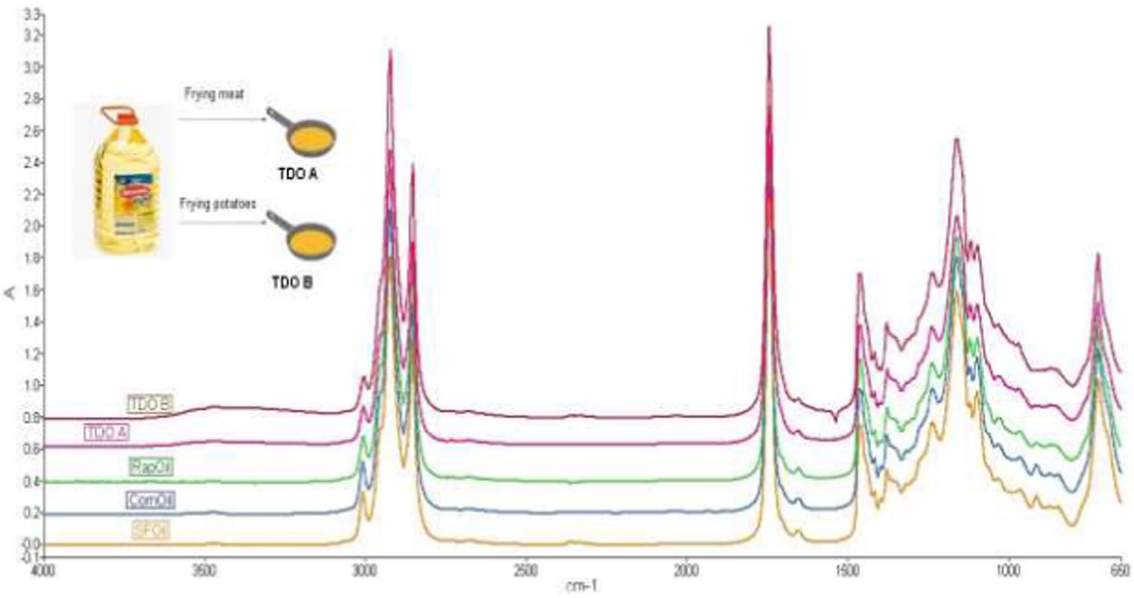
Abstract

Edible oils (EdO), such as sunflower, are preferably chosen for frying because they get soaked less and are very light. Nevertheless, there is the possibility that they can be adulterated with thermally deteriorated oil such as the leftover oil after the frying process of meat with breadcrumbs (TDO A) or potatoes (TDO B). It may harm our health and the environment, requiring a fast and reliable screening test for such adulterants. In this study, Fourier transform infrared spectroscopy based on the attenuated total reflectance (ATR–FITR) sampling technique was studied to directly determine TDO A or TDO B as adulterants in EdO-TDO binary mixtures. We proposed quantification methods based on the simple linear regression analysis of IR spectral intensity (peak height or peak area) on adulterant concentration 0 ÷ 70% (v/v). The methods proposed proved to be accurate (% recovery in the range of 98.0 ÷ 101.1%), precise (RSD < 2.7%), and technically simple (total analysis time of 5–10 min).

Graphical abstract



Keywords Edible oil · Adulteration · Thermally deteriorated oil · Infrared spectroscopy · Frying process · Peak height · Peak area · Screening test

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Introduction

"*Edible oils*" (also known as "cooking oils") are the term specifically ascribed to a group of plant, animal, or synthetic fatty liquids employed in food preparation such as frying, baking, and flavoring (salad dressings and bread dips). They are, in fact, an important component of the human diet as they are rich in liposoluble vitamins such as A, D, E, and K, among which vitamin E having antioxidant properties can devour free radicals blamed for carcinogenesis and aging (Zhou et al. 2020). The composition of edible oils is such that triacylglycerides (composed of different fatty acids) account for about 96% of their mass. The susceptibility to oxidative processes can render fatty acids, free and/or bound to glycerol degraded into volatile and non-volatile compounds in edible oils. Thus, a great number of studies have been dedicated to monitoring the quality of such products after processing until use by the consumer (Bunaciu et al. 2020).

The sunflower (*Helianthus annuus L.*) is a large annual forb of the Asteraceae family cultivated in many countries in the world for its edible oil and seeds (Raß et al. 2008; Rauf et al. 2017). Typically, the yield for oilseed sunflower and sunflower oil (SFO) is 68.40–74.35 bushels per acre (or 2.3–2.5 t/ha) and 1026–1227 pounds/acre (or 1.15–1.37 t/ha), respectively (Orlov 2022). SFO has high amounts of unsaturated fatty acids, of which 70% is linoleic acid. The domestic consumption of sunflower seed oil in 27 EU countries was reported to be 5,063,000 metric tons (Shahbandeh 2022). Thus, there is a possibility that sunflower oil could be used as an adulterant (Downey et al. 2002) or be adulterated with re-used frying oil as investigated for other edible vegetable oils (Zhang et al. 2012) given the fact that repeatedly heating edible oils at high temperatures is common practice during cooking. Ganesan et al. pointed out in a review that the consumption of repeatedly heated oils and inhalation of cooking fume may cause a high incidence of genotoxicity, mutagenicity, tumorigenicity and other types of cancers (Ganesan et al. 2019).

However, present regulations cannot require that traders and producers confirm the legitimacy of food or the analytical lower ability to identify adulteration.

Detection of adulteration involves a focus of interest, and counterfeiting has significant implications for consumer health. There may be consequences for customers who switch from pricey vegetable oils or diet oils to less expensive oils, underscoring the significance of this issue (Vlachos et al. 2006; Poiana et al. 2012; Mohammed et al. 2021).

In the literature, Fourier transform infrared spectroscopy (FTIR) has been successfully exploited for studying the oxidation of edible oils (Rohman et al. 2011; Russin et al. 2004; Guillén and Cabo 1999Guillén et al. 2000) and the effect of heating processing on edible oil quality (Innawong et al. 2004; Poiana et al. 2013; Tena et al. 2009). Recently, our research group has also demonstrated the applicability of FTIR spectroscopy for monitoring the oxidation process of lard during heating (Bunaciu et al. 2021, 2022a) and determining the adulteration of some edible oils with paraffin oil (Bunaciu et al. 2022b). With this study, we aim to further emphasize the suitability and applicability of FTIR spectroscopy for a fast, cost-effective and reliable determination of the adulteration of different edible oils (sunflower) with thermally degraded oil (TDO) obtained during the frying process of meat with breadcrumbs (TDO A) or potatoes (TDO B).

Materials and methods

Samples

SFOs were purchased in 1-L PET bottles from a local supermarket under the brand name "*Spornic*" (SFO 1, Prutul SA; produced in Galați district, Romania) or *"Floriol*" (SFO 2, Bunge Prio Romania, produced in Buzau district, Romania).

The adulterants were sunflower oil "*Spornic*" heated oils re-used after the frying process of meat with breadcrumbs (TDO A) and potatoes (TDO B) at the restaurant "Pikandy Pizza & Grill" (Romania, Bragadiru—Ilfov district).

All the samples were prepared in our laboratory by mixing fresh commercial edible oils, with the stock solution of one adulterant (either TDO A or TDO B) to have the concentration range under study of TDO 0 ÷ 70% (v/v). For this, fixed volumes of each adulterant (0.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0 ml, respectively) were put in 100 ml volumetric flasks and added to the mark with each fresh edible oil. These mixtures were manually shaken for homogenization and kept in a refrigerator between the analyses.

Measurement procedure

FTIR spectra were acquired with a PerkinElmer FTIR spectrometer equipped with an ATR sampling device, a detector of deuterated triglycine sulfate and a beam splitter of potassium bromide. For measurement, a small drop (~ 0.1 mL) of edible oil mixture was pipetted on the top of the ATR baseplate, which was kept at 27 °C. The spectra were then recorded in the range of 650–4000 cm^{-1} as absorbance values at each data point and were subtracted by air background air signal; the interferograms of 32 single scans were co-added at a resolution of 4 cm^{-1}. The collection time for each sample's spectrum was approximately 2 min. After every scan, a new background spectrum was taken. The ATR base was carefully cleaned in situ by scrubbing with hexane and then ethanol and dried with soft tissue before the next measurement. Unless stated otherwise, each sample was measured in triplicate to get the average spectrum for quantitative purposes. Spectrum software version 5.01 (PerkinElmer Co., Beaconsfield, Bucks, UK) and spectrum software version 10.5.1.581 (PerkinElmer Inc., Boston, MA, USA) were used for spectral acquisition and processing, respectively.

Results and discussion

Nowadays, deep frying in which food is submerged in edible oil at 176.7 ÷ 190.6 °C is one of the common cooking methods (LLC, 2022) because it can enhance the sensorial properties including crispy texture, golden brown color, and of course fried flavor. It is known that forced oxidation of edible oil could occur even at a moderate temperature (~58 °C) (Russin et al. 2004). It is obvious that the two oil adulterants used in our study definitely contain thermally degraded products. It may be evidenced by the growth of the absorption band and/or band shift as the oxidative processes take place. To quantify adulterants in different EdO, we searched for infrared spectral characteristics to reliably indicate the presence of TDO A or TDO B. Herein, our quantification method for TDOs in EdO mixtures was proposed using simple linear regression analysis. It means that IR signal intensity (peak height or peak area) at a specific wavenumber between TDO-EdO mixtures and pure EdO was regressed on the percentage of either adulterant. The proposed method was validated in terms of linearity, accuracy, precision, specificity, limit of detection and limit of quantification (Thompson et al. 2002).

Figure 1 displays the FTIR spectra of representative samples for fresh edible oils (sunflower "*Spornic*"—SFO 1, and "*Floriol*"—SFO 2) and the two adulterants (TDO A and TDO B) under the study. For a better visualization, they are all scaled vertically. It can be observed that it is difficult to find differences between these oils only by visual examination of their whole spectrum.

At the first analysis of these spectra, we noticed that:

- The peak at around 3472 cm^{-1} assigned to the ROOH absorption band (Russin et al. 2004) is present only in the re-used oils, due to the thermal oxidation process. The disadvantage of these peaks of TDOs is that they show

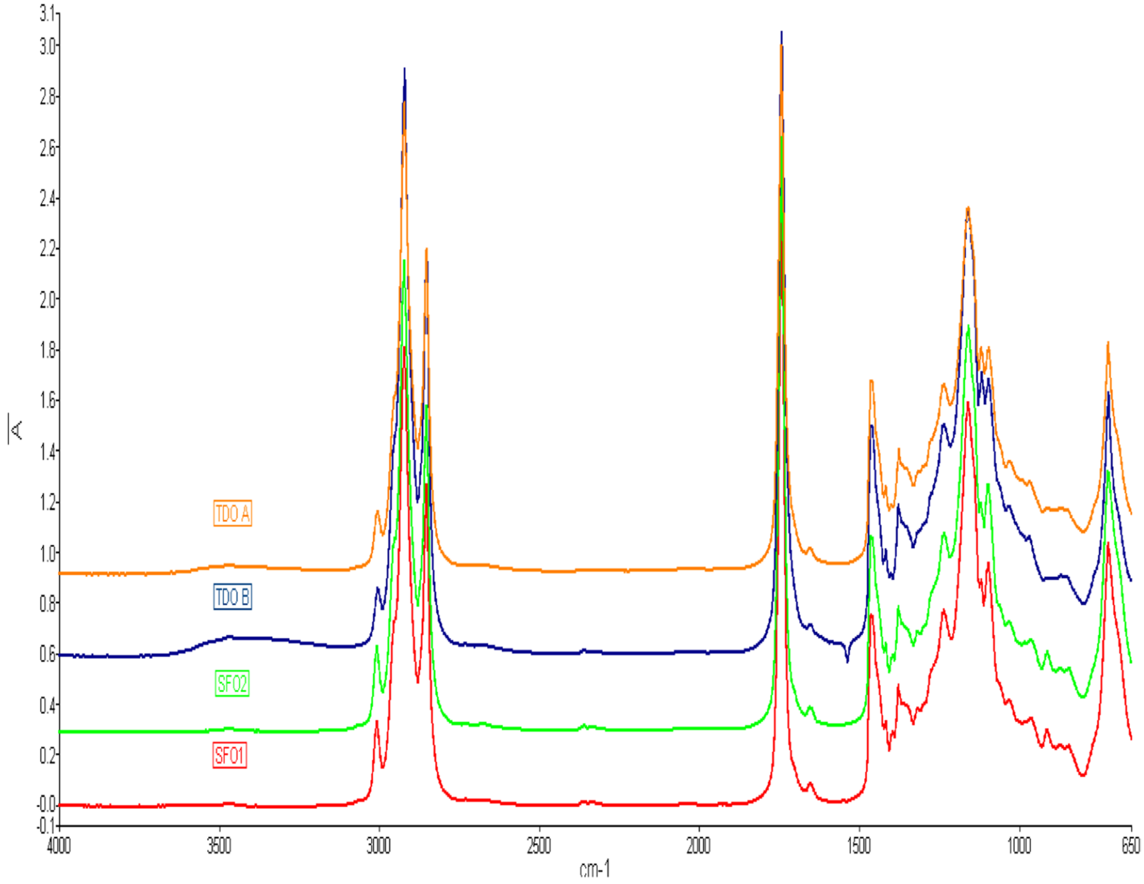

Fig. 1 FTIR spectra of the oils used in this study, SFO1, SFO2, TDO A and TDO B

only a slight increase in intensity, and so could not be used for quantification.

- In the region 3007–3004 cm^{-1}, there is a peak assigned to *cis* olefinic double bond (Guillén et Cabo, 1997)
- In the region 3000–2800 cm^{-1}, there are two peaks due to the asymmetric and symmetric stretching vibration of the aliphatic CH_2 functional group observed at around 2924 and 2852 cm^{-1} (Guillén et al. 2000).
- The peak around 1746 cm^{-1} is assigned to triglyceride ester linkage carbonyl absorption (van de Voort and A.A. Ismail, 1991).
- The peak around 914 cm^{-1} is assigned to a weak *cis* band situated in the *trans* region (van de Voort et al. 1995).

In Fig. 2A and B are presented the ATR–FTIR spectra for SFO1—TDO binary mixtures, similar curves being obtained for the other oil under the study.

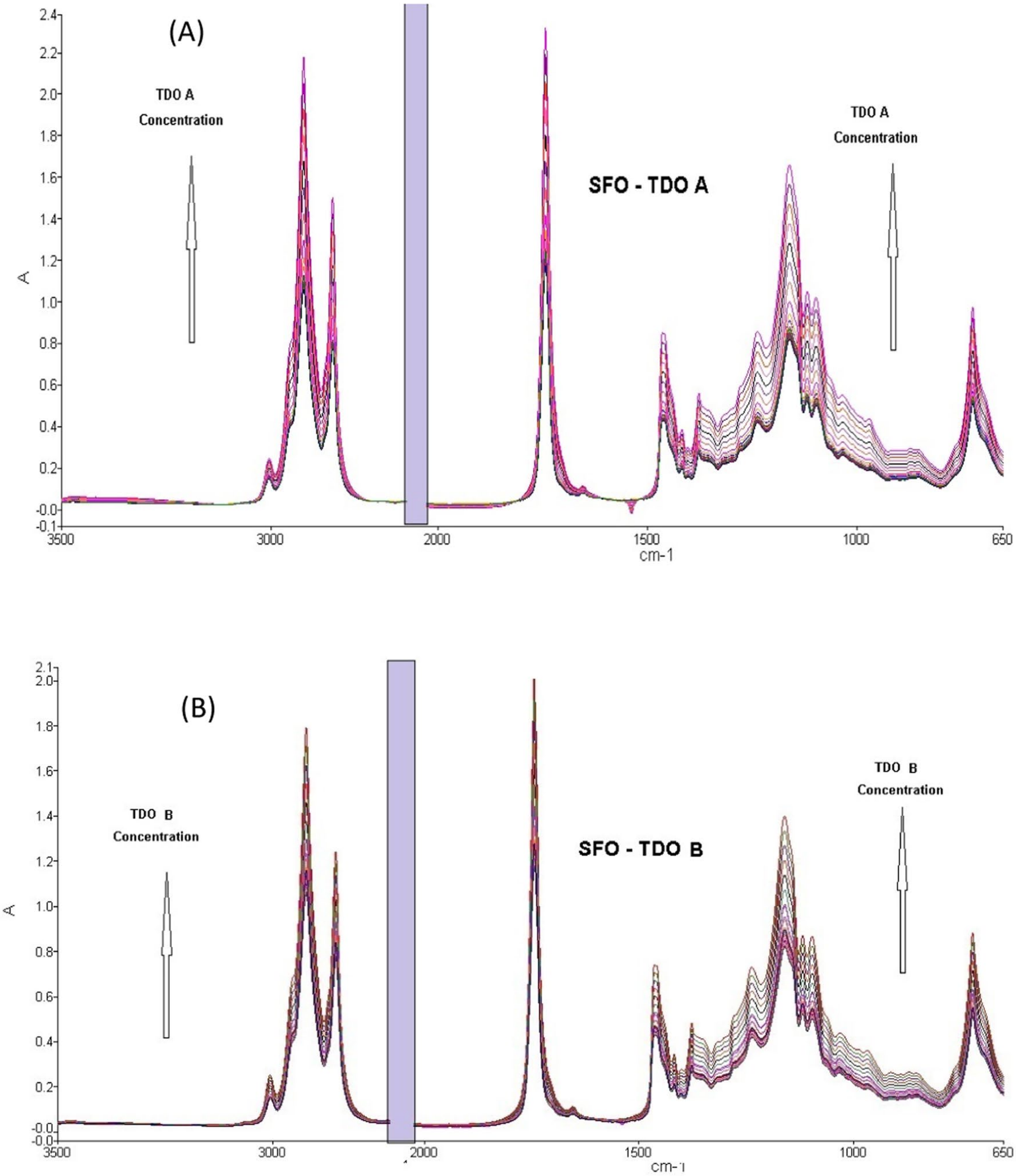

Fig. 2 ATR–FTIR spectra for SFO1 adulterated with **A** TDO A and **B** TDO B

In our study, the peak situated at 1746 cm^{-1} was used to quantify TDO A, while the peak at 2924 cm^{-1} was used to quantify TDO B. The peak area for the band at 1746 cm^{-1} was calculated using 1800 and 1682 cm^{-1} as points on the baseline, while the peak area for the band at 2924 cm^{-1} was calculated using 2949 and 2880 cm^{-1} as points on the baseline.

For TDO A, the peak situated at 2924 cm^{-1} presents a relatively small difference in intensity so it cannot be used for quantitative determinations, and similar for TDO B, in the case of the peak situated at 1746 cm^{-1}.

Statistical evaluation of the calibration curves is summarized in Table 1 for both adulterants. The coefficient of determination (R^2) for all the methods is, generally, greater than 0.990, suggesting a strong association between two variables (i.e., IR signal intensity (peak height or peak area) as the dependent variable, Y, and percentage of adulterant in EdO-TDO binary mixtures as the independent variable). It is noteworthy that the quantification methods based on IR peak area are more sensitive than those based on IR peak height as evidenced by their higher values of the regression slope.

The accuracy and precision of all the methods were also accessed by the quantification of TDOs as adulterants in the range of 3.5 ÷ 7.5% (v/v). TDOs in laboratory-made EdO-TDO binary mixtures are invisible to the naked eye at this concentration range. The results displayed in Table 2 show that all the methods are precise (RSD < 2.7%) and accurate (percent recovery in the range of 98.0 ÷ 101.1%). It is reasonably acceptable; in other words, the quantification of TDOs in EdO-TDO binary mixtures is considered to be specific (no significant influence of sample matrix existed). In comparison with chromatographic methods reported for identifying edible oil adulterants (Ghosh et al. 2005; Xing et al. 2019; Liao et al. 2017), our proposed methods proved to be more suitable as a reliable screening test for EdO adulterants because they are time-saving (the quantification could be performed in only about 5–10 min, taking into account from sample preparation to data acquisition) and cost-effective (solvent-free analysis and no sophisticated equipment requirement).

Table 1 Statistical evaluation of the regression analysis for the proposed method

Sample	Parameter	Peak measurements	
		Area	Height
		TDO A at 1746 cm^{-1}	
SFO1	Slope (a)	0.882	3.737
	Intercept (b)	14.71	28.25
	Coefficient of determination (R^2)	0.9992	0.9997
SFO2	Slope (a)	1.353	2.057
	Intercept (b)	10.25	39.30
	Coefficient of determination (R^2)	0.9994	0.9999
		TDO B at 2949 cm^{-1}	
SFO1	Slope (a)	−1.003	0.7101
	Intercept (b)	12.39	33.58
	Coefficient of determination (R^2)	0.9992	0.9999
SFO2	Slope (a)	−1.352	2.703
	Intercept (b)	18.33	29.68
	Coefficient of determination (R^2)	0.9997	0.9993

Conclusions

It was concluded that ATR–FTIR spectroscopy is a very useful technique for the direct determination of thermally deteriorated oil re-used as adulterants, TDO A and TDO B. In this study, the quantification of TDOs in SFO-TDO binary mixtures was done using the simple linear regression models describing the relationship between IR spectral intensity (peak height or peak area) at the wavenumber 1746 cm^{-1} and adulterant concentration. According to the validation data, our proposed quantification methods could serve as a screening test in the routine analysis of EdO adulteration with TDOs because they are labor-saving (easy to perform and quick), accurate, precise and specific.

Table 2 Quantitative determination of TDOs in SFO-TDO binary mixtures

		Found (%) (mean ± SD, $n = 5$)			
Taken (%)	Sample	peak area method		peak high method	
		TDO A	TDO B	TDO A	TDO B
3.50	SFO1	3.46 ± 0.01	3.43 ± 0.05	3.52 ± 0.09	3.55 ± 0.06
	SFO2	3.56 ± 0.05	3.53 ± 0.02	3.48 ± 0.09	3.50 ± 0.08
15.00	SFO1	15.02 ± 0.03	14.89 ± 0.04	15.09 ± 0.02	14.91 ± 0.04
	SFO2	15.09 ± 0.05	14.99 ± 0.07	15.11 ± 0.05	14.99 ± 0.07

Author contributions Andrei A. Bunaciu contributed to conceptualization, methodology, sampling and sample analysis, and writing the original draft. Lucia Mutihac, Vu D. Hoang and Hassan Y. Aboul-Enein contributed to data curation, supervision and writing—reviewing and editing.

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Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors declare no conflict of interest.

Ethical approval and Consent to participate Not applicable.

Human and animal rights No animals/humans were used for studies that are the basis of this research.

Consent for publication Not applicable.

Permission and/or credit for reproduced images Non-applicable.

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