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17 **Abstract**

18 This study examines the ability of fluorescence spectroscopy for monitoring the quality of 70
19 Moroccan virgin olive oils belonging to three varieties and originating from three regions of
20 Morocco. By applying principal component analysis and factorial discriminant analysis to the
21 emission spectra acquired after excitation wavelengths set at 270, 290, and 430 nm, a clear
22 differentiation between samples according to their storage time was observed. The obtained
23 results were confirmed following the application of four multivariate classification methods:
24 partial least squares regression, principal component regression, support vector machine, and
25 multiple linear regression on the emission spectra. The best prediction model of storage time
26 was obtained by applying partial least squares regression since a coefficient of determination
27 (R^2) and a root mean square error of prediction (RMSEP) of 0.98 and 24.85 days were
28 observed, respectively. The prediction of the chemical parameters allowed to obtain excellent
29 validation models with R^2 ranging between 0.98 and 0.99 for free acidity, peroxide value,
30 chlorophyll level, k_{232} , and k_{270} .

31

32 **Keywords:**

33 Fluorescence spectroscopy; Virgin olive oil; Freshness; Storage; Chemometric.

34

35 **Chemical compounds studied in this article:**

36 Acetic acid (PubChem CID: 176); Chloroform (PubChem CID: 6212), Cyclohexane
37 (PubChem CID: 8078); Diethyl ether (PubChem CID: 3283); Ethanol (PubChem CID: 702);
38 Phenolphthalein (PubChem CID: 4764); Potassium hydroxide (PubChem CID: 14797);
39 Potassium iodide (PubChem CID: 8475); Sodium thiosulfate (PubChem CID: 61501); Starch
40 solution (PubChem CID: 439341).

41

42 **1. Introduction**

43 Crude olive oil called virgin olive oil (VOO) is one of the well-consumed oil in the world
44 since it is consumed daily by the Mediterranean people in food as an ingredient, in different
45 culinary preparations, and raw with bread (Zaroual et al., 2019). Indeed, the excellent
46 organoleptic and nutritional properties of VOO make it the preferable and the most demanded
47 and consumed vegetable oil; this trend is confirmed by the increase of VOO production since
48 it passed from 1.4 to 3.2 million tonnes between 1990 and 2017 (COI, 2017).

49 Olive oil is produced only during the olive crop season that extends for two to three months
50 (October to December); thus, the producers and consumers kept VOO throughout the year
51 until the new season (Houlali et al., 2014). It is known that storage conditions, such as light
52 exposure and temperature, are the major factors that affects the chemical composition and
53 organoleptic parameters of VOO. Indeed, VOO is susceptible to oxidation that deteriorates its
54 quality (Sikorska et al., 2008).

55 The freshness state of VOO is of paramount importance for the consumer. In this context,
56 Pristouri et al., (2010) explored the use of free acidity (FA), peroxide value (PV), k_{232} , and
57 k_{270} parameters as indicators of VOO freshness level. The authors reported a significant
58 increase ($p < 0.05$) of these parameters determined on nine (9) VOO originating from the
59 Ionninna region (Greece) and kept during 12 months in different packaging (Transparent
60 glass, polyethylene, and polypropylene). Indeed, FA, PV, k_{232} and k_{270} passed, respectively,
61 from 0.63%, 12.92 meq O₂ kg⁻¹ oil, 2.25 and 0.14 to 0.83%, 18.86 meq O₂ kg⁻¹oil, 2.83 and
62 0.28 after 12 months of storage for samples kept at day-light. This increase impacted the
63 quality of VOO since it passed from the extra VOO class (FA ≤ 0.8%, PV ≤ 20 meq O₂ kg⁻¹
64 oil, $k_{232} \leq 2.50$ and $k_{270} \leq 0.22$) to lampante VOO class (FA > 3.3%, and no limit of PV, k_{232}
65 and k_{270}). Other parameters such as polyphenols and tocopherols, chlorophylls, and
66 carotenoids were suggested as indicators of the determination of the freshness level of VOO.

67 For instance, it was depicted that antioxidants and pigments decreased significantly during
68 storage of VOO, particularly, during their exposure to light (Esposito et al., 2017) and high
69 temperature (Silva et al., 2010). Morelló et al., (2004) found that α -tocopherol amounts
70 disappeared completely after VOO storage for 12 months. Indeed, polyphenol and chlorophyll
71 levels decreased significantly from 350.15 and 18 mg kg⁻¹ oil on days 7 to 48.5 and 7 mg kg⁻¹
72 oil after 12 months of storage, respectively. One of the main conclusions of this study was
73 that tocopherol levels could be considered as an effective antioxidant in the oxidation
74 induction period. In a similar approach, Méndez et al., (2007) reported an increase of stearic
75 acid and a decrease of oleic acid levels of 4 commercial VOO during storage in different
76 conditions (covered and transparent plastic, glaze and tetra brick aseptic bottles at 20-22 °C)
77 since they passed from 4.1 to 4.7% and from 76.3 to 73.3%, respectively, after 6 months of
78 storage. The most above-mentioned methods applied for quality determination of olive oil are
79 time-consuming, labour-intensive, require the use of high purity hazardous organic solvents,
80 and are not suitable for on-site analysis. Thus, new emerging techniques such as mid infrared
81 (Sinelli et al., 2007), near infrared (Casale & Simonetti, 2014), ultraviolet-visible (Lazzerini et
82 al., 2016), fluorescence, and so on, were used to determine the quality of olive oil during
83 storage. For example, synchronous fluorescence spectroscopy was used to monitor the quality
84 of 12 extra VOO samples in different storage conditions (dark, green, and clear glass bottles
85 exposed to daylight at 25 °C) (Sikorska et al., 2008). By applying principal component
86 analysis (PCA) to the emission spectra data recorded after excitation set at 290 nm, the
87 authors succeeded to differentiate between VOO according to their storage time and
88 condition. Recently, El Orche et al., (2020) accomplished to discriminate 27 VOO samples of
89 Moroccan Picholine variety originating from the Beni-Mellal/Khenifra region (Morocco)
90 according to their storage time. By applying a series of chemometric tools such as partial least
91 squares discriminant analysis (PLS-DA), linear discriminant analysis (LDA), and support

92 vector machine classification (SVM) on the data sets, 100% of correct classification was
93 obtained.

94 As already mentioned above, most of the research studies that explored fluorescence
95 spectroscopy coupled with chemometric tools for the determination of the quality of olive oil
96 during storage were performed on VOO purchased from a local supermarket without taking
97 into account the agronomic and industrial conditions of the olive oil (Méndez & Falqué,
98 2007).

99 To the best of our knowledge, no work has been reported on olive oil aging by taking into
100 account the impact of the geographic origin, variety, agronomic conditions, and extraction
101 mode. Thus, this study aimed to investigate the potentiality of front-face fluorescence
102 spectroscopy (FFFS) to: i) monitor the quality of 70 VOO belonging to 3 varieties (Moroccan
103 Picholine, Languedoc Picholine, and Arbequina) and originated from 3 regions of Morocco
104 (Fez/Meknes, Marrakech/Safi, and Eastern regions) during 18 months; and ii) predict their
105 chemical parameters (FA, PV, k_{232} , k_{270} , and chlorophyll level). To extract information
106 contained in the data sets, PCA, factorial discriminant analysis (FDA), principal component
107 regression (PCR), partial least squares regression (PLSR), support vector machine regression
108 (SVMR), and multiple linear regression (MLR) were applied. This kind of investigation is
109 necessary since the freshness of olive oil has become an urgent issue for producers,
110 researchers, governments, and consumers due to the increase of falsification of fresh VOO by
111 aged one and/or other oils of low quality inducing the loss of the consumer confidence.

112

113 **2. Materials and methods**

114 **2.1. Sampling**

115 Seventy (70) VOO peaked up during the crop season of 2015-2016 from 3 regions
116 (Fez/Meknes, Eastern, and Marrakech/Safi) in Morocco. The olives were irrigated by 3 modes

117 (rainwater, ponds, and dropping) and fertilised by traditional and modern modes. The VOO
118 samples belong to 3 varieties (Moroccan Picholine, Languedoc Picholine, and Arbequina) and
119 were extracted by 3 process modes (pressing discontinuous, three-phase, and two-phase
120 continuous systems) (**Table 1**).

121 Each VOO was kept in 50 mL sealed clear glass bottles, at room temperature (20 °C), and
122 exposed to daylight for 18 months.

123

124 **2.2. Chemical and colorimetric analyses**

125 The FA and PV are determined according to the official method of the International Olive Oil
126 Council under the code COI/T.20/Doc. N°34 and COI/T.20/Doc. N°35, respectively. The
127 k_{232} and k_{270} parameters are obtained according to the official method under the code
128 COI/T.20/Doc. N°19 (COI, 2016).

129 The level of chlorophyll, performed according to the method of Wolff (1968), is calculated
130 using the formula indicated below:

$$\text{Chlorophyll (mg kg}^{-1}\text{ oil)} = \frac{A_{670} - (A_{630} + A_{710})/2}{0.1086}$$

131 Where A_{630} , A_{670} , and A_{710} is the absorbance at 630, 670, and 710 nm, respectively.

132 To assess the oil colour, the Minolta Chroma Meter version CR-300 (Konica Minolta Sensing
133 Europe, Roissy Charles De Gaulle, France) was used. Olive oil samples were examined
134 without dilution to avoid colour variation and the oil colour is expressed as chromatic
135 ordinates L^* (lightness), a^* (redness), and b^* (yellowness) (Becerra-Herrera et al., 2018).

136 All the chemical and colorimetric analyses were made in triplicate.

137

138 **2.3. Fluorescence spectroscopy**

139 Fluorescence spectra were recorded using a Fluoromax-4 spectrofluorimeter (Jobin Yvon,
140 Horiba, NJ, USA) at 20 °C. The incidence angle of the excitation radiation was set at 60° to

141 ensure that reflected light, scattered radiation, and depolarisation phenomena were minimised
142 (Karoui et al., 2008).

143 For each VOO sample, 3 mL were poured in a quartz cuvette and fluorescence spectra were
144 recorded. The emission spectra of polyphenols (290-450 nm), tocopherols (305-450 nm), and
145 chlorophylls (450-800 nm) were acquired with the excitation wavelength set at 270, 290, and
146 430 nm, respectively. For each storage time (7 days, 3, 6, 12, and 18 months), three spectra
147 were acquired with different VOO samples.

148

149 **2.4. Statistical analysis**

150 Fluorescence spectra were normalised by reducing the area under each spectrum to a value of
151 1 to reduce scattering effects to compare VOO samples (Blecker et al., 2012). The principal
152 component analysis (PCA) was applied, separately, to the chemical, colorimetric, and
153 fluorescence data sets.

154 To improve the discrimination between VOO samples, factorial discriminant analysis (FDA)
155 was performed on the first 5 principal components (PCs) of the PCA. Before applying the
156 FDA with leave-one-out cross-validation, 5 groups corresponding to the storage time groups
157 (7 days, 3, 6, 12, and 18 months) were created.

158 Finally, the ability of fluorescence spectroscopy to predict the storage time and chemical
159 parameters was assessed by applying different chemometric methods namely PLSR, MLR,
160 PCR, and SVMR. The objective of this task was to determine the best regression model
161 allowing us to determine the chemical and age of VOO samples.

162 The 210 spectral measurements were divided into two groups of 188 and 22 spectra. The
163 former group was used for the establishment of the calibration models, whereas the latter
164 group was utilised for the validation of the established models. The first group (188 spectra)
165 designated as a calibration set and representing VOO samples belonging to the different

166 storage time was used. The calibration equation was determined for each parameter. The
167 robustness of the model was evaluated by determining the coefficient of determination (R^2),
168 root mean square error of calibration (RMSEC) and root mean square error of prediction
169 (RMSEP) (Zaroual et al., 2020a).

170 To validate the calibration, an independent set of 22 samples, representing all VOO storage
171 times were randomly selected from all sets representing the different class quality of VOO.

172 The PLSR, PCR, MLR, and SVMR were performed using The Unscramble X (V.10.4, Camo
173 Software AS, Oslo, Norway) software, while PCA and FDA were performed using MATLAB
174 (Version 6.5, Release 12, The MathWorks), and XLSTAT 2016 (Addinsoft SARL USA, New
175 York, NY, USA) software, respectively.

176

177 **3. Results and discussions**

178 **3.1. Chemical and colorimetric parameters of VOO during storage**

179 The chemical parameters (FA, PV, k_{232} , and k_{270}) of VOO samples determined on days 7
180 showed clear differences between samples ($P < 0.05$) (**Table 1**). Indeed, out of 14 samples, 9
181 samples are classified as EVOO, 4 as VOO, and 1 sample as lampante VOO. This could be
182 due to the difference in the maturity degree of olive fruit, the harvesting conditions, and/or
183 the extraction system (Bajoub et al., 2014).

184 The FA, PV, k_{232} , and k_{270} increased significantly ($p < 0.05$) during storage (**Table 1**). Indeed,
185 FA ranging between 0.21 and 1.64% on days 7 reached 6.52% after 18 months of storage.

186 These findings could be explained by the lipolysis of triglycerides that induce the liberation of
187 free acids. Indeed, olive fruits contain endogenous lipase enzymes that, although isolated from
188 the oil in intact fruit, react with the triacylglycerols just after crushing causing the production
189 of free fatty acids (Ayton et al., 2012). Our findings are in agreement with Iqdiam et al.,
190 (Iqdiam et al., 2020) who reported that light and storage time increased the FA level of olive

191 oil; the authors reported an increase of FA from 0.32 on days 7 to 0.99% after 12 months of
192 storage in a glass bottle at room temperature (25-28°C).

193 The PV, k_{232} , and k_{270} increased, likewise, during storage since they passed, mostly, from less
194 than 9.68 meq O₂ kg⁻¹ oil, 1.93 and 0.17 on days 7 to 24.65 meq O₂ kg⁻¹ oil, 3.07 and 0.31,
195 respectively, after 18 months of storage (**Table 1**). The increase of these parameters could be
196 explained by the oxidation of fatty acids that induce the formation of peroxides (Eymard,
197 2003). Furthermore, the oxidation reactions conduct to the formation of either carbon-carbon
198 bonds or carbon-oxygen bonds which cause an increase of absorption in the spectral region
199 between 225 and 325 nm, and for consequent the increase of both k_{232} and k_{270} values as
200 depicted by Ayton et al., (2012).

201 The samples originating from the high altitude of Fez/Meknes region (Bhalil zone) exhibited
202 the highest values of FA=6.52%, PV=24.65 meq O₂ kg⁻¹ oil, k_{232} =2.8, and k_{270} = 2.8 after 18
203 months of storage, while those belonging to low altitude orchards of Marrakech/Safi region
204 (Chiadma) showed the lowest values (FA=3.09%, PV=15.09 meq O₂ kg⁻¹ oil, k_{232} =2.41, and
205 k_{270} =0.26). These findings were in line with those of Houlali et al., (2014) who pointed out
206 that the FA of VOO samples (2%) aged less than 30 days and belonging to the plain region
207 were significantly lower than those originating from the piedmont and mountain (2.7 and
208 2.6%, respectively).

209 With respect to the extraction system, VOO samples extracted by using a three-phase system
210 are more oxidized than those extracted by pressing and a two-phase system. For instance,
211 after 18 months of storage of VOO belonging to Sefrou (Fez/Meknes region), the high values
212 of FA, PV, k_{232} , and k_{270} were ascribed to the samples extracted by a three-phase system
213 (3.88%, 17.92 meq O₂ kg⁻¹ oil, 2.29 and 0.31, respectively) followed by the pressing system
214 samples (2.77%, 12.86 meq O₂ kg⁻¹ oil, 2.12 and 0.25, respectively). VOO samples extracted
215 with a two-phase system are the most resistant to the oxidation and lipolysis since values of

216 1.21%, 8 meq O₂ kg⁻¹ oil, 2.14 and 0.19 of FA, PV, k₂₃₂, and k₂₇₀, respectively, were observed
217 after 18 months of storage. These findings are in agreement with Gimeno et al., (2002) who
218 pointed out that VOO samples obtained by a two-phase extraction system are resistant to
219 oxidation, contrary to those obtained with three-phase system. This could be due to the fact
220 that the latter system needs the use of water having a temperature higher than 35 °C during
221 olive dough mixing, which induce solubilisation of a part of polyphenols and vitamin E in
222 vegetation water (Zielinska & Nowak, 2014).

223 With respect to the chlorophyll level, the differences observed between VOO on days 7 could
224 be explained by the dissimilarity in irrigation, fertilisation, and particularly, extraction system
225 (Tamborrino et al., 2019). For instance, chlorophyll levels of VOO samples on days 7 ranged
226 between 1.22 and 5.64 mg kg⁻¹ oil, in agreement with the findings of Tanouti et al., (2011)
227 who observed chlorophyll levels in the 0.29-5.21 mg kg⁻¹ oil for 47 VOO aged less than 7
228 days. The amount of chlorophyll observed in the present study was less than 10 mg kg⁻¹ oil
229 avoiding their pro-oxidative action and thus ensuring a good preservation of olive oil during
230 storage (Trypidis et al., 2019).

231 During storage, VOO chlorophyll level decreased gradually since up to 50% of chlorophyll
232 level disappeared after only 6 months of storage, in agreement with the findings of Rigane et
233 al., (2013) who observed that the chlorophyll level decreased up to 90 % after 180 days of
234 storage. According to Giuliani et al., (2011), the decrease in the green pigments during the
235 storage is due to the activation of the lipoxygenase activity which catalyses the formation of
236 hydroperoxides leading to the oxidation of the green pigments of the drupe (bleaching) by
237 means of a co-oxidation mechanism.

238 The colour of VOO represents one of the main factors that influence the perception of quality
239 by consumers. **Table 1** showed the evolution of L*, a*, and b* parameters. By comparing
240 Sefrou (Fez/Meknes region) VOO samples, it seemed that the extraction system affected

241 significantly the colour since values of VOO extracted by pressing ($L^*=25.47$, $a^*=3.02$ and
242 $b^*=38.41$), a two-phase ($L^*=33.50$, $a^*=0.02$ and $b^*=46.50$) and a three-phase ($L^*=30.04$,
243 $a^*=2.66$ and $b^*=28.18$) systems were observed. Indeed, Giuliani et al., (2011) reported that
244 the type of the extraction system affects, considerably, the green pigments (chlorophyll A and
245 B) of VOO, which results in the variation of its colour.

246 The L^* and b^* decreased significantly ($p<0.05$) during storage, while a^* increased during the
247 first 6 months of storage and decreased after (**Table 1**). The decrease of the L^* and b^* values
248 during storage could be explained by the reduction of chlorophyll level in VOO as reported by
249 Cerretani et al., (2008). Indeed, the authors pointed out that an excellent correlation, with R^2
250 ranging between 0.95 and 0.97, was observed between L^* and b^* values and chlorophyll and
251 carotenoid levels.

252

253 **3.2. Fluorescence measurements**

254 **3.2.1. Emission fluorescence spectra recorded on VOO samples after excitation set at** 255 **430 nm**

256 Galeano-Díaz et al., (2003) reported that the excitation wavelength of chlorophylls is about
257 430 nm. **Figure 1a** shows the evolution of the emission fluorescence spectra recorded on
258 Moroccan Picholine VOO samples originated from Tafrata (Eastern region) and extracted by
259 a three-phase system during 18 months of storage. Fresh VOO samples aged 7 days, exhibited
260 two fluorescence intensity (FI) maxima located ~ 659 nm and 728 nm that could be attributed
261 to chlorophyll B and chlorophyll A, respectively (Zaroual et al., 2020b). The samples, stored
262 for 18 months, exhibited the highest FI ~ 686 that could be linked to the overlapping of
263 pheophytins A and B and the lowest FI at 728 nm attributed to chlorophyll A. The maximum
264 that appeared at 659 nm on days 7 shifted to ~ 670 nm on months 3 and 6 (**Figure 1a**). The

265 differences between spectra sharps could be explained by the transformation of chlorophyll A
266 and B to pheophytins A and B, respectively (Gandul-Rojas et al., 2000).

267 A similar trend was observed for VOO extracted by pressure system and belonging to the
268 same region (**Figure 1b**). Indeed, during storage the peak located ~ 654 nm linked to
269 chlorophyll B disappeared, while the FI observed ~734 related to chlorophyll A decreased.
270 The FI of maxima located ~695 and 666 nm linked to pheophytin A and B increased during
271 storage. A similar trend was also observed for VOO belonging to Arbequina and Languedoc
272 Picholine varieties.

273

274 **3.2.2. Emission fluorescence spectra recorded on VOO samples after excitation set at** 275 **290 nm**

276 **Figure 1c** shows the emission spectra acquired after excitation set at 290 nm of Moroccan
277 Picholine variety VOO originating from Chyadma (Marrakech/Safi region) and extracted by a
278 pressure system. It is clearly shown that the highest FI observed ~ 342 was noted for samples
279 on days 7, while the lowest ones are observed for those aged 18 months. This trend could be
280 ascribed to the difference in the tocopherol levels that decreased during storage as depicted by
281 Esposto et al., (2017) since fresh VOO aged less than 7 days had 250 mg kg⁻¹ and achieved 0
282 - 2 mg kg⁻¹ range after 12 months of storage. It could be also observed that ~ 438 nm, samples
283 aged 18 months exhibited the highest FI, while those aged 7 days noted the lowest FI
284 indicating the formation of the secondary oxidation products, in line with the findings of Tan
285 et al., (2017). From the obtained results, it could be concluded that the maximum observed ~
286 438 nm could be used as a marker of the oxidation level of VOO, in agreement with the
287 findings of Poulli et al., (2009) who pointed that the secondary oxidation products could be
288 excited at 290 nm with emission in the 400-500 nm range. These observations are in line with
289 the evolution of k_{270} that increased during storage since it passed from 0.17 on days 7 to 0.31

290 after 18 months of storage (**Table 1**). Similar results were obtained for the other VOO
291 varieties (**data not shown**). It could be concluded that emission spectra acquired after
292 excitation set at 290 nm could be used as fingerprint tool to monitor the quality of VOO
293 during their storage.

294

295 **3.2.3. Emission fluorescence spectra recorded on VOO samples after excitation set at** 296 **270 nm**

297 Polyphenols was used as a marker to trace the aging of VOO since they are influenced by
298 several factors such as packaging (Méndez & Falqué, 2007), light exposer (Esposito et al.,
299 2017), and heating (Silva et al., 2010). Galeano-Díaz et al., (2012) pointed out that vanillic
300 acid, syringic acid, gallic acid, p-coumaric acid, cinnamic acid, Tyrosol, o-coumaric acid, and
301 caffeic acid are the most known fluorescent phenolic compounds with the excitation
302 wavelength set at 270 nm. **Figure 1d** shows polyphenols fluorescence emission spectra
303 acquired on VOO samples originating from Eastern region (Tafrata zone) of Languedoc
304 Picholine variety extracted by a pressure system. The emission spectra presented two maxima
305 located ~ 375 and 442 nm. From **Figure 1d**, it is clearly shown that the highest FI ~ 375 nm
306 was observed for samples aged 7 days, 3, and 6 months, while the lowest FI was noted for
307 samples aged 18 months. The decrease of fluorescence intensity during storage could be
308 explained by the degradation of polyphenols that act as antioxidant against VOO oxidation
309 as depicted by Esposito et al., (2017) since the authors observed that after 165 days of olive
310 oil storage, polyphenol level passed from 1512 to 392 mg kg⁻¹ oil.

311 An inverse trend was observed ~442 since the highest fluorescence intensity was observed for
312 samples aged 18 months, while the lowest one was noted for samples aged 7 days. This
313 difference could be explained by the increase of oxidation product amounts during storage as
314 depicted by Tan et al., (2017).

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3.3. Discrimination based on the fluorescence spectra recorded on VOO samples

In order to extract information from the emission spectra acquired after excitation set at 270, 290, and 430 nm, PCA was applied, separately, to the normalised data sets. The similarity maps allowed a slight differentiation of VOO samples according to their storage time (Data not shown).

In a second step, FDA with leave-one-out cross-validation was performed on the 5 PCs of the PCA applied to each emission spectra. Before applying the FDA, 5 groups were defined corresponding to the storage time of VOO regardless of the other parameters (variety, geographic origin, crop season, agronomic factors, and extraction system): 7 days, 3 months, 6 months, 12 months, and 18 months. The similarity map defined by the two first discriminant factors (FD1 and FD2) of the FDA of the PCA applied on emission spectra acquired after excitation set at 430 allowed to discriminate VOO samples according to their storage time (**Figure 2a**). VOO aged 7 days and 3 months presented positive scores on FD1, while the others exhibited negative values. In addition, each group was separated from the others. An overall correct classification rate achieving 89.52% was observed (**Table 2a**). Indeed, VOO samples stored for 18 months were 100% correctly classified. Out of 42 samples aged 12 months, 2 samples were classified as belonging to the group aged 18 months giving a correct classification rate of 95.23%. Regarding samples aged 7 days, 6 samples were ascribed to samples aged 3 months. Out of 42 samples aged 3 months, 5 samples and 3 others were attributed to VOO aged 7 days and 6 months giving an overall correct classification of 83.33%.

339 The FDA applied to the 5 first PCs of the PCA performed on emission spectra acquired after
340 excitation set at 290 allowed a clear classification of VOO samples according to their storage
341 time (**Figure 2b**). Indeed: i) fresh samples aged 7 days presented positive values according to
342 the FD1 and FD2; ii) those aged 3 months exhibited positive and negative values according to
343 the FD1 and FD2, respectively; iii) VOO samples aged 12 months presented negative scores
344 according to the FD1 and FD2; and iv) VOO samples kept during 18 months presented
345 negative scores and mostly positive scores according to the F D1 and FD2, respectively. VOO
346 samples aged 6 months were close to the origin.

347 Correct classification amounting to 79.05% was observed with 95.29% and 80.95% of correct
348 classification for VOO aged 18 months and 7 days, respectively (**Table 2a**). The worst
349 classification was observed for VOO samples of 3 months since out 42 samples, 14 samples
350 were misclassified: 11 as belonging to samples aged 7 days and 3 others were attributed to
351 samples aged 6 months.

352 The similarity map of the FDA performed on emission spectra acquired after excitation set at
353 270 nm allowed some discrimination of samples according to their storage time. Indeed, only
354 fresh samples aged 7 days were well differentiated from those aged 18 months. The other
355 groups were overlapped on the map (data not shown). This trend was confirmed by the correct
356 classification rate since only 61.90% of correct classification was observed (**Table 2a**). The
357 worst correct classification was observed for samples aged 18 and 6 months with only 45.24%
358 and 52.38% of correct classification, respectively.

359 The data sets obtained from different fluorophores may give more information about the
360 freshness level of VOO samples when analysed jointly. Thus, FDA was applied to the first 5
361 PCs of the PCA performed to the emission spectra acquired after excitation set at 290 and 430
362 nm, since only 61.9% of correct classification was observed with excitation spectra set at 270
363 nm. The similarity map defined by the discriminant factors 1 and 2 accounting for 96.97% of

364 the total variance allowed clear separation of VOO samples according to their storage time
365 (**Figure 2c**). VOO samples aged 7 days and 3 months were located on the negative side of the
366 FD1, while the others presented mostly positives scores of the first discriminant factor. A
367 correct classification rate of 96.18% was observed with 100% of correct classification for
368 samples aged 7 days and 18 months. VOO aged 3, 6, and 12 months presented 95.21, 97.61,
369 and 88.09% of correct classification, respectively (**Table 2a**). These results are in line with
370 the findings of El Orche et al., (2020) who succeeded (100% of correct classification) to
371 discriminate 27 VOO samples of Moroccan Picholine variety originating from the Beni-
372 Mellal/Khenifra region according to their storage time (0, 12 and 24 months) by applying
373 PCA-LDA on laser conducted fluorescence spectra recorded after excitation set at 400 nm.

374

375 **3.4. Prediction of VOO storage time and chemical properties**

376 In order to establish calibration models for each excitation wavelength, four different
377 regression methods were separately used and their predictive abilities were compared. A
378 summary of the predictive performance of models developed for the determination of storage
379 time, FA, PV k_{232} , k_{270} and chlorophyll level is shown in **Table 2b**.

380

381 **3.4.1. Prediction of VOO storage time**

382 By using colorimetric parameters and according to the R^2 , the prediction of storage time can
383 be considered excellent by applying SVMR since R^2 of 0.95 and RMSEP=46.77 (**Figure 3a;**
384 **Table 2b**) days are obtained. The values of R^2 and RMSEP for the PCR model were 0.89 and
385 64.06 days, respectively; The MLR and PLSR gave approximate values of R^2 (0.77 and 0.64,
386 respectively). It could be concluded that applying SVMR builds better prediction models than
387 PLSR, MLR, and PCR. These results confirmed that applying non-linear regression model
388 tools such as SVMR on non-linear data sets (storage time) allow building a better prediction

389 model compared to linear model regression tools (PLSR and PCR) as depicted out by Thissen
390 et al., (2004).

391 Regarding fluorescence spectra, the excellent prediction was obtained with the excitation
392 wavelength set at 270, 290, and 430 nm (**Figure 3b; Table 2b**) with R^2 of 0.92, 0.97, and
393 0.98 and RMSEP of 53.78, 30.8, and 24.85 days, respectively. The application of PCR to the
394 emission spectra acquired after excitation set at 290 nm gave an excellent prediction of
395 storage time since R^2 and RMSEP of 0.97 and 29.50 days were observed, respectively. The
396 best result obtained with MLR was observed with the emission spectra recorded after
397 excitation set at 290 nm since a good prediction of storage time was observed ($R^2=0.88$;
398 RMSEP=88.44 days).

399 Comparatively, the results showed that PLSR (linear model regression tool) gave the best
400 predictive model of storage time basing on linear spectral data, in agreement with: i) Wei et
401 al., (2017) who reported that the PLSR should be the first choice for the prediction of storage
402 time of yogurt compared to SVMR. These results show that quantitative supervised
403 classification methods such as PLSR and PCR are more efficient than qualitative ones (FDA)
404 to build a robust predictive model of VOO storage duration.

405

406 **3.4.2. Prediction of free acidity**

407 Regarding the prediction of FA, the emission spectra recorded after excitation set at 430 nm
408 allowed an excellent prediction by applying PLSR ($R^2=0.99$; RMSEP=0.05%) (**Figure 4a;**
409 **Table 2b**) and PCR ($R^2=0.98$; RMSEP=0.12%) confirming the findings of Guzmán et al.,
410 (2015) who succeeded to predict FA ($R^2 = 0.93$; RMSEP = 1.77%) by applying PLSR on 90
411 VOO samples collected during 2010-2011 crop season. These results showed that excitation
412 at 430 nm could be used to monitor the quality of VOO during storage since they could be
413 used to predict the FA value. An only good and approximate prediction were obtained,

414 respectively, by applying SVMR ($R^2=0.82$ and $RMSEP= 0.42\%$) and MLR ($R^2=0.73$;
415 $RMSEP=0.84\%$) to the emission spectra recorded after excitation set at 430 nm. These results
416 were in agreement with those of Talpur et al., (2014) who pointed out that PLSR ($R^2=0.99$;
417 $RMSEP=0.03\%$) performed the best predictive model of FA of cottonseed oil compared to
418 PCR ($R^2=0.99$; $RMSEP=0.07\%$) and MLR ($R^2=0.90$; $RMSEP=0.18\%$).

419

420 **3.4.3. Prediction of peroxide value**

421 The emission spectra recorded after excitation set at 290 nm allowed an excellent prediction
422 of PV ($R^2=0.98$; $RMSEP=0.32$ meq O_2 kg^{-1} of oil) by applying PLSR (**Figure 4b**; **Table 2b**)
423 which confirm the results of Guzmán et al., (2015) who succeeded to predict PV of 90 VOO
424 samples since $R^2=0.96$ and $RMSEP = 8.17$ meq O_2 kg^{-1} oil were obtained by applying PLSR.
425 The obtained results could be explained by the fact that tocopherols, as antioxidant, are
426 inversely relative to PV that is one of oxidation parameter as depicted out by Bajoub et al.,
427 (2015), which uphold the results obtained in **Figure 1c**. An only good prediction of PV was
428 obtained after the application of MLR ($R^2=0.81$, $RMSEP= 1.85$ meq O_2 kg^{-1} oil) and SVMR
429 ($R^2=0.82$, $RMSEP= 1.97$ meq O_2 kg^{-1} oil) to the emission spectra acquired after excitation set
430 at 430 and 270 nm, respectively. The best results obtained from PCR allowed to give
431 approximate prediction of PV from the emission spectra acquired after excitation set at 430
432 nm ($R^2=0.74$, $RMSEP= 1.89$ meq O_2 kg^{-1} oil). From the obtained results, it could be
433 concluded that the model obtained after the application of PLSR to the emission spectra
434 recorded after excitation set at 290 nm could be used for the prediction of PV of VOO. These
435 results confirmed those obtained in **Figure 1c**, where an increase in the FI ~440 was observed
436 during the storage of VOO.

437

438 **3.4.4. Prediction of k_{232} and k_{270}**

439 Excellent prediction of k_{232} ($R^2=0.99$; $RMSEP=0.01$) (**Figure 4c**; **Table 2b**) and k_{270}
440 ($R^2=0.98$; $RMSEP=0.01$) (**Figure 4d**; **Table 2b**) were obtained from the emission spectra
441 recorded after excitation set at 290 nm by applying PLSR, in agreement with the results of
442 Guzmán et al., (2015) who succeeded to predict k_{232} ($R^2=0.9$; $RMSEP = 0.37$) and k_{270}
443 ($R^2=0.97$; $RMSEP = 0.06$) by applying PLSR on 90 VOO samples collected during 2010-
444 2011 crop season. These results confirmed those obtained in **Figure 1c**, where an increase in
445 the FI ~440, related to the formation of oxidation products, was observed during the storage
446 of VOO. A very bad prediction of k_{232} was obtained by applying MLR and PCR to the
447 different emission spectra sets (R^2 ranging between 0.04 and 0.15); while, as for the
448 prediction of k_{270} , good results were obtained by applying SVMR on the emission spectra
449 recorded after excitation set at 270 and 430 nm with R^2 of 0.87 and 0.88, respectively.

450

451 **3.4.5. Prediction of chlorophyll level**

452 Colorimetric parameters allowed to predict, perfectly, the chlorophyll level since excellent
453 values of R^2 (0.99) and $RMSEP$ ($0.09 \text{ mg kg}^{-1} \text{ oil}$) were obtained by applying SVMR (**Figure**
454 **4e**; **Table 2b**). Furthermore, excellent and good models were obtained by applying PCR,
455 MLR, and PLSR with R^2 of 0.98, 0.83, and 0.83, respectively. These results confirmed that
456 colorimetric parameters are strongly linked to pigment levels, in agreement with: i) Moyano
457 et al., (2008) who succeeded to predict the chlorophyll level by applying MLR to
458 colorimetric parameters since values of $R^2 > 0.9$ were obtained; and ii) Cerretani et al., (2008)
459 who pointed out a high correlation (R^2 ranging between 0.95 and 0.97) between colorimetric
460 parameters (L^* and b^*) and chlorophyll and carotenoid levels by applying PLSR.

461 The emission spectra recorded after excitation set at 430 nm allowed an excellent prediction
462 of chlorophyll level after applying PLSR ($R^2=0.98$; $RMSEP=0.16 \text{ mg kg}^{-1} \text{ of oil}$) and PCR
463 ($R^2=0.92$; $RMSEP=0.34 \text{ mg kg}^{-1} \text{ oil}$). These results are in agreement with Sikorska et al.,

464 (2008) who succeeded to predict chlorophyll level ($R^2 = 0.99$; RMSEP = 1.4 mg kg⁻¹ oil) by
465 applying PLSR on synchronous fluorescence spectra of 12 extra VOO stored for 7 days, 3, 6
466 and 12 months.

467

468 **Conclusion**

469 To our best knowledge, this study is the first one assessing the potential of FFFS to predict the
470 quality of VOO stored for 18 months using different regression chemometric tools. In the
471 present study, the determination of the quality of VOO stored up to 18 months in light was
472 performed by using FFFS, chemical and colorimetric methods. The emission spectra with
473 classification methods named FDA, PLSR, MLR, and SVMR were applied. Although data
474 collection needs the establishment of a robust model to predict the chemical and storage time
475 of VOO, the excitation wavelength set at 290 and 430 nm showed their ability to classify
476 VOO according to their freshness level, regardless of the geographic origin, variety,
477 fertilisation, and irrigation modes. As for the prediction of VOO aging, the chemical and
478 colorimetric parameters coupled with SVMR allowed an excellent prediction model since R^2
479 and RMSEP of 0.95 and 46.77 days were obtained, respectively. The application of PLSR to
480 the emission spectra acquired after excitation set at 430 nm demonstrated, also, its high
481 capability to predict the aging of VOO with $R^2=0.98$ and RMSEP=24.85 days. These findings
482 are also strengthened following the evaluation of the effectiveness of FFFS to predict some
483 chemical parameters of VOO. Indeed, the validation models obtained after the application of
484 PLSR and PCR to the different emission spectra allowed obtaining R^2 of 0.99, and 0.98 for
485 the prediction of FA and chlorophyll level with the excitation set at 430 nm; and R^2 of 0.98,
486 0.99, and 0.98 for PV, k_{232} , and k_{270} with the excitation wavelengths set and 290 nm. It was
487 concluded that PLSR and PCR could be considered as more efficient tools than SVMR and
488 MLR for the prediction of some chemical parameters of VOO.

489 It could be concluded that fluorescence spectroscopy as a fast and ecological method would
490 be useful for the monitoring of the quality of VOO during storage and to determine its
491 freshness level. However, the work reported here is only a preliminary study and further
492 studies using a large number of different VOO varieties and from different geographic origins
493 are required to provide robust models. The simplicity of the method offers rich opportunities
494 for the monitoring of VOO freshness at a very low cost.

495

496 **Declaration of competing interest**

497 The authors declare that they have no known competing financial interests or personal
498 relationships that could have appeared to influence the work reported in this paper.

499

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506

507

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665

666 **Tables captions:**

667 **Table 1:** Chemical and colorimetric parameters determined on VOO samples during 18
668 months of storage.

669

670 **Table 2:** (a) Classification table of factorial discriminant analysis (FDA) with leave-one-out
671 cross validation of VOO samples according to their storage time; and (b) Cross-validation
672 results of the storage time and the overall chemical parameters using partial least squares
673 regression (PLSR), principal component regression (PCR), support vector machine regression
674 (SVMR), and multiple linear regression (MLR) of the calibration and validation models.

675

676

677 **Figure captions:**

678 **Figure 1:** Normalised emission spectra acquired after excitation set at 430 nm of Moroccan
679 Picholine VOO originating from Tafrata (Eastern region) extracted by: (a) three-phase system
680 and (b) pressure; (c) normalized emission spectra acquired after excitation set at 290 nm of
681 VOO according to their storage time of Moroccan Picholine VOO originated from Chyadma
682 (Marrakech/Safi region) extracted by pressure; and (d) normalized emission spectra acquired
683 after excitation set at 270 nm of VOO according to their storage time of Moroccan Picholine
684 VOO originated from Ain Aicha (Fez/Meknes region) extracted by pressure.

685
686 **Figure 2:** Discriminant analysis similarity map determined by FD1 and FD2 of the FDA
687 performed on emission spectra acquired after excitation set at: (a) 430 nm, (b) 290 nm, and
688 (c) the concatenated emission spectra acquired after excitation set at 430 and 290 nm of VOO
689 samples stored during 7 days (◆), 3 months (■), 6 months (●), 12 months (○) and 12 months (⊕).

690
691 **Figure 3:** Scatter plot of measured versus predicted of storage time with full-cross validation
692 after applying: (a) support vector machine regression (SVMR) on chemical and colorimetric
693 parameters data; and (b) partial least square regression (PLSR) on the emission spectra
694 acquired after excitation set at 430 nm.

695
696 **Figure 4:** Scatter plot of measured versus predicted of : (a) free acidity; (b) peroxide value; (c)
697 k_{232} ; and (d) k_{270} of VOO samples with full-cross validation after applying partial least square
698 regression (PLSR); and (e) chlorophyll levels after applying support vector machine
699 regression (SVMR) on colorimetric parameters data.

700

701 **Table 1**

Region	Marrakech/ Safi	Fez/Meknes						Eastern						
zone	Chyadma	Ain Taoujdat	Bhalil	Sidi Moukhfi	Sefrou		Ain Aicha	Tafrata						
Extraction system	Pressing	Pressing	Three- phase	Pressing	Two- phase	Pressing	Three- phase	Pressing	Pressing		Three- phase	Pressing		
Variety	Moroccan Picholine											Languedoc Picholine	Arbequina	
Free acidity (%)														
7 days	1.58 ± 0.004	1.64 ± 0.007	1.57 ± 0.006	1.26 ± 0.06	0.31 ± 0.008	0.47 ± 0.027	0.37 ± 0.011	0.9 ± 0.012	0.21 ± 0.008	0.27 ± 0.015	0.71 ± 0.041	0.22 ± 0.004	0.4 ± 0.018	0.36 ± 0.015
	1.91 ± 0.018	1.86 ± 0.015	1.9 ± 0.006	1.45 ± 0.002	0.37 ± 0.001	0.62 ± 0.012	0.61 ± 0.041	1.02 ± 0.006	0.24 ± 0.001	0.43 ± 0.008	0.83 ± 0.021	1.19 ± 0.011	0.52 ± 0.027	0.5 ± 0.008
3 months	2.39 ± 0.004	2.18 ± 0.007	2.38 ± 0.006	1.72 ± 0.06	0.46 ± 0.008	0.85 ± 0.004	0.95 ± 0.008	1.19 ± 0.012	0.28 ± 0.008	0.56 ± 0.015	1 ± 0.06	1.4 ± 0.004	0.62 ± 0.015	0.7 ± 0.015
	2.51 ± 0.003	4 ± 0.007	5.12 ± 0.002	3.25 ± 0.005	0.95 ± 0.003	2.13 ± 0.003	2.89 ± 0.006	2.14 ± 0.001	0.53 ± 0.023	1.25 ± 0.044	1.98 ± 0.044	2.59 ± 0.003	1.21 ± 0.003	1.85 ± 0.004
6 months	3.09 ± 0.003	4.93 ± 0.025	6.52 ± 0.014	4.03 ± 0.004	1.21 ± 0.009	2.77 ± 0.008	3.88 0.002	2.63 ± 0.003	0.66 ± 0.005	1.61 ± 0.013	2.49 ± 0.006	3.2 ± 0.043	1.51 ± 0.007	2.45 ± 0.021
	Peroxide value (meq O₂ kg⁻¹ oil)													
7 days	8.76 ± 0.007	8.01 ± 0.008	5.45 ± 0.006	5.58 ± 0.025	7.31 ± 0.021	2.87 ± 0.005	4.05 ± 0.05	5.19 ± 0.012	4.51 ± 0.006	8.04 ± 0.006	8.39 ± 0.047	9.68 ± 0.141	5.11 ± 0.098	5.73 ± 0.002
	9.35 ± 0.147	8.6 ± 0.148	7.22 ± 0.066	6.39 ± 0.152	7.38 ± 0.306	3.79 ± 0.148	5.33 ± 0.193	6.08 ± 0.108	5.84 ± 1.486	8.9 ± 0.226	8.46 ± 0.238	14.01 ± 0.152	6.88 ± 0.149	6.71 ± 0.124
3 months	9.82 ± 0.05	9.07 ± 0.478	8.65 ± 0.1	7.04 ± 0.117	7.43 ± 0.005	4.54 ± 0.117	6.37 ± 0.003	6.79 ± 0.095	6.92 ± 0.009	9.32 ± 0.116	9.26 ± 0.054	9.78 ± 0.238	7.65 ± 0.149	7.51 ± 1.481
	11.92 ± 1.093	11.18 ± 0.025	15.04 ± 0.006	9.95 ± 0.098	7.66 ± 0.006	7.86 ± 0.141	10.98 ± 0.047	9.98 ± 0.005	11.73 ± 0.002	11.19 ± 0.007	12.84 ± 0.108	10.2 ± 0.148	11.08 ± 0.066	11.05 ± 0.306
6 months	15.09 ± 0.003	14.36 ± 0.152	24.65 ± 1.486	14.33 ± 0.149	8 ± 0.226	12.86 ± 0.152	17.92 ± 0.238	14.78 ± 0.148	18.97 ± 0.124	14 ± 0.147	18.22 ± 0.095	10.84 ± 0.478	16.24 ± 0.1	16.38 ± 0.005
	k₂₃₂													
7 days	1.64 ± 0.006	1.93 ± 0.001	2.8 ± 0.004	1.88 ± 0.001	1.63 ± 0.002	1.6 ± 0.02	1.94 ± 0.001	1.64 ± 0.014	1.93 ± 0.003	1.68 ± 0.058	1.88 ± 0.001	1.26 ± 0.044	1.59 ± 0.002	1.85 ± 0.075
	1.67 ± 0.063	1.94 ± 0.029	2.8 ± 0.004	1.9 ± 0.015	1.56 ± 0.016	1.62 ± 0.065	1.96 ± 0.006	1.66 ± 0.057	1.95 ± 0.008	1.92 ± 0.02	2.89 ± 0.147	2.94 ± 0.023	1.62 ± 0.005	1.95 ± 0.006

6 months	2.08 ±	2.19 ±	2.8 ±	2.1 ±	1.92 ±	1.9 ±	2.14 ±	1.93 ±	2.13 ±	2.12 ±	2.99 ±	2.99 ±	1.89 ±	2.29 ±
	0.145	0.096	0.004	0.062	0.004	0.005	0.01	0.056	0.062	0.01	0.003	0.054	0.013	0.022
12 months	2.23 ±	2.22 ±	2.8 ±	2.18 ±	2.03 ±	2 ±	2.21 ±	2.03 ±	2.21 ±	2.19 ±	3.03 ±	3.01 ±	1.99 ±	2.43 ±
	0.004	0.015	0.004	0.006	0.02	0.023	0.065	0.147	0.005	0.01	0.063	0.096	0.056	0.046
18 months	2.41 ±	2.31 ±	2.8 ±	2.27 ±	2.14 ±	2.12 ±	2.29 ±	2.15 ±	2.29 ±	2.28 ±	3.07 ±	3.03 ±	2.11 ±	2.57 ±
	0.005	0.062	0.004	0.022	0.01	0.054	0.005	0.003	0.063	0.096	0.01	0.046	0.004	0.056
k₂₇₀														
7 days	0.12 ±	0.17 ±	2.8 ±	0.19 ±	0.13 ±	0.04 ±	0.14 ±	0.15 ±	0.13 ±	0.16 ±	0.13 ±	0.17 ±	0.12 ±	0.15 ±
	0.002	0.001	0.004	0.004	0.003	0.001	0.002	0.001	0.002	0.003	0.001	0.001	0.001	0.002
3 months	0.12 ±	0.178 ±	2.8 ±	0.2 ±	0.14 ±	0.14 ±	0.14 ±	0.16 ±	0.13 ±	0.17 ±	0.16 ±	0.15 ±	0.14 ±	0.15 ±
	0.003	0.002	0.004	0.001	0.005	0.001	0.002	0.004	0.004	0.002	0.001	0.02	0.041	0.041
6 months	0.13 ±	0.185 ±	2.8 ±	0.25 ±	0.14 ±	0.17 ±	0.18 ±	0.21 ±	0.14 ±	0.17 ±	0.19 ±	0.2 ±	0.17 ±	0.16 ±
	0.001	0.002	0.004	0.002	0.003	0.001	0.001	0.021	0.001	0.002	0.002	0.002	0.004	0.001
12 months	0.14 ±	0.19 ±	2.8 ±	0.26 ±	0.15 ±	0.19 ±	0.2 ±	0.27 ±	0.16 ±	0.19 ±	0.2 ±	0.22 ±	0.18 ±	0.19 ±
	0.041	0.022	0.004	0.005	0.002	0.002	0.005	0.008	0.005	0.003	0.004	0.002	0.001	0.02
18 months	0.26 ±	0.26 ±	2.8 ±	0.26 ±	0.19 ±	0.25 ±	0.31 ±	0.31 ±	0.29 ±	0.2 ±	0.23 ±	0.24 ±	0.18 ±	0.21 ±
	0.000	0.006	0.004	0.001	0.002	0.001	0.003	0.001	0.001	0.002	0.001	0.002	0.002	0.002
Chlorophyll level (mg kg⁻¹ oil)														
7 days	2.76 ±	4.2 ±	1.62 ±	2.04 ±	5.02 ±	3.23 ±	5.64 ±	2.06 ±	3.16 ±	2.11 ±	1.25 ±	4.49 ±	1.22 ±	4.61 ±
	0.021	0.01	0.005	0.023	0.097	0.015	0.019	0.008	0.019	0.04	0.024	0.043	0.073	0.004
3 months	1.75 ±	4.01 ±	1.03 ±	2.04 ±	4.13 ±	2.41 ±	4.67 ±	0.8 ±	2.13 ±	1.14 ±	1 ±	0.79 ±	0.95 ±	1.91 ±
	0.088	0.043	0.073	0.099	0.004	0.021	0.013	0.024	0.05	0.093	0.011	0.098	0.066	0.322
6 months	1.33 ±	3.81 ±	0.39 ±	1.7 ±	3.15 ±	1.13 ±	3.54 ±	0.75 ±	1.66 ±	0.98 ±	0.36 ±	0.75 ±	0.96 ±	1.59 ±
	0.12	0.057	0.048	0.124	0.08	0.089	0.012	0.022	0.17	0.0087	0.024	0.043	0.002	0.025
12 months	0.98 ±	2.4 ±	0.39 ±	0.64 ±	1.39 ±	0.98 ±	3.14 ±	0.32 ±	1.58 ±	0.85 ±	0.32 ±	0.31 ±	0.85 ±	0.87 ±
	0.002	0.099	0.002	0.047	0.093	0.005	0.219	0.002	0.21	0.0032	0.092	0.002	0.002	0.032
18 months	0.57 ±	0.24 ±	0.31 ±	0.29 ±	0.33 ±	0.87 ±	2.63 ±	0.26 ±	0.22 ±	0.56 ±	0.21 ±	0.30 ±	0.49 ±	0.26 ±
	0.009	0.124	0.005	0.017	0.043	0.001	0.125	0.004	0.165	0.005	0.026	0.054	0.013	0.003
L*														
7 days	26.02 ±	24.54 ±	30.06 ±	32.7 ±	33.50 ±	25.47 ±	30.04 ±	33.49	22.63 ±	32.31 ±	26.97 ±	31.22 ±	29.67 ±	28.06 ±
	0.29	0.47	1.39	0.57	0.29	0.65	2.27	0.81	1.83	0.55	0.25	0.74	0.74	0.19
3 months	19.08 ±	13.69 ±	23.40 ±	31.11 ±	33.02 ±	24.33 ±	27.21 ±	30.38 ±	18.64 ±	31.71 ±	23.89 ±	29.24 ±	28.74 ±	23.34 ±
	1.19	1.33	1.09	0.20	0.56	0.08	0.03	0.69	1.12	0.72	1.70	0.78	0.27	0.99
6 months	16.2 ±	11.15 ±	20.54 ±	30.4 ±	31.81 ±	24.03 ±	24.52 ±	28.415 ±	15.79 ±	30.48 ±	19.23 ±	27.73 ±	28.10 ±	22.66 ±
	0.28	0.04	0.81	0.43	0.79	0.41	0.65	0.48	0.53	1.14	0.63	0.92	0.11	0.46
12 months	15.975 ±	11.96 ±	18.05 ±	28.44 ±	28.10 ±	25.65 ±	23.40 ±	25.72 ±	16.79 ±	29.37 ±	14.65 ±	22.99 ±	26.39 ±	20.595
	0.74	0.11	0.21	0.88	0.83	0.56	0.70	0.46	0.51	0.34	0.07	1.13	2.06	0.56

18 months	13.73 ±	10.28 ±	17.70 ±	27.28 ±	26.80 ±	21.25	22.04 ±	24.84	11.62 ±	24.19 ±	10.84 ±	21.47 ±	15.15 ±	18.50 ±
	1.27	1.38	0.88	0.52	0.61	0.43	0.91	0.61	1.00	0.69	1.23	0.89	0.80	0.97
a*														
7 days	-0.3 ±	0.13 ±	-3.02 ±	-0.83 ±	0.02 ±	3.02 ±	2.66 ±	0.69 ±	0.79 ±	0.00 ±	0.00 ±	-0.68 ±	0.13 ±	-0.03 ±
	0.008	0.011	0.004	0.001	0.006	0.003	0.004	0.008	0.001	0.006	0.002	0.003	0.006	0.004
3 months	0.86 ±	1.67 ±	-2.43 ±	-0.75 ±	0.86 ±	3.47 ±	3.15 ±	1.85 ±	0.96 ±	0.81 ±	0.33 ±	-0.32 ±	0.98 ±	0.55 ±
	0.001	0.002	0.027	0.001	0.004	0.003	0.005	0.000	0.002	0.005	0.002	0.001	0.003	0.001
6 months	1.05 ±	1.91 ±	1.36 ±	-0.63 ±	1.4 ±	3.92 ±	3.89 ±	1.87 ±	1.25 ±	1.45 ±	0.61 ±	-0.24 ±	1.42 ±	0.76
	0.004	0.006	0.031	0.007	0.027	0.027	0.004	0.009	0.004	0.029	0.010	0.010	0.020	0.012
12 months	0.47 ±	1.07 ±	-2.92 ±	-1.62 ±	-2.44 ±	0.18 ±	3.35 ±	0.64 ±	0.76 ±	-2.63 ±	-0.73 ±	-1.6 ±	-1.42	-0.97
	0.006	0.005	0.004	0.009	0.002	0.000	0.029	0.025	0.028	0.003	0.018	0.007	0.005	0.012
18 months	-0.43 ±	0.37 ±	-3.47 ±	-2.92 ±	-2.74 ±	0.12 ±	-0.69 ±	-2.89 ±	-3.22 ±	-3.04 ±	-3.27 ±	-2.61 ±	-2.14 ±	-2.63
	0.005	0.006	0.016	0.004	0.010	0.008	0.010	0.011	0.009	0.011	0.008	0.005	0.009	0.007
b*														
7 days	40.20 ±	36.55 ±	36.03 ±	45.16 ±	46.50 ±	38.41 ±	28.18 ±	46.24 ±	35.51 ±	43.53 ±	38.64 ±	46.09 ±	43.13 ±	40.87 ±
	1.74	2.71	1.67	0.78	0.12	0.29	0.71	0.40	1.00	0.15	0.77	0.49	0.23	1.18
3 months	28.69 ±	20.29 ±	30.47 ±	42.86 ±	45.36 ±	35.81 ±	37.25 ±	43.02 ±	28.18 ±	45.73 ±	28.61 ±	43.12 ±	40.18 ±	33.39 ±
	0.72	0.64	0.71	0.49	0.30	0.08	0.67	0.18	0.71	0.31	1.17	0.38	0.16	0.17
6 months	23.93 ±	14.98 ±	26.09 ±	42.08 ±	43.12 ±	35.47 ±	37.36 ±	40.26 ±	23.71 ±	42.84 ±	21.83 ±	40.01 ±	39.08 ±	29.41 ±
	0.02	0.08	0.25	0.27	0.37	0.16	0.11	0.20	0.10	0.11	0.45	0.47	0.17	0.21
12 months	21.12 ±	15.36 ±	18.01 ±	37.79 ±	35.27 ±	31.42 ±	30.84 ±	35.45 ±	18.36 ±	31.45 ±	15.53 ±	30.78 ±	37.95 ±	24.81 ±
	0.15	0.11	0.02	0.06	0.09	0.29	0.09	0.08	0.34	0.35	0.26	0.10	0.75	0.14
18 months	10.08 ±	16.95 ±	14.85 ±	24.64 ±	22.89 ±	23.00 ±	20.34 ±	28.59 ±	10.67 ±	26.34 ±	14.45 ±	13.84 ±	7.10 ±	16.35 ±
	0.66	0.89	0.66	0.40	0.22	0.20	0.40	0.21	0.54	0.23	0.66	0.36	0.33	0.42

702 **Table 2a**

Predicted / Observed	7 days	3 months	6 months	12 months	18 months	Total	% correct classification
Fluorescence emission spectra acquired after excitation at 430 nm							
7 days	36	6	0	0	0	42	85.71%
3 months	5	35	2	0	0	42	83.33%
6 months	0	4	35	3	0	42	83.33%
12 months	0	0	0	40	2	42	95.23%
18 months	3	0	0	0	42	42	100.00%
Total	41	45	37	43	44	210	89.52%
Fluorescence emission spectra acquired after excitation at 290 nm							
7 days	34	7	1	0	0	42	80.95%
3 months	11	28	3	0	0	42	66.67%
6 months	1	8	31	2	0	42	73.80%
12 months	0	0	6	33	3	42	78.57%
18 months	0	0	1	1	40	42	95.29%
Total	45	43	42	36	43	210	79.05%
Fluorescence emission spectra acquired after excitation at 270 nm							
7 days	27	15	0	0	0	42	64.29%
3 months	1	30	6	5	0	42	71.43%
6 months	0	0	22	14	6	42	52.38%
12 months	0	0	10	32	0	42	76.19%
18 months	0	0	5	18	19	42	45.24%
Total	28	45	43	69	25	210	61.90%
Concatenation data of emission spectra acquired after excitation set at 430 and 290 nm							
7 days	42	0	0	0	0	42	100.00%
3 months	2	40	0	0	0	42	95.21%
6 months	0	0	41	1	0	42	97.61%
12 months	0	0	4	37	1	42	88.09%
18 months	0	0	0	0	42	42	100.00%
Total	44	40	45	38	43	210	96.18%

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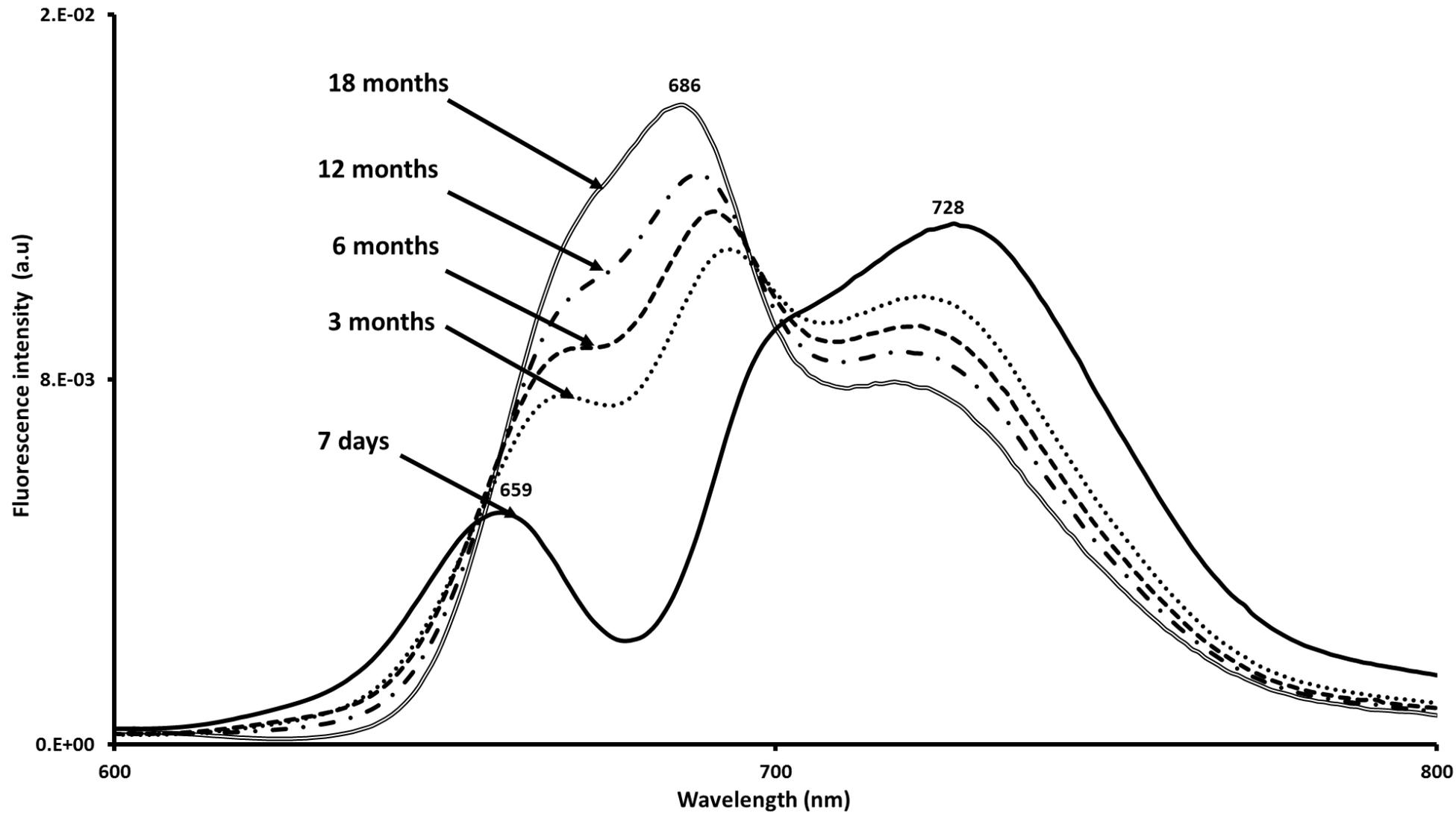
705 Table 2b

Data	PLSR				MLR				PCR				SVMR			
	Calibration		Validation		Calibration		Validation		Calibration		Validation		Calibration		Validation	
	R ²	RMSEC	R ²	RMSEP	R ²	RMSEC	R ²	RMSEP	R ²	RMSEC	R ²	RMSEP	R ²	RMSEC	R ²	RMSEP
Storage time																
Chemical parameters	0.93	43.11 days	0.87	72.85 days	0.77	92.98 days	0.82	84.72 days	0.89	61.45 days	0.89	68.56 days	0.94	45.07 days	0.43	221.69 days
Colorimetric parameters	0.89	62.05 days	0.77	90.18 days	0.68	108.13 days	0.64	118.01 days	0.89	63.36 days	0.89	64.06 days	0.95	45.77 days	0.95	46.77 days
Excitation 430 nm	0.98	20.51 days	0.98	24.85 days	0.99	16.86 days	0.88	88.44 days	0.68	107.09 days	0.82	83.72 days	0.93	50.68 days	0.96	42.91 days
Excitation 290 nm	0.97	29.50 days	0.97	30.8 days	0.94	77.11 days	0.39	194.07 days	0.61	121.07 days	0.60	119.98 days	0.64	120.84 days	0.89	65.20 days
Excitation 270 nm	0.97	28.60 days	0.92	53.78 days	0.96	88.76 days	0.52	223.51 days	0.97	30.80 days	0.97	29.50 days	0.94	48.14 days	0.90	65.44 days
Free acidity																
Excitation 430 nm	0.99	0.05%	0.99	0.05%	0.99	0.43%	0.72	1.35%	0.98	0.15%	0.98	0.12%	0.88	0.43%	0.82	0.42%
Excitation 290 nm	0.82	0.42%	0.79	0.45%	0.87	1.13%	0.73	0.84%	0.63	0.71%	0.58	0.78	0.72	0.63%	0.62	0.76%
Excitation 270 nm	0.66	0.69%	0.56	0.68%	0.93	0.98%	0.19	1.51%	0.82	0.46%	0.76	0.57%	0.82	0.44%	0.78	0.55%
Peroxide value																
Excitation 430 nm	0.83	1.55 meq O ₂ kg ⁻¹ oil	0.67	2.33 meq O ₂ kg ⁻¹ oil	0.99	0.46 meq O ₂ kg ⁻¹ oil	0.81	1.85 meq O ₂ kg ⁻¹ oil	0.80	1.69 meq O ₂ kg ⁻¹ oil	0.74	1.89 meq O ₂ kg ⁻¹ oil	0.78	1.81 meq O ₂ kg ⁻¹ oil	0.64	2.11 meq O ₂ kg ⁻¹ oil
Excitation 290 nm	0.98	0.33 meq O ₂ kg ⁻¹ oil	0.98	0.32 meq O ₂ kg ⁻¹ oil	0.94	2.01 meq O ₂ kg ⁻¹ oil	0.63	2.47 meq O ₂ kg ⁻¹ oil	0.37	3.04 meq O ₂ kg ⁻¹ oil	0.42	2.8 meq O ₂ kg ⁻¹ oil	0.50	2.91 meq O ₂ kg ⁻¹ oil	0.53	2.67 meq O ₂ kg ⁻¹ oil
Excitation 270 nm	0.88	0.98 meq O ₂ kg ⁻¹ oil	0.80	1.42 meq O ₂ kg ⁻¹ oil	0.92	2.89 meq O ₂ kg ⁻¹ oil	0.15	5.79 meq O ₂ kg ⁻¹ oil	0.70	2.05 meq O ₂ kg ⁻¹ oil	0.60	2.69 meq O ₂ kg ⁻¹ oil	0.86	1.86 meq O ₂ kg ⁻¹ oil	0.82	1.97 meq O ₂ kg ⁻¹ oil
k₂₃₂																
Excitation 430 nm	0.2	0.35	0.12	0.4	0.99	0.13	0.15	5.73	0.12	0.39	0.12	0.43	0.21	0.39	0.17	0.45

Excitation 290 nm	0.99	0.01	0.99	0.01	0.81	0.39	0.04	0.64	0.14	0.38	0.13	0.45	0.85	0.21	0.92	0.10
Excitation 270 nm	0.07	0.0007	0.05	1.08	0.88	0.37	0.09	1.30	0.02	0.42	0.04	0.39	0.23	0.37	0.23	0.37
k₂₇₀																
Excitation 430 nm	0.67	0.028	0.33	0.038	0.99	0.04	0.76	0.16	0.59	0.31	NA	0.13	0.58	0.36	0.87	0.41
Excitation 290 nm	0.98	0.004	0.98	0.004	0.66	0.58	0.41	0.77	0.86	0.18	0.86	0.18	0.32	0.36	0.21	0.43
Excitation 270 nm	0.19	0.044	0.13	0.161	0.97	0.19	0.41	0.52	0.86	0.14	0.65	0.25	0.40	0.40	0.88	0.11
Chlorophyll level																
Colorimetric parameters	0.92	0.26 mg kg ⁻¹ oil	0.83	0.48 mg kg ⁻¹ oil	0.83	0.39 mg kg ⁻¹ oil	0.83	0.40 mg kg ⁻¹ oil	0.98	0.11 mg kg ⁻¹ oil	0.98	0.11 mg kg ⁻¹ oil	0.99	0.07 mg kg ⁻¹ oil	0.99	0.09 mg kg ⁻¹ oil
Excitation 430 nm	0.98	0.12 mg kg ⁻¹ oil	0.98	0.16 mg kg ⁻¹ oil	0.99	0.24 mg kg ⁻¹ oil	0.57	0.76 mg kg ⁻¹ oil	0.93	0.31 mg kg ⁻¹ oil	0.92	0.34 mg kg ⁻¹ oil	0.72	0.66 mg kg ⁻¹ oil	0.71	0.64 mg kg ⁻¹ oil
Excitation 290 nm	0.72	0.61 mg kg ⁻¹ oil	0.71	0.65 mg kg ⁻¹ oil	0.91	1.16 mg kg ⁻¹ oil	0.24	2.91 mg kg ⁻¹ oil	0.63	0.73 mg kg ⁻¹ oil	0.67	0.68 mg kg ⁻¹ oil	0.72	0.67 mg kg ⁻¹ oil	0.70	0.64 mg kg ⁻¹ oil
Excitation 270 nm	0.78	0.56 mg kg ⁻¹ oil	0.7	0.64 mg kg ⁻¹ oil	0.94	1.17 mg kg ⁻¹ oil	0.64	2.45 mg kg ⁻¹ oil	0.71	0.65 mg kg ⁻¹ oil	0.78	0.61 mg kg ⁻¹ oil	0.77	0.57 mg kg ⁻¹ oil	0.83	0.59 mg kg ⁻¹ oil

706 *RMSEC, Root mean square error of calibration; RMSEP, Root mean square error of prediction.*

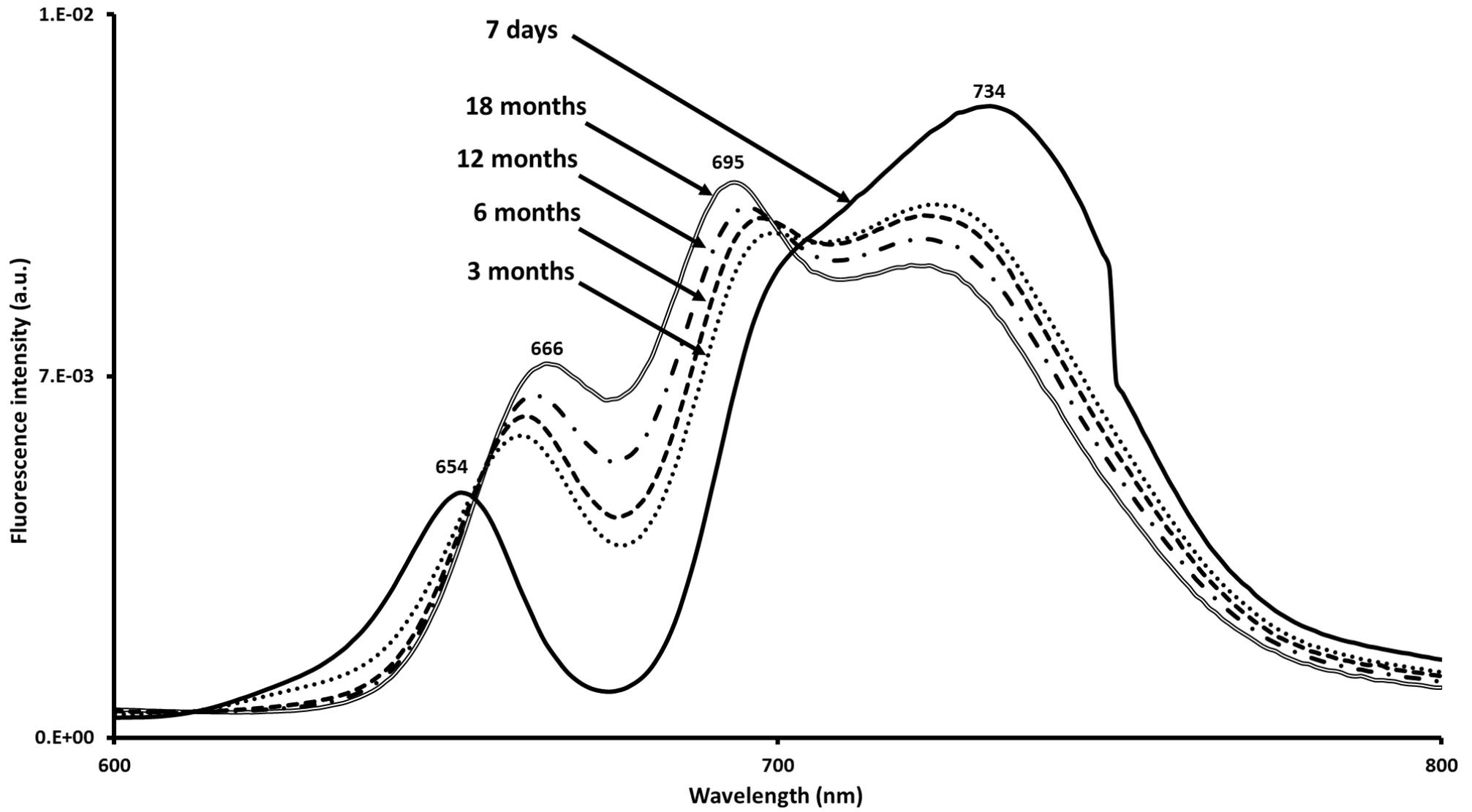
707 **Figure 1a**



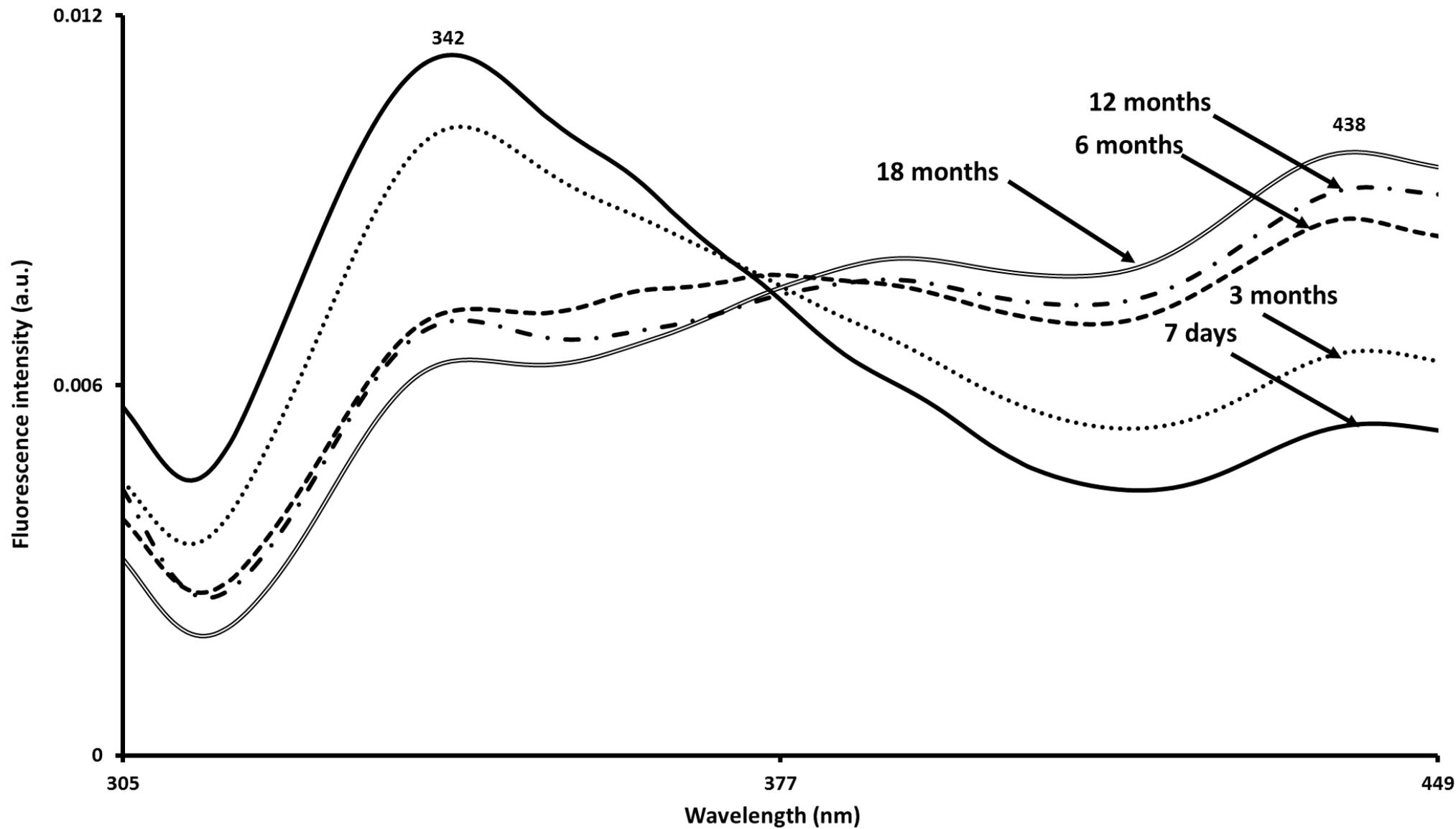
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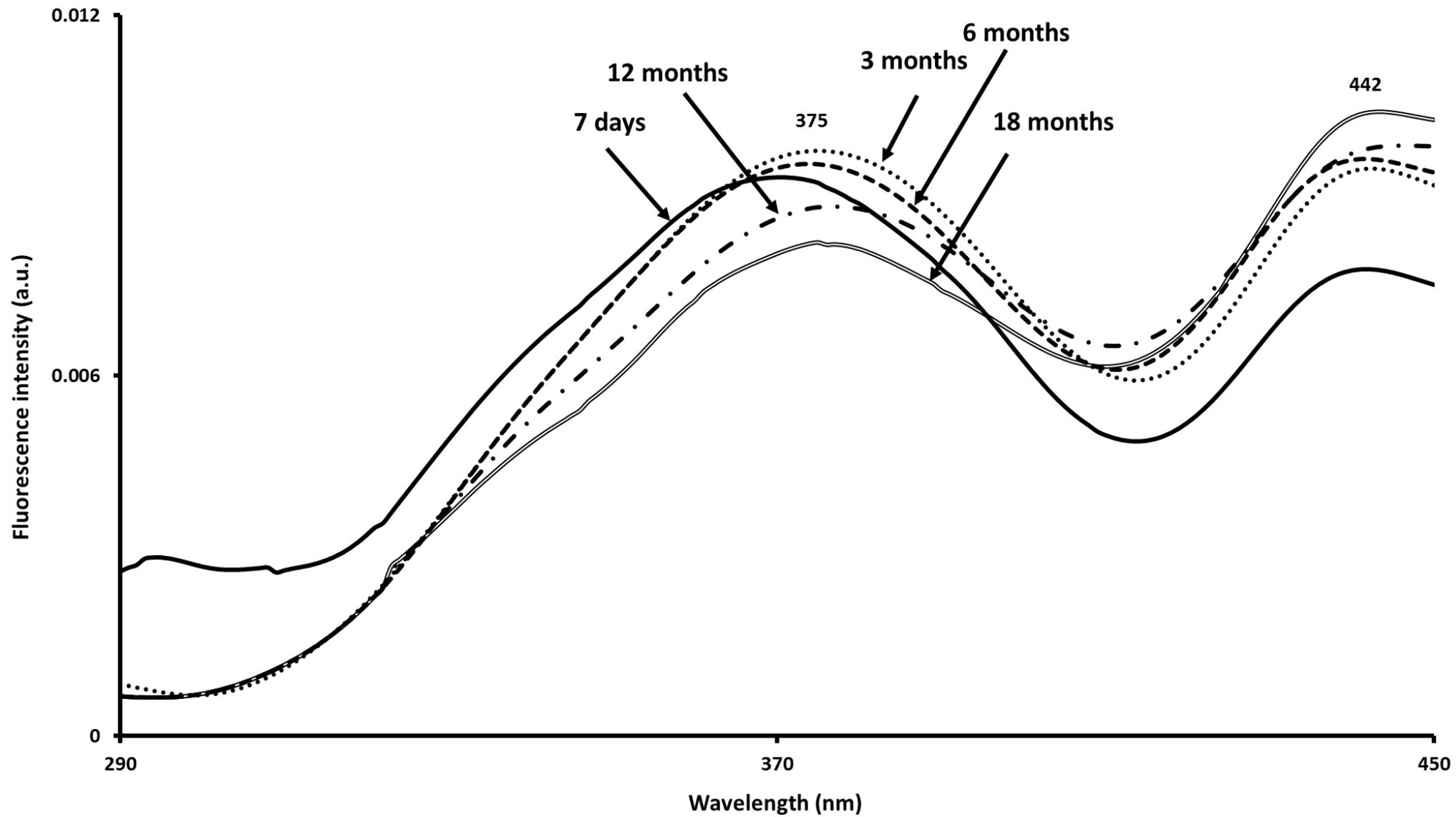
710 **Figure 1b**



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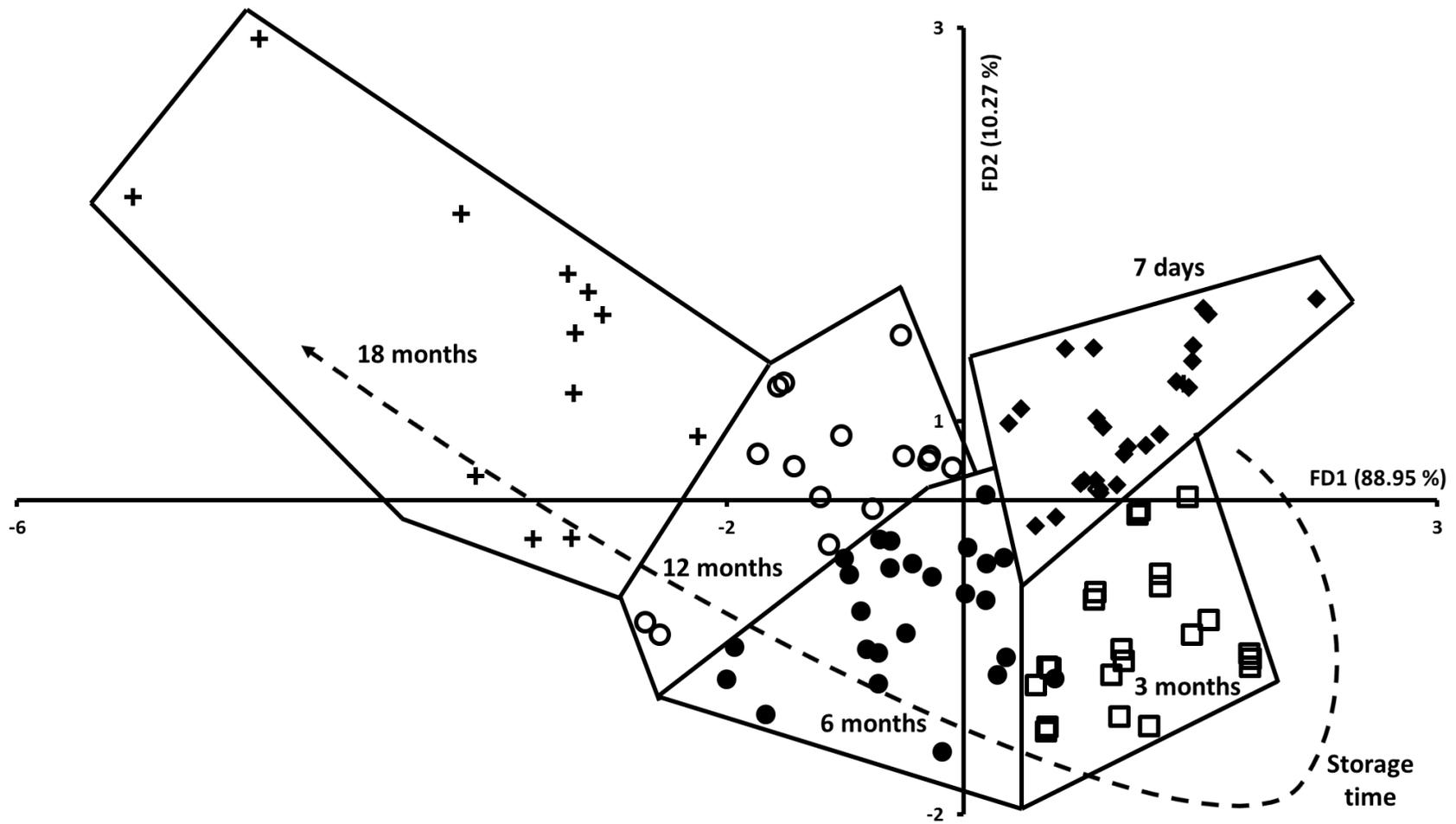


715 **Figure 1d**



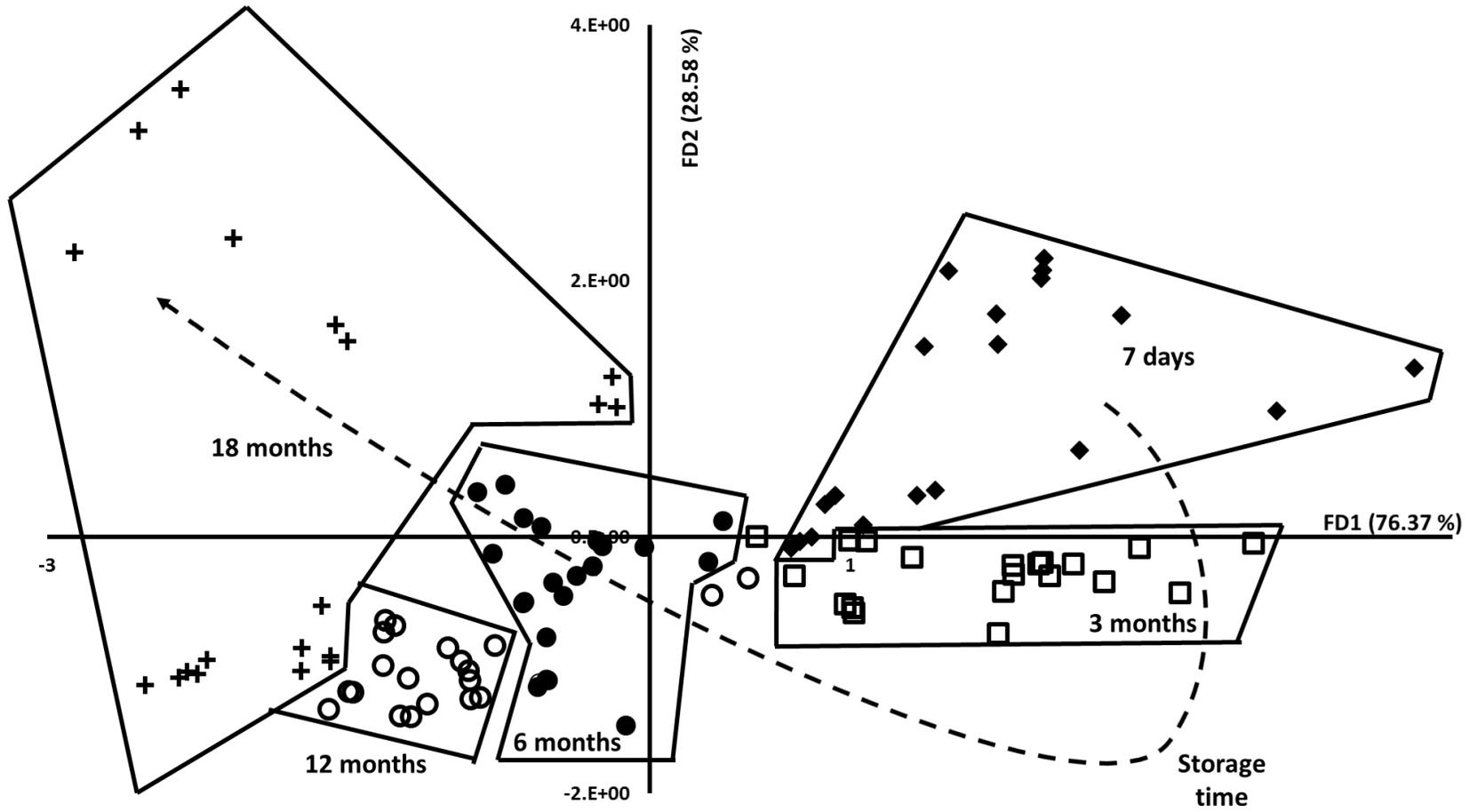
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718 **Figure 2a**



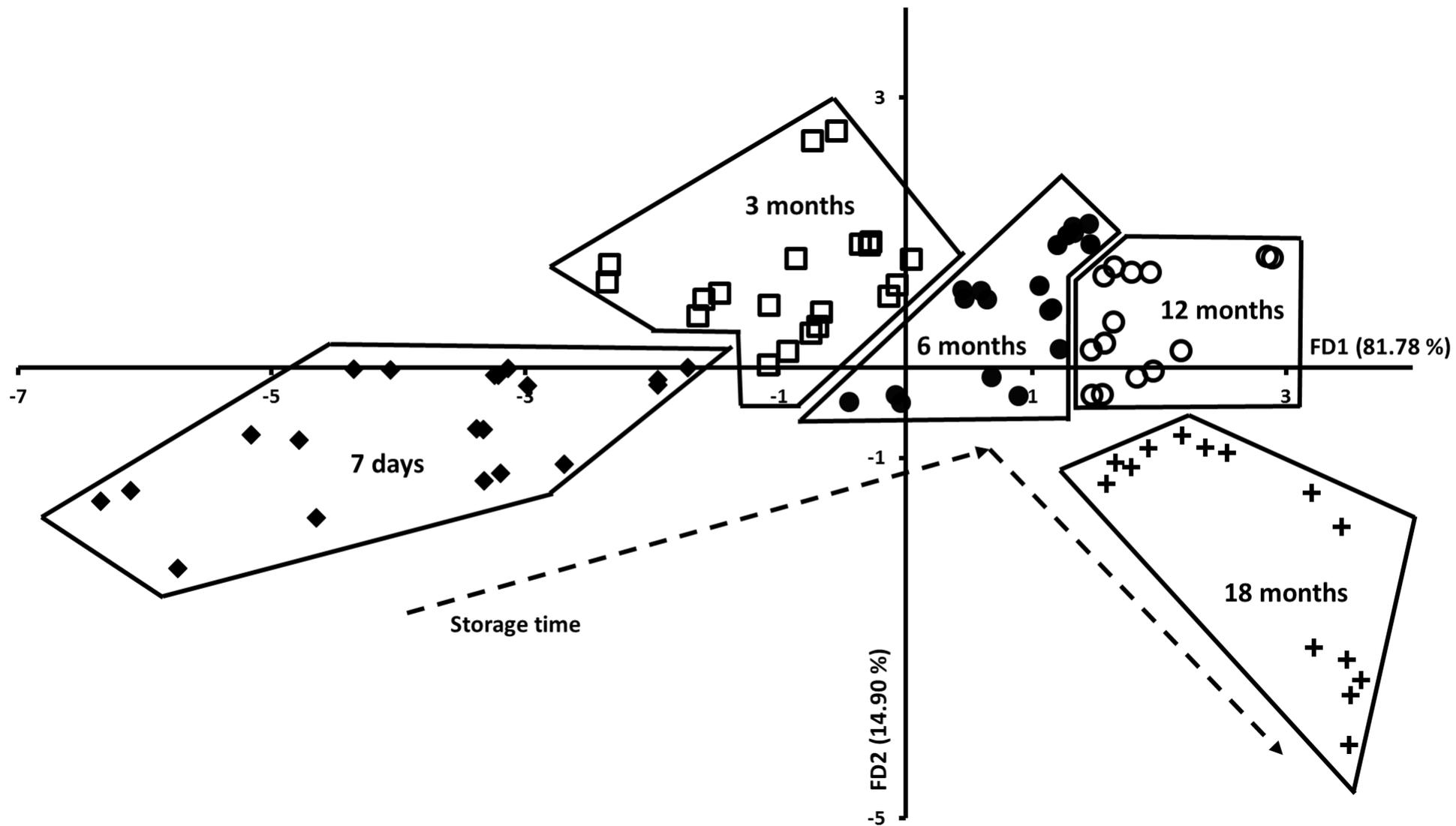
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720 **Figure 2b**



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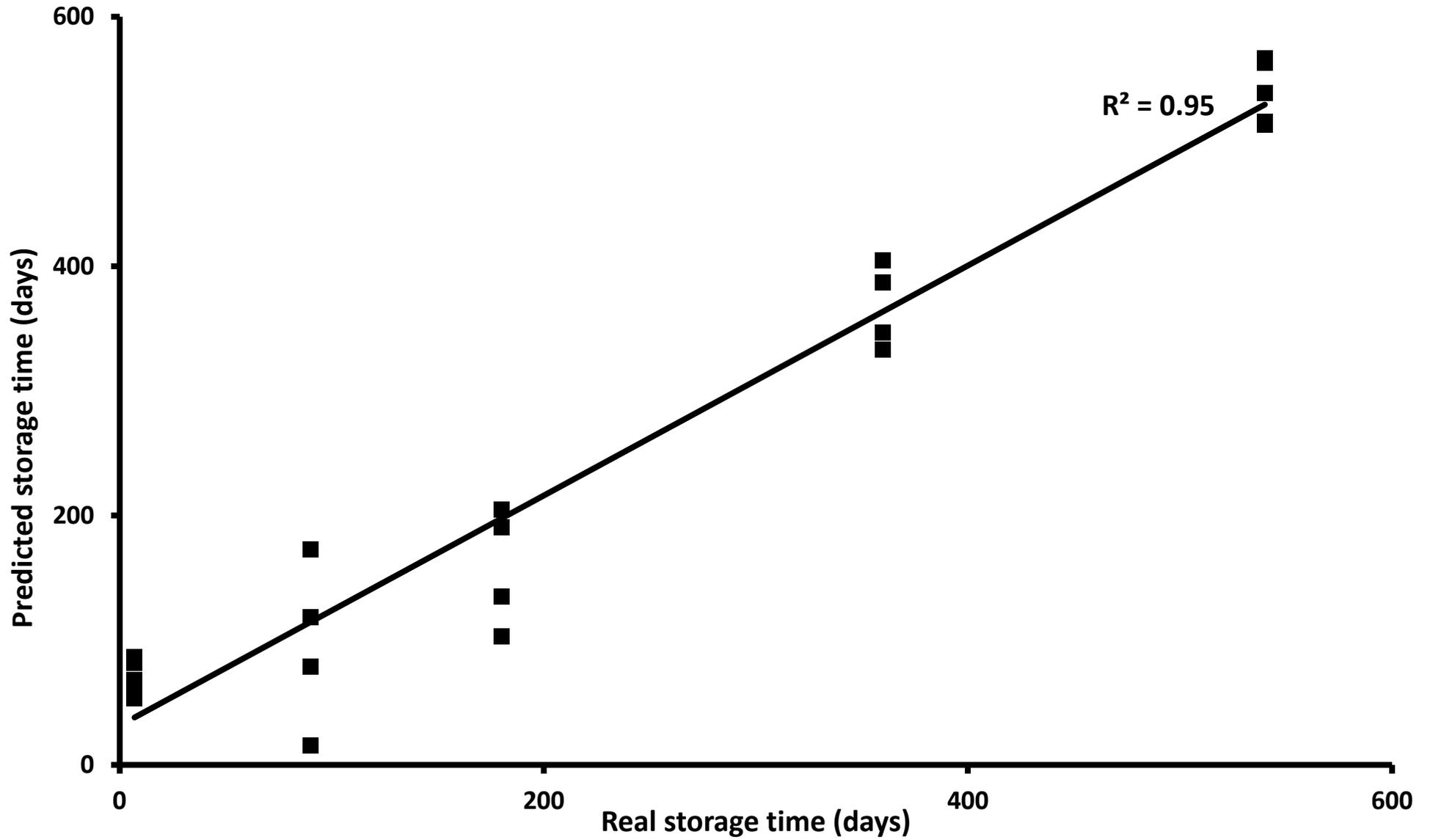
722 Figure 2c



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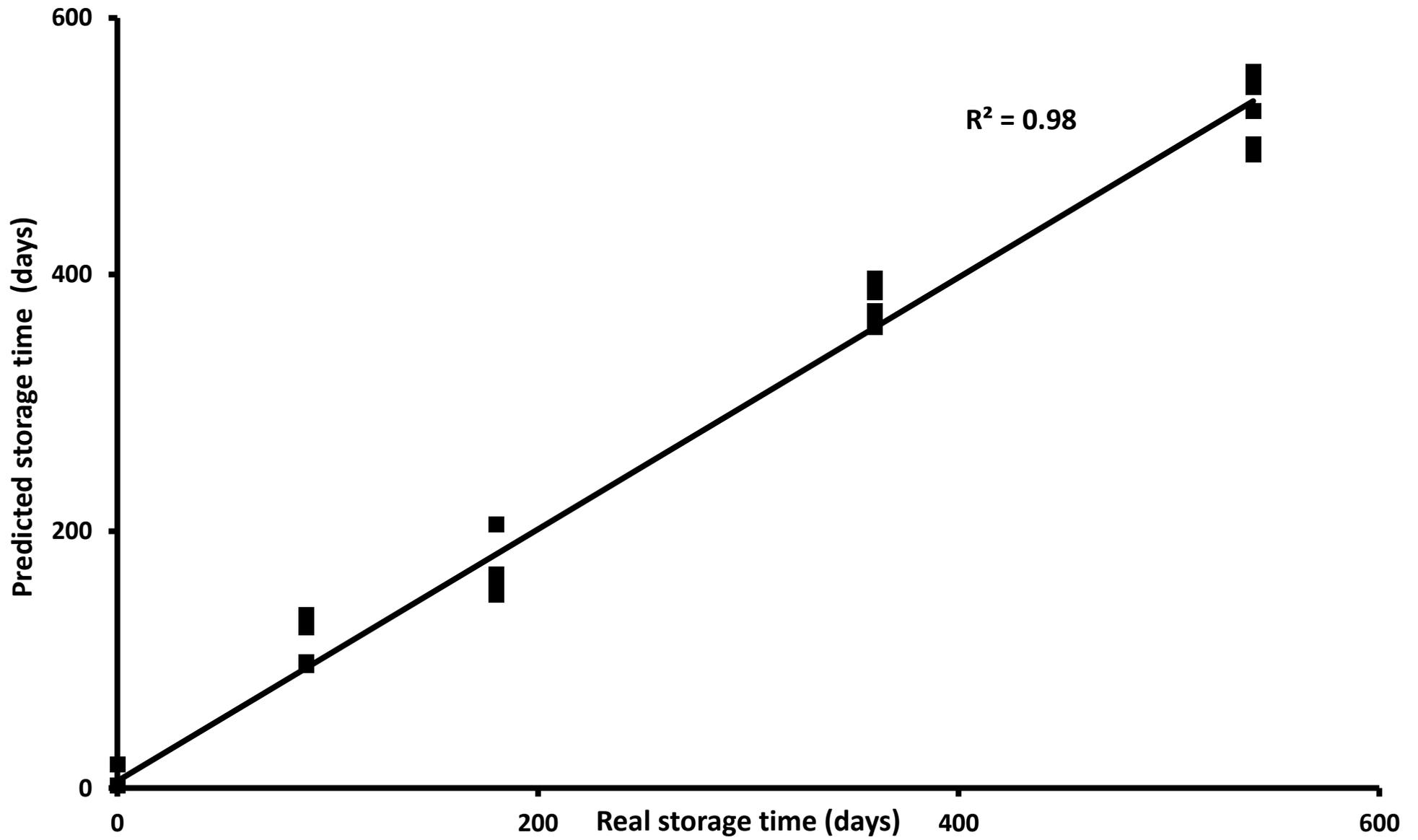
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725 Figure 3a

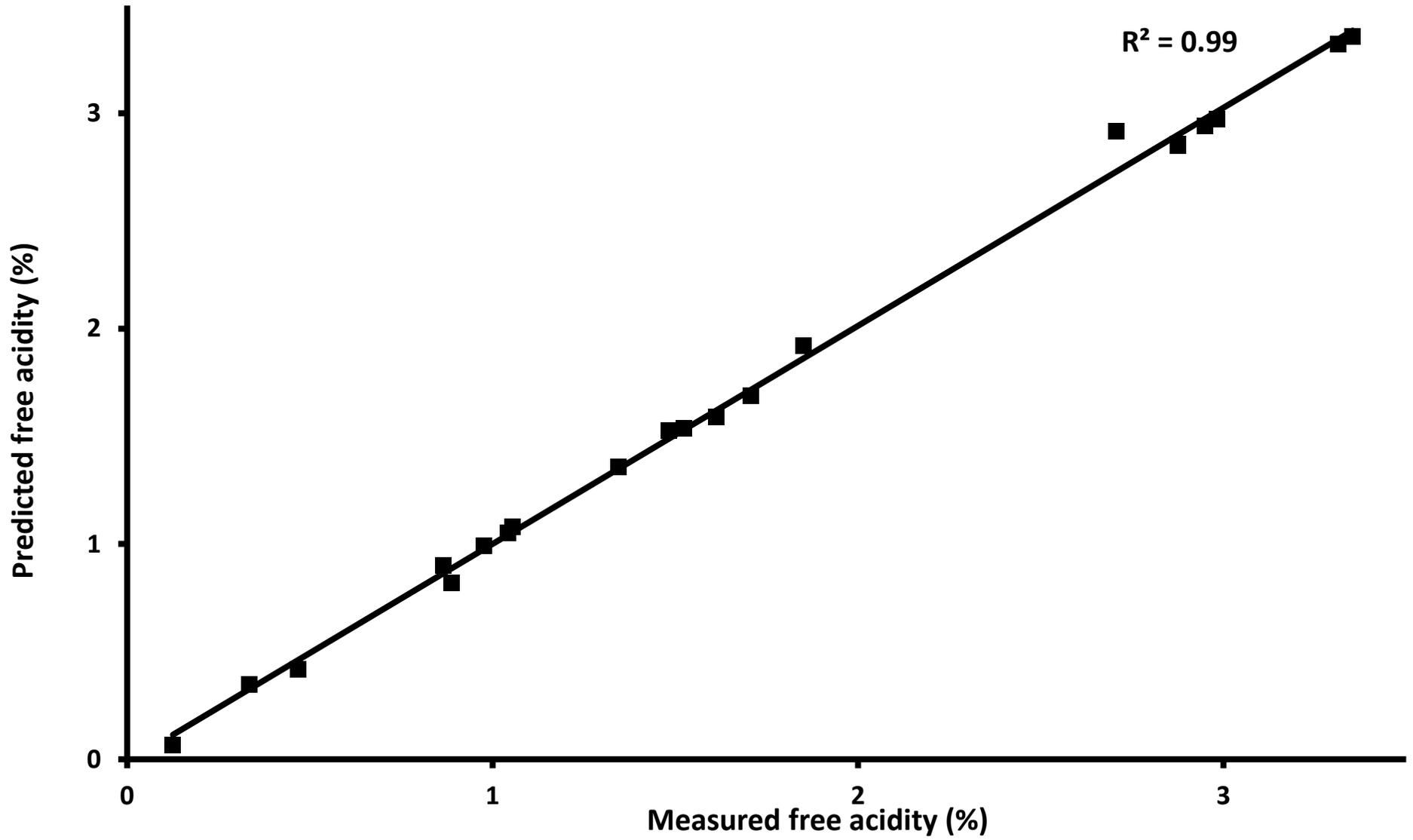


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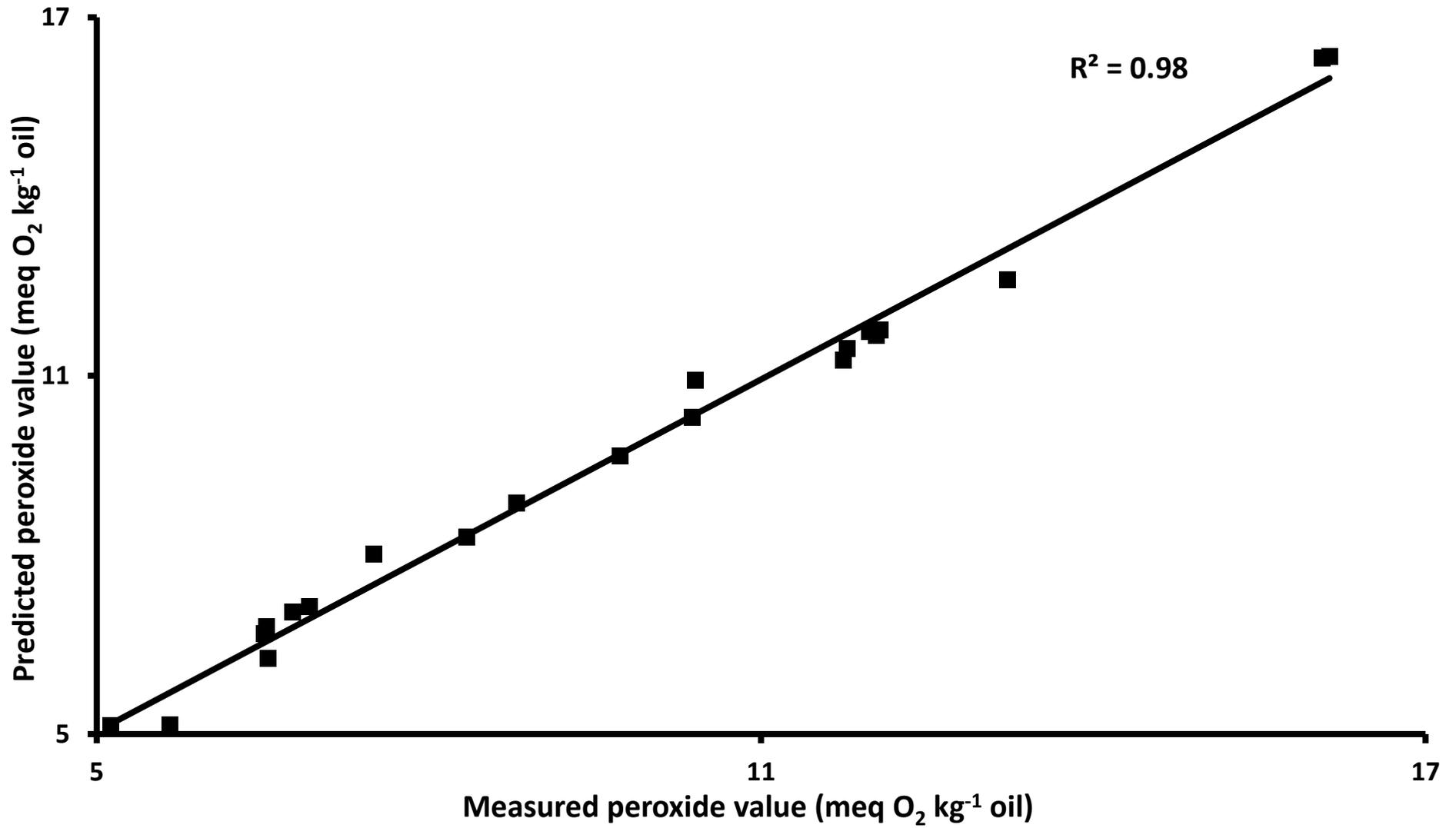
728 Figure 3b



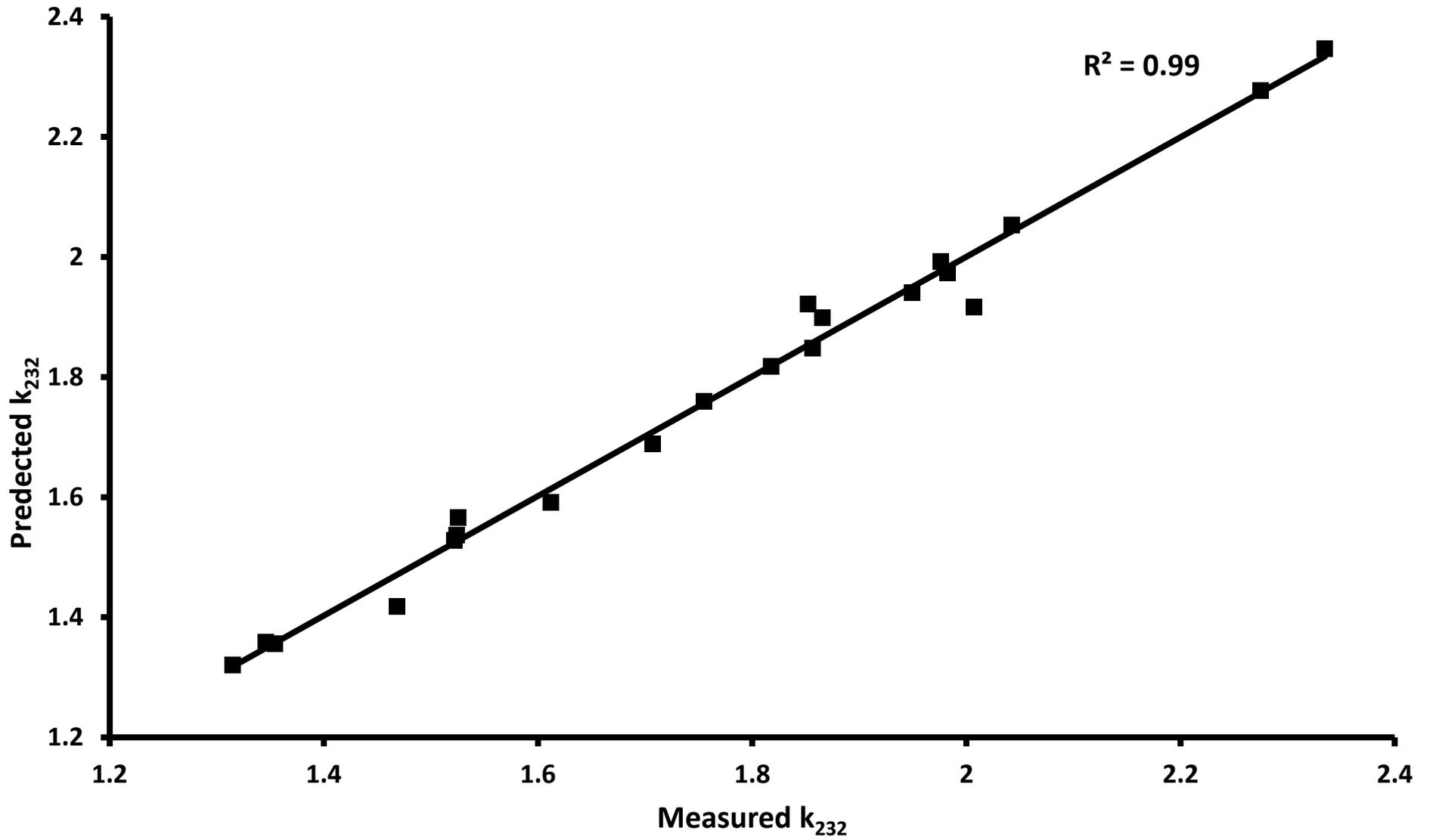
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736 Figure 4c



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