



Raman spectroscopy and machine-learning for edible oils evaluation

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ABSTRACT

Because of the important advantages as rapidity, cost effectiveness and no sample preparation necessity, encountered in most of the cases, Raman spectroscopy gained more and more attention during the last years with regard to its application in food and beverages authenticity. Vegetable cold-pressed oils obtained from: sesame, hemp, walnut, linseed, pumpkin and sea buckthorn have gained increased attention in consumer interest due to their high nutrient value and health benefits. The high commercial value of these, brought the temptation from some unfair producers and sellers to gain an illegal profit by replacing the raw material of these oils by cheaper ones (i.e. sunflower). Here a new approach based on the rapid processing of Raman spectra using Machine Learning algorithms, for edible oil authentication was developed and successfully tested. Through this approach, not only the adulteration detection was achieved but also an initial estimation of its magnitude.

1. Introduction

During the last years, vegetable cold-pressed oils obtained from sesame, hemp, walnut, linseed and sea buckthorn have gained increased attention in consumer interest due to their high nutrient value and health benefits. From nutritional point of view, two polyunsaturated fatty acids – linoleic and linolenic are very important, as they are considered essential for the human body and must be obtained from exterior sources like plant materials [1]. The fatty acids composition of oils is also of significant interest for nutrition due to their influence on the blood cholesterol levels [2]. Besides their nutritional qualities, some of the edible oils are popular given their benefits for health. Thus, hemp oils are known for their influence onto the cardiovascular functions [3], sesame oils for their help in rheumatoid arthritis or for lowering blood pressure [4,5], linseed oils for reducing cholesterol and even for fighting cancer [6,7], sea buckthorn for skin regeneration or protection against infection and allergies prevention [8]. Most of these oil types are premium products, having a higher price as compared with the regular edible oils (i.e. refined sunflower oil). In these conditions, the temptations of some unfair producers or sellers to replace high priced oils by cheap ones in order to gain an illegal benefit occur. Apart of economic consequences related to the replacement of some raw materials with cheaper ingredients without their proper indication on the label, some harmful effects can be caused by this type of replacements. For example, a “dilution” with common oils of the antioxidants’ amounts (e.g. quercetin) from the sea buckthorn oils affects their therapeutic effects, hindering their health benefits and protection

[9–11]. In order to discourage this type of actions, the development of rapid and cheap analysis methods represents a strength point for control laboratories.

Edible oils are complex food containing mono, di or triglycerides, free fatty acids, phospho- and glycolipids, but also proteins, pigments, sterols, metals and oxidized materials [12], depending on the type of oil and the extraction method. Most of edible oils are vegetable oils that, after the initial extraction method, are subjected to different processes (neutralization, bleaching and deodorization) to become suitable for human consumption [13]. Different methods have been employed for analysis of edible oils; these methods involve titration, colorimetric or potentiometric investigations, gas chromatography (GC), gas liquid chromatography (GLC), high-performance liquid chromatography (HPLC) or non-destructive analytical methods as spectrophotometric methods (infrared - IR, near infrared - NIR and nuclear magnetic resonance - NMR) [13,14]. Raman spectroscopy can be also applied to investigate the edible oils for their characterization [15], authentication [16] or even for the quantitative analysis of total unsaturation [17,18], cis/trans isomers [17,19,20] and free fatty acid [21]. Moreover, Raman spectroscopy was used to detect the adulteration of oils [22] and to provide information about the extent of lipid oxidation in oils [23]. A rapid protocol for carotenoids and fat quantification in salmon has been also established using Raman spectroscopy [24].

However, the Raman collected data are large and, due to the high similarity of most of the edible oils, their Raman spectra resemble a lot, making the qualitative or quantitative information extraction very difficult. In this situation, the statistical investigations can help by

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allowing the classification and authentication of certain oils [25]. Among the statistical methods that are employed to Raman data, the Principal Component Analysis (PCA) has been one of the most successfully used both for the edible oils' authentication or detection of olive oil adulteration [15,26–29].

In the last thirty years, the Machine Learning (ML) methods have been proved to be effective for the discrimination of Raman spectra of minerals [30] and the classification of high dimensional spectroscopic data [31]. They have been successfully applied in different area as food or material analysis, bacteria identification or diagnostic application [32]. In the field of oils investigations, some studies have demonstrated the robustness of ML and Laser Induced Breakdown Spectroscopy for olive oils classification [33] or the fast edible oil classification by using ML for analysis of Infrared spectra [34].

The present work aims the use of Machine Learning for analysis of Raman spectra of some less common edible oils, commercialized on the Romanian market (i.e. Sesame, Hemp, Walnut, Linseed (Flaxseed), Sea Buckthorn and Pumpkin) as food natural supplements. To the best of our knowledge, this combination of techniques is applied for the first time for the biological discrimination of these edible oils and the identification of oils adulteration too. The main advantage of the proposed approach consists in a rapid and accurate detection of adulterated oil samples which allow, in the same time, an estimation of the adulteration degree.

2. Materials and methods

2.1. Sample description

Seven types of oils, Sunflower, Sesame, Hemp, Walnut, Linseed (Flaxseed), Sea Buckthorn and Pumpkin seeds, have been chosen for investigation by Raman spectroscopy. Thus, six Sunflower samples (SF1 – SF6) obtained by two types of extraction procedures (refined, SF1 and SF2 or cold-pressed, SF3 – SF6) were compared with the other types of cold-pressed oils, Sesame – five samples (SES7 – SES11), Hemp – four samples (HEM12 – HEM15), Walnut – four samples (WAL16 – WAL19), Linseed – four samples (LIN20 – LIN23), Sea Buckthorn – three samples (SB24 – SB26), and four Pumpkin seed oils (PUP27 – PUP30). Due to the fact that a Sea Buckthorn sample, SB24, is commercialized by producer as a mixture of Sea Buckthorn - Sunflower in the ratio 80-20%, this sample will be treated as a distinct class and denoted SBi in the section of ML investigation. Excepting the Sea Buckthorn SB25 and SB26 (acquired from a pilot-private Romanian producer that used mechanic cold-pressed methods for extraction of oils), all the other samples have been purchased from the market. Most of them have the Romanian origin, purchased from known Transylvanian producers but some of them are of Chinese (SES7) or German (SES10, LIN23) origin. All samples were freshly prepared or within the warranty periods at the moment of Raman investigations.

The Mix1set contains three binary mixtures having the ratio between the Sunflower, SF5, and the Sea Buckthorn, SB26, oils of 20–80% v/v, 50-50% v/v and 80-20% v/v respectively.

The Mix2 set contains eight ternary mixtures having the following ratios between the Sunflower, S5, the Sea Buckthorn, SB26, and the Pumpkin, PUP28, oils (SF5-SB26-PUP28): M1 – 40-27-33% v/v; M2 – 30-20-50% v/v; M3 – 24-16-60% v/v; M4 – 60-15-25% v/v; M5 – 48-12-40% v/v; M6 – 40-10-50% v/v; M7 – 34-9-57% v/v; M8 – 30-7.5-62.5% v/v.

2.2. Raman measurements

Raman investigations were performed on a JASCO NRS-3300 equipped with CCD detector (–69 °C). A 785 nm laser wavelength, 600 lines/mm grating and an objective lens UMPLFL 20x were used to record the spectra between 330 and 2010 cm^{-1} , with an exposure time of 120 s and 3 accumulations per spectrum. The Si 521 cm^{-1} peak was

used for calibration. 3 mL for the simple oil or 3–8 mL for the oils' mixtures were placed in a glass vessel and the Raman spectra were recorded in two different points. The Raman spectra of the oils' samples have been collected at different times under different laser power levels, varying from 122.9 to 163.6 mW. The normalization process has been applied to all spectra in order to correct the differences in intensity levels of the spectra.

2.3. Experimental data processing

After the mean spectrum calculation, all spectra have been background corrected (to subtract the fluorescence background) and they have also normalized in the range of [0, 1].

Due to the specific fingerprint of the oil matrix, the interest range selected was 600–1800 cm^{-1} for general Raman spectra analysis and 1120-1800 cm^{-1} for the ML investigations. The Raman spectra analyses were conducted by OriginPro 2017 (OriginLab, Northampton, USA), while the Machine Learning studies were performed using the Classification learner app implemented in MATLAB R2017b (MathWorks, Natick, Massachusetts, USA).

3. Results and discussion

3.1. Raman spectroscopy characterization of oils

Fig. 1 shows the characteristic Raman frequencies of the seven types of investigated oils. Except for the Sea Buckthorn oils, they are dominated by the typical signals of fatty acids, as i) the CH in-plane deformation vibration of the cis $-\text{CH}=\text{CH}-$ unit, $\delta(\text{CH})_{\text{in plane}}$, located at about 1265 cm^{-1} , ii) the stretching vibration of cis C=C bond, $\nu(\text{C}=\text{C})_{\text{cis}}$, closed to 1656 cm^{-1} and iii) the two specific deformation vibrations of saturated CH_2 group, $\tau(\text{CH}_2)$ and $\delta(\text{CH}_2)$, around 1302 cm^{-1} and 1440 cm^{-1} , respectively. When the oils are obtained from seeds containing large amounts of polysaccharides in the cell walls, a broad peak appears at 1460 cm^{-1} , due to the symmetric deformation of the $-\text{O}-\text{CH}_3$ group, $\delta(\text{CH}_3)$ [35]. The stretching vibration of the C=O bond of the esters appears at about 1745 cm^{-1} ; this vibration is clearly seen in almost all spectra, with some exception from the Hemp, Sea Buckthorn and Pumpkin samples. In Table 1 are reported the main frequencies' values and more details on their vibrational assignments for each type of the investigated oils.

After a brief analysis of Fig. 1, three different Raman characteristic spectra appear to be distinguished for the seven studied oils, taking into account their specific bands intensities. The first Raman spectra type (Fig. 1a,b,g) are dominated by the 1440 cm^{-1} peak, associated to the CH deformation of the CH_2 group and seems to be specific to the Sunflower (SF1-SF6), Sesame (SES7-SES11) and Pumpkin (PUP27-PUP30) oils. This predominance brings to mind the idea that the saturated fatty acids are dominant in this type of oils; however, the presence of the other CH deformation vibration in the region 1302-1304 cm^{-1} , clearly indicates that the main components of Sunflower, Sesame and Pumpkin oils are the unsaturated fatty acids (this band is shifted to 1295 cm^{-1} in saturated fatty acids) [35].

The second Raman spectra profile (Fig. 1c–e) is not very different from the Sunflower and Sesame oils, but contrary to these oils, the vibrational Raman spectra of Hemp (HEM12-HEM15), Walnut (WAL16-WAL19) and Linseed (LIN20-LIN23) oils reveal a significant peak at about 1266 cm^{-1} (e.g. in HEM15), associated to the CH deformation vibration from cis $-\text{CH}=\text{CH}-$ units, promoting the idea of a high level of unsaturated fatty acids, Fig. 1 and Table 1.

This difference between the two Raman spectra types described above could be correlated with the saturated (SFA), monounsaturated (MUFA) and polyunsaturated (PUFA) mean levels of fatty acids from various vegetable oils [40–46]. Thus, the CH_2 deformation mode (1440 cm^{-1}) seems to be preponderate in the Raman spectra of oils containing high levels of saturated compounds (at least higher than

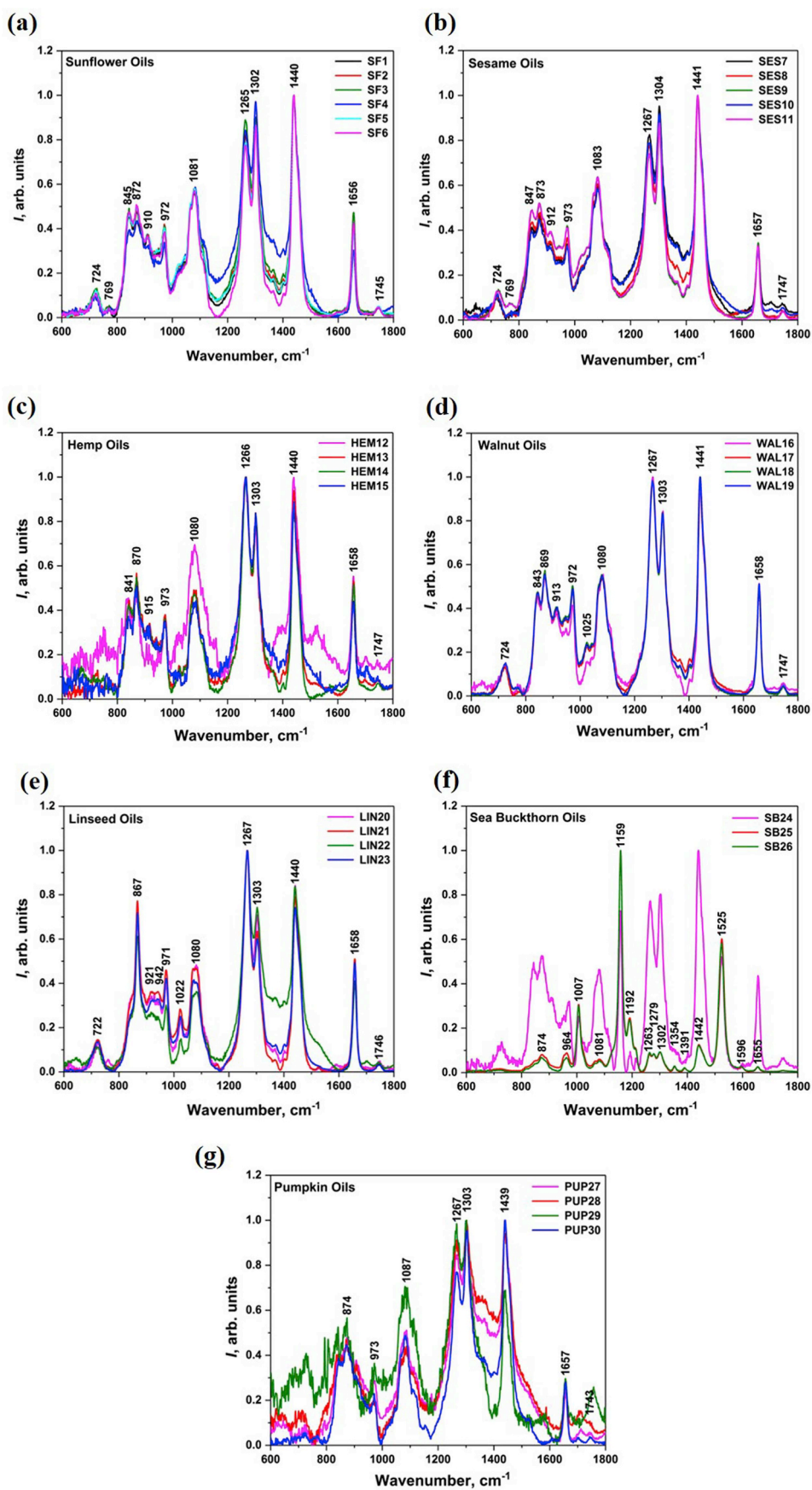


Fig. 1. Raman spectra of Sunflower (a), Sesame (b), Hemp (c), Walnut (d), Linseed (e), Sea Buckthorn (f) and Pumpkin (g) oils.

Table 1

Raman data of different types of oils (Sunflower, Sesame, Hemp, Walnut, Linseed, Sea Buckthorn, Pumpkin) and their peaks assignments.

Type of oil/Raman vibrations (cm^{-1})							Assignments
Sunflower SF6	Sesame SES11	Hemp HEM15	Walnut WAL17	Linseed LIN21	Sea Buckthorn SB25	Pumpkin PUP27	
724	724	–	724	722	–	–	CH ₂ rocking vib.[36]
769	769	–	–	–	–	–	CH wagging vib. from cis –CH=CH-[36]
845	847	841	843	–	–	–	C–C/C–O stretching[36]
872	873	870	869	867	874	874	C–C/C–O stretching
910	912	915	913	921	–	–	C–C stretching[36]
–	–	–	–	942	–	–	C–C/C–O stretching[36]
972	973	973	972	971	964	973	CH wagging from cis –CH=CH-[36]
–	–	–	–	–	1007	–	C–CH ₃ rocking vib.[37]
–	–	–	1025	1022	–	–	C–O/C–C stretching[36]
1081	1083	1080	1080	1080	1081	1087	Skeletal C–C stretching
–	–	–	–	–	1159	–	C–C stretching vib. (C–H in-plane bending mode) [37]
–	–	–	–	–	1192	–	C–C stretching, C–H in plane bending[38]
1265	1267	1266	1267	1267	1263	1267	CH deformation vib. from cis –CH=CH- [15,36]
–	–	–	–	–	1279	–	C–H bending coupled with C=C stretching (7-cis) [39]
1302	1304	1303	1303	1303	1302	1303	CH deformation of CH ₂ [15,36]
–	–	–	–	–	1354	–	C–CH ₃ stretching, sym. Deformation of methyl group[38]
–	–	–	–	–	1391	–	sym. deformation of methyl group[38]
1440	1441	1440	1441	1440	1442	1439	CH deformation (scissor vib. of CH ₂ group)[15,36]
–	–	–	–	–	1525	–	C=C stretching vib.[37]
–	–	–	–	–	1596	–	C=C stretching vib., in-plane bending of the C–H bond[38]
1656	1657	1658	1658	1658	1655	1657	C=C stretching from cis –CH=CH-[15]
1745	1747	1747	1747	1746	–	1743	C=O stretching from RC = OOR[15]

10%), SFA > 10% (Sunflower oils – mean SFA 10.1%, Sesame oils – mean SFA 14.2%, Pumpkin – SFA 18% [40,42,45,47]. A lower percentage of SFA (SFA < 10%) led to an increase of the peak from 1266 cm^{-1} , associated with the cis = C–H in-plane deformation mode and, in consequence, with a higher unsaturation degree of oils (Hemp oils – 7–10%, Walnut oils – mean 9.1%, Linseed oils – mean 9.4% [40–43,45,46,48].

Unlike the other two spectra shapes, the third one (Fig. 1f) is characteristic to carotenoids species, possessing their main Raman skeletal features at 1007, 1159 and 1525 cm^{-1} , which correspond to the rocking vibration of the methyl groups, $\delta(\text{C–CH}_3)$ and the stretching mode of the single and double carbon-carbon bonds, $\nu(\text{C–C})$ and $\nu(\text{C=C})$, as appear in the Sea Buckthorn(SB24-SB26) samples, Fig. 1 and Table 1 [37]. These Raman characteristics of the Sea Buckthorn samples have been obtained from oils employing the Sea Buckthorn fruits and the cold-pressed method in the preparation process.

However, one of the Sea Buckthorn samples, SB24, stands out from the others by the preponderance of some peaks specific to the first type of oils (namely SF, SES and PUP). At an initial analysis, this situation is not uncommon since, on the oils supplements' market, some products are commercialized by the producer as a mixture of the oils possessing health benefits and cheaper sunflower oils. The ratio between these oils is difficult to control by a rapid and accessible method, so it can be an easy way for fake products commercialization.

An exhaustive analysis of the raw Raman spectra of the SB24 (labeled by the producer as 80% SB oil and 20% SF oil) and SB26 (a cold-pressed SB oil) emphasizes, even more, the dissimilarity level between the two SB samples, Fig. 2a. As expected, the Raman spectrum of SB24 sample contains the characteristic profile of the SF oil in the region of 1264 and 1301 cm^{-1} bands, associated with the preponderance of 1439 cm^{-1} peak. However, this profile is significant in the SB24 sample, Figs. 1f and 2a.

Moreover, due to the high fluorescence background observed, it became evident that the SB24 oil cannot be only a mixture of the SB and SF; the presence of a fluorescent oil to this mixture is mandatory to

obtained such fluorescence of the spectra. From all investigated oils produced by the company which manufactured SB24 sample, a substantial fluorescence was remarked for the Pumpkin seeds oil, Fig. 2a.

Therefore, to obtain a similar spectrum with the SB24, different mixtures of oils were prepared, Fig. 2b and c. Firstly, a set of three samples having the ratio between SF and SB 20–80% (v/v), 50–50% (v/v) and 80–20% (v/v) has been prepared and measured. This binary mixture (Mix1) spectra are presented in Fig. 2b (in this case, for comparison, the normalization by mean has been applied to raw spectra). It is evident that there is a change in the Raman intensities with the variation of the oils' concentrations. Thus, the decrease of SB concentration leads to a reduction of the characteristic bands from carotenoids (1007, 1159 and 1523 cm^{-1}) as indicated by orange-colored arrows in Fig. 2b, while the peaks specific to SF oils (1264, 1302, 1442 cm^{-1}) rise with its concentration augmentation, olive-colored arrows from Fig. 2b.

The lack of fluorescence from these spectra must be also noted, and, in consequence, the investigation of a trinary mixture Sunflower – Sea Buckthorn – Pumpkin seeds (Mix2) oils became mandatory. Fig. 2c contains the spectra of the SF–SB 80–20% (v/v), SF–SB – PUP 30–7.5–62.5% (v/v) oils mixtures and the SB24 oil (presented on the market by producer as Sunflower – Sea Buckthorn 20–80%). By comparison of all spectra shapes presented in Fig. 2c, there are reasons to suspect the use of another ratio between SF and SB than that it was written on the oil label, namely a higher percentage of SF, and the presence of Pumpkin seed oil in the mixture.

3.2. Machine Learning for the oils' investigation

In this experiment, we used the Machine Learning implemented in Matlab with the aim to build a model that will be applied further to make prediction and analysis of a test dataset. As the training dataset, we have used the Raman spectra of the seven types of investigated oils (SF, SES, HEM, WAL, LIN, SB, PUP), the Sea Buckthorn traded by producer as a mixture 80–20% SB–SF (Sbi), the binary (Mix1) mixture

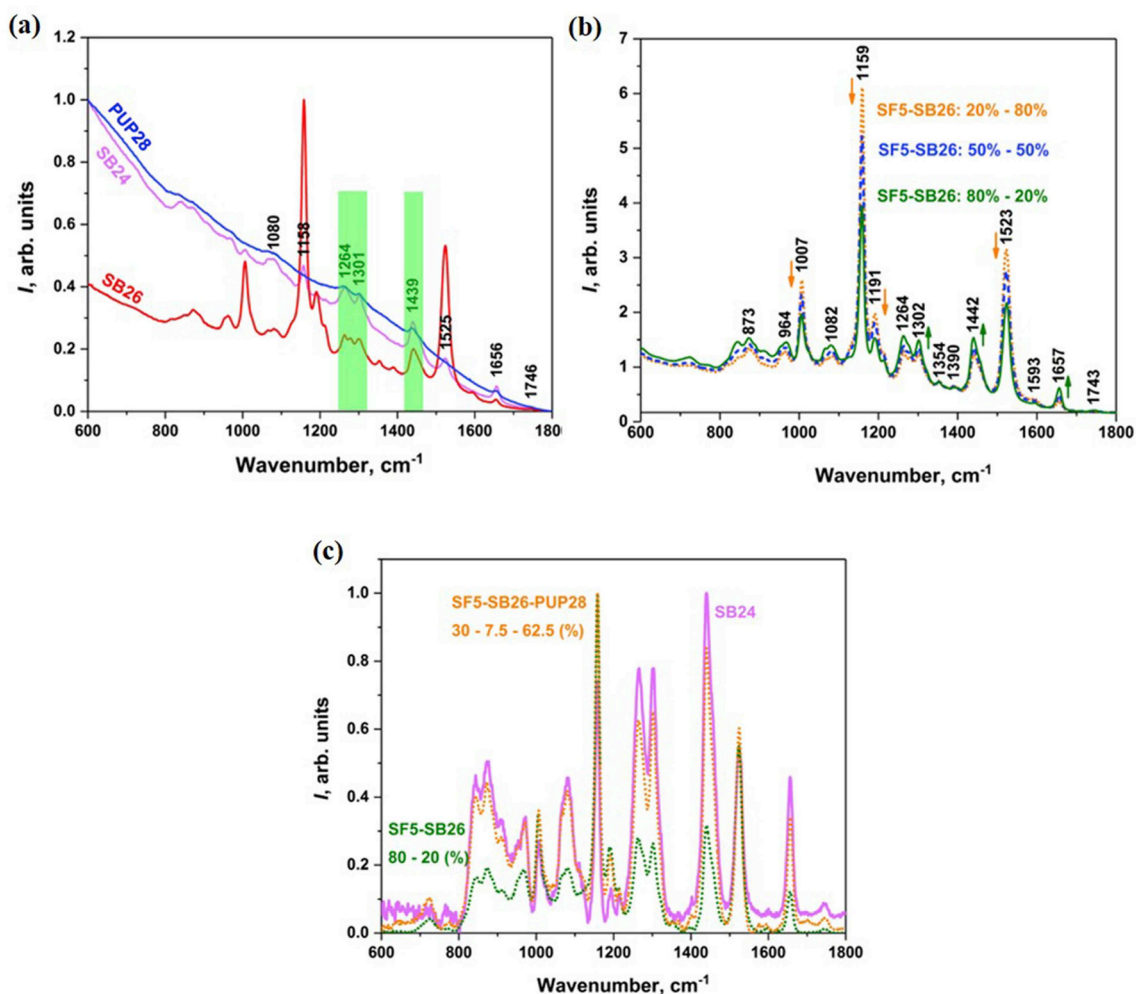


Fig. 2. Raman spectra of two Sea Buckthorn (SB24 and SB26) oils compared with the Pumpkin seeds (PUMP28) oil (a); influence of the Sunflower oil - SF5 concentration augmentation onto the Raman spectra of SB26 oil (b); Normalized Raman spectra of different oils mixtures (Sunflower – Sea Buckthorn and Sunflower – Sea Buckthorn – Pumpkin seeds) compared with the spectrum of SB24 oil, claimed by the producer as preponderant Sea Buckthorn oil (c).

SF5-SB26 (20–80% v/v, 50–50% v/v and 80–20% v/v) and the first three samples of the ternary (Mix2) mixture, SF5-SB26-PUP28 (40–27–33% v/v; 30–20–50% v/v; 24–16–60% v/v), a totally number of 36 samples. The test dataset was created for investigation of the contamination or adulteration of oils from the SBi oil producer. Thus, the test dataset contains the Raman spectra of SF, PUP and SBi oils from the same producer, the spectra Sea Buckthorn (SB26) used for the ternary mixtures' preparation, and five samples of the ternary (Mix2) mixtures SF5-SB26-PUP28 (totally 8 samples). Both the reference and test datasets contain the Raman data from the region 1120–1800 cm⁻¹, obtained after the baseline subtraction and normalization to [0 1].

We trained the Classification learner on the 36 samples of the reference dataset, having as variables the Raman data and as response, the seven oils species, SBi (for the Sea Buckthorn traded by producer as a mixture 80–20% SB-SF), and Mix1 or Mix2 (for the two types of our prepared mixtures). An 8 folds cross-validation technique has been employed for the process validation and we have trained all the classification types to classify these data. The best model that worked for the oils' classification (better accuracy) has been investigated by the confusion matrix chart and it has been exported to the Matlab workspace in order to make prediction on the test data. The model that worked well (accuracy 88.9%) for this approach is an ensemble classifier - subspace KNN when the PCA was disabled. Figs. 3–5 present the confusion matrices obtained for the trained data.

As can be seen, this technique is able to separate successfully the investigated oils into classes. There are some exceptions related to one Linseed (LIN) oil that is attributed to Walnut (WAL) class, while the Sea Buckthorn oil (SB24) and one sample of Sunflower (SF) are assigned to Sesame (SES) class. To these, one sample of ternary oils mixtures - Mix2 (SF-SB-PUP) is associated to Mix1 (SF-SB) type, mainly due to a high similarity between the two mixtures when the ternary composition contains very low concentration of the Pumpkin oil (Fig. 3).

According to the results from Fig. 4, several classes of the oils, namely Hemp, Pump, Sea Buckthorn, Sesame, Walnut and also Mix1 have a 100% recognition rate (sensitivity), while Sea Buckthorn SB24 (denoted in the charts as SBi) has 100% false negative percentage. This means that the SB24 (the oils indicated by producer as 80% SB and 20% SF) is separated by the SB class, but, in the same time, it is not associated to SF too. This sample SB24 (SBi) is classified as Sesame type (SES). The similarity observed in the Raman spectra (Fig. 1a) between the two types of oils can justify this classification results. This similarity also provides a positive predictive value of only 71% for SES (Fig. 5), due to the assignment of one SF sample to the SES class too.

This model has been employed further to make prediction on the test dataset; the results are presented in Table 2.

These results highlight not only the possibility for an accurate identification of some less common edible oils, even on low signal-to-noise spectra (e.g. Pumpkin, PUP case), but also the capability of the

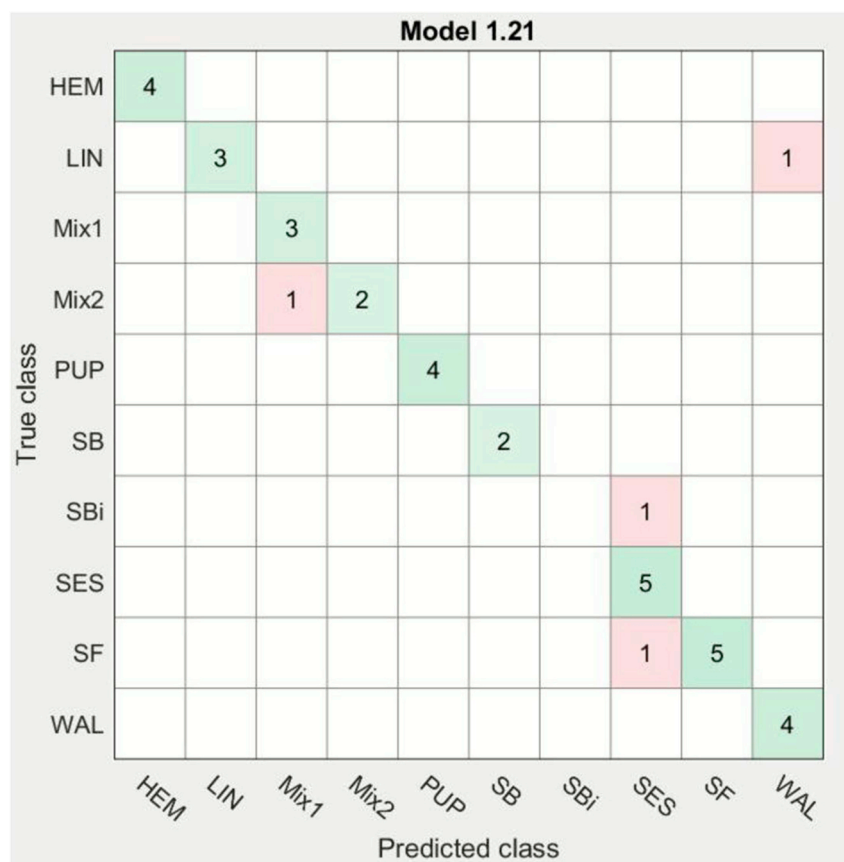


Fig. 3. Confusion matrix chart of the classification results.

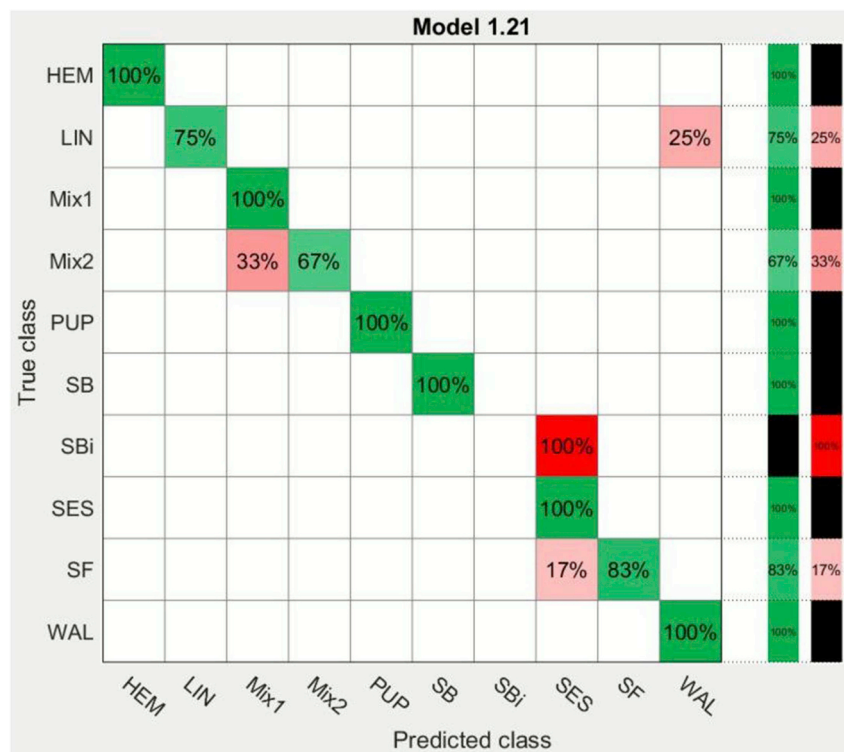


Fig. 4. Confusion matrix displaying the percentage values of true positive and false negative rates.

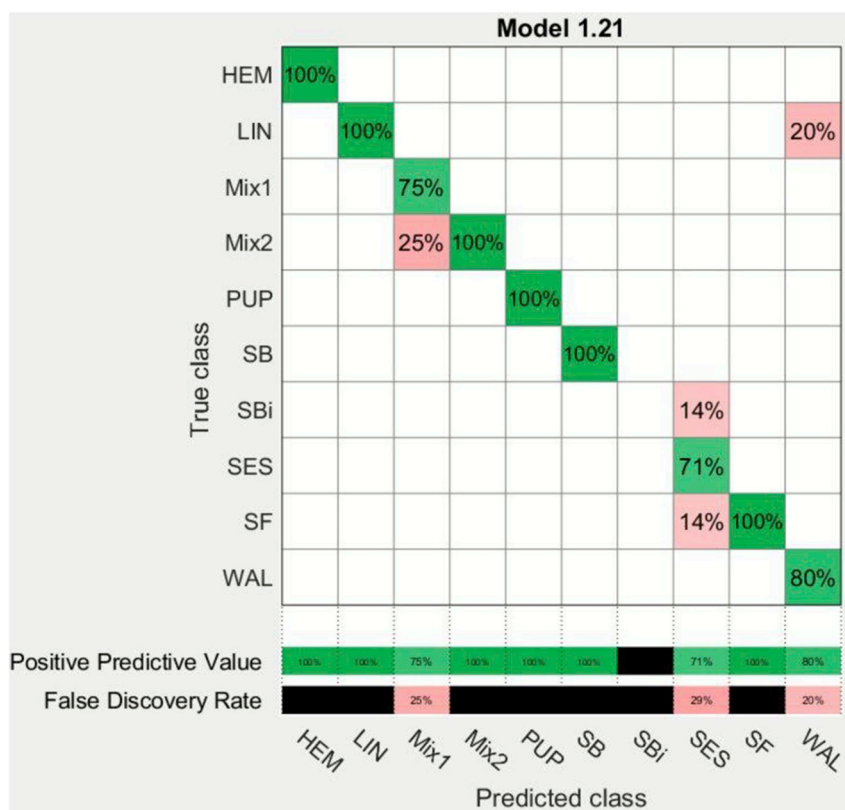


Fig. 5. Confusion matrix displaying the percentage of the positive predictive value and the false discovery rates.

Table 2

Prediction results obtained for the test datasets together with the sample types and their composition.

Sample type	Predicted class	Composition
SF5	SF	SF ^a
PUP28	PUP	PUP ^a
SB24	SBi	SF-SB: 20–80% ^a
SB26	SB	SB ^a
M4	Mix2	SF5-SB26-PUP28: 60-15-25% v/v ^b
M5	Mix2	SF5-SB26-PUP28: 48-12-40% v/v ^b
M6	Mix2	SF5-SB26-PUP28: 40-10-50% v/v ^b
M7	Mix2	SF5-SB26-PUP28: 34-9-57% v/v ^b
M8	SBi	SF5-SB26-PUP28: 30–7.5–62.5% v/v ^b

^a As indicated by producer.

^b Prepared by us before Raman measurements.

ML analysis of Raman data to be used for discrimination between a pure oil from a mixture of oils. Using two types of mixtures, we prove that our approach is also useful to differentiate between them and to get a first idea about the degree of adulteration.

4. Conclusions

In this study, a new approach for edible oil authentication was developed and successfully tested, being based on the rapid processing of Raman spectra using Machine Learning algorithms. The main advantages for using Raman spectroscopy in food authentication purposes are related to the features of this technique which do not require a sample preparation step, is a very rapid one and the analysis costs are relatively low. In this regard, distinct varieties of edible oils, some of them being considered as natural food supplements, like: Sesame, Hemp, Walnut, Linseed (Flaxseed), Pumpkin and Sea Buckthorn were included in this study.

Our approach is very simple; it is based on the collection of the oils

Raman spectra and the creation of a training dataset based on data that doesn't require special or time-consuming pretreatments. It employs the use of the Classification learner app and allows the identification of the most relevant model for the oils' classification by a simple analysis of their Raman spectra.

Moreover, through this approach, not only the adulteration detection was achieved but also an initial estimation of its magnitude. It was demonstrated that in the case of the sample SB24 (labeled by the producer as 80% Sea Buckthorn oil and 20% Sunflower oil) the proportion between the two oils types was not the claims one. In this case the cheaper ingredient (Sunflower oil) was present in a much higher percentage than it was labeled. Moreover, the obtained fluorescence for this sample suggested the presence of Pumpkin seeds oil, this being also produced in the frame of the same manufacture.

All these results, demonstrated the potential of this approach to be used as a rapid and sensitive tool for edible oils investigation.

Author statement

Camelia BERGHIAN-GROSAN: Conceptualization, Methodology, Validation, Investigation, Formal analysis, Writing- original draft preparation, Writing -reviewing and editing, Dana Alina MAGDAS: Conceptualization, Methodology, Writing- original draft preparation, Writing -reviewing and editing, Supervision, Project administration.

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Declaration of competing interest

None.

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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