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Rapid Authentication of Olive Oil Adulteration by Raman Spectrometry

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The authentication of olive oil and its adulteration with lower priced oils are still serious problems in the olive oil industry. In this study, a method based on the intensity ratio of the Raman spectroscopy vibration bands, especially on the intensity ratio of the cis (=C—H) and cis (C=C) bonds normalized by the band at 1441 cm^{-1} (CH_2), was established to authenticate genuine/fake olive oil. These intensity ratios of the vibration bands given in the form of a two-dimensional chart allow first the discrimination between the various grades of olive oil and the seed oils and then the detection of olive oil fraud by the line of $y = 0.7$, which is observed under most experiments and dot charts. This method can reliably distinguish the genuine olive oils from the olive oils containing 5% (volume percentage) or more of other edible oils, such as soybean oil, rapeseed oil, sunflower seed oil, or corn oil. Compared to the traditional principal component analysis method, this method is more intuitive, more precise, and easier to use. Moreover, this method also has the advantages of simplicity efficiency and has no need for sample preprocessing, being especially suitable for on-site testing in field applications.

KEYWORDS: Raman spectroscopy; intensity ratio; vibration bands; authentication; olive oil; edible oil

INTRODUCTION

Olive oil is a type of fruit oil obtained through a process called cold press or centrifugation, which is quite different from the processes of other edible oils, such as soybean oil, corn oil, and rapeseed oil. In the world market, olive oils are the most valuable ones with a price tag normally 3−5 times those of regular edible oils. The high commercial value has prompted some merchants to sell inferior olive oils, blended with a large amount of other cheap edible oils or outright fake, under genuine labels, which, in addition to being unfair to the consumer in terms of the cost of this apparent premium commodity, may also cause severe health and safety problems.

Consequently, there is no doubt that the detection of olive oil adulteration needs to be addressed to ensure olive oil quality. Several techniques have been developed to authenticate and detect olive oil adulteration, such as chromatographic techniques, including gas chromatography (GC) (*1−3*), gas chromatography−mass spectrometry (GC-MS) (*4−6*), and high-performance liquid chromatography (HPLC) (*7−9*). Nuclear magnetic resonance spectroscopy (NMRS) (*10−12*) has also been widely used to aid in the authentication, quality control, and adulteration detection of edible oils. Although these methods are widely used analytical techniques with low detection limits, they not only require complicated and expensive laboratory facilities but also involve complicated process steps and consume a great deal of time and money. Therefore, there is an urgent need to develop a simple, cheap, and rapid alternative to determine adulterants in olive oil.

Vibration spectroscopy such as infrared (IR) (*13*), near-infrared (NIR) (*14−16*), and Raman techniques, combined with chemometric (*17*) methods is an emerging analytical technique for the determination of adulterants in olive oils. Especially, Raman spectral bands represent vibrations characteristic for chemical bonds and structural units within the molecules of the examined sample (*18−22*). In combination with principal component analysis (PCA), partial least-squares (PLS), mode recognition, or neural network techniques, Raman spectroscopy has been successfully used to identify and quantitate adulteration in olive oils adulterated with corn oil, soybean oil, olive pomace oil, and even hazelnut oil and so on (*23−27*). However, these techniques require professional chemometric knowledge and sophisticated data processing, which are very difficult to employ in practice.

In this paper, a method was established to authenticate genuine/fake olive oil on the basis of the intensity ratio of the Raman spectroscopy vibration bands using a portable Raman spectrometer. By means of other edible oils such as soybean oil, rapeseed oil, sunflower seed oil, and corn oil containing higher percentages of unsaturated fatty acids in comparison to olive oil, this method was used to distinguish olive oil from olive oil adulterated with these four edibles oils. The intensity ratios of

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Table 1. Sample Information

sample	source	place of origin	brand	grade
1	USA	Italy	Carapelli	extra virgin olive oil
2	USA	Italy	Carapelli	extra virgin olive oil
3	USA	Italy	Berio	extra virgin olive oil
4	USA	Italy	Berio	olive oil
5	USA	Spain	Star	virgin olive oil
6	USA	Spain	San Gallio	olive oil
7	China	Italy	Berio	extra virgin olive oil
8	China	Spain	Oliterra	extra virgin olive oil
9	China	Italy	Argosy	pure olive oil
10	China	Spain	Fortune	extra virgin olive oil
11	China	Italy	Michty	extra virgin olive oil
12	China	Greece	Wordbest	virgin olive oil
13	China	Italy	Olivoilà	extra virgin olive oil
14	China	Spain	Ybarra	extra virgin olive oil
15	China	Italy	Bertolli	pure olive oil
16	China	Spain	La Española	pure olive oil
17	China	Italy	Bertolli	virgin olive oil
18	China	Spain	Mueloliva	extra virgin olive oil
19	China	Italy	Michty	pure olive oil
20	China	Italy	Berio	pure olive oil
21	Spain	Spain	Núñez de Prado	extra virgin olive oil
22	Spain	Spain	Carbonell	extra virgin olive oil
23	Spain	Spain	Núñez de Prado	extra virgin olive oil
24	China	Spain	Don Quijote	olive pomace oil
25	China	China	Gold Fish	soybean oil
26	China	China	Fu Lin Men	soybean
27	China	China	Hui Fu	soybean
28	China	China	Michty	sunflower oil
29	China	China	Fu Lin Men	sunflower
30	China	China	Gold Fish	sunflower
31	China	China	Jiangjiayoufang	rapeseed oil
32	China	China	Lotus Super Center	rapeseed oil
33	China	USA	American Cchef	corn oil
34	China	China	Fu Lin Men	corn oil
35	China	China	Hui Fu	corn oil

the cis-(=C—H) and cis-(C=C) Raman vibration bonds normalized by the band at 1441 cm^{-1} (CH_2) were given in the form of a two-dimensional (2D) chart, which allowed first the discrimination between the various grades of olive oil and the seed oils and then the detection of olive oil fraud.

EXPERIMENTAL PROCEDURES

Instrument. A portable RamTracer Raman spectrometer (OptoTrace Technologies, Inc., Sunnyvale, CA) was used to collect the spectral data. The data were processed with OptoTrace proprietary software. The instrument's physical dimensions are 20 (W) × 18 (L) × 9 (H) cm, and the instrument weights about 3 kg. The light source is a diode laser operating at 785 nm with the scanning range from 250 to 2400 cm^{-1}. The spectral resolution of the instrument is better than 6 cm^{-1}. Sample vials were purchased from National Scientific (USA).

Samples. The tested samples included different brands and grades and were produced in different places. They were all purchased at major supermarkets from the United States, Spain, and Mainland China for a total of 23 samples. There were also 11 edible oil samples of soybean oil, sunflower seed oil, rapeseed oil, and corn oil that were purchased from several large supermarkets in Mainland China. One sample of olive pomace oil was purchased from a supermarket in Beijing, China. A detailed list of the sample information is shown in **Table 1**. Edible oil samples with volume percentages of 5, 10, 20, 30, 40, and 50% were blended into two sample olive oils purchased from the United States that were labeled 1 and 6, which were chosen stochastically, resulting in a total of 48 blended samples. To verify the accuracy of this experiment, we further blended edible oil samples of soybean oil, sunflower seed oil, rapeseed oil, and corn oil with volume percentages of 5, 10, and 20%, respectively, into four sample olive oils labeled 1−4 that were purchased from the United States. Thus, the total number of samples is 131. A 1.5 mL vial was used for each sample.

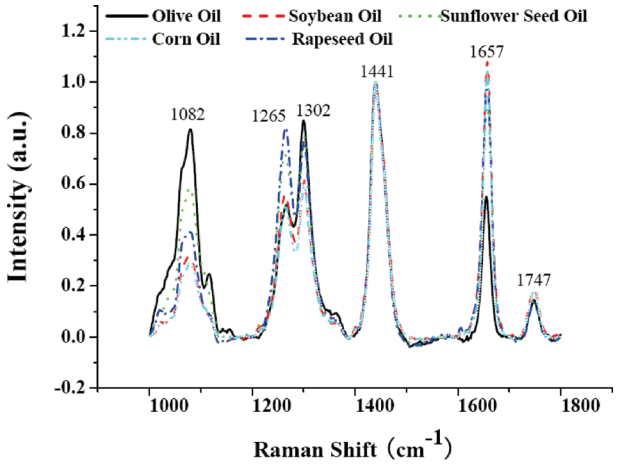

Figure 1. Normalized Raman spectra of olive oil, soybean oil, sunflower seed oil, rapeseed oil, and corn oil.

Table 2. Characteristic Raman Spectra from the Sample

frequency (cm^{-1})	molecule	vibration mode	intensity
1082	$-(CH_2)_n-$	C—C stretch	medium
1265	cis-RHC=CHR	=C—H stretch	medium
1302	$-CH_2$	C—H bend (twist)	medium
1441	$-CH_2$	C—H bend (shear)	strong
1657	cis-RHC=CHR	C=C stretch	medium
1747	RC=OOR	C=O stretch	weak

Data Collection. The samples were measured with a portable Raman spectrometer with a near-infrared laser operating at 785 nm as excitation light source. The laser power was set at 200 mW, and the data acquisition time was set at 10 s to achieve optimal Raman peak intensity. The Raman spectrum of each sample is the average of five repeated scans, which is also the average spectrum of five times operation by software. The relative standard deviation (RSD) of intensity for each band (measured five times) is below 5%.

The scan is done by placing the sample vial in the sample holder, where the light is focused onto the sample. The scanning range for each test is from 250 to 2400 cm^{-1}. The scan resolution is about 6 cm^{-1}. The time required for completing each sample measurement is about 2 min.

RESULTS AND DISCUSSION

Figure 1 shows the normalized Raman spectra of olive oil, soybean oil, sunflower oil, rapeseed oil, and corn oil. The normalized spectra are processed as follows: first, to carry out intensity calibration by system built-in software and the related database, make background subtraction, due to lack of interesting characteristics in the spectrum regions of 250−1000 and 1800−2400 cm^{-1}, the region of 1000−1800 cm^{-1} is selected for analysis, then use the band intensity of Raman shift at 1441 cm^{-1} (I_{1441}), related to the deformation vibration of the group C−H ($-CH_2$ molecule), as 1 to normalize the spectra. The characteristic bands and their corresponding vibration modes are well established according to the literature (*13*, *24*, *28*, *29*) and are listed in **Table 2**; that is, the major bands of Raman shifts are at 1082 cm^{-1} [ν(C—C)], 1265 cm^{-1} [in-plane δ (=C—H) deformation in unconjugated cis double bond], 1302 cm^{-1} (in-phase methylene twisting motion), 1441 cm^{-1} δ [(CH_2)], 1657 cm^{-1} [ν(C=C)], and 1747 cm^{-1} [(ν(C=O))]. Obviously, the band intensities of Raman shifts at 1082 cm^{-1} (I_{1082}), 1265 cm^{-1} (I_{1265}), 1302 cm^{-1} (I_{1302}), and 1657 cm^{-1} (I_{1657}) of the olive oil are quite different from the peak intensities of the other four edible oils. The biggest difference occurred at 1657 cm^{-1}; the peak intensities of olive oils are all <0.7, whereas the peaks of other oils are all >0.7. This may

be due to the fact that olive oil contains less polyunsaturated fatty acid than other oils. Therefore, characteristic band intensities of normalized Raman spectroscopy can be used as an important criterion to evaluate the quality of olive oil.

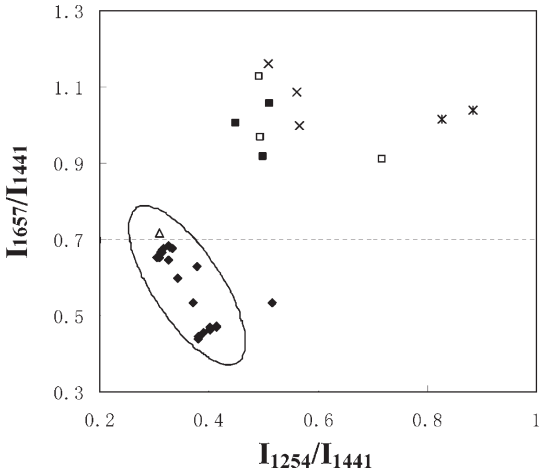

Figure 2. Intensity ratio of the Raman spectroscopy vibration band distribution charts of olive oil (◆), olive pomace oil (△), sunflower seed oil (□), soybean oil (×), rapeseed oil (∗), and corn oil (■). Genuine edible oils are delimited by ellipses of confidence of confidence at α = 0.90.

It is well-known that the Raman shifts of the vibration bands at 1265 cm^{-1} (I_{1265}) and 1657 cm^{-1} (I_{1657}), due to the cis-(=C—H) vibration and cis-(C=C) vibration, respectively, have a high correlation with monounsaturated and polyunsaturated fatty acids in the oils (*30−32*). Olive oil mainly consists of monounsaturated oleic acid, whereas soybean oil, sunflower seed oil, rapeseed oil, and corn oil show a high content of linoleic acid, which has the same chain length as oleic acid but contains one more C=C double bond. As a result, the Raman intensity of the cis-(=C—H) vibration and cis-(C=C) vibration is changed with the ratio change of olive oil adulterated with other edible oils. Accordingly, by calculating the band intensity of the Raman shifts at 1265 and 1657 cm^{-1}, olive oil can be detected from olive oil fraud with other edibles oils characterized by different contents of unsaturated fatty acids from olive oil.

Figure 2 shows the intensity ratio of the Raman spectroscopy vibration band distribution chart of olive oil, olive pomace oil, soybean oil, sunflower seed oil, rapeseed oil, and corn oil. The ratio of I_{1265} to I_{1441} was used as the horizontal coordinate for the chart, and the ratio of I_{1657} and I_{1441} was used as the vertical coordinate. Thus, each oil sample's data dot appears on the chart with its unique *x*,*y* coordinate. All olive oil samples' data dots

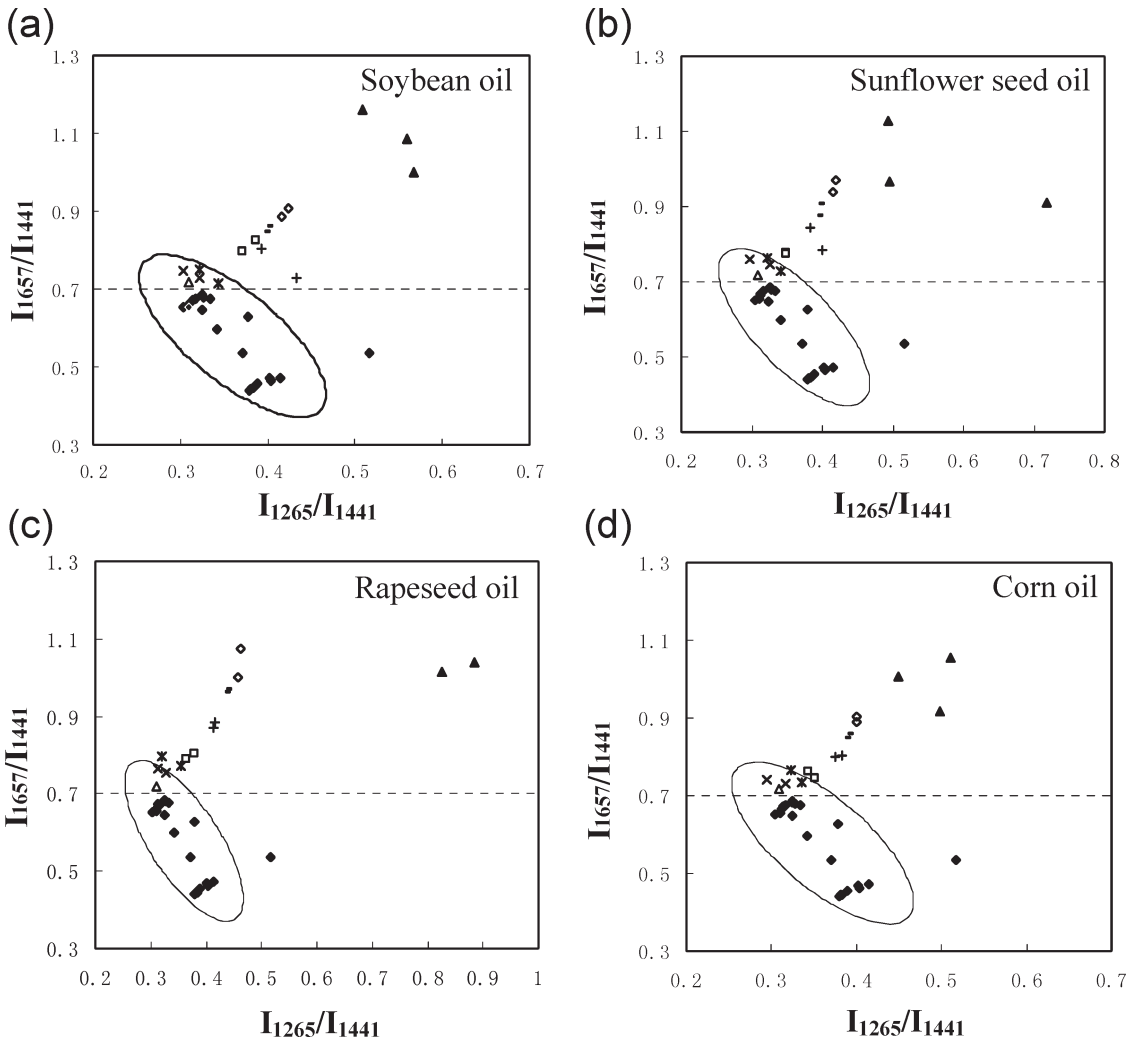

Figure 3. Intensity ratio of the Raman spectroscopy vibration band distribution charts of olive oil (◆) and its blended versions with other four edible oils in various volume percentages: olive oil blended with (a) soybean oil (▲), (b) sunflower seed oil (▲), (c) rapeseed oil (▲), and (d) corn oil (▲) in various volume percentages [5% (×); 10% (∗); 20% (□); 30% (+); 40% (-); 50% (◇)], respectively. △ represents olive pomace oil. Genuine edible oils are delimited by ellipses of confidence at α = 0.90.

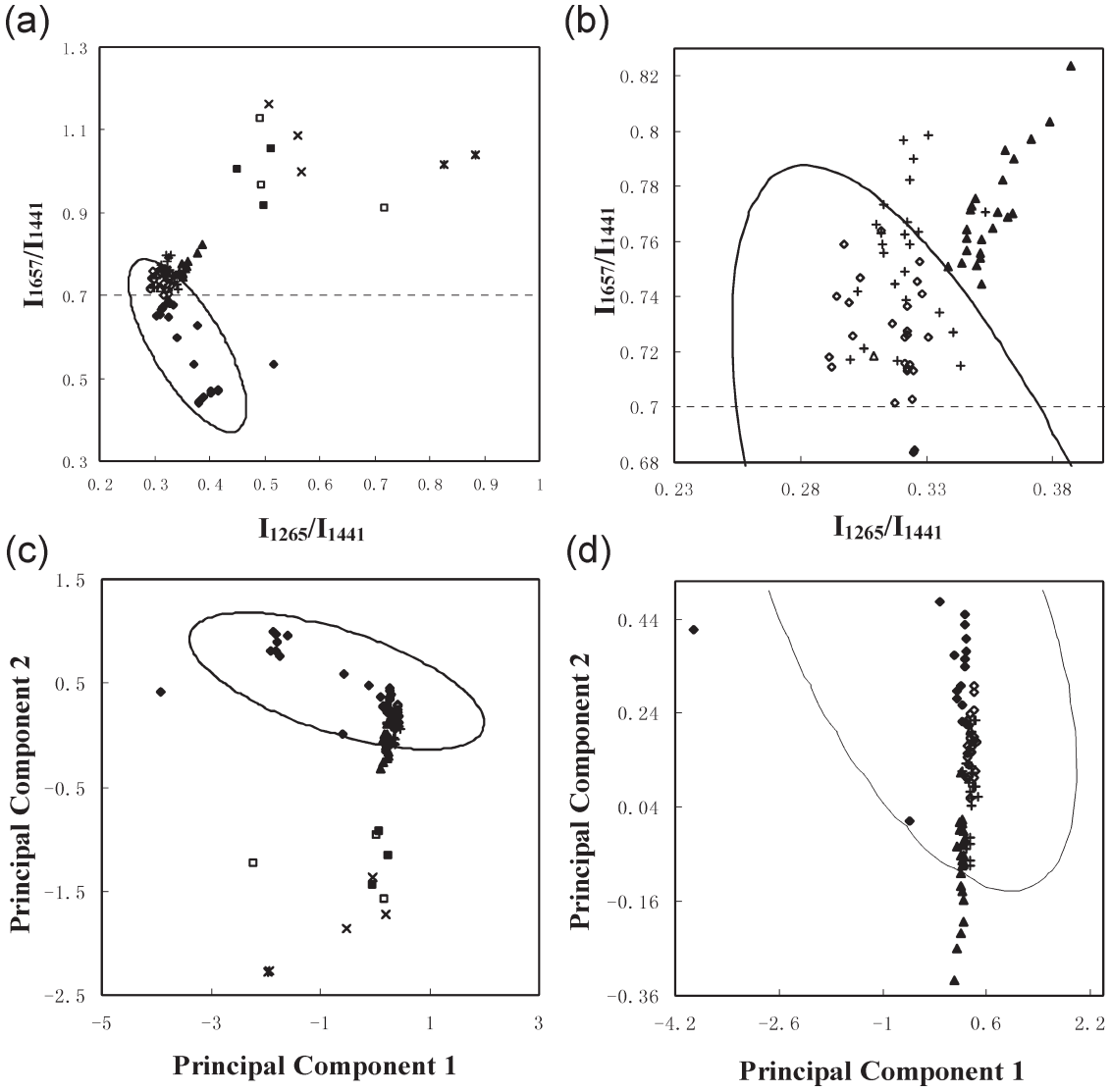

Figure 4. Intensity ratio of the Raman spectroscopy vibration bands (**a**, **b**) and PCA (**c**, **d**) distribution charts of olive oil (◆) and its blended version with 5% (◇), 10% (+), and 20% (▲) of soybean oil (×), sunflower seed oil (□), rapeseed oil (∗), and corn oil (■), and their local enlarged drawing, respectively. △ represents olive pomace oil. Genuine edible oils are delimited by ellipses of confidence at $\alpha = 0.90$.

appear blow the line of $y = 0.7$; most of them locate at the left side of the distribution chart. On the other hand, soybean oil, sunflower seed oil, rapeseed oil, and corn oil sample data dots all appear above the line of $y = 0.7$ and locate at the right side of the distribution chart. The olive pomace oil data dot appears near the line of $y = 0.7$, but it is above the line. Apparently, olive pomace oil can be distinguished from olive oil by the different distribution region on the chart. An ellipse of confidence (90%) of genuine olive oils, the centers of which have been calculated from the means of the genuine olive oil coordinates, contains the sample data dot of olive pomace oil. This is because the concentrations of the various unsaturated fatty acids in olive pomace oil and virgin olive oil are almost not different. There are also small differences in trans fatty acid content (the content of oleic acid is ≤0.20% in olive oil, whereas that in olive pomace oil is ≤0.40%; linoleic acid and linolenic acid are ≤0.30% in olive oil, whereas in olive pomace oil they are ≤0.40%), total sterol content, and so on. These results suggest that the more olive oil fraud with edible oils characterized by higher content of unsaturated fatty acids than olive oil, such as soybean oil, sunflower seed oil, rapeseed oil, and corn oil, the easier it is to detect.

Following the above study, the intensity ratios of the Raman spectroscopy vibration band distribution charts of olive oil and its blended versions with other four edible oils in various volume percentages were investigated in detail as follows. First, the genuine olive oil samples and olive pomace oil, as well as fake olive oil, which include the genuine olive soil samples 1 and 6 blended with 5, 10, 20, 30, 40, and 50% (volume percentage) of soybean oil, sunflower seed oil, rapeseed oil, and corn oil, respectively, were used as the tested samples. Then the distribution coordinates for each sample were obtained by the same procedures as described above, and the distribution charts were sketched as in **Figure 3**. From these distribution charts, genuine olive oil sample data dots were below the line of $y = 0.7$, whereas olive pomace oil and all blended oil sample data dots appeared above the line of $y = 0.7$. Moreover, as the volume percentage of blended edible oil increases, the normalized intensity ratio of vibration bands coordinate moves away from the line and toward the top of the right side. While an ellipse of confidence (90%) of genuine olive oils includes the sample of olive oils adulterated with 5% and 10% of soybean oil (**Figure 3a**), sunflower seed oil (**Figure 3b**), and corn oil (**Figure 3d**) except for rapeseed oil (**Figure 3c**), and olive oils adulterated with 20% of four edible

oils are all outside the 90% confidence regions, among them, only that with 20% corn oil is nearer the edge of the ellipse. Therefore, distribution charts can be used to easily distinguish an olive oil sample from those blended with other edible oils and to qualitatively show the amount of other edible oils.

To certify the accuracy of the method described in above sections, principal component analysis (PCA) method, which is a classical method of sample classification and identification (*17*), was used for comparison. In this section, fake samples were prepared by blending soybean oil, sunflower seed oil, rapeseed oil, and corn oil with low volume percentages of 5, 10, and 20%, respectively, into genuine olive oil samples, which were labeled 1, 2, 3, 4, 5, and 6, respectively. These samples along with genuine olive oil and olive pomace oil were measured with the portable Raman spectrometer. Then the distribution charts were obtained according to the procedures described in above section, as shown in **Figure 4a**,**b**. The same measurement results also analyzed using PCA method with MATLABR2007a are shown in **Figure 4c**,**d**. The first principal component (PC1) and the second principal component (PC2) were used as horizontal coordinates and vertical coordinates, respectively. Panels **a** and **b** of **Figure 4** show that olive pomace oil and olive oils adulterated with 5 and 20% of other edible oils are all inside and outside of ellipse confidence regions, respectively, and that olive oils adulterated with 10% of other edible oils are partly inside and partly outside of ellipse confidence regions; the outside samples with 10% oils should be adulterated with rapeseed oil. The method of the intensity ratio of vibration bands can separate the genuine olive oils from the olive oils that were blended with other edible oils by the line of $y = 0.7$. The method of intensity ratio of the Raman spectroscopy vibration bands is much clearer in authenticating olive oil than PCA. Moreover, the method offers a much more intuitive and reliable means to authenticate olive oil, and it is also much easier to operate and does not require one having a chemometric background to carry out the analysis. Therefore, it is well-suited for field authentication of the genuine/fake olive oil.

In conclusion, with a portable Raman spectrometer, Raman spectra of olive oil samples were tested real time and on-site. By distribution charts based on the intensity ratio of the Raman spectroscopy vibration bands, the genuine olive oils can be reliably distinguished from the olive oils containing 5% (volume percentage) or more of other edible oils, such as soybean oil, rapeseed oil, sunflower seed oil, or corn oil. The results obtained through this method are better than that achieved by the traditional PCA method. It appears that this method is confined to the detection of olive oil fraud with edible oils characterized by a higher content of unsaturated fatty acids than olive oil, such as the four edible oils used in this study. However, the method was more intuitive (1), more convenient and more time-saving (2) , more sensitive (3), and easier to use than existing methods (4): (1) Distribution charts of the sample measurement results from such method showed that the line of $y = 0.7$ could separate the genuine olive oils from the olive oils that were blended with other edible oils. (2) The method does not need sample preprocessing and takes only about 2 min to complete each sample measurement. (3) The method of intensity ratio of the vibration bands described here can reliably identify olive oil blended with 5% (volume percentage) or more of other edible oils. (4) The test data are easy to process and do not need complicated statistical analysis and chemometric knowledge. Therefore, this method is well-suited for field authentication of genuine/fake olive oils. We are doing further study to detect olive pomace oil and hazelnut oil, which have fatty acid profiles similar to that of olive oil, and the existence of them as impurities at higher percentage in olive oil.

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