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Chemometric classification and quantification of olive oil in blends with any edible vegetable oils using FTIR-ATR and Raman spectroscopy

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1 **CHEMOMETRIC CLASSIFICATION AND QUANTIFICATION OF OLIVE OIL**
2 **IN BLENDS WITH ANY EDIBLE VEGETABLE OILS USING FTIR-ATR AND**
3 **RAMAN SPECTROSCOPY**

4

5 Ana M. JIMÉNEZ-CARVELO¹ ✉, María Teresa OSORIO², Anastasios KOIDIS²,

6 Antonio¹ GONZÁLEZ-CASADO, Luis CUADROS-RODRÍGUEZ¹

7 ¹ Department of Analytical Chemistry, University of Granada, c/ Fuentenueva, s.n. E-
8 18071 Granada, Spain.

9 ² Institute for Global Food Security, Queen's University, 18-30 Malone Road, Belfast
10 BT9 5BN, Northern Ireland, UK

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15 spectroscopic techniques

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19 ✉ Corresponding author: phone: +34 958240797; fax: +34 958243328; email:
20 amariajc@ugr.es

21

22

23 **Abstract**

24 Samples of olive oils (n=67) from different qualities and samples of other vegetable
25 edible oils (including soybean, sunflower, rapeseed, corn oil etc; n=79) were used in
26 this study as pure oils. Previous to spectroscopy analysis, a transesterification step
27 was applied to the pure vegetable oil samples and all the different oil blends were then
28 prepared to create in-house blended samples. Spectral acquisition was performed with
29 typical parameters to collect the FTIR and Raman fingerprints. For the olive/non-olive
30 classification model, three classification strategies have been applied: (i) one input-
31 class (1iC) classification; (ii) two input-class (2iC) classification; and (iii) one input-class
32 plus one 'dummy' class classification (or *pseudo* two input-class (*p2iC*) classification).
33 The multivariate classification methods used were k-nearest neighbours (kNN), partial
34 least squared-discriminant analysis (PLS-DA), one-class partial least squares
35 (OCPLS), support vector machine classification (SVM-C), and soft independent
36 modelling of class analogies (SIMCA). The multivariate quantification method used was
37 partial least square-regression (PLS-R). FTIR fingerprints showed excellent
38 classification ability to distinguish pure olive from non-olive oil. When PLS-DA or SVM-
39 C techniques are applied, 100% of olive oil samples and 92% of other vegetable edible
40 oils are correctly classified. In general FTIR fingerprints were more discriminative than
41 Raman's in both classification and regression scenarios.

42

43 1. INTRODUCTION

44 As a natural product that is produced using 'only mechanical means' from olive drupes,
45 olive oil is protected by various regulations and institutions such as the EU Regulations
46 (Regulation UE, 2016; Regulation UE, 2011; Commission Regulation EEC, 2016) and
47 Codex Alimentarius (Codex Stan, 2015). Due to its increasing popularity, it has always
48 been the target for fraudulent practises such as substitution fraud with cheaper oils
49 (blends). To prevent that, authenticity of olive oil is described adequately in the
50 legislation. The top two qualities of olive oil that exist are the extra-virgin and the virgin
51 olive oil and both of them must comply to certain well defined physical, chemical and
52 sensorial parameters. There are several standard methods that are used to determine
53 these parameters. For example, with the use of chromatographic techniques detection
54 of several major and minor constituents of olive oil (fatty acids, tocopherols,
55 carotenoids etc.) is achieved. Nowadays rapid and novel methods are continuously
56 developed (such as those based on spectroscopy), as alternatives to the standard
57 methods offering speed, efficiency (less resources required) and accuracy in
58 authenticity testing.

59 Actually, studies about authentication of olive oil using spectroscopic techniques are
60 based on the application of chemometric tools to develop multivariate models that are
61 able to differentiate pure olive oils from adulterated olive oil with other vegetable edible
62 oil. Then, the proportion of olive oil in these blends is quantified; therefore, although
63 blends of olive oil with other vegetable oils are allowed by the legislation, there is a
64 restriction of labelling them as "olive oils" if the olive oil in the blend does not exceed
65 50% (Regulation UE, 2016). Consequently, a proper method of control must be
66 established. Sun, Lin, Li, Shen and Luo (2015) reported: (i) a principal component
67 analysis (PCA) model to discriminate extra virgin olive oil from binary blends of olive oil
68 with camellia oil, soybean oil, sunflower oil and corn oil; and (ii) a quantification model
69 using partial least squares (PLS) to quantify the olive oil in binary blends. López-Díez

70 and Goodacre (2003) described a PCA model to differentiate pure extra virgin olive oil
71 from adulterated olive oil with hazelnut oil, and a PLS model to quantify the amount of
72 olive oil in the mixtures. Similar studies to the above mentioned ones are shown in
73 Table 1. This table shows five papers using FTIR to detect adulteration of olive oil with
74 other vegetable oil in blends binary, only Gurdeniz and Ozen (2009) develop a model
75 to quantify olive oil in ternary blends. For Raman spectroscopy five works are reported,
76 as in FTIR all the authors detect and quantify olive oil in blends binary, except Rohman
77 and Che Man (2012) which quantifies olive oil in quaternary blends.

78

Table 1

79

80 The main disadvantage of the reported models to authenticate olive oil using
81 spectroscopic techniques, such as FTIR and Raman, is the low number of different
82 botanical species used to build the blends of olive oil with other edible vegetable oils.
83 Most authors employ a small set of oils to elaborate the blends, and sometimes using a
84 single olive oil or a limited number of vegetable edible oil (non-olive oil) in the different
85 mixtures prepared. For example, Tay, Singh, Krishnan and Gore (2002) reported a
86 method to authenticate olive oil using only thirty two olive oil and seven vegetable
87 edible oils (non-olive oil) to build the different blends (Tay et al.,2002). Thus, the
88 resulting models cannot be considered as global methods to detect adulteration of olive
89 oil (independently of the cultivars) with any edible vegetable oil. Moreover, some
90 authors erroneously apply PCA as discriminant analysis technique to develop and
91 validate classification models of olive oil (Sun et al.,2015). PCA is an unsupervised
92 data analysis technique used to explore the variability in the dataset and to evaluate if
93 there are different groups of samples when the dimensionality of the data decreases.
94 This exercise should not be used for classification purposes. In the literature there is
95 only one published study where it is developed a classification model to distinguish

96 pure olive oil from other pure vegetable oil using FTIR or Raman spectroscopy. De la
97 Mata et al. (2012) reported a partial least squares discriminant analysis (PLS-DA)
98 aiming to distinguishing between olive oil and binary mixture of non-olive samples
99 applying ATR-FTIR.

100 The aims of this study are: (i) discrimination of pure olive oil/non-pure olive oil, (ii)
101 detection of adulterated olive oil and (iii) quantification of olive oil in blends (from binary
102 to heptenary mixtures) with other vegetable edible oils using a number of chemometric
103 techniques. For this purpose, we have developed a global and comprehensive
104 analytical method to differentiate, detect and quantify olive oil in blends with any edible
105 oils. The number of oils used in this work is wide, and spread worldwide. Although, in
106 the "real world" the usual blends of olive oil with other seed oil are binary, a quality
107 control laboratory does not know which was and/or how many were the seed oils used
108 in adulteration, if any. For this reason, the proposed method aims at covering binary
109 and higher-order blends which could be found.

110

111 **2. MATERIALS AND METHODS**

112

113 **2.1. Chemicals**

114 Isopropanol, *n*-hexane, methanol and tert-butyl methyl ether (TBME) were purchased
115 from VWR International Eurolab, S.L. (Barcelona, Spain) and all of them were of HPLC
116 grade. Other reagents, such as sodium methoxide, citric acid monohydrate, and
117 anhydrous sodium sulphate were purchased from Merck (Darmstadt, Germany). The
118 nitrogen (99.9999 %) used was provided by Air Liquid (Madrid, Spain).

119

120 **2.2. Instrumentation**

121 FT-IR spectra were obtained on a NICOLET iS5 spectrometer (Thermo Scientific,
122 Waltham, Massachusetts, USA) equipped with a DTGS detector and KBr beam splitter.
123 Spectra were obtained in the range of 4000 cm^{-1} to 550 cm^{-1} with a resolution of 2 cm^{-1}
124 using a monolithic diamond attenuated total reflectance (ATR iD7) accessory. All the
125 spectra were recorded at room temperature with 32 scans.

126 Raman measurements were carried out using IDRAMAN Reader (Ocean Optics,
127 Oxford, UK) with 785 nm emission of a laser (23.4 mW at sample) for excitation. The
128 laser was focused on the sample contained in 2 mL vial. For signal detection, a 2048-
129 element NIR-enhanced CCD array with thermoelectric cooling to 10 °C was employed.
130 An averaged spectrum for each sample was recorded in the range of 200 to 3200 cm^{-1} ,
131 using an integration time of 10 s each 3 scans.

132 NIR spectra were obtained using Antaris II (Thermo Electron Corporation, Waltham,
133 Massachusetts, USA) FT-NIR analyzer, equipped with a diffuse reflection fibre optic
134 and InGaAs detector. All the spectra, in the range of 4000 to 10000 cm^{-1} , were
135 recorded at room temperature with 32 scans.

136 In all cases, each sample was analysed in triplicate.

137

138 **2.3. Samples**

139 *Pure vegetable edible oils used to the classification models*

140 67 samples of olive oils and 79 samples of other vegetable edible oils were used in this
141 study. The samples of olive oils were constituted by 52 extra virgin olive oils (EVOO)
142 samples, including 41 samples from 10 different monovarietals ("Arbequina",
143 "Hojiblanca", "Picual", "Royal", "Manzanilla", "Cornicabra", "Empeltre", "Frantoio",
144 "Verdial" and "Blanqueta") and 26 samples of varietal mixtures, 4 virgin olive oil
145 samples (VOO), 5 olive oils, blend of virgin and refined (OO) and 6 pomace olive oil
146 samples (POO). Vegetable edible oil samples (non-olive oils) consisted of 8 hazelnut

147 oils, 5 peanut oils, 10 canola oils, 2 safflower oils, 12 sunflower oils, 2 flax oils, 5 corn
148 oils, 9 palm oils, 8 seeds oils (marketing mixture of unidentified seeds), 4 sesame oils,
149 8 soybean oils, 1 wheat oil and 4 grapeseed oils. In addition, a speciality olive oil
150 extracted from previously dehydrated olive fruits was also added in this group. All
151 samples were collected from marketed edible oils, purchased in food stores and
152 sourced from respective partners from multiple geographical locations.

153

154 *Blends of olive oil with other vegetable edible oils*

155 To build the blends were used 27 olive oil samples, of which 22 EVOO (including 16
156 monovarietal oils), 3 VOO and 2 OO. In addition, 52 edible oils samples of 8 botanical
157 origins, obtained each one from different suppliers, were used: 8 soybean oils, 11
158 sunflower oils, 10 rapeseed (canola) oils, 5 corn oils, 5 seeds oils (commercial blends
159 of unknown seed oils), 5 peanut oils, 4 sesame oils and 4 grapeseed oils. Table 2
160 shows details on the composition of the different blends.

161

Table 2

162

163 All the oil samples were stored at 4 °C until the sample preparation in order to provide
164 realistic testing conditions.

165

166 **2.4. Sample preparation**

167 Previous to the spectrometric analysis, a transesterification reaction was applied to the
168 pure vegetable oil samples and all the different oil blends prepared. This reaction was
169 carried out using 0.1 g/mL sodium methoxide in a methanol/TBME mixture, 4:6
170 (mL:mL), and then the extraction was performed with *n*-hexane. In this alkaline

171 medium, the free fatty acids presents in the oil are not methylated (Li & Watkins, 2001).
172 A modification of the original procedure described by Biedermann *et al.* was applied
173 (Bierdermann *et al.*, 1993). A detailed description of the procedure followed is
174 described elsewhere (Jímenez-Carvelo, Pérez-Castaño, González-Casado & Cuadros-
175 Rodríguez, 2017). The subsequent solution was stored at -25° C until analysis with
176 less than 5% headspace under nitrogen.

177

178 **2.5. Chemometrics**

179 The FTIR and FT-NIR raw data files were exported to MATLAB (Mathworks,
180 Massachusetts, USA, version R2013a). In order to reduce the variability associated to
181 the intensity and derived from baseline, or other sources such as scattering effects,
182 source or detector variations, or other general instrumental sensitivity effects, standard
183 normal variate (SNV) and smoothing applying the Savitzky-Golay algorithm (second
184 order polynomial filter with a 9-point window and first derivative) were used. Different
185 chemometric tools have been applied for classification, including k-nearest neighbours
186 (kNN), partial least squares discriminant analysis (PLS-DA), support vector machine-
187 classification (SVM-C), one-class partial least squares (OCPLS) and soft independent
188 modelling of class analogies (SIMCA). The classification results from each method
189 have been evaluated on the basis of several quality metrics, such as: (i) sensitivity, (ii)
190 specificity, (iii) positive (or precision) and negative predictive values, (iv) efficiency (or
191 accuracy), (v) AUC (area under the receiver operating curve), (vi) Matthews correlation
192 coefficient and (vii) Kappa coefficient. The meaning and way to calculate these metrics
193 was recently reviewed [(Cuadros-Rodríguez, Pérez-Castaño & Ruiz-Samblás, 2016)].

194 Partial least squares regression (PLS-R) has been applied for quantification. Root
195 Mean Square Error of Validation (RMSEV), Mean Absolute Error of Validation (MAEV)
196 and Median Absolute Error of Validation (MdAEV) were used for accuracy assessment
197 of the quantification methods.

198

199 *Olive/non-olive classification models*

200 Three classification strategies have been applied: (i) one input-class (1iC)
201 classification; (ii) two input-class (2iC) classification; and (iii) one input-class plus one
202 'dummy' class classification (or *pseudo* two input-class (*p*2iC) classification).

203 The main difference between the strategies pursued is the number of class used to
204 build the classification model. More detailed information can be found at the references
205 Jiménez-Carvelo, Pérez-Castaño, González-Casado and Cuadros-Rodríguez (2017)
206 and Jiménez-Carvelo, González-Casado, Pérez-Castaño and Cuadros-Rodríguez
207 (2017).

208 For each strategy applied (2iC, *p*2iC and 1iC) the original vector data set of pure
209 vegetable oil was divided into different groups to perform the classification model. The
210 selection was carried out using the Kennard-Stone (KS) algorithm [Kennard & Stone,
211 1969]. For 2iC, the training set was made up of 98 samples (44 olive oils and 54 non-
212 olive oils), and the remaining oil samples (23 olive oils and 25 non-olive oils) composed
213 the validation set. For *p*2iC, the training set which was made up of 61 samples (44 olive
214 oils and 17 analytical blanks), and the validation set composed by 102 samples (23
215 olive oils and 79 non-olive oils). For 1iC, the training set was composed by 44 olive oils
216 samples and the validation set by 102 samples (23 olive oils and 79 non-olive oils).

217 Once it was done, the classification models were developed. PLS_Toolbox (version
218 8.02, Eigenvector Research, Wenatchee, WA) for MATLAB environment was applied
219 for reducing of variables and classification methods: principal component analysis
220 (PCA) (Bro, 2014), k-nearest neighbours (kNN) (Steinbach & Tan, 2009), partial least
221 squares-discriminant analysis (PLS-DA) (Ballabio & Consonni, 2013) soft independent
222 modelling of class analogies (SIMCA) (Bylesjö et al., 2006), and support vector
223 machine-classification (SVM-C) (Luts et al., 2010). Moreover, one-class partial least

224 squares classification (OCPLS) (Xu, Yan, Cai & Yu, 2013) was performed applying the
225 three variants of the function: (i) conventional ordinary linear OCPLS, (ii) nonlinear
226 radial basis function (RBF) OCPLS, and (iii) partial robust M-regression (PMR) OCPLS,
227 using the software provided by Xu *et al.*,(2013). All the options offered by the software
228 were tested.

229

230 *Adulterated olive oils detection models*

231 Classification models to detect adulterations of olive oil with other vegetable edible oils
232 were developed in order to apply a screening classification method previous to carry
233 out the quantification. In this case, it was only applied the 2iC strategy. The training set
234 was composed by 56 samples (44 pure olive oils and 12 adulterated olive oils) and
235 validation set was made up of 35 samples (23 pure olive oils and 12 adulterated olive
236 oils). As in the olive/non-olive classification models, PCA was used to reduce the
237 variables, kNN, PLS-DA, SIMCA, SVM-C and OCPLS techniques were applied to
238 developed the different classification models.

239

240 *Olive oil quantification model*

241 The original analytical data were divided in different groups to perform the statistical
242 analysis. The calibration data set was made up of 18 samples whose adulteration
243 levels were from 20 to 80 (g olive oil/100 g blend oil). The validation set for olive oil
244 quantification was composed of 12 samples. The composition of the different samples
245 is shown in Table 2. Partial least squares-regression (PLS-R) was used to build the
246 model of quantitative prediction using standard parameters.

247

248 **3. RESULTS AND DISCUSSION**

249 Figure 1 shows a spectral fingerprint of the transesterified fraction of an EVOO sample
250 with the three different spectroscopic techniques used. The FTIR and Raman
251 fingerprints of EVOO show strong molecular vibrations and good variability between
252 samples, the NIR fingerprints appear non selective. Therefore, classification and
253 quantification models in FT-NIR were not developed due to the low specificity of the
254 spectra of the transesterified fraction from the different vegetable edible oil samples.

255

Figure 1

256

257 **3.1. Selection of variables**

258 In order to reduce the number of variables and visualise the data a PCA model was
259 obtained using FTIR and Raman fingerprints. In both spectroscopic techniques the
260 selection of variable was performed examining the PCA loading plot. For that purpose,
261 the regions of the spectra where the intensity of the loading was high were selected.
262 Although the initial region of the Raman spectrum ($2900\text{-}2800\text{ cm}^{-1}$) shows a high
263 value of the loadings, it was not finally selected since it did not improve the
264 performance of the classification and quantification models.

265 The PCA model from FTIR data was developed with four principal components (PCs)
266 which explain 98.87% of the variance. Figure 2 shows both the plot for FTIR spectrum
267 and PCA loading plot with the three regions selected. The frequencies of the regions 1,
268 2 and 3 were $3100\text{-}2700\text{ cm}^{-1}$, $1800\text{-}1600\text{ cm}^{-1}$ and $1205\text{-}1080\text{ cm}^{-1}$ respectively.

269

Figure 2

270

271 The Raman spectra of all 146 samples were recorded. For the PCA model, four PCs
272 were enough to explain 99.84% of the variance. Only the 950-650 cm^{-1} range, as
273 shown in Figure 3, was chosen for analysis.

274

Figure 3

275

276 **3.2. Olive/non-olive classification models**

277

278 *FTIR*

279 In order to differentiate pure olive oils from other pure vegetable edible oils, different
280 models were tested using the three regions selected; however, the best performance
281 statistics were obtained for the models generated using the region 2.

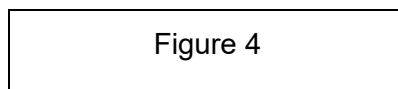
282 The two-input class (2iC) strategy was used to develop the model applying the
283 chemometric methods: kNN, PLS-DA, SVM-C and SIMCA. One-input class (1iC)
284 strategy was applied when OCPLS and SIMCA models were performed and lastly,
285 *pseudo* two-input class (*p*2iC) strategy was only applied to SIMCA model.

286 The target class was "olive oil" and the non-target class was "non-olive". In kNN,
287 PLS-DA and SVM-C the olive class was assigned to samples with a predicted
288 probability value equal to 1 and the non-olive class was defined by samples with a
289 probability of 0. $K=3$ was enough to decide the neighbour distance in the kNN model.
290 Classification of the samples of the validation set was performed directly by the
291 software. There were only five samples misclassified, two olive oils samples and three
292 non-olive oils samples (canola, peanut and hazelnut oils).

293 The PLS-DA model was built using six latent variables (LV), with 75.68% of the
294 variance explained. Only one sample was not well classified corresponding to non-olive

295 oil (canola oil). The efficiency, area under the receiver operating curve (AUC) and
296 Matthews's correlation coefficient were 0.98, 0.98 and 0.96 respectively. Figure 4
297 shows the classification plot obtained from the PLS-DA method.

298



299

300 The SVM-C model was developed optimizing the "C" and "nu" operational parameters.
301 There are two commonly used versions of SVM classification, 'C-SVC' and 'nu-SVC'.
302 "C" represents the penalty associated with errors. "Nu" is an alternative parameter for
303 specifying the penalty associated with errors. It indicates a lower bound on the number
304 of support vectors to use, given as a fraction of total calibration samples, and an upper
305 bound on the fraction of training samples which are errors (misclassified) (SVM
306 Function Settings, Eigenvector Documentation wiki. URL
307 <http://wiki.eigenvector.com/index.php?title=Svmda>. Accessed 13.06.17). The results
308 obtained in all the cases were similar. Moreover, all the models were tested with and
309 without variable reduction using PCA and PLS. This variable reduction is named X-
310 block compression by PLS_Toolbox software. The best results were obtained when an
311 X-block compression with PLS was applied. The samples were directly classified by the
312 software.

313 The 2iC, *p*2iC and 1iC strategies were tested to generate the SIMCA models.
314 Classification of samples was performed using means of the normalised (also called,
315 reduced) statistics values of residual- Q_r and Hotelling- T_r^2 (Marini, 2010). The samples
316 with values lower than 1 for both statistics were classified as olive oil. Firstly, a 2iC
317 SIMCA classification was carried out. PCA model was built with 4 PCs and 5 PCs for
318 olive and non-olive oil classes, respectively. Secondly, a *p*2iC SIMCA model was
319 developed. In this case, 4 PCs and 3 PCs were chosen for olive oil and 'dummy'

320 classes respectively. At last, a 1iC SIMCA was performed with a 4 PCs for olive oil
321 model.

322 An OCPLS class-model was also developed. Conventional OCPLS was built with 4
323 LVs, RBF OCPLS with 5 LVs and PMR OCPLS with 6 LVs. The regions for the
324 samples classification were pre-established by the software.

325 To sum up, the 2iC strategy gave good results for all the discriminant methods. PLS-
326 DA and SVM with reduction of variable using PLS were the best models; yielding the
327 same classification results. The sensibility and specificity of all models were 1.00 and
328 0.96 respectively. In contrast, to SIMCA model lead to better classification results when
329 1iC strategy was used. The results for each model are shown in Table 3.

330

Table 3

331

332 *Raman*

333 In a similar way to FTIR, the 2iC strategy was applied with all the chemometric
334 methods, *p*2iC strategy only with SIMCA and 1iC strategy with SIMCA and OCPLS.
335 The classification criteria were the same as for FTIR with the different chemometric
336 methods.

337 kNN classification model was built with $k=3$. Seven oil samples were misclassified (4
338 olive oils and 3 non-olive oils). The values of the quality performance metrics were
339 similar with those obtained from FTIR models. Four LVs explaining 99.99% of the
340 variance were enough to develop the PLS-DA model. This model was less efficient
341 than PLS-DA model from FTIR.

342 As in the previous case of FT-IR spectra, SVM-C classification models were developed
343 and tested with and without X-Block compression (reduction of variables). The results
344 of all the models were the same excepting the (nu)-SVM-C model with reducing the

345 variable by PLS. In this model all the samples were classified in both classes (olive and
346 non-olive oil classes) and the values of the quality performance metrics were not
347 satisfactory.

348 The SIMCA classification model was built with 3 PCs and 4 PCs for olive and non-olive
349 oil classes applying the 2iC strategy. On the contrary to FTIR model, this SIMCA model
350 classified better the samples of the validation set. 3 PCs for each class were enough to
351 develop the *p*2iC SIMCA model. This model classified all the oil samples in the class of
352 non-olive oils. At last, the 1iC SIMCA model was built with 4 PCs for olive oil model.

353 OCPLS classification models were developed. In this case partial robust M-regression
354 (PMR) OCPLS was the best model.

355 As in the case of FT-IR, the discriminant analysis methods gave good classification
356 results; PLS-DA model was the best model. In contrast with the results for FTIR,
357 SIMCA provided better results when the 2iC strategy was applied. Table 4 shows the
358 results for each model.

359

Table 4

360

361 **3.3. Adulterated olive oils detection models**

362 Discriminant analysis and class-modelling methods were used for the discrimination of
363 pure EVOO and EVOO adulterated with several vegetable edible oils. The
364 chemometric techniques used and the criteria for classification were the same that to
365 olive/non-olive classification models. Table 5 and 6 show the classification results of
366 the different models tested from FTIR and Raman techniques. From FTIR, the best
367 results were obtained when PLS-DA was applied. On the contrary, from Raman, the
368 best models were obtained when SVM-C (optimizing with 'nu' operational parameter)

369 without and with X-Block compression by PLS was used. Only four EVOO adulterated
370 samples were misclassified.

371

Table 5

372

Table 6

373

374 **3.4. Olive oil quantification model**

375 Quantitative analysis of blends of olive oil with other vegetable edible oils was
376 performed building a specific PLS-R model from FTIR and Raman fingerprints on the
377 regions previously selected (see section 3.1). In order to achieve more realistic
378 conditions of the composition of olive oil, the proportion of olive oil in the blends of the
379 training and validation set is different, in contrast to some research work about
380 quantification of olive oil using spectroscopic techniques in which the composition is
381 similar in both set.

382 The reliability of the different models was established on the basis of: (i) the
383 determination coefficient (R^2) and (ii) the errors of quantification (validation errors) were
384 evaluated with the Root Mean Square Error of Validation (RMSEV), Mean Absolute
385 Error of Validation (MAEV) and Median Absolute Error of Validation (MdAEV)
386 (Hyndman & Koehler, 2006; ASTM E1655-05, 2012). The results obtained (g
387 EVOO/100 g blend) in terms of R^2 , RMSEV, MAEV and MdAEV were 0.86, 17.6, 14.6
388 and 16.0 respectively from FTIR and 0.93, 34.2, 27.8 and 29.6 respectively from
389 Raman. Figure 5 shows the concentration values obtained from the PLS model vs. the
390 actual concentration of any vegetable edible oil in olive oil samples using FTIR-ATR.

391

Figure 5

392

393 Although the R^2 obtained from FTIR is not sufficiently good, the validation errors
394 (about 15-17%) are better than the validation errors obtained from Raman (about 28-
395 34%).

396

397 **4. CONCLUSION**

398 Methyl-transesterified provides the information needed to authenticate of olive oil. The
399 method developed could be named “global method” of detection, discrimination and
400 quantification of olive oil in blends with other vegetable edible oils. Moreover, due to a
401 transesterification step prior to spectroscopic analysis the problem of the low selectivity
402 of these techniques has been resolved. Using FTIR and applying PLS-DA is
403 performed without the need of any resource intensive chromatographic analysis.
404 Discriminant analysis classified well the 100% olive oils samples and in addition, the
405 proportion of olive oil in blends with other vegetable edible oils has been successively
406 quantified using PLS-R.

407

ABBREVIATIONS AND ACRONYMS

408

1iC, one input-class classification

2iC, two input-class classification

ATR, attenuated total reflectance

AUC, area under the receiver operating curve

Bay-LS-SVM, Bayesian-least squares-support vector machine

BOM, bean with omega

CAM, camellia oil

CAN, canola oil

COG, corn germ oil

COR, corn oil

COT, cottonseed oil

EVOO, extra virgin olive oil

FLA, flaxseed oil

FT-IR, Fourier transform-infrared spectroscopy

FT-NIR, Fourier transform-near infrared spectroscopy

GAR, garlic oil

GSO, Grapeseed oil

HAZ, hazelnut oil

kNN, k-nearest neighbors

KS, Kennard-Stone

LDA, linear discriminant analysis

LS-SVM, least squares-support vector machine

LV, latent variables

MAE, Mean absolute error

MAEV, mean absolute error of validation

MdAEV, median absolute error of validation

MDVO, mixture of different vegetable edible oils (non-olive oil)

MLR, multiple linear regression

OCPLS, one class partial least squares classification

OO, olive oil

$p2iC$, *pseudo* two input-class classification

PC, principal component

PCA, principal component analysis

PCR, principal component regression

PLS-DA, partial least squares-discriminant analysis

PLS-R, partial least squares regression

PLS-R, partial least squares regression

PMR, partial robust M-regression

POO, pomace olive oil

R^2 , determination coefficient

RBF, radial basis function

RBO, rice bran oil

RMSE, Root mean square error

RMSEV, root mean square error of validation

RPS, rapeseed oil

SAF, safflower oil

SES, sesame oil

SIMCA, soft independent modelling of class analogy

SNV, standard normal variate

SOY, soybean oil

SUN, sunflower oil

SVM-C, support vector machine classification

TBME, tert-butyl methyl ether

VOO, virgin olive oil

WGE, wheat germ oil

WO, walnut oil

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Table 1. Chemometric methods using FTIR or Raman for the authentication of olive oil found in the literature

Nº	Analytical technique	Amount and types of edible oils	Blends	Aims	Chemo-metrics	Results (Quality Features)	Ref.
1	FTIR (4000-650 cm ⁻¹)	EVOO ^t (40), CAM ^a (5), SOY ^b (5), SUN ^c (5) and COR ^d (5) oils	EVOO-CAM, EVOO- SOY, EVOO-SUN, EVOO-COR	Classification model of EVOO and binary blends of EVOO with edible oil Quantification of EVOO in binary blends	PCA and PLS	R ² : 0.98 - 0.99 RMSE: 1.9 % (EVOO-SUN); 9.5% (EVOO-CA); 1.72 % (EVOO-SOY); 2.2% (EVOO-COR)	{{Sun,Lin, Li, Shen & Luo, 2015}}
2	FTIR (1200-900 and 2949-2885 cm ⁻¹)	EVOO (1), GSO ^e (1), RBO ^f (1), WO ^g (1) oils	GSO-WO, EVOO-RBO, EVOO-RBO-GSO-WO	Quantification of EVOO in quaternary mixture	PLS	R ² : 0.99 ; RMSE : 3.7%	{{Rohman & Che Man, 2011}}
3	FTIR (1207-1018, 1517-1222 and 3050-2927 cm ⁻¹) GC	EVOO, CAN ^h , COR, GSO, SOY, SES ⁱ , SUN and WO oils	EVOO-SES	Classification model of EVOO and other pure edible oil based on their fatty acids profiles. Quantification of EVOO in blends of EVOO-SES	PLS and PCR	R ² : 1.00 ; RMSE : 7.0% (PLS) R ² : 0.997; RMSE: 1.1% (PCR)	{{Rohman & Che Man, 2012}}
4	FTIR (4000-1000 cm ⁻¹)	EVOO (6), HAZ ^j (6), SUN (6), COR (3), COG ^k (2) and SOY (6) oils	EVOO-HAZ, EVOO-SUN, EVOO-CORN, EVOO-SOY	Classification of vegetable oils using LDA Determination of EVOO adulteration	LDA and MLR	R ² : 0.91; MAE: 2.0 (EVOO-HAZ) R ² : 0.99; MAE: 1.7 (EVOO-SUN) R ² : 0.99; MAE: 1.5 (EVOO-CORN) R ² : 0.98; MAE: 1.9 (EVOO-SOY)	{{Lerma-García, Ramis-Ramos, Herrero-Martínez & Simó-Alfonso, 2010}}

5	FTIR (3080-2800 cm ⁻¹)	EVOO (25), COR, SUN, RPS and COT ^s oils	EVOO-SUN-COR, EVOO-COT, EVOO-RPS	Classification model of EVOO and adulterated EVOO Quantification of EVOO in the mixtures	SIMCA and PLS	R ² : 0.99; RMSE: 10.4% (EVOO-SUN-COR) R ² : 0.95; RMSE: 14.0% (EVOO-COT) R ² : 0.93; RMSE: 13.2% (EVOO-RPS)	{{Gurdeniz & Ozen, 2009}}
6	Raman (1000-3000 cm ⁻¹)	EVOO (31) and HAZ (10) oils	EVOO-HAZ	Quantification of EVOO in blends with hazelnut oil	PCA and PLS	R ² = 0.98 RMSE 10.94%	{{López-Diez , Bianchi & Goodacre, 2003}}
7	Raman (800-1800 and 2850-3020 cm ⁻¹)	EVOO (18), RPS ^l , SES, GAR ^m , BOM ⁿ , SUN (3), WO, SAF ^o (2), SOY, WGE ^p , and FLA ^r oils	EVOO-SUN#1, EVOO-SUN#2, EVOO-SUN#3	Discrimination model of EVOO and adulterated EVOO. Estimation of the SUN oil content in EVOO	PCA and PLS	R ² : 0.99; RMSE(cross-valid): 9.81% R ² : 0.99; RMSE(cross-valid): 9.88% R ² : 0.98; RMSE (cross-valid): 9.71%	{{El-Abassy, Donfack & Materny, 2009}}
8	Raman (1000-1800 cm ⁻¹)	EVOO (6), POO ^u (1), SOY (3), SUN (3), RPS (2) and COR (2) oils	EVOO-SOY, EVOO-SUN, EVOO-RPS, EVOO-COR	Model to detect adulterated EVOO	PCA	Intensity ratio	{{Zhou et al., 2009}}
9	Raman (800-1800 cm ⁻¹)	EVOO (5), SOY (3), corn (3) and SUN (3) oils	EVOO-SUN, EVOO-SOY, EVOO-COR	Quantification of EVOO in binary blends	Bay-LS-SVM, LS-SVM and PLS	R ² : 0.99; RMSE: 5.1% (Bay-LS-SVM) R ² : 0.99; RMSE: 6.9% (LS-SVM) R ² : 0.99; RMSE: 8.4% (PLS)	{{Dong, Zhang, Zhang & Wang, 2012}}
10	Raman (1000-1800 cm ⁻¹)	EVOO and SOY oil	EVOO-SOY	Quantification of SOY adulteration in EVOO	PLS	R ² = 0.99; RMSE: 1.3%	{{Tiryaki & Ayvaz, 2016}}

414 ^a Camellia; ^b Soybean; ^c Sunflower; ^d Corn; ^e Grapeseed; ^f Rice bran; ^g Walnut; ^h Canola; ^l Sesame; ^j Hazelnut; ^k Corn germ; ^l Rape seed; ^m Garlic; ⁿ Bean with Omega 3; ^o Safflower; ^p Wheat germ; ^r
415 flaxseed; ^scottonseed, ^tExtra virgin olive oil, ^u Pomace olive oil

416 RMSE: Root mean square error; MAE: Mean absolute error

Table 2. Percentage and composition of the olive oil and other vegetable edible oil in the oil blend samples.

N°	Composition	
<i>(a) Calibration set</i>		
1	100% MDVO ^a	20% seed#1 oil, 20% peanut#1 oil, 20% sunflower#1 oil, 20% canola#1 oil and 20% corn#1 oil
2	100% MDVO	20% soybean#1 oil, 20% soybean#2 oil, 20% sunflower#2 oil, 20% canola#2 oil and 20% grapeseed#1 oil
3	100% MDVO	20% seed#2 oil, 20% sesame#1 oil, 20% peanut#2 oil, 20% corn#2 oil and 20% grapeseed#2 oil
4	20% EVOO ^b + 80% MDVO	10% EVOO#1, 5% EVOO#2, 5% EVOO#3, 13% soybean#3 oil, 13% canola#3 oil, 13% corn#1 oil, 13% seed#3 oil, 13% grapeseed#3 oil and 13% peanut#2 oil
5	15% EVOO + 5% OO ^c + 80% MDVO	5% OO#4, 5% EVOO#5, 5% EVOO#6, 5% EVOO#7, 8% sunflower#3 oil, 8% sunflower#4 oil, 8% canola#1 oil, 8% canola#4 oil, 16% corn#3 oil, 16% sesame#2 oil and 16% peanut#3 oil
6	15% EVOO + 5%VOO ^d + 80% MDVO	5% EVOO#8, 5% EVOO#9, 5% EVOO#11, 5% VOO#10, 13% sunflower#5 oil, 13% sunflower#2, 26% corn#2 oil and 26% grapeseed#2 oil
7	30% EVOO + 10% OO + 60% MDVO	10% OO#12, 10% EVOO#5, 10% EVOO#7, 10% EVOO#14, 15% soybean#4 oil, 15% canola#5 oil, 15% seed#3 oil and 15% peanut#4 oil
8	30% EVOO + 10% OO + 60% MDVO	10% EVOO#6, 10% EVOO#13, 10% EVOO#8, 10% OO#4, 15% sunflower#6 oil, 15% canola#5 oil, 15% corn#4 oil and 15% grapeseed#2 oil
9	30% EVOO + 10% VOO + 60% MDVO	10% EVOO#1, 10% EVOO#3, 10% EVOO#2, 10% VOO#15, 15% sunflower#7 oil, 15% corn#1 oil, 15% sesame#1 oil and 15% peanut#4 oil
10	60% EVOO + 40% MDVO	15% EVOO#6, 15% EVOO#7, 15% EVOO#13, 15% EVOO#14, 5% soybean#1 oil, 5% soybean#5 oil, 10% canola#6 oil, 10% sesame#3 oil and 10% grapeseed#4 oil
11	36% EVOO + 12% OO + 12% VOO + 40% MDVO	12% EVOO#6, 12% EVOO#2, 12% EVOO#5, 12% OO#12, 12% VOO#15, 8% canola#7 oil, 8% corn#5 oil, 8% seed#4 oil, 8% grapeseed#8 oil and 8% peanut#3 oil
12	40% EVOO + 10% VOO + 10% OO + 40% MDVO	10% EVOO#9, 10% EVOO#11, 10% EVOO#1, 10% EVOO#8, 10% VOO#10, 10% OO#12, 7% sunflower#8 oil, 6.6% canola#8 oil, 6.6% corn#2 oil, 6.6% sesame#2 oil, 6.6% seed#2 oil and 6.6% peanut#5 oil
13	40% EVOO + 20% VOO + 20% OO + 20% MDVO	20% EVOO#5, 20% EVOO#2, 20% VOO#15, 20% OO#12, 5% sunflower#9 oil, 5% corn#3 oil, 5% seed#1 oil and 5% grapeseed#3 oil
14	80% EVOO + 20% MDVO	30% EVOO#6, 25% EVOO#7, 25% EVOO#9, 5% seed#5 oil, 5% peanut#1 oil, 5% canola#9 oil and 5% canola#2 oil
15	60% EVOO + 20% OO + 20% MDVO	20% EVOO#11, 20% EVOO#1, 20% EVOO#13, 20% OO#12, 5% soybean#6 oil, 5% corn#1 oil, 5% sesame#4 oil and 5% grapeseed#1 oil

16	100% EVOO	100% EVOO#16
17	100% EVOO	100% EVOO#17
18	100% VOO	100% VOO#18

(b) Validation set

1	68% EVOO + 32% MDVO*	68% EVOO#6, 25% corn#5 oil, 3% peanut#3 oil and 4% grapeseed#4 oil
2	17.50% VOO + 82.50% MDVO	17.50% VOO#15, 17% sunflower#8, 11% soybean#4 oil, 28% canola#6 oil, 26% peanut#1 oil and 0.5% seed#5 oil
3	93% VOO + 7% MDVO	93% VOO#19, 2% corn#3 oil and 5% sesame#4 oil
4	44% EVOO + 56% MDVO	44% EVOO#20, 13% peanut#3 oil, 8% canola#5 oil and 35% canola#4 oil
5	5% EVOO + 95% MDVO	5% EVOO#27, 40% canola#9 oil, 23% soybean#2 oil, 7% grapeseed#2 oil, 15% canola#4 oil and 10% sunflower#3 oil
6	68% EVOO + 32% MDVO	68% EVOO#21, 10% sesame#4 oil, 7% soybean#7 oil and 15% seed#3 oil
7	70% VOO + 30% MDVO	70% VOO#10, 1% sunflower#2 oil, 9% sesame#1 oil, 17% corn#1 oil and 3% sunflower#1
8	31% EVOO + 69% MDVO	31% EVOO#22, 24% sunflower#3 oil, 13% sesame#4 oil, 20% soybean#7 oil, 2% peanut#5 oil and 10% grapeseed#2
9	52% EVOO + 48% MDVO	52% EVOO#23, 28% canola#7, 13% soybean#6 oil, 5% grapeseed#1 oil and 2% sesame#4 oil
10	25% EVOO + 75% MDVO	25% EVOO#24, 25% corn#1 oil, 25% sunflower#2 oil and 25% peanut#3 oil
11	90% EVOO + 10% MDVO	90% EVOO#25, 5% canola#2 oil and 5% soybean#2 oil
12	40% EVOO + 60% MDVO	40% EVOO#26, 30% peanut#1 oil and 30% canola#6

417 ^a MDVO: Mixture of different vegetable edible oils (non-olive oils)

418 ^b EVOO: Extra virgin olive oil

419 ^c OO: Olive oil

420 ^d VOO: Virgin olive oil

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Table 3. Values of the quality performance metrics from the different FTIR olive/non-olive classification methods

Performance features Region 2 (1680-1800 cm ⁻¹)	kNN	PLS-DA	(nu)SVM-C			(c)SVM-C			SIMCA			OCPLS		
			None	PCA	PLS	None	PCA	PLS	2iC	p2iC	1iC	Ordinar y linear	RBF	PRM
			2iC	2iC	2iC	2iC	2iC	2iC	2iC	2iC	2iC	1iC	1iC	1iC
Sensibility (Recall)	0.91	1.00	1.00	0.83	1.00	1.00	0.87	1.00	0.91	0.87	0.96	0.74	0.87	0.57
Specificity	0.88	0.96	0.88	0.88	0.96	0.92	0.84	0.96	0.32	0.76	0.71	0.80	0.20	0.94
Positive predictive value (Precision)	0.88	0.96	0.88	0.86	0.96	0.92	0.83	0.96	0.55	0.51	0.49	0.52	0.24	0.72
Negative predictive value	0.92	1.00	1.00	0.85	1.00	1.00	0.88	1.00	0.80	0.95	0.98	0.91	0.84	0.88
Efficiency (Accuracy)	0.90	0.98	0.94	0.85	0.98	0.96	0.85	0.98	0.60	0.78	0.76	0.78	0.35	0.85
AUC (Correctly classified rate)	0.90	0.98	0.94	0.85	0.98	0.96	0.85	0.98	0.62	0.81	0.83	0.77	0.54	0.75
Matthews correlation coefficient	0.79	0.96	0.88	0.71	0.96	0.92	0.71	0.96	0.29	0.54	0.56	0.48	0.08	0.55
Kappa coefficient	0.79	0.96	0.88	0.71	0.96	0.92	0.71	0.96	0.23	0.50	0.50	0.46	0.04	0.54

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Table 4. Values of the quality performance metrics from the different Raman olive/non-olive classification methods

Performance features (650-950 cm ⁻¹)	kNN	PLS-DA	(nu)SVM-C			(c)SVM-C			SIMCA			OCPLS		
			None	PCA	PLS	None	PCA	PLS	2iC	p2iC	1iC	Ordinar y linear	RBF	PRM
			2iC	2iC	2iC	2iC	2iC	2iC	2iC	2iC	2iC	2iC	1iC	1iC
Sensibility (Recall)	0.83	0.88	0.83	0.83	1.00	0.83	0.83	0.83	0.67	0.00	0.50	0.42	0.46	0.33
Specificity	0.88	0.88	0.88	0.88	0.00	0.88	0.88	0.88	0.88	1.00	0.94	0.29	0.23	0.95
Positive predictive value (Precision)	0.87	0.88	0.87	0.87	0.49	0.87	0.87	0.87	0.84	-	0.71	0.15	0.15	0.67
Negative predictive value	0.85	0.88	0.85	0.85	-	0.85	0.85	0.85	0.73	0.76	0.86	0.62	0.58	0.82
Efficiency (Accuracy)	0.86	0.88	0.86	0.86	0.49	0.86	0.86	0.86	0.78	0.76	0.83	0.32	0.28	0.80
AUC (Correctly classified rate)	0.86	0.88	0.86	0.86	0.50	0.86	0.86	0.86	0.77	0.50	0.72	0.36	0.34	0.64
Matthews correlation coefficient	0.71	0.76	0.71	0.71	-	0.71	0.71	0.71	0.56	-	0.50	-0.25	-0.29	0.37
Kappa coefficient	0.71	0.76	0.71	0.71	0.00	0.71	0.71	0.71	0.55	0.00	0.48	0.24	-0.19	0.34

The hyphen "-" is signifying that the performance feature cannot be determined

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Table 5 Values of the quality performance metrics from the different FTIR adulterated olive oils detection models

Performance features	kNN	PLS-DA	SIMCA	(nu)SVM-C			(c)SVM-C		
				None	PCA	PLS	None	PCA	PLS
				2iC	2iC	2iC	2iC	2iC	2iC
Region 2 (1680-1800 cm⁻¹)									
Sensibility (Recall)	0.83	0.70	0.70	1.00	1.00	1.00	1.00	1.00	0.87
Specificity	0.50	0.92	0.58	0.00	0.00	0.00	0.00	0.00	0.67
Positive predictive value (Precision)	0.76	0.94	0.76	0.66	0.66	0.66	0.66	0.66	0.83
Negative predictive value	0.60	0.61	0.50	-	-	-	-	-	0.73
Efficiency (Accuracy)	0.71	0.77	0.66	0.66	0.66	0.66	0.66	0.66	0.80
AUC (Correctly classified rate)	0.66	0.81	0.64	0.50	0.50	0.50	0.50	0.50	0.77
Matthews correlation coefficient	0.34	0.58	0.27	-	-	-	-	-	0.55
Kappa coefficient	-0.11	0.55	0.27	0.00	0.00	0.00	0.00	0.00	0.55

The hyphen "-" is signifying that the performance feature cannot be determined

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Table 6. Values of the quality performance metrics from the different Raman adulterated olive oils detection models

Performance features (650-950 cm ⁻¹)	kNN	PLS-DA	SIMCA	(nu)SVM-C			(c)SVM-C		
				None	PCA	PLS	None	PCA	PLS
				2iC	2iC	2iC	2iC	2iC	2iC
Sensibility (Recall)	0.83	0.92	0.46	1.00	1.00	1.00	0.88	0.71	0.83
Specificity	0.08	0.67	0.33	0.67	0.00	0.67	0.67	0.00	0.67
Positive predictive value (Precision)	0.65	0.85	0.58	0.86	0.67	0.86	0.84	0.59	0.83
Negative predictive value	0.20	0.80	0.24	1.00	-	1.00	0.73	0.00	0.67
Efficiency (Accuracy)	0.58	0.83	0.42	0.89	0.67	0.89	0.81	0.47	0.78
AUC (Correctly classified rate)	0.46	0.79	0.40	0.83	0.50	0.83	0.77	0.35	0.75
Matthews correlation coefficient	-0.11	0.61	-0.20	0.76	-	0.76	0.55	-0.35	0.50
Kappa coefficient	-0.10	0.61	-0.19	0.73	0.00	0.73	0.55	-0.33	0.50

The hyphen "-" is signifying that the performance feature cannot be determined

430 **FIGURE CAPTIONS**

431

432 Figure 1. Examples of vibrational spectra of extra virgin olive oil (EVOO) acquired from:
433 (a) FTIR (b) Raman and (c) FT-NIR

434

435 Figure 2. (a) Superposed FTIR spectra and (b) loading plot of the 146 vegetable oil
436 samples showing the three regions selected.

437

438 Figure 3. Plot of (a) superposed Raman spectra and (b) loading plot of all the vegetable
439 edible oil samples showing the region selected.

440

441 Figure 4. Classification plot from FTIR applying two input-class (2iC) classification
442 strategy on PLS-DA. The green squares (■) and the red triangles (▼) represent the
443 olive and non-olive class, respectively.

444

445 Figure 5. Concentration values for adulteration obtained from the PLS model vs. the
446 actual concentration of olive oil using FTIR-ATR.

Figure 1

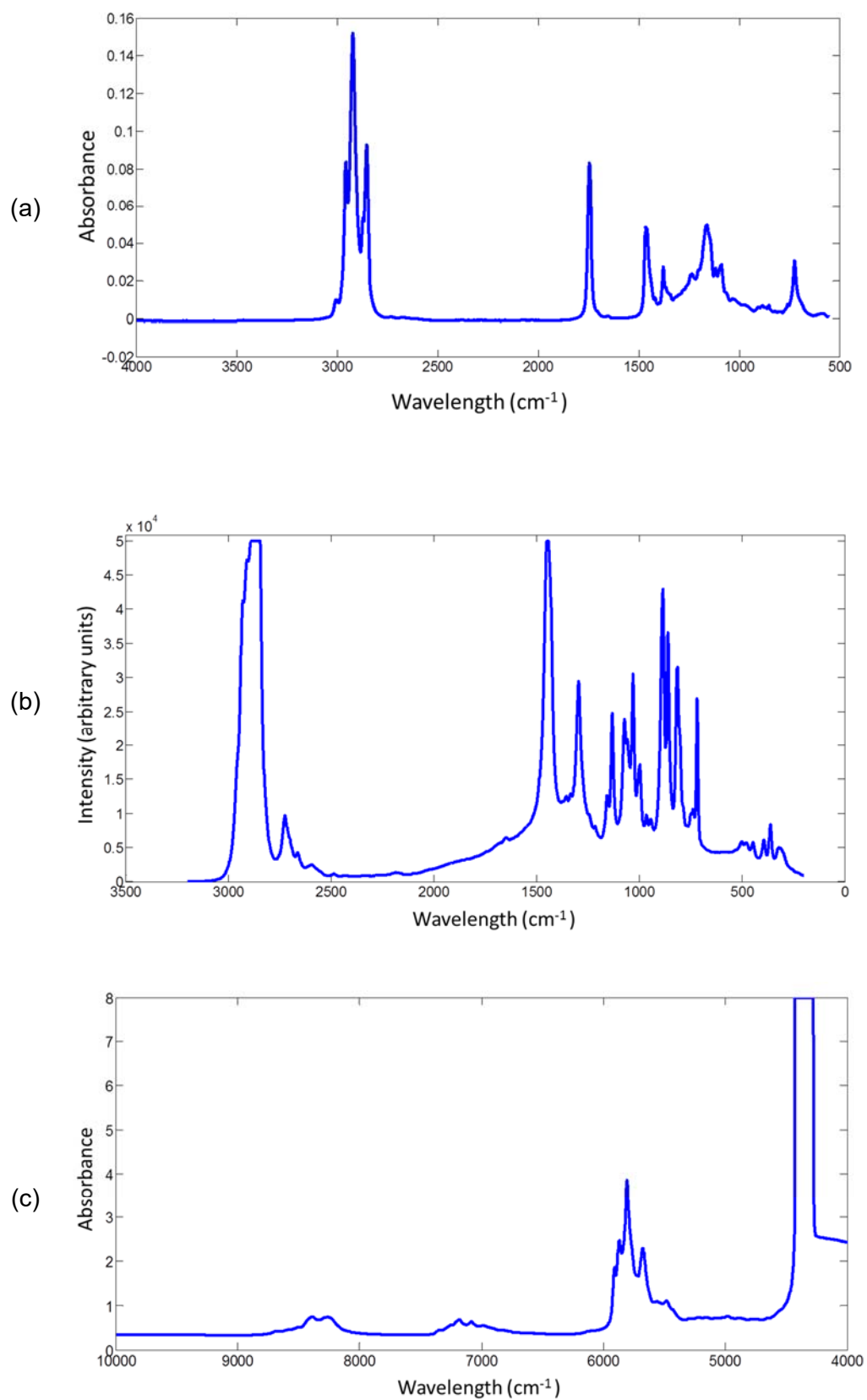
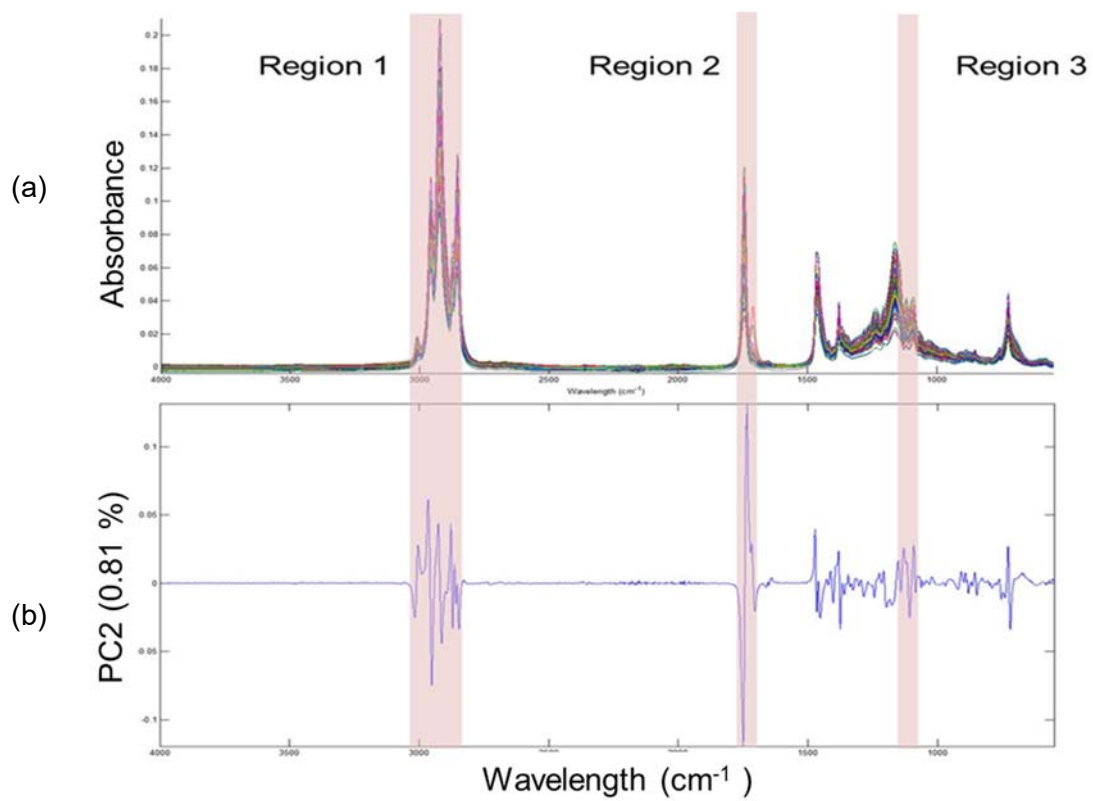
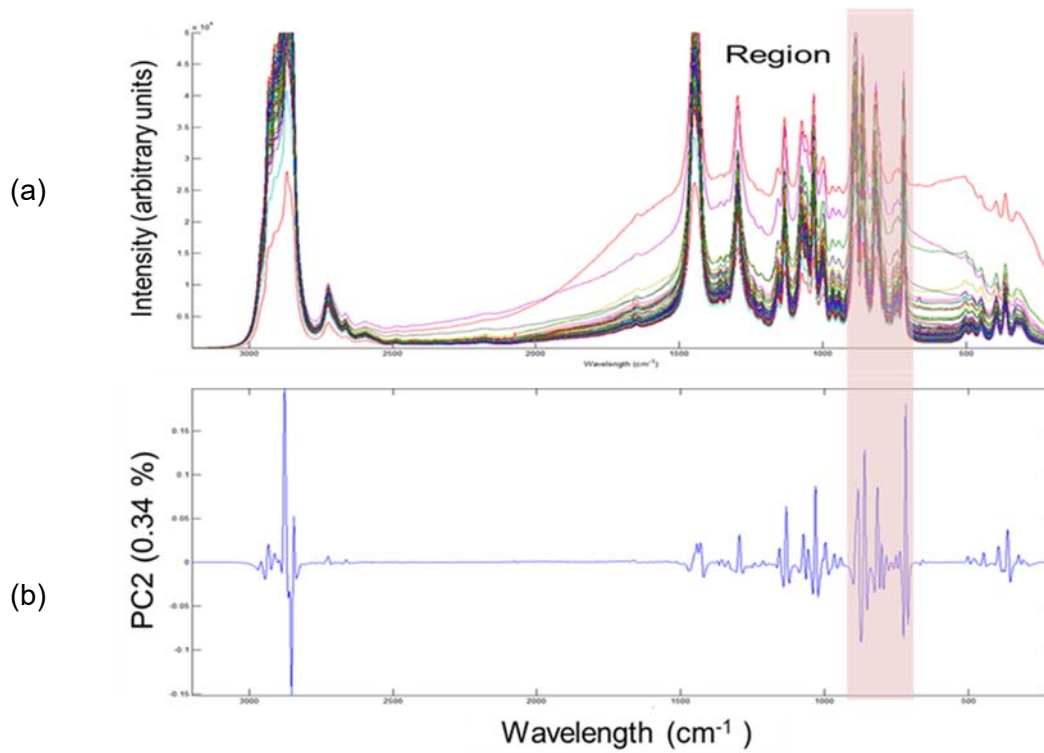


Figure 2



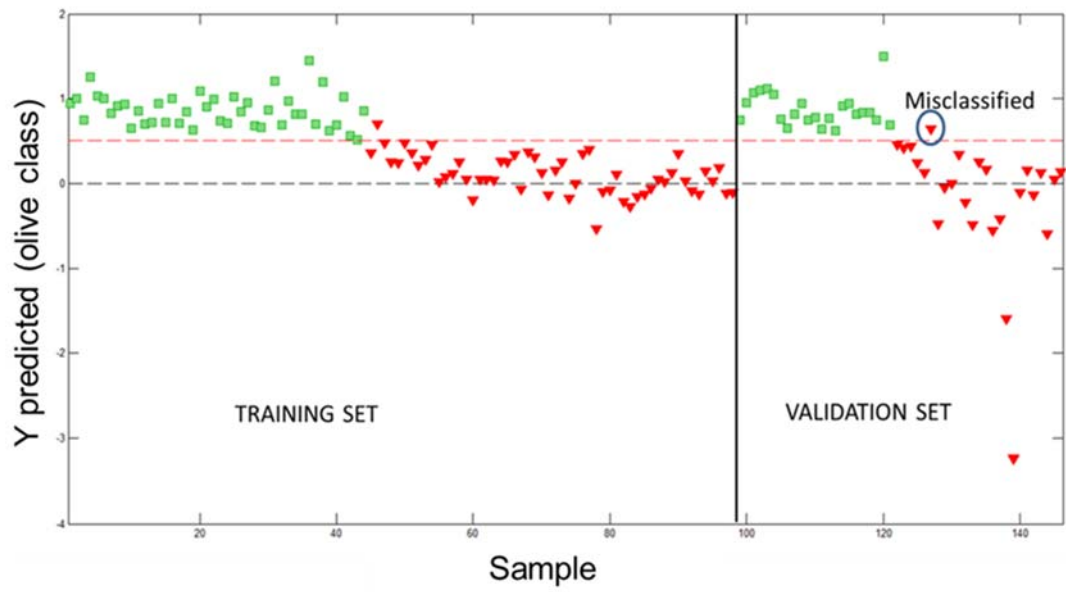
448

Figure 3



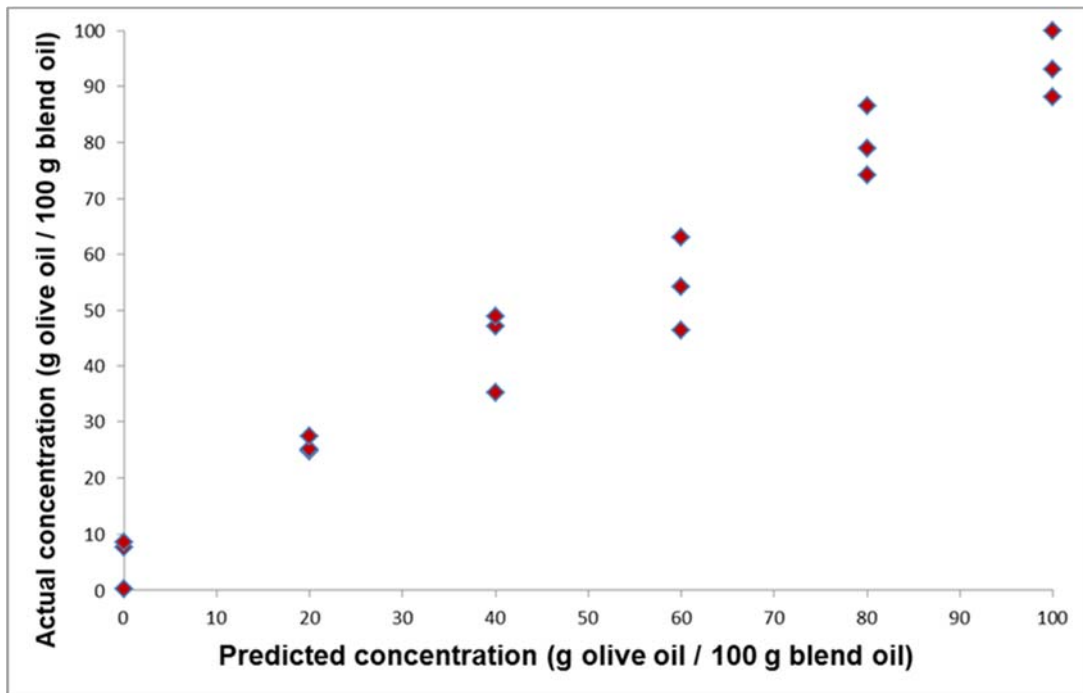
449

Figure 4



450

Figure 5



451

452

Graphical abstract

