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FT-IR and untargeted chemometric analysis for adulterant detection in chia and sesame oils

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1 **FT-IR and untargeted chemometric analysis for adulterant detection in chia and**
2 **sesame oils.**

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19
20
21 **Abstract**

22 Chia (*Salvia hispanica* L.) and sesame (*Sesamum indicum* L.) oils are valorized for their
23 health benefits and both are extensively used as ingredients in different food
24 formulations and/or processes. Their retail prices are higher than those of other edible
25 oils and might promote fraudulent adulterations. Spectroscopic methods associated to
26 untargeted analysis are appropriate and faster than traditional techniques, requiring less
27 time to prepare and run the samples. In the present study Fourier transform infrared
28 spectroscopy was used in combination with one class partial least squares and soft
29 independent modelling by class analogy to detect the presence of four possible
30 adulterants: corn, peanut, soybean and sunflower oils, in four different proportions
31 (pure+adulterant: 90+10, 95+5, 98+2 and 99+1, in volume). Untargeted approaches
32 were successful in the detection of adulterated chia and sesame oils with acceptable
33 prediction errors ranging between 1% and 5%.

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35
36 **Keywords:** *FT-IR; untargeted analysis; chia oil; sesame oil; food adulteration; OC-*
37 *PLS; SIMCA.*

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51 **1. Introduction.**

52 Chia (*Salvia hispanica* L.) and sesame (*Sesamum indicum* L.) oils have been
53 gaining attention among consumers due to their nutritional and health benefits
54 associated to their fatty acid profile and other lipophilic phytochemicals. Chia oil is rich
55 in polyunsaturated fatty acids (PUFAs), containing about 60% of α -linolenic acid
56 (C18:3, n-3), 20% of linoleic acid (C18:2, n-6) and 6% of oleic acid (C18:1, n-9)
57 (Dąbrowski et al., 2017). On the other hand, sesame oil has a unique high oxidative
58 stability and contains about 45% of oleic acid (C18:1, n-9), 40% of linoleic acid (C18:2,
59 n-6), 9% of palmitic acid (16:0) and 6% of stearic acid (18:0) (Kamal-Eldin &
60 Appelqvist, 1994). Chia and sesame oils have been extensively used as ingredients in
61 different food formulations and/or processes (Perveen et al., 2014; Rojas et al., 2019;
62 Ullah et al., 2016; Zettel & Hitzmann, 2018; Zhuang et al., 2016). Despite the health
63 benefits of these oils, their retail prices are higher than those of other edible oils and this
64 fact might promote fraudulent adulterations made by unscrupulous producers or
65 suppliers.

66 Adulteration may be achieved by adding less expensive edible oils. Therefore,
67 several efforts have been made to detect the presence of these adulterants. Adulteration
68 of extra-virgin and virgin olive oils is the most studied because many fraud cases have
69 been reported in the last decades (Aparicio et al., 2013; Moore et al., 2012; Peng et al.,
70 2017). Additionally, other oils have been considered as potential targets for
71 adulteration, such as those extracted from rapeseed, walnut, hazelnut, coconut, peanut
72 and sesame, among others (Fadzilillah et al., 2014; Jović et al., 2016; Li et al., 2015;
73 Ozen & Mauer, 2002; Ozulku et al., 2017; Rohman & Che Man, 2012; Rohman et al.,
74 2010; Xu et al., 2011; Zhao et al., 2015).

75 The official techniques to detect the presence of possible adulterants in oil
76 samples include a separation step, typically using gas or liquid chromatography,
77 followed by quantification of the acyl lipids and fatty acids (Aparicio et al., 2013; Lee et
78 al., 2013; Zhang et al., 2015, Zhang et al., 2017). Some drawbacks of these techniques
79 are the high amount of time required to prepare and run the samples, the consumption of
80 solvents and the use of standard compounds needed in some cases for quantification
81 purposes. In contrast, spectroscopic techniques, such as; NMR or any vibrational
82 spectroscopy (i.e. NIR, FT-IR or Raman) require less sample preparation time, are rapid
83 and non-destructive. In recent years, these advantages have triggered the use of
84 vibrational spectroscopy as alternative procedure to detect the presence of adulterants in
85 oil samples. Moreover, FT-IR in the region of mid infrared is one of the most used
86 characterization methods of edible oils (de la Mata et al., 2012; Georgouli et al., 2017;
87 Gurdeniz & Ozen, 2009; Jiménez-Carvelo et al., 2017; Lerma-García et al., 2010;
88 Maggio et al., 2010).

89 The spectral information described by FT-IR (or any vibrational spectroscopy)
90 could be used as a fingerprint. Multivariate statistical methods (also known as
91 chemometric methods) transforms the spectral information (i.e. the intensities at every
92 wavelength) into new variables or class responses according to the similarities of the
93 samples. The most used methods for exploratory analysis and classification purposes
94 are principal component analysis, cluster analysis and any type of discriminant analysis
95 (linear, quadratic or partial least squares, among others) (Gómez-Caravaca et al., 2016).
96 However, discriminant analysis is considered as a targeted method, which uses the
97 information of adulterated samples as a class previously specified by the user. In
98 contrast, in recent years, untargeted methods are gaining attention among food scientist
99 and chemists (Aparicio et al., 2013; Li et al., 2015; Rodionova et al., 2016; Xu et al.,

2011; Zhang et al., 2015, Zhang et al., 2017). Untargeted methods, such as one class partial least squares (OC-PLS) and soft independent modelling by class analogy (SIMCA), use the spectral information to fix the boundaries of the pure oil class with a specified confidence level. Then, with the boundaries for the pure samples, a class prediction of a new sample can be done by the algorithm (Rodríguez et al., 2019).

To the best of our knowledge a method to detect adulterants in chia oil has never been reported and the use of untargeted analysis for detection of adulterants in sesame oil has not been fully explored yet. The aim of the present work is to challenge FT-IR spectra as input of two different chemometric untargeted analysis (SIMCA and OC-PLS) to evaluate the authenticity of chia and sesame oils, by detecting the presence of less expensive oils.

2. Materials and methods.

2.1 Materials.

Five batches of cold pressed chia and non-roasted sesame oils were provided from a local oil producer company (*Alimentos Sturla, Buenos Aires, Argentina*). Pure commercial oils (corn, peanut, soybean and sunflower) were purchased in a local market in *Buenos Aires, Argentina*. All other reagents used were analytical grade.

2.2 Specific gravity and refractive index determination.

Specific gravity (apparent) and refractive index were determined by the methods described in AOAC 920.212 and AOAC 921.08, respectively, for every oil (AOAC, 2016). Refractive index was measured at a temperature of 25°C, using an automatic digital refractometer (RE40D, Mettler Toledo Inc., Japan). Both determinations were

124 done by quintuplicate for every oil type. Specific gravity and refractive index results are
125 reported in Table SM1 (*Supplementary Material Section*).

126

127 *2.3 Quantification of acyl lipids by gas chromatography (CG-FID).*

128 Fatty acid composition of pure oils was measured by gas chromatography, after
129 hydrolysis of the acyl glycerols. The methyl esters for the determination of the fatty
130 acids (FAME) were prepared according to AOCS Official Method Ce 2-66 (AOCS,
131 2009). The separation of FAMEs was performed on a CLARUS 500 (Perkin Elmer,
132 Norwalk, CT) gas chromatograph equipped with a flame ionization detector and
133 automatic sampler. A polyethylene glycol phase capillary column Elite Wax (Perkin
134 Elmer, Norwalk, CT) with a length of 30 m, 0.32 mm inner diameter and 0.25 μm film
135 thickness was used. The analysis conditions were as follows: column temperature was
136 set from 190 $^{\circ}\text{C}$ to 240 $^{\circ}\text{C}$ rising at 3 $^{\circ}\text{C}/\text{min}$, injector temperature was 240 $^{\circ}\text{C}$ and
137 detector was set at 300 $^{\circ}\text{C}$; nitrogen was used as carrier gas at a linear velocity of 20
138 cm/s and the injection volume was 1 μL . FAMEs were identified by comparison of their
139 retention times versus pure standards analysed under the same conditions. They were
140 quantified according to their percentage area, obtained by the integration of the peaks
141 using TotalChrom software suite (Perkin Elmer, Norwalk, CT).

142

143 *2.4 Preparation of adulterated samples.*

144 Five replicates (one for each batch of pure oil) of each adulterated type of
145 sample were prepared by mixing during 10 minutes at room temperature in a 10 mL
146 glass vial with magnetic stirring the necessary volumes of pure oil (chia or sesame) with
147 an adulterant oil (corn, peanut, soybean or sunflower). Four types of adulterated

148 samples were prepared using the four adulterants in four proportions (pure+adulterant:
149 90+10, 95+5, 98+2 and 99+1 in volume) for each pure oil tested.

150

151 *2.5 Fourier Transform infrared spectroscopy measurements.*

152 Pure and adulterated oils samples were scanned in a FT-IR (Spectrum 400,
153 Perkin Elmer Inc., Shelton CT, USA) with DTGS detector and an attenuated total
154 reflectance accessory (ATR, PIKE Technologies, Inc., Madison WI, USA). A few drops
155 of each oil sample were poured on the diamond/ ZnSe of a reflectance ATR crystal with
156 an angle of 45°. Spectra were collected accumulating a total of 64 scans per sample with
157 a resolution of 4 cm⁻¹ from 600 to 4000 cm⁻¹. Every spectrum was base-line corrected
158 (cubic spline function method), transformed to absorbance units and normalized (min-
159 max normalization) using the Spectrum Software ver. 6.3 (Perkin Elmer, Inc.). For
160 detailed information about the type of samples prepared and the number of
161 measurements performed, see Table 1.

162

163 *2.6 Multivariate Statistical methods.*

164 Principal component analysis (PCA) is one of the most used of the multivariate
165 methods and was well described in many studies. The data set is arranged in a matrix \mathbf{X}
166 with I rows (samples of oils) and J columns (FT-IR normalized absorption intensities).
167 PCA finds new variables (also known as principal components) from \mathbf{X} , according to \mathbf{X}
168 $= \mathbf{TP}^T + \mathbf{E}$, where \mathbf{T} , \mathbf{P} are matrices containing the score vectors (related to the principal
169 components) and the loading vectors respectively. Additionally, \mathbf{E} is a matrix
170 containing the residuals for each sample. Every principal component is a linear
171 combination of scores and loading values and is related, in decreasing order, to an
172 amount of variance of the original data (Bro & Smilde, 2014). The aim of using PCA in

173 the present work was to find similarities among the samples scanned with FT-IR by
174 plotting the most relevant components to describe the data set (chia data set or sesame
175 data set). Additionally, the analysis of the loading values was used to find the most
176 relevant wavenumbers for the grouping of samples according to their similarities. PCA
177 on the covariance matrix was performed on the two data sets (chia and sesame)
178 considering the intensities at each wavenumber (normalized and in absorbance units) of
179 the spectra as original variables and each type of sample representing a row of the
180 original matrix data set. PCA was performed using GNU Octave for Windows ver.
181 4.4.1.

182 Soft independent modelling class analogy (SIMCA) is a supervised method (i.e.
183 use the information of the samples' class) based on PCA. A single PCA was modelled
184 for each class (pure oils or adulterated samples) of the data set matrix. To show how a
185 sample would fit in each class, two scalar statistics are calculated for each sample, Q-
186 residual and Hotelling's T^2 . Q-residuals are calculated according to $Q_i = e_i e_i^T$, where e_i
187 is the residual of sample i after applying the model and it is related to the amount of
188 original information not included in the model. In the other hand, Hotelling's T^2 is
189 related to the information of each sample within the model according to $T_i^2 = I(x_i - x_{avg})S^{-1}$
190 $(x_i - x_{avg})'$, where I is the number of samples, x_i the multivariate measurement of the
191 sample i , x_{avg} the mean value and S the standard deviation. Q and T^2 limit values can be
192 calculated at a specific α (level of significance), often set at 0.05. A relevant number of
193 components were used to set the boundaries (Q-residual limit value vs. Hotelling's T^2
194 limit value) for the classification of the samples and then predict the class of a new
195 sample (not included in the training step) (Luna et al., 2016). If only one class is used in
196 the training step the approach is considered as untargeted and the boundaries can be
197 used as an accepted/rejected limit (Rodríguez et al., 2019). SIMCA was run using

198 Classification Toolbox ver. 5.0 (Ballabio & Consonni, 2013) with a confidence level of
 199 95% ($\alpha = 0.05$) under GNU Octave for Windows ver. 4.4.1.

200 One class partial least squares (OC-PLS) is another untargeted approach based
 201 on PLS algorithm using a distance-based sample density measurement as the response
 202 variable. OC-PLS computes a regression as $1 = \mathbf{X}b_{PLS} + e$, where 1 is the response
 203 vector, \mathbf{X} is the original data set, b_{PLS} contains the regression coefficients and e is the
 204 vector of model's residuals. After the model is built the Hotelling's T^2 (based on score
 205 distances) and the absolute centered residual (ACR) can be calculated according to ACR

206 $= |1 - y_j - \mu_e|$ and $T^2 = \sum_{i=1}^K \frac{(t_i - t_{i,avg})^2}{S_{t,i}^2}$, where y_j is the response of sample j , μ_e is the mean

207 of the training errors, $t_{i,avg}$ and $S_{t,i}^2$ are the mean and sample variance of the i th latent
 208 variable and t_i , respectively; and K is the number of significant latent variables. The

209 standard deviation of the model can be calculated as

210 $\sigma_e = \sqrt{\sum_{i=1}^N (1 - y_i - \mu_e)^2 / (N - 1)}$, where N is the total number of left-out samples

211 during cross validation and y_i is the predicted response of the i th left-out sample. When

212 a confidence level (α) is set the limit values for ACR and T^2 can be calculated as ACR_L

213 $= Z_{\alpha/2} \cdot \sigma_e$ and $T_L^2 = \frac{(n^2 - 1)}{n(n - K)} F_{\alpha(K, n - K)}$, where $Z_{\alpha/2}$ is the upper critical point of the

214 standard normal distribution, and $F_{\alpha(K, n - K)}$ is the upper critical point of the F -distribution

215 with $(K, n - K)$ degrees of freedom. The plot of SD versus ACR including the limits are a

216 useful tool to screen outlier diagnosis and predict adulterated samples from pure ones

217 (Xu et al., 2013; Zhang et al., 2017). OC-PLS was computed using OC-PLS algorithm

218 under Octave for Windows ver. 4.4.1, with a confidence level of 95% and a *leave one*

219 *out* cross validation (LOOCV) to fix the number of the latent variables (LVs) (Xu et al.,

220 2014).

221

222 3. Results.

223 3.1 Gas chromatography with flame ionization detection (GC-FID).

224 Table 2 recovers the GC-FID results expressed as the ratio of total areas. Chia
225 oil major components were unsaturated fatty acids: linolenic (68.3 %) and linoleic acid
226 (20.7 %), in agreement with other studies that indicated that linolenic acid contents
227 might be up to 69 % (Ayerza & Coates, 2004; Ixtaina et al., 2011). The most abundant
228 fatty acids in sesame oil were oleic, linoleic, palmitic and stearic acids with high
229 predominance of unsaturated fatty acids. The proportions of different fatty acids are
230 within the reported ranges (El khier et al., 2008; Thakur et al., 2017). In corn and
231 sunflower oils, the major fatty acids were palmitic, oleic, and linoleic acids and were in
232 the range described by FAO/WHO Codex Alimentarius Commission (Codex
233 Alimentarius Commission CODEX STAN 210, 1999). As for peanut the oil used had
234 oleic acid content slightly higher than the maximum stated by FAO (80%). While
235 soybean oil presented high content of linoleic acid as compared with reported
236 specifications (Spencer et al., 1976; Codex Alimentarius Commission CODEX STAN
237 210, 1999).

238

239 3.2 Fourier transform infrared spectroscopy (FT-IR).

240 The assignments of the bands in the FT-IR spectra (shown in Fig. SM1
241 (Supplementary Material Section, for the cases of adulteration of chia oil (a) and for
242 sesame oil (b)) agreed with those previously reported in literature for many pure oil
243 types. In this work, the relevant signals were labelled from #1 to #12. The first region of
244 bands was associated to hydrogen's stretching (C–H stretching) signals from about 3000
245 to 2850 cm^{-1} . The first band (labelled as #1) was assigned to the *cis* double bond =C–H
246 stretching vibration. In addition, the signals labelled as #3 and #4 were reported as

247 symmetric and asymmetric (respectively) stretching vibrations of the aliphatic CH₂
248 group. The shoulder marked as #2 was associated to the symmetric stretching of the
249 aliphatic CH₃ group. The second region of signals (from about 1750 to 1650 cm⁻¹) was
250 previously reported as the region of double bond's stretching. This region includes the
251 highest band in all spectra (#5), associated to the stretching vibration of ester carbonyl
252 groups present in the triglycerides (–C=O). Furthermore, a small signal was present (#6)
253 and attributed to the C=C stretching vibration of the *cis*-oleofins. A third region of
254 signals was denoted as the region of other bond's deformations and bendings ranging
255 from about 1470 to 1370 cm⁻¹. Bands labelled as #7 and #8 were found in this region
256 and are associated to the bending vibration of CH₂ and CH₃. Finally, the fourth region
257 of signals (from about 1240 to 700 cm⁻¹) is the so-called fingerprint region. This last
258 region includes three bands (#9, #10 and #11) linked with the stretching vibration of the
259 C–O ester groups. And, the last band labelled as #12, was associated to the overlapping
260 of two vibrations, the CH₂ rocking and the out-of-plane vibration of the *cis*-disubstituted
261 oleofins (Guillén & Cabo, Guillén & Cabo, 1997b; Vlachos et al., 2006).

262 The average values of the wavenumbers recovered from FTIR spectra for pure
263 oil samples used in this work are reported in Table 3. Significant differences (one-way
264 ANOVA, $p < 0.05$) were only found in signals #3, #11 and #12. In the case of the band
265 number 3, the wavenumber value reported for chia, soybean and sunflower was 2923
266 cm⁻¹ and the values found in the case of sesame, corn and peanut oils were lower (2915,
267 2917 and 2915 cm⁻¹ respectively). The band labelled as #11 showed a lower value of
268 1092 cm⁻¹ for peanut oil in comparison with all other oils with values of 1096 cm⁻¹. The
269 last shift was observed at the band marked as #12 with a lower value of 713 cm⁻¹ in the
270 case of the chia oil in contrast with the value of 721 cm⁻¹ reported for all the other oils.
271 According to the works published by Guillen and Cabo (1997a and 1997b) and

272 references therein, the frequencies of the bands could change in agreement with the
273 profile of acyl lipids of the oils.

274 Moreover, the intensities of the bands could vary also with the type of acyl lipids
275 and other components of the oils. In order to display a better visualization of those
276 intensity differences, the insets in Fig. SM1(a) and (b) show different zooms of three
277 different regions from the same spectra depicted in the main figure. FT-IR spectrum of
278 chia oil (insets in Fig. SM1(a)) showed lower intensities for the bands marked as #2, #3,
279 #4 and #7 and higher intensities for bands #1, #5, #6, #9, #10, #11 and #12 in
280 comparison with all other pure oils used as adulterants (corn, peanut, soybean and
281 sunflower). The band labelled as #8 showed lower intensities than the other oil except
282 for peanut oil, which showed no significant difference. In the case of sesame oil (Fig.
283 SM1(b)), the trend is more complex, intermediate intensity values for sesame oil
284 occurred in bands #1, #2, #3, #4, #7, #11 and #12. Lower intensities were observed in
285 the case of bands marked as #5 and #10 and higher in the case of band #9. No
286 significant differences were found in the bands #6 and #8 with in relation to adulterant
287 oils except for peanut, which presented lower values in both bands.

288

289 *3.3 Principal component analysis.*

290 FT-IR spectra of the pure oil samples and the adulterated oil samples were used
291 as input for principal component analysis (PCA) for a better visualization and
292 exploratory purposes of the data. Fig. SM2 (*Supplementary Material Section*) shows the
293 scatter plot of the two first principal components (PC_1 vs. PC_2) for the case of chia (part
294 (a)) or sesame (part (b)) and the oils used as adulterants. The visual discrimination
295 observed in Fig. SM2(a) and (b) is quite similar and the amount of accumulated
296 variance was 98.5% and 96.1% respectively. PCA was able to discriminate the samples

297 according to their similarities and separate the pure oils used as adulterants and the
298 target oil (chia or sesame) into three well defined groups. One group of samples
299 correspond to chia or sesame pure oils, the second one to corn, soybean and sunflower
300 oils and the third one representing only peanut oil.

301 PCA results obtained by FT-IR spectra are in good agreement with the results
302 showed using GC-FID for quantification of the acyl lipids. Fig. SM3 (*Supplementary*
303 *Material Section*) shows a PCA using as input the average relative percentage of the
304 total chromatographic area for the five FAMES (reported in Table 2). The similarities of
305 the fatty acid profile match with the similarities obtained with FT-IR (Fig SM2 a) and
306 b)), where the sample of sesame oil is near to corn, soybean and sunflower oils and
307 distant from peanut oil. In the case of chia, the sample is located far from all others.
308 According to Fig. SM3 a detection method based on the use of FAMES profile would
309 find more difficulties to detect adulteration of sesame than chia oil for three of the four
310 adulterants used in the present work (corn, soybean and sunflower).

311 Fig. 1(a) and (b) show the three-dimensional PCA score plot (PC1 vs. PC2 vs.
312 PC3) for the cases of chia (88.2% of cumulative variance) and sesame (72.0% of
313 cumulative variance) oils using FT-IR frequencies for pure and adulterated oils. Despite
314 some samples are superimposed in some places of the plots, there is a clear trend in both
315 cases (chia and sesame). Pure chia or sesame oil samples are grouped in a confined area
316 of the plot and adulterated samples are placed in a different region. The proximity of
317 adulterated samples from pure oil samples are in good agreement with the proportion
318 used as adulterant (corn, peanut, soybean or sunflower oils). The samples with the
319 lowest proportion of adulteration (99+1) are near the pure oil samples and the samples
320 with the highest proportion of adulteration (90+10) are more distant. The good

321 discrimination results showed by PCA in both cases (chia and sesame) motivated the
322 use of SIMCA, which is a PCA-based method.

323

324 *3.4 Soft independent modelling class analogy (SIMCA).*

325 Fig. 2(a) and 3(a) show the plots of Q residuals vs. Hotelling T^2 outcoming from
326 SIMCA analysis performed for chia and sesame adulteration respectively using a
327 confidence value of 0.05 and 3 latent variables (LVs). Using the target class (pure oils)
328 and the confidence level, SIMCA defines the boundaries (red dotted lines), which forms
329 the lower and left square (insets in Fig. 3a and 4a for a better visualization). Once the
330 limits were established, prediction of the class of new samples can be done. Any sample
331 of the target class predicted as adulterated is considered a false negative (FN), and any
332 adulterated sample predicted as the pure oil is considered as false positives (FP).
333 Samples with correct prediction are considered as true positives (TP) or true negatives
334 (TN). Performance parameters can be calculated using the number of FN, FP, TP and
335 TN. Sensitivity (SEN), also known as Type I error, is a performance parameter related
336 to the target class and is equals to $TP/(TP+FN)$. In contrast, specificity (SPEC), or type
337 II error, is a parameter which gives information about the samples that do not belong to
338 the target class and is equal to $TN/(TN+FP)$. Using the information of the samples
339 wrongly classified Table 4 recovers SEN and SPEC values using SIMCA for chia and
340 sesame cases. SEN values were identical in both cases (0.967), with only 1 sample
341 wrongly classified of a total of 30. And SPEC values were 1.00 and 0.948 (21 wrong
342 classified samples of a total of 400) for chia and sesame respectively. SPEC values
343 reflect the difficulties to achieve an appropriate prediction using SIMCA for the
344 adulterated samples with a proportion of 99+1 in the case of sesame adulterated oil.

345

346 3.5 One class partial least squares (OC-PLS).

347 Fig. 2(b) and 3(b) represent the plot of the two classifier distances (ACR and
348 OCPLS score distance) obtained using OC-PLS (with a confidence level of 0.05) in the
349 cases of chia and sesame respectively. The inset inside the main graph in Fig. 3b show a
350 zoom, for a better visualization of the pure sample limit square (limited by the red
351 dotted lines), which is no necessary in the Fig. 3(b). The numbers of LVs (5 and 4 for
352 chia and sesame cases respectively) were selected according to the instructions given by
353 the developers of the algorithm using a leave-one-out cross validation method
354 (LOOCV) (Xu et al., 2014). SEN and SPEC values were calculated following the same
355 equations given in Section 3.4 and reported in Table 4. The use of OC-PLS shows
356 excellent discrimination results for the prediction step with SEN values of 1.00 in both
357 cases (chia and sesame). And SPEC values of 1.00 and 0.992 (less than 1% of error) in
358 the cases of chia and sesame respectively. The last SPEC value of 0.992 (sesame case)
359 represents only 3 wrongly classified samples (adulterated samples with a proportion of
360 99+1) of a total of 400.

361

362 4. Discussion.

363 According to the results showed in this work, SIMCA and OC-PLS were
364 successful in the detection of adulterated samples of chia oil with cheaper oils (corn,
365 peanut, soybean and sunflower) with acceptable errors prediction at any level of
366 adulterant proportion (90+10, 95+5, 98+2 and 99+1 in volume). In the case of sesame
367 adulterated samples, only OC-PLS showed a successful detection for all the proportions
368 of adulterant with lower acceptable error; while SIMCA failed only in the case of 99+1
369 adulteration proportion with a SPEC value of 0.948 (error rate of slightly more than

370 5%). The difficulties observed in the detection of adulterants in the case of sesame oil
371 could be explained by FAMES profile similarities with the adulterants used.

372 The results obtained for chia and sesame oils are in good agreement and in some
373 cases better than those found by other authors and for other materials in the literature.
374 For example, in the case of extra virgin olive oil adulteration studies the most used
375 methods were discriminant analysis (Linear or PLS-based) or regression based methods
376 (partial least squares or principal component regressions) using FT-IR as the input data,
377 and the lower proportion detected of adulterant was about 1% to 5% (Downey et al.,
378 2002; Gurdeniz & Ozen, 2009; Jiménez-Carvelo et al., 2017; Lerma-García et al., 2010;
379 Rohman & Man, 2010; Tay et al., 2002). Moreover, discriminant analysis and
380 regression-based methods were performed to detect adulterants in hazelnut, walnut and
381 sesame oils with a limit of detection between 0.53 – 10% (Fadzillillah et al., 2014; Li et
382 al., 2015; Ozen & Mauer, 2002; Ozulku et al., 2017; Rohman & Man, 2011; Zhao et al.,
383 2015).

384 In spite of the general good adulterant detection results showed by discriminant
385 analysis-based methods, several authors discuss about the robustness of these
386 techniques. The main weakness is that during the optimization step, SPEC parameter
387 (type II error) is minimized instead of the SEN parameter (type I error). Thus,
388 discriminant-based methods are considered as a compliant approach instead of a robust
389 approach (Granato et al., 2018; Oliveri & Downey, 2012; Rodionova et al., 2016).

390 Based in this concept, the present work showed a better performance than other
391 studies using untargeted analysis. OC-PLS and a partial least squares class model
392 (PLSCM, similar to OC-PLS) were used to detect adulterants in olive, peanut and
393 sesame oils with as much as 3% of adulterant proportion in all the cases (Deng et al.,
394 2012; Xu et al., 2011; Zhang et al., 2017). The slight better performance showed in the

395 present work by PLS-based algorithm (OC-PLS) in comparison to a PCA-based
396 algorithm (SIMCA) relies on the different way the two methods fix the LVs. SIMCA
397 calculates the components according to the direction of the maximum variance of the
398 target class and OC-PLS calculates the LVs by maximizing the component's correlation
399 between the original variables and the response variable (Deng et al., 2012; Rodríguez
400 et al., 2019; Xu et al., 2011). Moreover, another possible reason is that the use of
401 LOOCV (or other cross validation performed in OC-PLS) leads to a higher number of
402 LVs. In the present work the number of LVs were 5 and 4 for chia and sesame
403 respectively using OC-PLS in comparison to 3 using SIMCA for both cases.

404

405 **5. Conclusions.**

406 Both models for the analysis of FT-IR measurements (using the untargeted
407 methods: SIMCA and OC-PLS) were able to successfully detect the presence of four
408 adulterants (corn, peanut, soybean and sunflower oils) in chia and sesame oils. OC-PLS
409 showed a slightly better performance than SIMCA with a limit of 99+1 (proportion of
410 target+adulterant oils, in volume) for chia and sesame samples. The difference in the
411 performance for both untargeted methods (OC-PLS and SIMCA) could be associated to
412 the different way of fixing the latent variables (LVs) and the number of these used to
413 model the data set. FT-IR coupled to untargeted chemometric analysis may be
414 implemented to determine impurities in oils, avoiding time-consuming sample
415 preparation, harmful reactants and expensive materials. These techniques could be also
416 extended to ensure product authentication in other foods and ingredients and for
417 classifying food quality into different grades, providing the corresponding validation
418 steps are fulfilled. Food industry and control bodies would be also favoured by the
419 expected technical and economic benefit and product's quality improvement.

420

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429

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437

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650 **Figure captions**

651 **Fig. 1.** Principal component three-dimensional score plot (PC_1 vs. PC_2 vs. PC_3) for pure
652 and adulterated oil samples. Part (a): pure chia oil (blue dots), adulterated chia in 90+10
653 proportion (red squares), adulterated chia in 95+5 proportion (green diamonds),
654 adulterated chia in 98+2 proportion (black pointing down triangles) and adulterated chia
655 in 99+1 proportion (pink pointing up triangles). Part (b): pure sesame oil (blue dots),
656 adulterated sesame in 90+10 proportion (red squares), adulterated sesame in 95+5
657 proportion (green diamonds), adulterated sesame in 98+2 proportion (black pointing
658 down triangles) and adulterated sesame in 99+1 proportion (pink pointing up triangles).
659 Variance values associated to each component are between parentheses.

660

661 **Fig. 2.** Samples of pure chia oil (blue dots and blue crosses), adulterated chia in 90+10
662 proportion (red squares), adulterated chia in 95+5 proportion (green diamonds),
663 adulterated chia in 98+2 proportion (black pointing down triangles) and adulterated chia
664 in 99+1 proportion (pink pointing up triangles) represented in a scatter plot of Q

665 residuals vs. Hotelling T^2 values obtained using SIMCA (part (a)) and a scatter plot of
666 centered model residuals (ACR) vs. OC-PLS score distance using OC-PLS (part (b)).

667

668 **Fig. 3.** Samples of pure sesame oil (blue dots and blue crosses), adulterated sesame in
669 90+10 proportion (red squares), adulterated sesame in 95+5 proportion (green
670 diamonds), adulterated sesame in 98+2 proportion (black pointing down triangles) and
671 adulterated sesame in 99+1 proportion (pink pointing up triangles) represented in a
672 scatter plot of Q residuals vs. Hotelling T^2 values obtained using SIMCA (part (a)) and
673 a scatter plot of centered model residuals (ACR) vs. OC-PLS score distance using OC-
674 PLS (part (b)).

Table 1. Detailed number of measurements for each type of sample: Ch = chia oil, Se = sesame oil, Co = corn oil, Pe = peanut oil, So = soybean oil, Su = sunflower oil.

Type of sample	Number of samples per each class					Total
	pure oils	90+10	95+5	98+2	99+1	
Ch	30 [*]					30
Ch+Co		25 ^{**}	25 ^{**}	25 ^{**}	25 ^{**}	100
Ch+Pe		25 ^{**}	25 ^{**}	25 ^{**}	25 ^{**}	100
Ch+So		25 ^{**}	25 ^{**}	25 ^{**}	25 ^{**}	100
Ch+Su		25 ^{**}	25 ^{**}	25 ^{**}	25 ^{**}	100
Se	30 [*]					30
Se+Co		25 ^{**}	25 ^{**}	25 ^{**}	25 ^{**}	100
Se+Pe		25 ^{**}	25 ^{**}	25 ^{**}	25 ^{**}	100
Se+So		25 ^{**}	25 ^{**}	25 ^{**}	25 ^{**}	100
Se+Su		25 ^{**}	25 ^{**}	25 ^{**}	25 ^{**}	100
Co	30 [*]					30
Pe	30 [*]					30
So	30 [*]					30
Su	30 [*]					30
Total	180	200	200	200	200	980

* 6 measurements for each batch of oil (5 batches prepared).

** 25 samples produced with all the possible combinations of 5 batches of pure oils and 5 batches of adulterant oils.

Table 2. Fatty acid relative composition of pure oils expressed as percentage of total chromatographic area.

Oil type	Fatty acid relative composition (%)				
	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)
Chia	7.30 ± 0.06	3.00 ± 0.02	0.70 ± 0.01	20.70 ± 0.11	68.30 ± 0.15
Sesame	9.50 ± 0.08	5.30 ± 0.03	43.30 ± 0.27	41.50 ± 0.23	0.40 ± 0.00
Corn	10.10 ± 0.08	2.20 ± 0.01	33.00 ± 0.20	53.90 ± 0.30	0.90 ± 0.01
Peanut	6.10 ± 0.05	2.00 ± 0.01	85.00 ± 0.53	6.80 ± 0.01	0.20 ± 0.00
Soybean	13.70 ± 0.11	6.00 ± 0.04	1.40 ± 0.01	69.80 ± 0.38	9.10 ± 0.02
Sunflower	6.00 ± 0.05	3.30 ± 0.02	30.20 ± 0.19	60.40 ± 0.33	0.10 ± 0.00

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Table 3. Mean wavenumber values in cm^{-1} of the twelve peaks labelled in Fig. SM1 (*Supplementary Material Section*) obtained from FT-IR spectra of the pure oil samples.

Oil sample	Number of the peak from the spectra											
	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12
Ch	3006 ± 3^a	2951 ± 2^a	2923 ± 3^a	2850 ± 1^a	1742 ± 1^a	1649 ± 2^a	1456 ± 2^a	1372 ± 2^a	1233 ± 1^a	1156 ± 1^a	1096 ± 1^a	713 ± 1^a
Se	3004 ± 2^a	2949 ± 3^a	2915 ± 1^b	2850 ± 1^a	1742 ± 1^a	1652 ± 2^a	1459 ± 1^a	1374 ± 1^a	1233 ± 1^a	1156 ± 1^a	1096 ± 1^a	721 ± 1^b
Co	3004 ± 2^a	2948 ± 2^a	2917 ± 3^b	2850 ± 1^a	1742 ± 1^a	1652 ± 2^a	1459 ± 1^a	1374 ± 2^a	1233 ± 1^a	1156 ± 1^a	1096 ± 1^a	721 ± 1^b
Pe	3004 ± 1^a	2949 ± 1^a	2915 ± 1^b	2850 ± 1^a	1742 ± 1^a	1652 ± 1^a	1459 ± 2^a	1374 ± 2^a	1233 ± 1^a	1156 ± 1^a	1092 ± 2^b	721 ± 1^b
So	3004 ± 2^a	2949 ± 2^a	2923 ± 2^a	2850 ± 1^a	1742 ± 1^a	1652 ± 2^a	1459 ± 1^a	1374 ± 1^a	1233 ± 1^a	1156 ± 1^a	1096 ± 1^a	721 ± 1^b
Su	3004 ± 3^a	2949 ± 4^a	2923 ± 1^a	2850 ± 1^a	1742 ± 1^a	1649 ± 1^a	1459 ± 2^a	1374 ± 1^a	1233 ± 1^a	1156 ± 1^a	1096 ± 1^a	721 ± 1^b

* shared superscripts represent statistically significance differences ($p < 0.05$).

Table 4. Performance parameters recovered from SIMCA and OC-PLS results for chia and sesame adulterated data sets.

Case	Method	LV's*	SEN**	SPEC***
Chia	SIMCA	3	0.967	1.00
	OC-PLS	5	1.00	1.00
Sesame	SIMCA	3	0.967	0.948
	OC-PLS	4	1.00	0.992

* LV's: Number of latent variables used in each case.

** SEN: Sensitivity performance value, calculated as $SEN = TP/(TP+FN)$, where TP is the number of true positives and FN is the number of false negatives.

*** SPEC: Specificity performance value, calculated as $SPEC = TN/(TN+FP)$, where TN is the number of true negatives and FP is the number of false positives.

Fig. 1

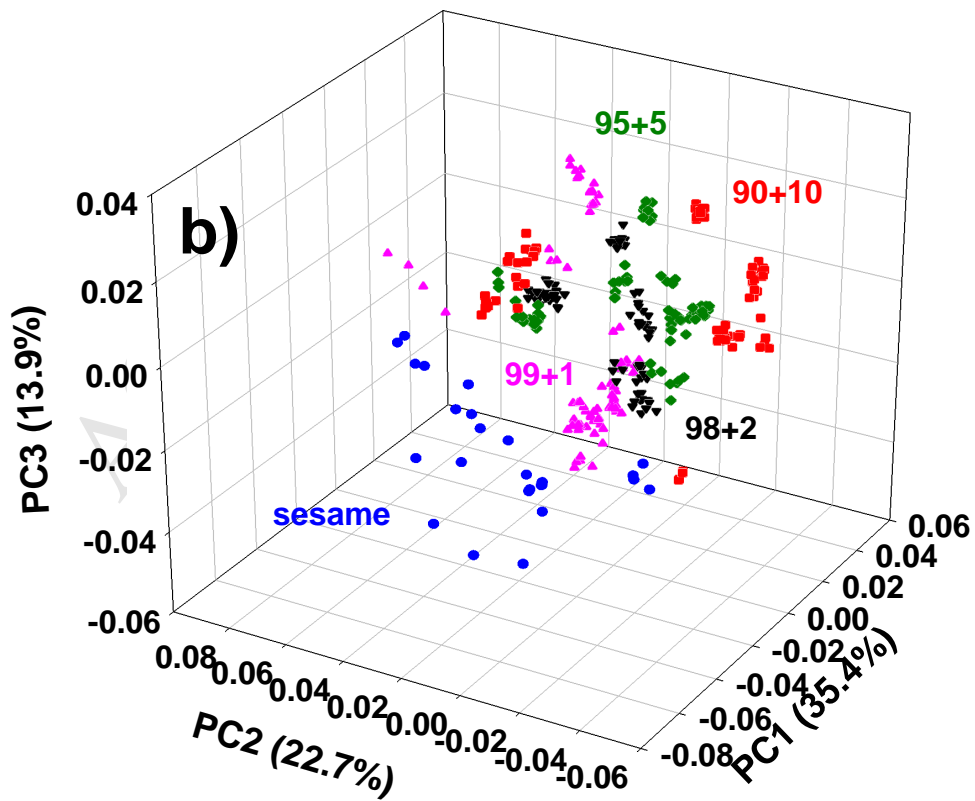
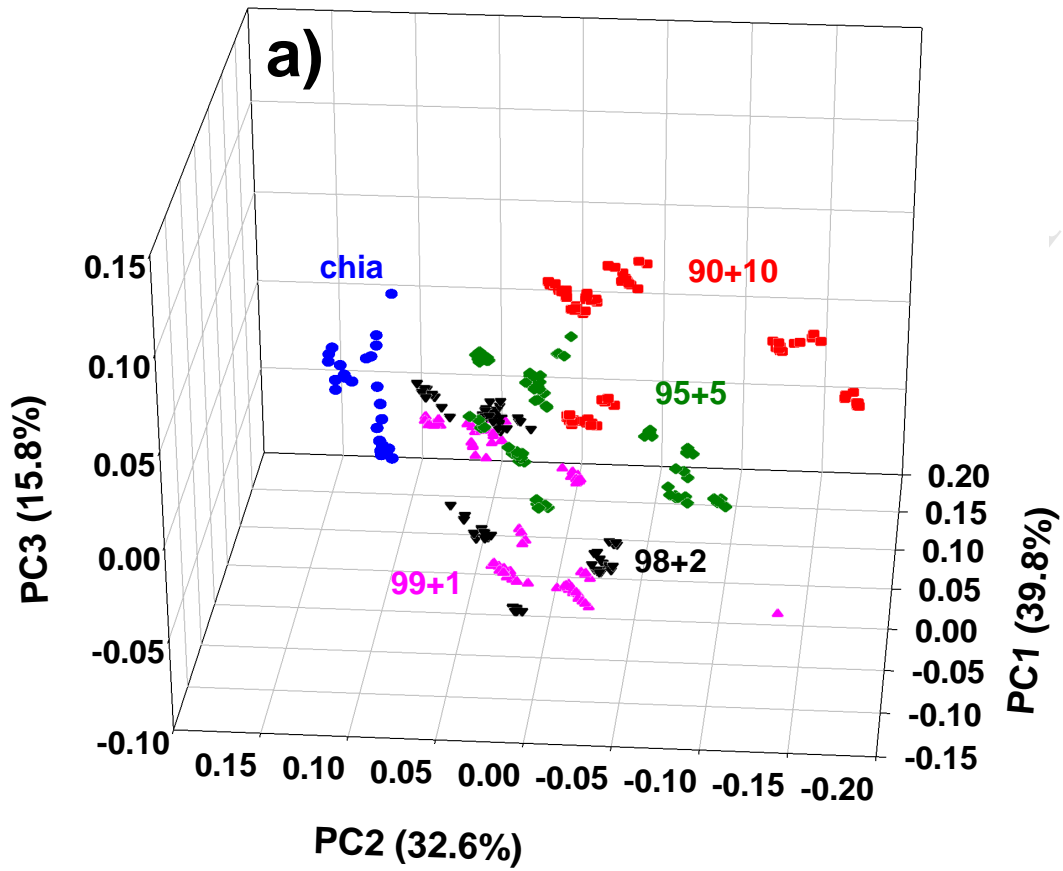


Fig. 2

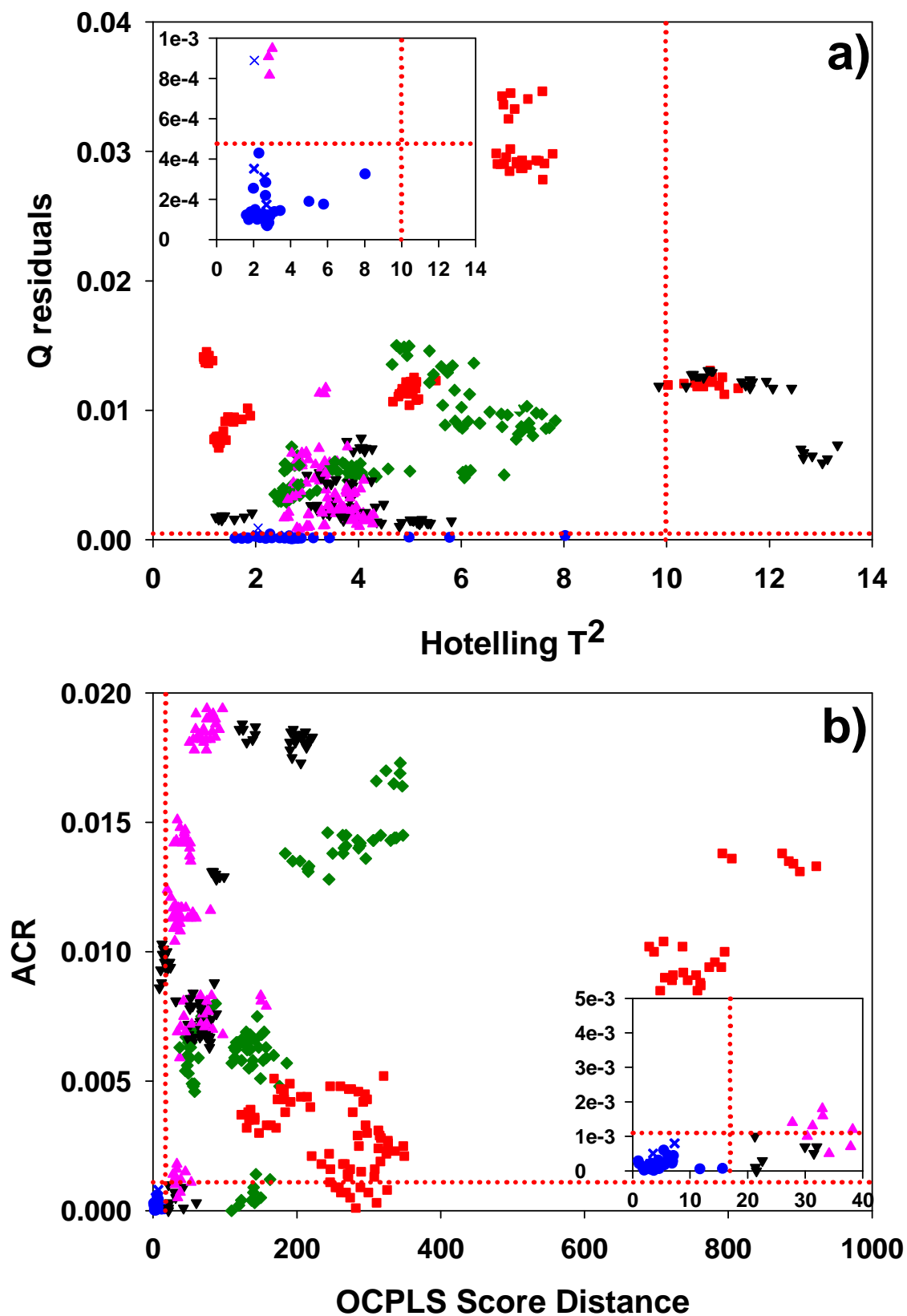
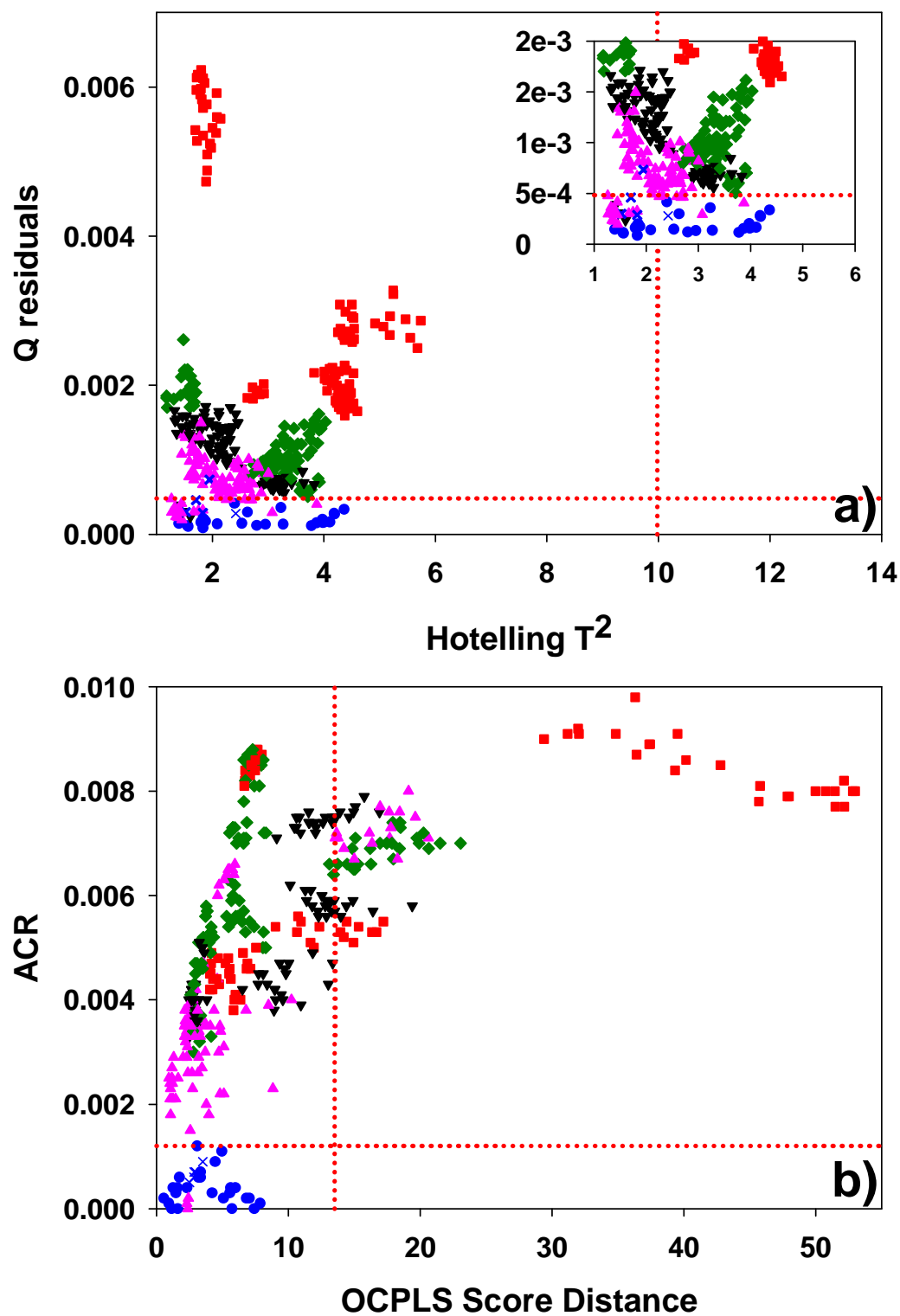


Fig. 3



Highlights

- FT-IR measurements were obtained for pure oils and adulterated chia and sesame oils.
- SIMCA and OC-PLS were performed as untargeted methods with an error of prediction below 5%.
- An adulteration proportion as low as 99+1 could be detected with minimum error of prediction.
- GC-FID explained the differences obtained by the FT-IR and untargeted methods for chia and sesame oil adulteration.

Conflict of interest statement

Silvio David Rodríguez, Maite Gagnetten, Abel E. Farroni and María del Pilar Buera declare to have no conflict of interest.

Ethical approval: This article does not contain any study with human participants or animals performed by any of the authors.

ACCEPTED MANUSCRIPT