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Detection of refined sunflower and rapeseed oil addition in cold pressed rapeseed oil using Mid Infrared and Raman Spectroscopy

Daniel McDowell, Maria Teresa Osorio, Christopher T. Elliott and Anastasios Koidis*

Institute for Global Food Security, Queen's University Belfast, Northern Ireland, UK.

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***Corresponding author:** Dr Anastasios (Tassos) Koidis,

Institute for Global Food Security,

Queen's University Belfast,

18-30 Malone Road,

Belfast, BT9 5BN, Northern Ireland, UK,

tel: +44 28 90975569

email: t.koidis@qub.ac.uk

Abstract

In this study, a new screening technique for the detection of two types of oil adulterants in cold pressed rapeseed oil was investigated. The calibration models built with four different multivariate classifiers (SIMCA, PLS-DA, LDA-KNN, and LDA-SVM) were based on spectral fingerprints from either FT-IR and Raman instruments from authentic pure oils and in-house admixtures of the oils involved. When refined sunflower oil was the adulterant, both FT-IR and Raman produced effective models with high sensitivity of 86%, 93% respectively, when refined rapeseed oil was the adulterant the sensitivity decreased. This was explained by the chemical differences of the two adulterants. PLS-R quantification analysis estimated minimum detection levels of 15% (Raman) and 9% (FT-IR) when refined sunflower oil was the adulterant, and 22% (Raman) and 64% (FT-IR) when refined rapeseed oil was the adulterant. This initial study shows the potential of Raman spectroscopy to be utilized for the screening of cold pressed rapeseed oil authenticity.

Practical Applications:

It has been well documented in the past that high-value edible oils can be easily adulterated with lower cost oils for economic gain. Although the cold pressed rapeseed oil industry has not experienced such fraud, it would be prudent to have analytical techniques available to authenticate genuine oils quickly. This would further strengthen cold pressed rapeseed oils reputation as a product free from substitutional fraud. These calibration models can tool the industry and regulatory bodies with a screening method to detect authenticity in realistic levels.

1. Introduction

Cold pressed rapeseed oil (CPRO) is produced when the seeds harvested from the oilseed rape crop (also known as canola depending on geographical region) are mechanically crushed at low temperature. The oil is collected and the sediment removed through filtration or sedimentation tanks. Once free from sediment the oil is bottled and ready for sale. The advantages to this type of processing are that the oil has a pleasant taste, bright color, and can be used in both hot and cold cooking. Manufacturing cold pressed rapeseed oil is still a relatively new industry, the earliest producers in Britain started production around mid-2000's. Cold pressed rapeseed oil is marketed as a high-quality product, and consequently its retail value is at the high end of the edible oil market [1]. High-value edible oils are an easy target for adulteration as they can be mixed with low-value edible oils without critically changing either the taste or the appearance of the original oil. To secure the burgeoning cold pressed rapeseed oil industry from any future threats it would be sensible to develop a screening technique capable of quickly and accurately detecting adulterants.

With regards to the cold pressed rapeseed oil adulteration, there has been little work which looks specifically at analytical methods to detect authentication. There has been some research which has investigated the differences between refined rapeseed oil (RRO) and cold pressed edible oils including rapeseed [2]. For clarity when this paper refers to a "refined" oil it is regarding oils which have been conventionally solvent extracted, refined, bleached and deodorised, as is common with many low-cost edible oils. Common oil components which are found in refined rapeseed oil and not cold pressed rapeseed oil are trans fatty acids[3], steradienes[4], cis-phytol [2] and 3-MCPD-esters [5]. The detection above certain levels of any of these in cold pressed rapeseed oil would point towards adulteration. The advantage of using a targeted chemical technique is that low levels (<10%) of adulteration can be confidently identified and quantified. These techniques include gas chromatography[6], liquid

chromatography[7] and genomic analysis [8]. The disadvantages are that these techniques are often costly, require skilled technicians and take long periods of time to generate results. Cold pressed rapeseed oil has yet to be analyzed for purity using commonly available spectroscopic techniques. With the aid of chemometrics, spectroscopy can be adapted to become a non-target technique which can be an alternative to traditional wet chemistry procedures. Vibrational spectroscopy techniques can replace targeted molecular techniques if the prediction model is particularly strong, it can also be used as a screening method in tandem with chemical quantitative methods. Both Raman and Fourier transform-infrared spectroscopy (FT-IR) have been shown to be effective tools for the authentication of many edible oils. Raman spectroscopy has been successfully used to classify different types of vegetable oils [9,10]. It has also been used extensively to detect adulteration of extra virgin olive oil with low value oils [11–14]. On the other hand, FT-IR has been shown to be able to classify vegetable oils [15,16], and detect adulterants in extra virgin olive oil [17–19]. There has currently been no work which has yet explored the feasibility of spectroscopy to control cold pressed rapeseed oil authentication. Although one study has used FT-IR to detect waste cooking oil in refined rapeseed oil [20].

Raman peaks are formed when there are changes to the polarizability of a bond, while FT-IR spectra peaks are formed when there is a change in the dipole movement of a bond. This means that some molecular bonds can be Raman active but not FT-IR active and vice versa, therefore they could be viewed as complementary techniques [21]. It should be stated that this study focuses on comparing the two spectroscopies, rather than an investigation into their tandem use. This research is testing two types of spectroscopy and four types of chemometric techniques which are essential for multivariate data analysis and classification, to evaluate their suitability for cold pressed rapeseed oil authentication.

This study consists of strategically designed binary oil mixtures of a) cold pressed rapeseed oil and refined rapeseed oil, b) cold pressed rapeseed oil and refined sunflower oil (RSO), c) cold

pressed rapeseed oil and either refined rapeseed oil or refined sunflower oil. These adulterants were chosen after input from industry insiders because both exhibit properties which make them attractive to potential fraudsters; they are low cost and readily available while refined rapeseed oil has the added advantage of being very similar in its chemical composition to cold pressed rapeseed oil [22]. Refined, bleached, deodorized rapeseed oil was chosen over partially refined rapeseed oil (degummed and solvent extracted oil) because these oils are not commercially available and are therefore unlikely to be readily available to potential fraudsters because they are not commercially sold. Few if any large refining plants produce cold pressed rapeseed oil as well. The probability of a partially refined oil being used as an adulterant is slim at this present time.

Vibrational spectroscopy was chosen as a technique because it already has some applications and a great potential for further development in the food industry; analysis points can be set up at many points of the manufacturing process to offer quick, constant feedback regarding the quality of the product. In summary, the overall aim of this study is to develop a first of its kind rapid spectroscopic screening technique based on either FTIR or Raman which can detect refined rapeseed oil or refined sunflower oil substitution fraud in cold pressed rapeseed oil with high confidence.

2. Materials and Methods

2.1. Sample Preparation and study design

The cold pressed rapeseed oils (CPRO), refined rapeseed oils (RRO) and refined sunflower oils (RSO) used for this study were all donated by producers of reputable oil processors and spanned across two production years (2014-2016). All the cold pressed rapeseed oils were from British or Irish origins and were produced only by cold pressing and no additional refining

processes were used. All oils were measured for general quality parameters including peroxide value [23] acid value [24] and fatty acid composition [1] using typical methods and the values were found nominal (see Supplementary Material). All samples fell within expected parameter ranges for such oils. The oils were then frozen at -20°C and defrosted when required. Three separate cases were studied: RSO as an adulterant in CPRO, RRO as an adulterant in CPRO and either RSO or RRO as adulterants in CPRO with RSO or RRO. To achieve that three calibration sets were constructed: a) with binary mixtures of CPRO:RRO, b) with binary mixtures of CPRO:RSO and c) with binary mixtures of CPRO:RSO and CPRO:RRO. These calibration sets had corresponding independent validation sets which were approximately a third smaller in size. The calibration set containing CPRO and RRO contained mixtures made from seven CPRO's and five RRO. The corresponding validation set contained mixtures made with three different CPRO's and two RRO's. The calibration set containing CPRO and RSO also contained mixtures made from seven CPRO's and five RSO's. The corresponding validation set contained three CPRO's and RSO's. The mixtures were made from different brands of CPRO in each validation and calibration set i.e., the seven CPRO's used in the CPRO/RRO calibration set were different from the CPRO's used in the CPRO/RSO calibration set. The oils present in the calibration sets were not used in the validation sets and vice versa, this ensured no bias within the model. A complete gradient of oil mixtures was used for the calibration and validation (4-97% and 7-98%) because no previous work on cold pressed rapeseed oil spectroscopic analysis has been done before, therefore approximate limits of detection were unknown.

2.2. Raman and FT-IR spectral acquisition

A DeltaNu Advantage 1064 Raman Spectrometer was used along with NuSpec software to acquire the spectra. The 1064 nm laser power was set to “high”, integration time was “10

seconds”, and the number of spectra for each acquisition was set to “2”. Each sample was taken in duplicate and averaged. The FT-IR instrument used was a Thermo Scientific Nicolet iS5 spectrometer (Thermo Fisher Scientific, MA, USA) equipped with a standard Id5 ATR accessory. The number of scans was 32 and the data spacing set to 0.482 cm^{-1} . Each sample was taken in triplicate and averaged. The spectral acquisition took place across several days.

2.3. Data Analysis: Pre-processing, Classification, and Quantification

For the spectra pre-processing, Standard Normal Variate (SNV) and 1st derivative were applied to reduce the scattering effect of the spectra. The smoothing technique Savitzky-Golay was then employed followed by Pareto scaling. The Raman and FT-IR spectra were cut at certain places to remove areas that held no information. The areas of the FT-IR spectra which were included ranged from $654.32 - 1875.43\text{ cm}^{-1}$ and from $2520.02 - 3120.74\text{ cm}^{-1}$. The Raman areas for inclusion were from 800.314 to 1800.22 cm^{-1} . A trial data fusion system was also investigated, where the Raman and FT-IR spectra were fused and analyzed with the same method as for the single spectroscopy techniques. All chemometric data analysis was performed with in-house Matlab routines (Mathworks inc., USA). For classification analysis four different techniques were used to illustrate the most effective, these were; partial least squares – discriminant analysis (PLS-DA)[25], soft independent modeling of class analogy (SIMCA)[26], linear discriminant analysis - k-nearest neighbor (LDA-KNN)[27], and linear discriminant analysis - support vector machine (LDA-SVM) [28].

PLS-DA is a chemometric technique often paired with spectroscopic data to predict the probability that a sample belongs to a certain class [29]. Soft independent modelling of class analogies is another technique which this paper also investigates. In SIMCA, a principal component analysis is first performed on each class in the dataset to establish principal components which account for a large part of the variation within the classes. The residual

variance from an unknown sample is then compared with the calculated variance of each class and a prediction is made as to the likelihood that the unknown sample belongs to a certain class [30]. LDA-KNN is a completely non-parametric approach which compares calibration and validation datasets. It classifies validation samples according to the classes of the k closest calibration samples, where k is the number of neighbours for the decision [31]. Support vector machines (SVM's) define a function that describes the decision boundary that optimally separates two classes by maximising the distance between them. The support vectors are selected in the calibration set and the classification rule is derived from these objects [32]. The four classifiers will be compared to establish which technique produces the most promising results based on sensitivity, specificity, precision and false positive rate, the equations for which can be found in Oliveri and Downey [33]. For quantification analysis, partial least squares – regression (PLS-R) was used to produce a root mean square error of prediction (RMSEP) value. The RMSEP can then be used to estimate levels of detection as shown in Downey and Kelly [34].

3. Results and Discussion

3.1. Initial Spectra Exploration

Principal component analysis (PCA) was used as an unsupervised data exploration step to visualize the differences between the various classes of edible oils of the study. The PCAs were built using datasets of Raman and FT-IR spectra (Figs. 1, 2) and contain both pure oils and oil mixtures. The PCA plot of Raman spectral data in Fig. 1A showed a clear separation between pure oil classes, with some samples of the mixture class close to pure sunflower oil and some close to pure cold pressed rapeseed oil. In Fig. 2A the separation is much less defined, although the refined rapeseed oils are loosely congregated towards the top and cold pressed appear more towards the bottom of the PCA plot. When all five classes were combined in a PCA plot of

Raman spectral data, sunflower oil and its admixtures are separate from the three classes containing only rapeseed oil which are tightly grouped (Fig. 3). The PCA plot of FT-IR spectral data of cold pressed rapeseed oil, refined sunflower oil and mixtures of the two (Fig. 2A) showed a clear separation between the two pure oils with mixtures occupying the space between the two pure oils. The PCA plot of refined rapeseed oil, cold pressed rapeseed oil and its mixtures (Fig. 2B) showed there was little grouping of the three classes. The pure oil classes appear close together, suggesting that both cold pressed rapeseed oil and refined rapeseed oil produce very similar FT-IR spectra. When five classes were visualised the sunflower oil and its admixtures formed clear groups while cold pressed rapeseed oil and refined rapeseed oil remained congregated together (Fig. 3). These diagrams illustrate the difficulties in clearly separating refined rapeseed oil from cold pressed rapeseed and it would therefore be expected to be a harder adulterant to detect than refined sunflower oil.

A spectral comparison of the oils can indicate a difference in chemical composition, therefore an initial visual comparison of the spectra was observed. The wavelength at which spectral variation(s) occur can be used to indicate what compound(s) are responsible for specific regions of absorption. Any difference between the mixtures should show a gradual change in spectra composition as the ratio of oils changes. The raw Raman spectra were not suitable for a visual comparison analysis (Fig. 4a) therefore the pre-processed spectra were superimposed (Fig. 4 b/c). Superimposed pre-processed spectra of cold pressed rapeseed oil and refined rapeseed oil admixtures (4-97%) were similar apart from variation around the regions at 1150-1200 cm^{-1} and 1500-1600 cm^{-1} (Fig. 4b).

It is established both in-house (data not shown) and in the literature that cold pressed rapeseed oil and refined rapeseed oil have almost identical fatty acid compositions. The areas of spectral variation are not taken up by large peaks corresponding to fatty acids, therefore the variation is likely to come from minor compounds within in the oils. A study by *Baeten et al.*[35], using

Raman spectroscopy identified these areas as parts of the spectra where the carotenoids β -carotene and lutein absorb. One of the main differences between cold pressed rapeseed oil and refined rapeseed oil is their pigment composition. Pigments including chlorophyll and carotenoids are removed during the bleaching stage of refinement while cold pressed rapeseed oils retain their pigments [36]. These compounds are likely to be very important when using vibrational spectroscopy to differentiate between the two oils. When cold pressed rapeseed oil and refined sunflower oil mixtures spectra were superimposed (Fig. 4c), there were more regions of variation than when refined rapeseed oil and cold pressed oil were superimposed (Fig. 4b). The regions between 1150-1200 cm^{-1} and 1500-1600 cm^{-1} again showed variation which would indicate differences in pigment levels. This explanation would be further strengthened by the fact that the refining process removes nearly all of the pigments in refined sunflower oil [37]. The other areas of variation in this oil set are likely down to the difference in fatty acid composition between the two oils [38]. The variation in the spectra around 800-1100 cm^{-1} corresponds to the $-\text{CH}_2-$ group [9]. The difference in fatty acid composition between the two oils and therefore the difference in $-\text{CH}_2-$ chain lengths within the oil mixtures are likely to be responsible for this variation. There is also variation around the region 1660 cm^{-1} which corresponds to *cis*- carbon double bonds. The number of double bonds between the two oils differs significantly; rapeseed oil 110-143 cm^{-1} and sunflower oil 188-193 cm^{-1} [39]. There was no variation in the region of trans double bonds (1670 cm^{-1}), probably because their levels are so small that they fall below the limits of detection and resolution of this spectroscopy.

The superimposed raw FT-IR spectra of cold pressed rapeseed oil and refined rapeseed oil showed no variation within the spectra of oil mixtures. When typical pre-processing techniques were applied to the spectra, there was still no visible distinction achieved. The Raman spectra suggests that pigments can cause variation between these oil admixtures, and because of this

the infrared regions where pigments would be expected to influence, were analyzed for variation. A study by Baranska *et al.* [40] found β -carotene to be associated with peaks in the infrared spectrum at 965 and 950 cm^{-1} . Close visual inspection of this region, showed no variation with regards to cold pressed rapeseed oil and refined rapeseed oil mixtures. The regions of the FT-IR spectra which may assist in discrimination between these two oils, does not appear to be visible with only visual inspection.

When the FT-IR spectra of admixtures containing refined sunflower oil and cold pressed rapeseed oil were superimposed (Fig. 5) there was clear variation in the region 880-1050 cm^{-1} . This area of the spectra has been identified as corresponding to saturated fatty acids content [41]. The two oils differ in their saturated fatty acid content with cold pressed rapeseed oil having around 7% [42] while refined sunflower oil has between 9-13%, which would explain the variation. This could be an important area of spectral information with regards to classification analysis. The reason that FT-IR does not appear to show the same variation associated with pigmentation that Raman shows, is that the different energy sources emitted from the instruments excite molecules in different ways. Therefore it is possible the infrared signal is not as readily absorbed by pigment molecules as the Raman signal. It is also possible the other peaks in the FT-IR spectra are blocking the pigment variation peaks.

2.2. Classification Analysis

Four types of supervised classification techniques (SIMCA, PLS-DA, LDA-KNN, LDA-SVM) were used to build the chemometric models. These classification techniques were used to classify three distinct dataset scenarios. The suitability of each model was shown by the successful classification of samples in a validation dataset. The results showed that successful classification is dependent upon multiple variables including; the type of adulterant, the number of classes and the classifier technique used (Table 1, 2).

Scenario #1 (3 classes with 2 different types of oils): CPRO adulterated with RRO

The results showed that Raman spectroscopy was able to achieve an average model sensitivity of 93% (Table 1) while FT-IR achieved 86% average sensitivity (Table 2). Raman spectroscopy also produced a lower FPR across the three classes than FT-IR. It would seem that Raman spectroscopy is better suited than FT-IR spectroscopy for this three-class problem. It should, however be noted that the FT-IR spectra was able to obtain a respectable classification rate, although the regions of spectra associated with this remain unclear. The reason for Raman spectroscopy better performance compared to FT-IR may be down to the ability of the spectra to show absorbance peaks associated with pigmentation (Fig. 4b) that should be discriminative due to the different pigment profiles of the two oils [37]. Also, subtle variations in fatty acid composition could contribute to the differentiation between the three classes even if they are largely invisible to the naked eye (spectral pre-processing usually enables enhancement of these minute differences). With regards to the individual classifiers, LDA-KNN and LDA-SVM performed best for both Raman and FT-IR, regarding this scenario.

Scenario #2 (3 classes with 2 different types of oils): CPRO adulterated with RSO

Raman spectroscopy exhibited an average sensitivity of 93% (Table 1) while FT-IR produced an average sensitivity of 96% (Table 2). FT-IR was also able to produce a lower FPR across the three classes. The most successful combination was shown to be FT-IR spectroscopy coupled with LDA-SVM modeling. Although less sensitive than FT-IR, Raman spectroscopy still achieved competitively high classification rates, also with LDA-SVM classification. There were many regions of the Raman spectra which were likely to be important for discriminating classes (Fig. 4c) as discussed earlier.

Scenario #3 (5 classes, with 3 different types of oils): CPRO adulterated with either RSO or RRO

The final dataset tested was a combination of the two datasets previously mentioned, resulting in five classes; CPRO, RRO, RSO, CPRO:RRO and CPRO:RSO. Ternary oil mixtures were not investigated because classification accuracy decreases with an increasing number of adulterants [43] and in fact, binary adulteration is a more common form of adulteration. As a result of the increased class number in this scenario, the accuracy of the models decreased, compared with the previous three class datasets (scenario 1 and 2). Raman spectroscopy was found to be considerably more effective than FT-IR when dealing classifying five possible classes, as it achieved 88% average model sensitivity compared to 69% produced by FT-IR. This may be due to multiple factors including the ability of Raman to detect pigment variation and differences in molecule activity to Raman and FT-IR. The most accurate classification models for this scenario were LDA-KNN for Raman and PLS-DA for FT-IR spectroscopy. It should be noted that simple data fusion techniques to combine the two types of spectra serially produced inadequate classification regarding the three scenarios when compared with single spectroscopic techniques (experiments conducted but data not shown).

3.3. PLS-R quantification analysis

Partial least squares regression (PLS-R) is a quantitative modeling technique which generates predictor components against known variables in a linear output. The relationship between the two variables can be used to show variability between calibration and validation datasets. The analysis can only be utilized for three class analysis i.e., 0-1 where 0 is the first pure oil and 1 is the second pure oil, with the binary mixtures of the two being the values between 1 and 0. The PLS-R results (Table 3) reflect the classification results with regards to the success of the spectroscopy technique and classification problem. When concerning sunflower oil as an adulterant, FT-IR produced the highest R^2 value (0.99) with an estimated minimum detection limit of 9%. The dataset where refined rapeseed oil was the adulterant showed that Raman

spectroscopy produced spectra better suited for accurate quantification ($R^2=0.95$). The minimum detection levels with refined rapeseed oil as an adulterant was 22% which is higher compared to refined sunflower oil as an adulterant. The similarities between refined rapeseed oil and cold pressed rapeseed oil meant that it was likely to be more difficult to quantify than any other type of edible oil adulterant. With regards to comparable studies, there has been little published that looks at pre-determined mixtures of cold pressed rapeseed oil and refined rapeseed oil, as this study does. A study by Vetter [2] showed that a cis-phytol level above 0.5% could be used as a marker for refinement in cold pressed oils. The study used only pure cold pressed oils and pure refined oils, therefore it was not known to what level cis-phytol could be detected in admixtures of cold pressed rapeseed oil and refined rapeseed oil would have. Bruhl [3] claimed that $>0.1\%$ trans fatty acids in cold pressed rapeseed oil would confer adulteration, however, the study did not pursue this opportunity to test this concept on admixtures and therefore could not establish a limit of detection of adulteration of cold pressed rapeseed oil with refined rapeseed oil.

This paper is the first to investigate specifically, cold pressed rapeseed oil authentication with current spectroscopic techniques and advanced multivariate analysis. It indicates there is a niche that spectroscopy could occupy in cold pressed rapeseed oil authentication. Its strengths are speed, low maintenance and non-destructive technique. More specifically, Raman spectroscopy was shown to be the most promising in this study and it showed a sound ability to classify pure cold pressed rapeseed oil from admixtures of cold pressed rapeseed oil and adulterants (Table 1). Other advantages of Raman spectroscopy over other techniques e.g. FT-IR, is that it can be utilised as a portable device, which would allow flexible on-site analysis. For quantifying the amount of cold pressed rapeseed oil adulterated with refined rapeseed oil, it is unlikely spectroscopy would be suitable. Even wet chemistry techniques previously mentioned [2,3] were not tested on admixtures of cold pressed rapeseed oil and refined

rapeseed oil. However, when viewed from a real-world perspective this is not a pressing issue, as classification of an adulterated oil would be enough to raise concerns in the screening step as developed here, and it could then be further analysed with targeted analytical techniques such as GC-MS or LC-MS to ascertain how much adulterant is in the oil.

4. Conclusions

The various combinations of vibrational spectroscopy and chemometric analysis produced outputs which varied in performance regarding this analytical problem. Both FT-IR and Raman spectroscopy showed clearly the ability to detect adulteration in cold pressed rapeseed oil with sunflower oil at relatively low levels. Raman spectroscopy produced, however, consistently higher classification rates than FT-IR, with all of the three top performing classifiers reaching above 88% model sensitivity, which was also coupled with low error margins. Detection of refined rapeseed oil addition proved more challenging due the chemical similarities between it and cold pressed rapeseed oil. Regarding this adulteration scenario, Raman spectroscopy coupled with LDA modelling was able to achieve an average model sensitivity of 93%. The performance of the four classifiers showed that both LDA and PLS-DA models performed much better than SIMCA. The LDA-KNN and LDA-SVM models produced higher classification rates than the often used PLS-DA model, which would suggest there is room to improve the already established models. This feasibility work shows the potential of vibrational spectroscopy, and especially Raman, as rapid screening techniques to identify common oil replacement fraud in cold pressed rapeseed oil. They are techniques which could easily transferred into an industrial setting and screen large sample numbers, quickly with little-specialised training need.

Abbreviations:

CPRO – Cold Pressed Rapeseed Oil; RRO – Refined Rapeseed Oil; RSO – Refined Sunflower Oil.

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Conflict of Interest

The authors declare no conflict of interest.

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