Discrimination of olive oil adulterated with vegetable oils using dielectric spectroscopy

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ABSTRACT

The study focused on application of dielectric spectroscopy to identify the adulteration of olive oil. The dielectric properties of binary mixture of oils were investigated in the frequency range of 101 Hz–1 MHz. A partial least squares (PLS) model was developed and used to verify the concentrations of the adulterant. Furthermore, the principal component analysis (PCA) was used to classify olive oil sample as distinct from other adulterants based on their dielectric spectra. The results showed that the dielectric spectra of binary mixture of olive oil spiked with other oils increased with increasing concentration of soy, corn, canola, sesame, and perilla oils from 0% to 100% (w/w) over the measured frequency range. PLS calibration model showed a good prediction capability for the concentrations of the adulterant. For olive oil adulterated with soy oil, the results showed that the RMS was 0.053, sd(RMS), 0.017 and Q^2 value was 0.967. PCA classification plots for all oil samples showed clear performance in the differentiation for the different concentrations of the adulterant. Each of the oil samples could be easily grouped in different clusters using dielectric spectra. From the results obtained in this research, dielectric spectroscopy could be used to discriminate the olive oil adulterated with the different types of the oils at levels of adulteration below 5%.

1. Introduction

Adulteration of edible oils is generally blended cheaper or lower quality oil to premium oil such as extra-virgin olive oil. It was reported that in Italy seven olive oil plants were closed for allegedly adding sunflower and soybean oil to olive oil and selling it as extra-virgin olive oil in Italy and abroad. Some 25,000 litres of fake olive oil were confiscated that sunflower oil was mixed with chlorophyll and beta-carotene to give it olive oil's characteristic colour.[1] It is estimated that in the European Union 4 million Euros per year are lost because of this adulteration (Tay et al., 2002; Fujida, 2003). It is not only a major economic fraud but can also have major healthy implications for consumers. In 1998, the consumption of fake cooking oil (mustard oil) led to cases of dropsy and more than forty people died and hundreds were admitted to hospitals in India.[2] Therefore, detection of edible oil adulteration is of vital important in food quality, safety control and vegetable oil product trade.

On the other hand, a study of dielectric properties of lipid mixtures is important both from the points of view of dielectric theory and practical applications. The dielectric properties of binary mixture of solid and liquid have been researched and the several formulas are available for calculation of the dielectric constant of binary mixtures of liquids depending on different blending state (Gorur, 2003). Among the edible oil products, the most of them are formulated from blends of one or more oil stocks in order to obtaining optimum functional and nutritional aspects of oil products, so that the properties of binary mixture of oils are very important for evaluation of oil quality in oil processing.

Various physical and chemical procedures have been established and used to the authentication of oils such as UV spectroscopy, mass spectrometry (MS), GC, near-infrared spectroscopy (NIR), and Fourier-transform infrared spectroscopy (FTIR), the most of them are based on the analysis of fatty acid profile and the other minor components. The determination limit is in the range of 1–20% (Wenzl et al., 2002; Ramón and Ramón, 2000; Zabaras and Godon, 2004). Generally, the methods of conventional analysis and some instruments are complex, time-consuming, tedious chemical treatment of the oil samples. Therefore, it is still a major challenge to develop a new method for the authentication of the adulteration of edible oils.

In this study, dielectric spectroscopy was adopted for the quantitative determination of the levels of adulterant in olive oil. As a simple, rapid and non-destructive measuring technique,

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dielectric spectroscopy provides the information about the dielectric response of materials to electromagnetic fields. It is a convenient method for evaluating food quality, especially for detecting moisture content in foods (Toyoda, 2003). This technology has been studied and used extensively in analysis and monitoring quality of various agricultural products and food materials (Nelson, 1991, 2005; Christopher, 1997; Venkatesh and Raghavan, 2004). Dielectric method has also been studied and applied to determine frying oil deterioration. It was reported to be a useful tool in determining heat abuse for frying fats and oils in comparison with conventional analytical techniques (Fritsch et al., 1979; Billek et al., 1978; Inoue et al., 2002; Paul and Mittal, 1996; El-Shaml et al., 1992; Stier, 2004). In the previous studies, dielectric properties of edible oils and fatty acids as a function of frequency, temperature, moisture and composition were investigated (Lizhi et al., 2008), the dielectric constants of the oils showed bigger difference among different types of oils, this result suggested that the discrimination of adulteration of edible oils would be possibly made using dielectric method. Therefore, in this research, the dielectric properties of binary mixture of edible oils were further investigated and the quantitative determination of the levels of adulterant in extra-virgin olive oil was researched using dielectric spectroscopy.

2. Materials and methods

2.1. Samples

The oil samples were prepared by mixing the extra-virgin olive oil with different types of oils (Table 1), i.e., the oleic acid type: safflower and virgin olive oils, the linoleic and low-content linolenic acid type: sesame, canola, soybean and corn oils and the linolenic acid type: perilla oil.

2.2. Methods

Dielectric parameters of oil samples were measured with a precision liquid test fixture (Agilent, 16452A, Agilent Technologies, Hyogo, Japan) and a precision LCR meter (Agilent, 4284A, Agilent Technologies, Hyogo, Japan) that was connected to a personal computer for control and data logging. The dielectric parameters were measured at 21 logarithmically distributed frequencies between 100 Hz and 1 MHz. The measured data were recorded and plotted as a Bode diagram with a Matlab program. Dielectric measurements of oil samples were taken at 25 ± 0.5 °C.

The ε' values of the oil samples were calculated using the following equation by the software

$$\varepsilon' = \alpha \left(\frac{C_p}{C_0} \right) \tag{1}$$

where ε' is the dielectric constant (−); α is the correction coefficient (−) (Agilent Technologies, 2000); C_p is the oil capacitance (pF) and C_0 is air capacitance (pF).

2.3. Statistical analysis

All the measurements were carried out in triplicate and mean values and standard deviations were calculated. The R Project for Statistical Computing (R version 5.2.0) and Matlab (version 7.0) were used to carry out PCA classification, PLS analysis, statistical and linear regression analysis of experimental data. The effects of frequency and concentration on dielectric parameters were determined by paired samples t-test and significance of differences was defined at $p < 0.05$.

3. Results and discussion

3.1. Dielectric properties of binary admixture of edible oils

In the frequency range of 101 Hz–500 kHz, the dielectric spectra of binary mixture of oils indicated a general plateau and the maximum value, which is much like the values measured at static electric field. As dielectric dispersion occurred, the dielectric spectra diminished from 500 kHz to 1 MHz, significantly ($p < 0.05$) (Fig. 1).

The dielectric spectra of binary mixture of the oils increased with increasing concentration of adulterant over the measured frequency range, significantly ($p < 0.05$). For example, as shown in Fig. 1, the dielectric spectra of olive oil spiked with soy oil increased with increasing concentration of soy oil from 0% to 100% (w/w) in the frequency range of 101 Hz to 1 MHz. Fig. 2 presents that the ε' of binary mixture of oils increased linearly with increasing concentration of the spiked oils (canola, corn, sesame and soy oils) in olive oil. For instance, the ε' values of olive oil spiked with soy oil increased from 3.049 to 3.071 with increasing concentration of soy oil from 0% to 100% (w/w). The dielectric spectra of the olive oil spiked with linolenic acid type of oil (perilla oil) also increased linearly with increasing concentration of perilla oil over the measured frequency range (Fig. 3).

Fig. 4 shows the dielectric spectra of binary mixture of same type of the oils (oleic acid type), i.e., olive oil was spiked with safflower oil. The results showed that the dielectric spectra of the olive oil and the olive oil spiked with same type of oil (safflower oil) exhibited a little difference over the measured frequency range. At 1 MHz, the difference between ε' values of the olive oil and the olive oil mixed with 50% safflower oil was around 0.003. It is difficult to discriminate the adulteration of the oil mixed with same type of oils directly by dielectric constants. It needs to be further investigated using PCA and PLS analysis.

The relationship between ε' of binary mixture of oils and concentration of spiked oils can be described by a first-order polynomial equation. Although several formulas are available for calculation of the ε' of binary mixtures of liquids according to different blending states, the binary mixtures of edible oils can be assumed as the parallel or homogeneous dielectrics, accordingly, the ε' of binary mixtures of oils can be calculated simply from the following equation:

$$\varepsilon'_m = (\varepsilon'_1 - \varepsilon'_2)\text{wt.\%} + \varepsilon'_2 \tag{2}$$

where ε'_m is the ε' of the oil mixture; ε'_m and ε'_1 are the dielectric constants of the individual oil components, and the weight fraction of blended oil is denoted by wt.%.

3.2. Discrimination of adulteration of olive oil

Discrimination of olive oil adulterated with soy oil (linoleic and low-content linolenic acid type) and perilla oil (linolenic acid type)

Table 1
Tested adulterated oil samples.

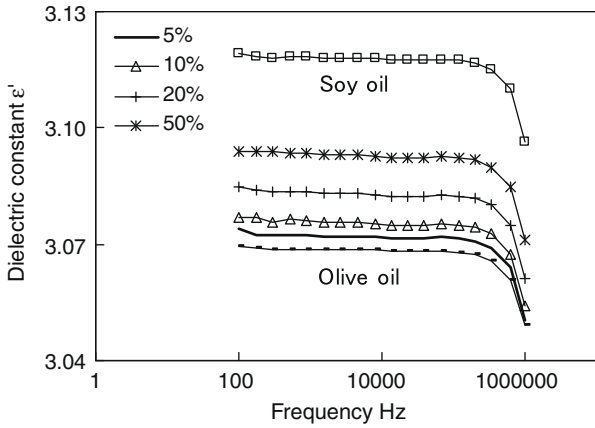| Adulterated oils	Original oil	Spiked oil	Ratio % (w/w)
Test oil group 1 (Oleic type + linoleic type)	Olive oil	Soy, corn, canola, sesame oils	5–50
Test oil group 2 (Oleic type + linolenic type)	Olive oil	Perilla oil	2–50
Test oil group 3 (Oleic type + oleic type)	Olive oil	Safflower oil	50

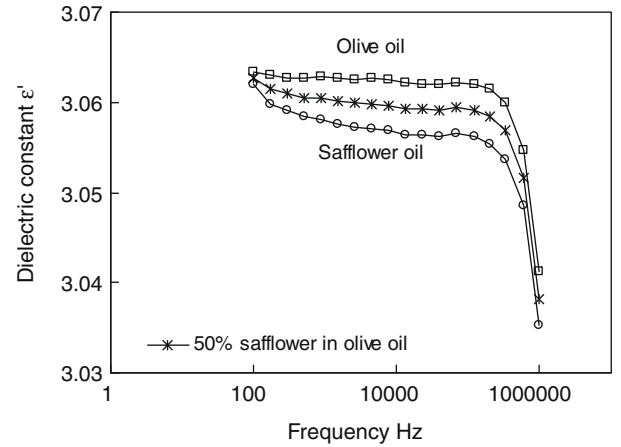Fig. 1. Dielectric spectra of olive oil spiked with soy oil at 25 °C.

Fig. 4. Spectra of dielectric constants of olive oil spiked with safflower oil at 25 °C.

was carried out using PCA classification and PLS calibration models.

3.2.1. PCA classification model

PCA is an exploratory multivariate technique and involves a mathematical operation that determines the transformation of a set of predictable variables (possibly correlated) into a (smaller) set of new uncorrelated variables called principal components. The unique feature of these principal components is that the first

accounts for the most variability in the data, the second component accounts for the most of the remaining variability in the data, and each succeeding component takes accounts for less variability in the data. The method can be used for classification as well as for description and interpretation. Fig. 5 shows the PCA score plot (first [Comp.1] versus second [Comp.2] principal component) related to 18 samples based on dielectric spectra in the frequency range of 174 Hz–1 MHz, i.e., 17 variables, 18 observations, and 306 data sets. PCA classification results for olive oil adulterated with soy oil, the importance of components (Comp.1): Standard deviation was 4.116, Proportion of Variance, 0.996 and Cumulative Proportion, 0.996.

The observation of PCA score plots (between PC scores 1 and 2) for all oil samples showed clearer and better performance in the differentiation and identification for the different concentrations of adulterant from 0% to 100% (w/w). Each of the oil samples could be easily grouped in different clusters using dielectric spectra. Fig. 6 presents the PCA score plot of the olive oil adulterated with
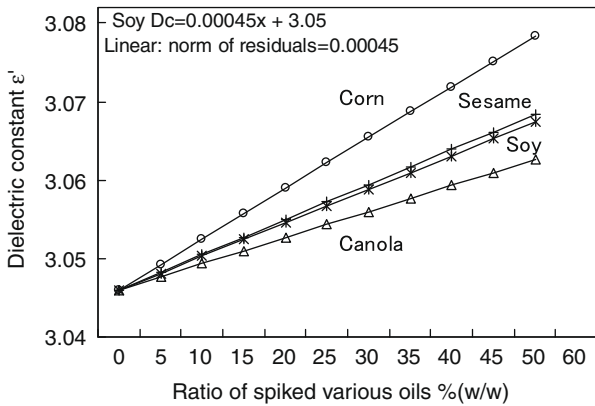

Fig. 2. Correlation between ε' of binary mixture of oils and concentration of spiked oils at 25 °C and 1 MHz.
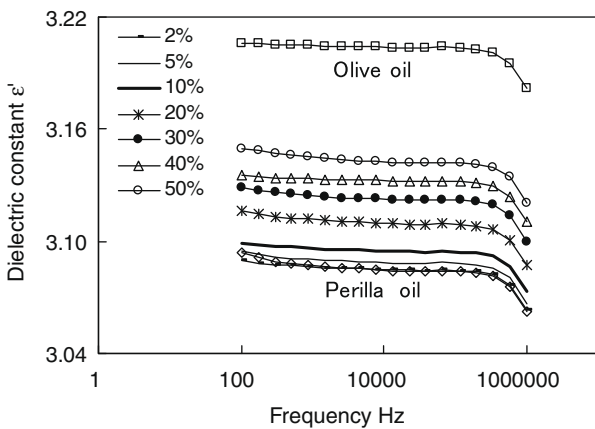

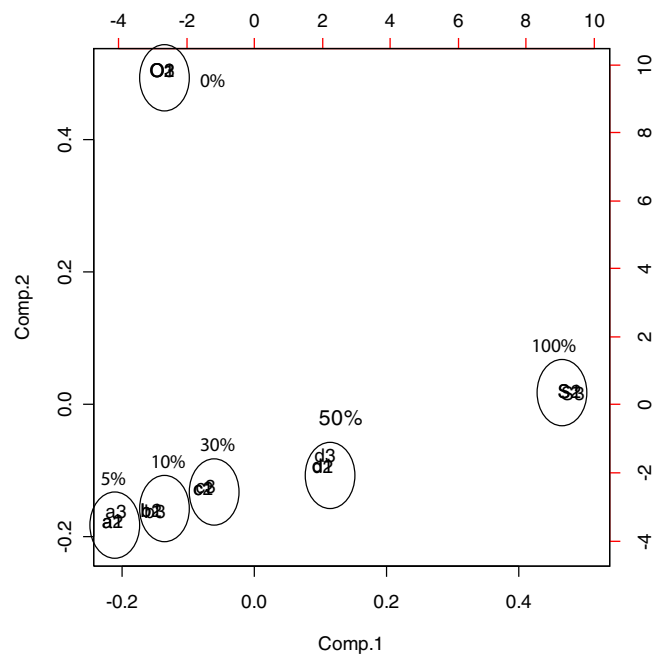Fig. 3. Dielectric spectra of olive oil spiked with perilla oil at 25 °C.

Fig. 5. PCA score plot for different concentration of soy oil in olive oil (between Comp. score 1 and 2).

linolenic acid type of oil (perilla oil). The similar results were obtained from the PCA classification model (17 variables and 30 observations), the importance of components (Comp.1): Standard
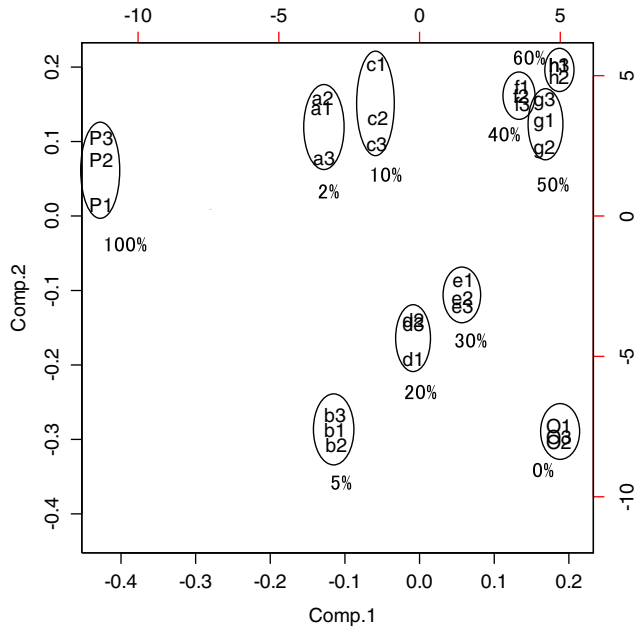
deviation was 4.122, Proportion of Variance, 0.999, and Cumulative Proportion, 0.999.

These results showed that the differences in the dielectric spectra of the genuine olive and adulterated olive oils were magnified and discriminated each other by chemometrics (PCA covariance technique).

3.2.2. PLS calibration model

The results from the discriminate analysis were further confirmed and assessed using PLS algorithm. In this analysis, 11 samples and 198 data sets measured were used, i.e., independent variables, X, were dielectric constants of oil samples measured over the measured frequencies (18 frequencies between 101 Hz and 1 MHz, X dimension: 11:18), while the dependent variables, Y, were concentration of soy oil in olive oil (11 samples with different concentration variables from 0% to 100%, Y dimension: 11:1). The prediction capability of the regression model was assessed by cross-validation, i.e., the root mean square (RMS), standard error of root mean square sd(RMS) and Q^2 value. The cross-validation was done by removing one standard at a time. Q^2 value is determined by the following equations:

$$\text{PRESS} = \sum_{i-1}^{n}(y_i - \hat{y}_i)^2 \tag{3}$$

$$Q^2 = 1 - \frac{\text{PRESS}}{\sum_{i-1}^{n}(y_i - \bar{y})^2} \tag{4}$$

Fig. 6. PCA score plot for different concentration of perilla oil in olive oil (between Comp. score 1 and 2).
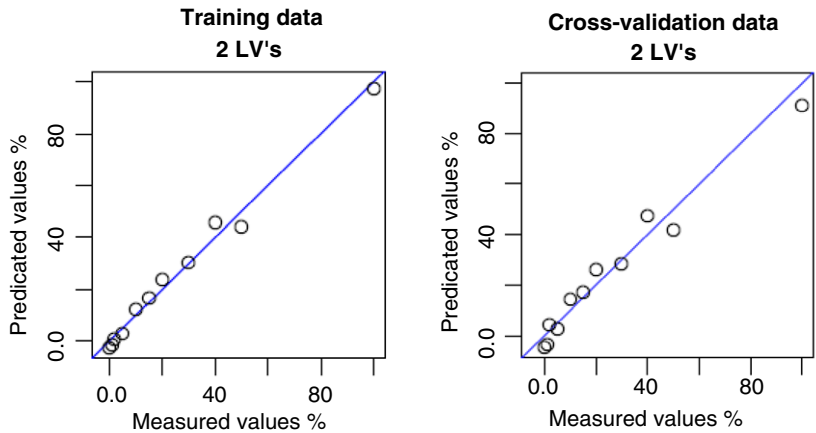

Fig. 7. Predicted values for adulteration obtained from PLS calibration model versus actual concentration of soy oil.
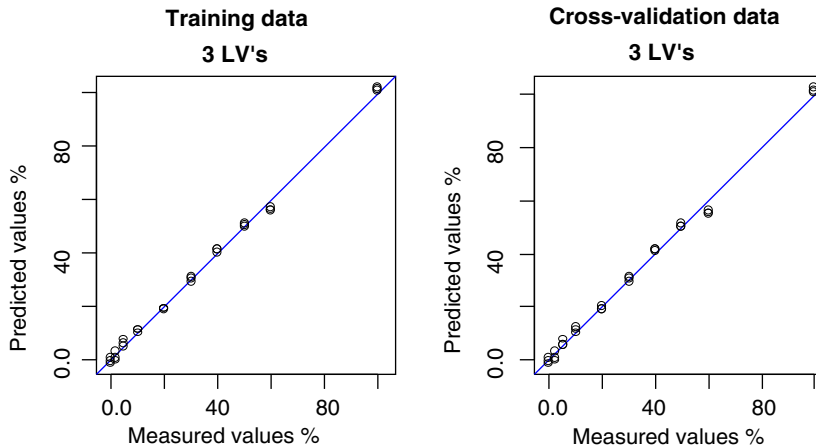

Fig. 8. Predicted values for adulteration obtained from PLS calibration model versus actual concentration of perilla oil.

where PRESS is the Predicted Residual Sum of Square; $\hat{y}$ is the fitted value; y is the response value and $\bar{y}$ is the mean value.

In this analysis, PLS algorithm was practiced in the number of latent variables considered from 1 to 8, the best model was developed from training and cross-validation analysis, yielding the lowest root mean square (RMS) and standard error of root mean square sd(RMS) of prediction, and the maximum values of percent variance explained after 2 numbers of latent variables. A plot of predicted versus actual concentrations for the training and cross-validation sets using this number of latent variables is given in Fig. 7. A summary of the results obtained from the calibration model indicated that the RMS was 0.053, sd(RMS), 0.017, and Q^2, 0.967. The values of percent variance explained obtained from training data for X, 99.99, Y, 98.72. The PLS model showed reliable prediction of the percentage of adulterant in olive oil.

In this research, the olive oil adulterated with linolenic acid type of oil (perilla oil) was also investigated using PLS multivariate analysis (X dimension: 30:18; Y dimension: 30:1; number of latent variables considered: 1–8). Fig. 8 shows the predication results of the percentage of perilla oil in olive oil by PLS calibration model. The results showed that the RMS was 0.019, sd(RMS), 0.0035, and Q^2, 0.996. The values of percent variance explained obtained from training data for X, 100.00, Y, 99.71. It showed the similar prediction results with that of olive oil adulterated with linoleic and low-content linolenic acid type of oil (soy oil).

From the results obtained in this research, dielectric spectroscopy is helpful in the discrimination the adulteration of olive oil adulterated with different types of oils. The detection limit could be at levels of adulteration below 5%.

4. Conclusions

The dielectric spectra of binary mixture of edible oils increased linearly with increasing concentration of spiked oils over the measured frequency range, significantly, ($P < 0.05$). PCA classification plots for all oil samples showed clear performance in the differentiation and identification for the different concentrations of adulterated oil. Each of the oil samples could be easily grouped in different clusters using dielectric spectra. PLS calibration models showed a good prediction capability for different concentrations of the adulterant in olive oil. The identification of olive oil adulterated with same type of oils needs to be further investigated using PCA and PLS analysis.

Dielectric spectroscopy could be helpful in the quantitative determination of the levels of adulterant in olive oil. It could also be used to control the quality of oil blend in oil processing.

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