

Determination of some edible oils adulteration with paraffin oil using infrared spectroscopy

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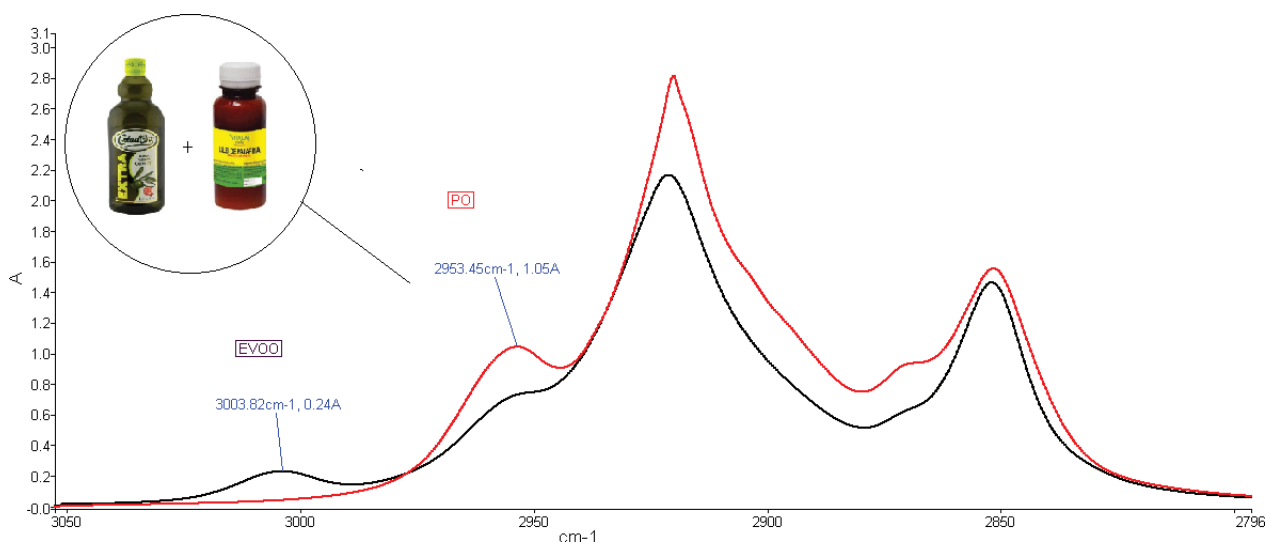
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Abstract

The spectroscopy of molecular vibrations using mid-infrared or near-infrared techniques was used more and more to characterize different compounds, including edible oil, in order to monitor any changes and to detect fraudulent modifications. This article presents a new method for quantitative adulteration of extra virgin olive oil (EVOO) or corn germ oil (CGO) with a mineral oil, such as paraffin oil (PO). A Fourier transform infrared (FT-IR) spectrometric method, using ATR spectra, was developed for the rapid, direct measurement of edible oils adulteration. The results indicate the efficiency of the proposed method for the detection of paraffin oil in adulteration of EVOO and CGO with RSD (< 3.0%).

Graphical abstract:



Keywords

FT-IR analysis, mineral oil, olive and corn germ, oil adulteration analysis, Beer's law

Introduction

The term “edible oils” (also possibly referred to as “cooking oils”) describes a group of fatty liquids physically extracted from several vegetables, some animal tissues or microorganisms (Bunaciu et al. 2020). In an overview presenting the principal sources of oils, it was concluded that most edible oils are obtained after extraction from seeds, while olive, coconut and palm, are extracted from fruits (Issaoui and Delgado 2019).

Vegetable oils are some of the most important and used agricultural products worldwide, existing a great variety of oils that can contribute to the human diet. Edible oils and fats are known to be essential nutritional requirements for humans. An adult needs approximately 5 g daily of linolenic and unsaturated fatty acids, which cannot be manufactured within the body (Pitts et al. 2007).

Extra-virgin olive oil (EVOO) is a well-known vegetable oil extracted from fruits only by using physical and mechanical processes (Council Regulation (EC) No 1513/2001). The literature data presents several methods for determination of adulteration of olive oil using infrared spectroscopy (Vancancelous et al. 2015; Meenu et al. 2019), while in another review are presented the critical parameters for determination of EVOO purity (Gómez-Caravac et al. 2016).

Corn germ oil (CGO) is a by-product of the corn oil milling process. Most corn that is harvested is used as feed but the proportion of the corn that is milled is increasing due to the bioethanol production (Dijkstra 2016). The literature data presents several methods for CGO determination including a relevant review for determination of adulteration of corn germ oil (Rohman et al. 2020).

Mineral oils (such as paraffinum liquidum or white oil, PO), which consist of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH), are widely applied in various consumer products such as medicines and cosmetics.

Adulteration represents an unhealthy and unethical act of adding prohibited substances to food with a profit motive. In these conditions it is necessary to ensure the authenticity of the food that we consume has intensified more and more in the last period of time all over the world. Usually, low priced oils are mixed with premium oils. Many analytical techniques, such as: chromatographic methods, differential scanning calorimetry, Fourier transform infrared spectroscopy, etc. can be used to discriminate different oils as well as to detect adulteration (Libish et al. 2011; Rohman 2017; Valand et al. 2019; Jamwal et al. 2021).

The main purpose of this work was to develop a spectrophotometric procedure for the fast and accurate determination of two types of extra-virgin olive oil (EVOO) and corn germ oil (CGO) adulterated with paraffin oil (PO) in commercial products using Lambert-Beer's law reducing in this way the sample pretreatment, and providing direct FTIR measurement.

Experimental

Apparatus

Data acquisition was performed using a Spectrum1000 FT-IR spectrometer equipped with Spectrum for Windows v.5.01 (Perkin Elmer Co., Beaconsfield, Bucks, UK). The commercial softwares used to generate analysis for the principal component analysis were QUANT+ expert v.4.51 and Spectrum Beer's law v.10.7.2.1360 (Perkin Elmer Co. UK).

Reagents and materials

The commercial products, two types of EVOO (Extra Virgin Olive Oil – Costa d'Oro, Italy and respectively Extravirgin Olive Oil – Primadonna, Italy, both blend of Olive from European Union origin and not of European Union origin), a type of CGO (Italy, obtained exclusively by physical means, pressing without the use of solvents) and a type of PO (Vitalia Pharma Ploiesti district – Romania), were acquired from Romanian commercial stores. All solvents (hexane and acetone) were reagent grade and were obtained from Aldrich Chemical Co. (Milwaukee, WI).

Recommended procedures

All samples were homogenized and a small amount of sample was spread onto the ATR crystal to give total coverage. For each sample, the absorbance spectrum was collected against a background obtained with a dry and empty ATR cell, before each day of measurements. The spectra were scanned in triplicate at room temperature over the wavenumber interval of 4000–650 cm^{-1} , averaging 16 scans at a resolution of 4 cm^{-1} or 8 cm^{-1} , and then were averaged before calculations. After acquiring each spectrum, the ATR crystal was cleaned with a cellulose tissue soaked in hexane and then rinsed with acetone.

Experimental parameters, such as resolutions and calibration methods were compared and recommendations for the best options in edible oils analysis were made.

Stock solutions for paraffin oil with the appropriate concentration (C, %) in edible oils, in order to cover the range of detection 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100% (v/v) with EVOO 1, EVOO 2 and CGO, respectively, were prepared.

Results and discussions

Figure 1 shows comparatively, the FTIR spectra of paraffin (PO), extra virgin olive (EVOO 1 and 2) and respectively corn germ oil (CGO).

As can be noticed from this figure, there are no significant differences between the spectra of EVOO 1, EVOO 2 and CGO. The single major difference is the position of the peak assigned to *cis* double bond observed at about 3003 cm^{-1} , in the spectrum of EVOO1, EVOO2 and respectively 3007 cm^{-1} for CGO samples. In the spectrum of PO, the characteristic peak assigned to

methyl asymmetrical stretching vibration, observed at 2953 cm^{-1} , it was used for quantitative determination, as can be seen, in details, in Fig. 2 (Guillén and Cabo 1997). For a better quantitative determination of the presence of EVOO1, EVOO2 and CGO, was used the peak situated at about 1743 cm^{-1} , assigned to stretching vibrations of ester carbonyl band, as can be seen, in details, in Fig. 3 (Guillén and Cabo 1997). At these wavelengths, the contribution is major for a single component of the two in the mixture, EVOO, CGO and respectively PO.

Taking into account the small differences between the FTIR spectra of edible oils and the mineral one, we tried to develop a new spectrophotometric method for quantitative determination of adulteration of edible oils with the mineral oil.

Using the standards prepared by us, noticed in Recommended procedures, we obtained calibration curves for quantitative determination of the adulteration.

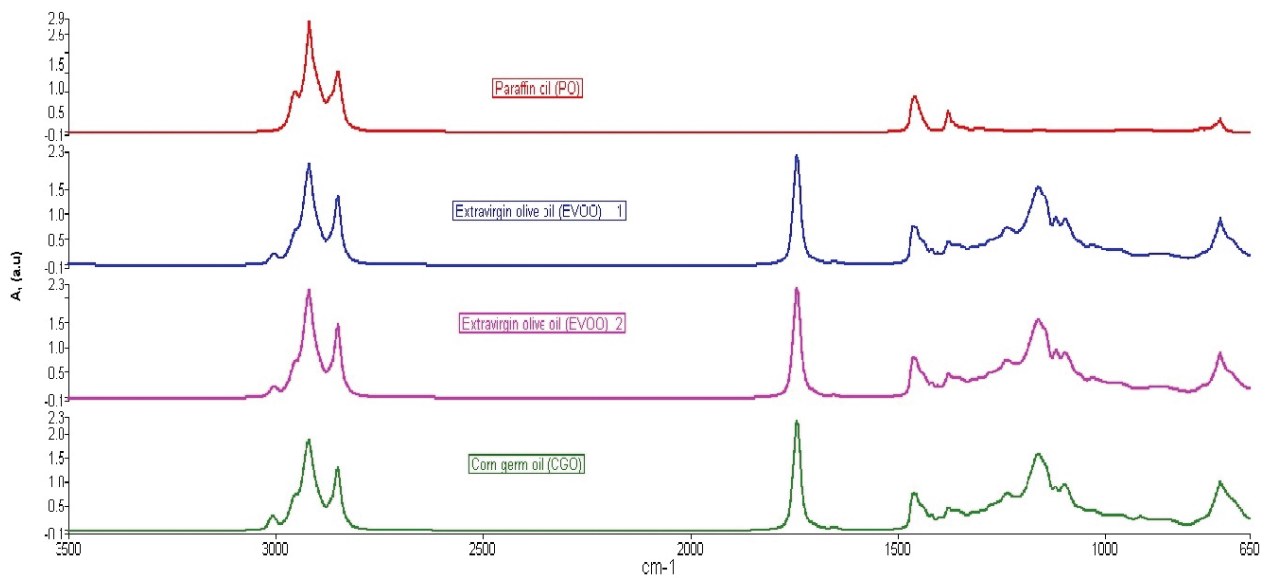


Figure 1. ATR spectra of extra virgin olive oil (EVOO), corn germ oil (CGO) and paraffin oil (PO) used in this study.

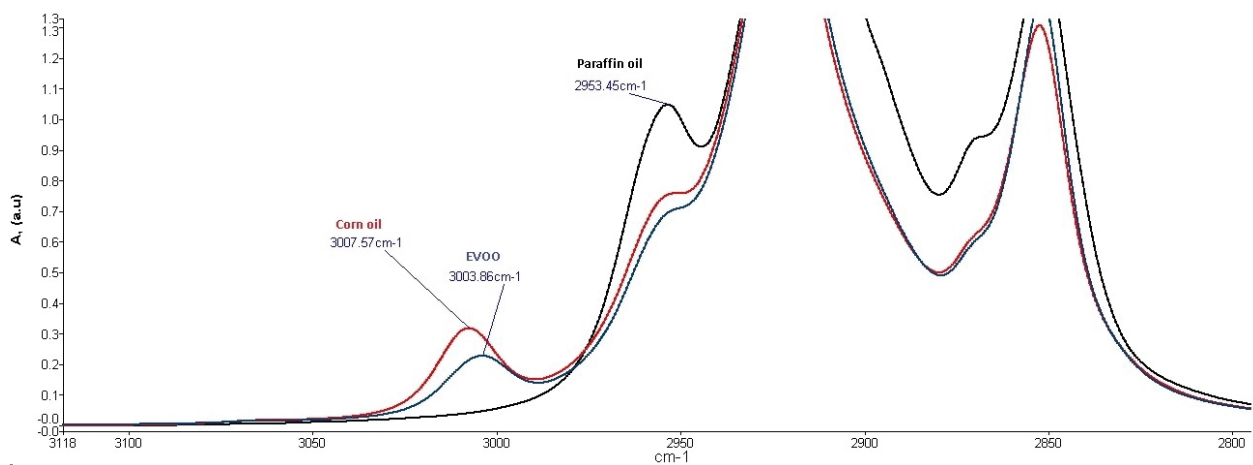


Figure 2. FTIR peaks used for quantitative determination of PO (black line) against EVOO1 (purple line) and CGO (red line).

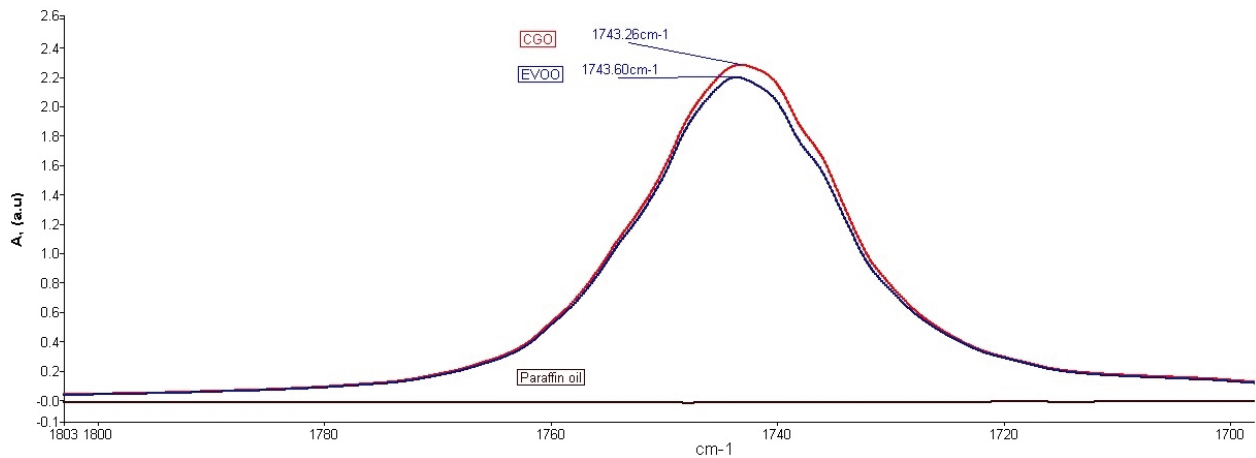


Figure 3. FTIR peaks used for quantitative determination of EVOO1 (purple line) and CGO (red line) against PO (black line).

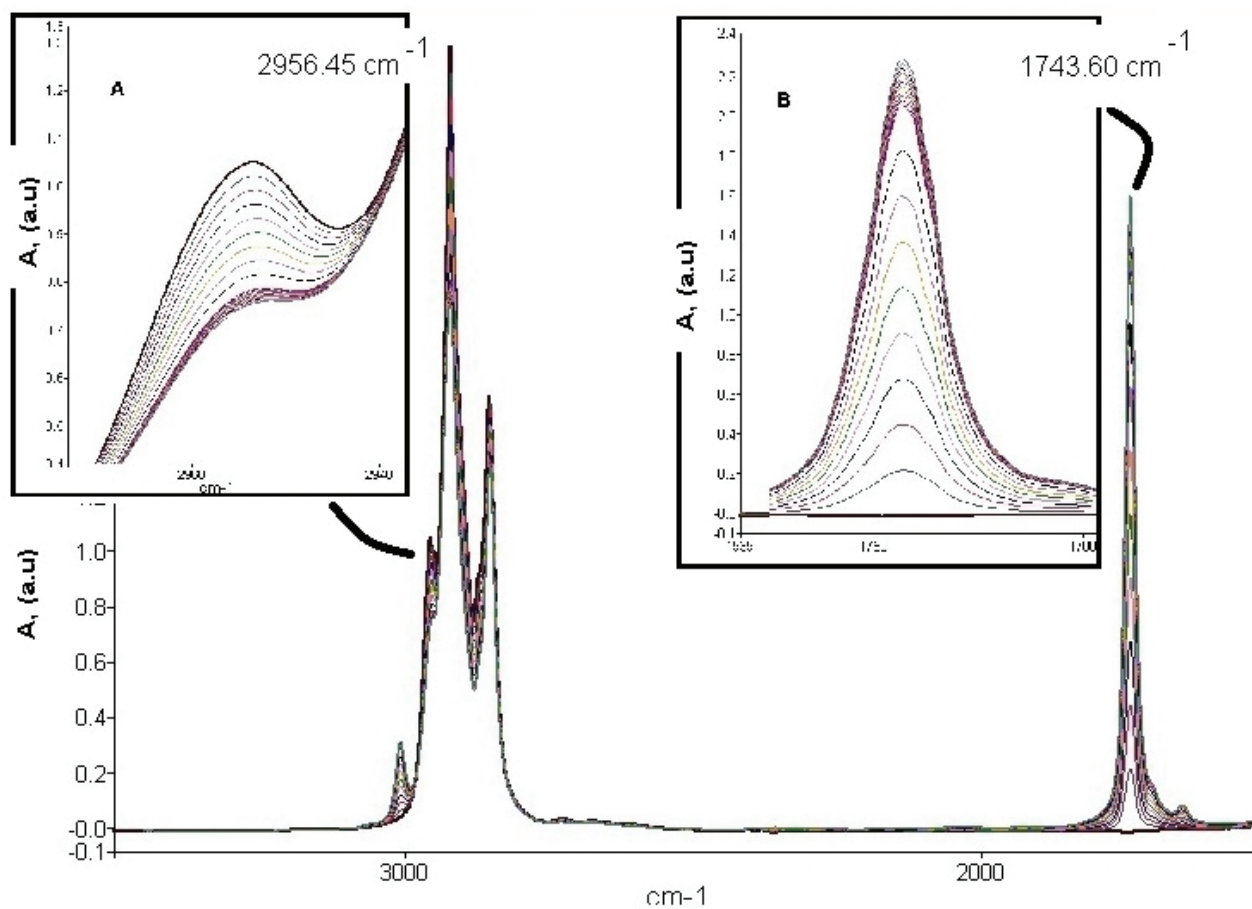


Figure 4. FT-IR spectra regions of pure PO, CGO and their mixtures studied.

In Fig. 4 ATR – FTIR spectra for the binary mixtures of CGO and PO are presented, while Fig. 5 presents the calibration curves, for measurements performed at 1743.60 cm^{-1} .

As can be observed, the calibration graph can be divided into two linear domains, where slopes change depending on the concentration: one for the adulteration with 1–10%, and the other one in the range of 10–100% adulteration, each of them being characterized by specific linear equations.

Similar results were obtained for the binary mixtures of EVOO and PO.

In Table 1 are presented the results for calibration graphs for the binary mixtures, EVOO – PO and respectively CGO – PO.

For the quantitative determinations of edible oils adulteration with mineral oil (paraffin oil), were used both variants. The results presented in Tables 2, 3 are the averages of 5 determinations, for same samples prepared by us, and having the following quantities of adulterant, such

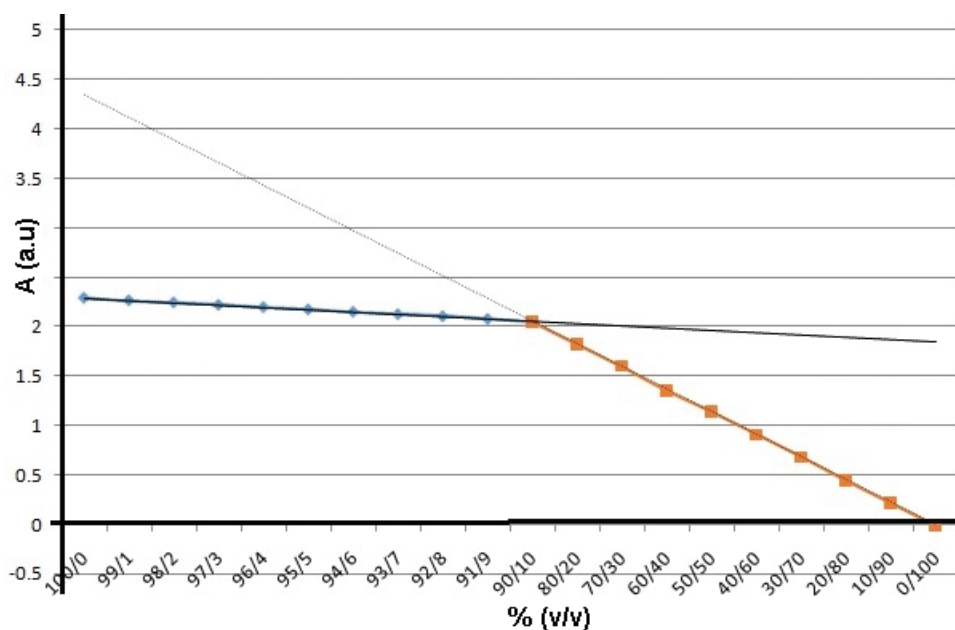


Figure 5. Calibration graph for Paraffin oil determination in a mixture of corn germ oil and paraffin oil, for measurements performed at 1743.60 cm^{-1} .

Table 1. Calibration results.

Parameter	Binary mixtures			
	EVOO – PO		CGO – PO	
	Range % (v/v)			
	0–10 PO	10–100 PO	0–10 PO	10–100 PO
Slope	-0.001	-0.018	-0.023	-0.228
Intercept	0.232	0.234	2.313	2.278
Correlation coefficient	0.998	0.997	0.998	0.999

Table 2. Quantitative determination of extravirgin olive oil adulteration with paraffin oil.

Taken (%)	Found at 1743.60 cm^{-1}		Found at 2956.45 cm^{-1}	
	(%)	RSD, %	(%)	RSD, %
3.5	3.53	0.32	3.44	0.88
15.0	14.90	0.24	15.08	1.15
25.0	25.24	0.48	25.34	1.78

Table 3. Quantitative determination of corn germ oil adulteration with paraffin oil.

Taken (%)	Found at 1743.26 cm^{-1}		Found at 2956.45 cm^{-1}	
	(%)	RSD (%)	(%)	RSD
3.5	3.49	0.33	3.57	0.70
15.0	15.36	0.27	15.58	1.06
25.0	25.12	0.59	25.56	1.42

as: 3.5 (3.5%PO + 96.5% EVOO and respectively 3.5%PO + 96.5% CGO), 15 (15%PO + 85% EVOO and respectively 15%PO + 85% CGO) and respectively 25 (25%PO + 75% EVOO and respectively 25%PO + 75% CGO).

The limit of quantification (LOQ) was determined by the analysis of samples with known concentration of PO and by establishing the minimum level at which the analyte can be quantified with acceptable accuracy and

precision, 3% v/v PO. The limit of detection (LOD), 1% v/v, was considered as the signal to noise ratio of 3:1 (Shrivastava et Gupta 2011; Moldovan et al. 2017).

As can be seen in these Tables, the results are very similar, and so, we suggest the use of this method, especially for the determination of the major component of the mixture, EVOO or CGO, because of the smaller value of RSD (< 1.0%). Also, for the determination of paraffin oil quantity, the results are also good, even the RSD value is a little higher.

Conclusions

It is clear that FT-IR spectrometry is capable of direct determination of EVOO and CGO in several mixtures when adulterated with a mineral oil, PO. With the commercial software involving Beer-Lambert law, the method proposed is simple, precise and not time-consuming compared to chromatographic methods. Quantification could be done in about 5–10 minutes, including sample preparation and spectral acquisition.

Conflict of interest

Andrei A. Bunaciu declares that he has no conflict of interest. Serban Fleschin declares that he has no conflict of interest. Hassan Y. Aboul-Enein declares that he has no conflict of interest.

Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

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