Fluorescing olive oil: characterization by means of EEMs-PARAFAC technique, sample group discrimination and relations with oil quality

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Some components of olive oil are fluorescent (Guimet et al. 2005; Tena et al., 2009; Sikorska et al., 2012) and, therefore, may serve as natural markers in characterizing oil samples, their quality and origin. Olive oil characterization is of great interest due to the recognized health, nutrition and gastronomic value of the oil. Its characterization may also help in detecting and preventing possible adulteration by other types of oil that may be cheaper, have lower quality and even not necessarily eatable. Not least important, examination of olive oil fluorescence may contribute to better understanding of natural fluorophores that may find their way to the environment, soil and various water bodies. Despite olive oil fluorescence being well-known, limited studies dealt with excitation-emission matrices (EEMs) of fluorescence specifically analyzed by means of parallel factor analysis (PARAFAC; e.g., Guiment et al. 2005). In addition, proper examination of olive oil fluorescence is complicated by its strong absorbance in the UV region, thus producing significant inner filter effect, not necessarily taken into account in the literature.

This paper presents examination of a series of 63 olive oil samples distributed into 6 groups. The groups represent either a certain source of olive oil, i.e., a specific location of olive mill, or include commercial oil (available in supermarkets). In addition, between and within those 6 groups, oil samples differed by the extent of intended or natural sensorial defect. Olive oil samples were subjected to the following examinations: (i) EEMs of fluorescence of diluted solutions in cyclohexane at the 250-700 nm range followed by a PARAFAC analysis, (ii) absorbance spectra of native oil samples and their solutions in cyclohexane obtained in the 200-700 nm range, (iii) chemical analysis (content of free fatty acids, peroxide value, total phenolic content) and (iv) organoleptic panel evaluation. The objectives of this examination included (1) testing the ability of spectroscopic tools, and foremost fluorescence, to differentiate olive sample groups, (2) examining correlations of spectrally derived compositional indices with the results of the panel evaluation, and (3) checking relations between the above compositional indices and some oil chemical parameters.

Three major fluorescent components, characterized by excitation and emission maxima at 280/310, 665/674 and 260/358 nm, were detected. The first (C1) and the third (C3) components appear to be related to some phenolic compounds (possibly, tocopherols); in the whole set of samples, concentration scores of both components were strongly correlated. The concentration scores of the second component (C2) which seems to represent chlorophyll pigment fluorescence showed no correlation with components C1 and C3. Absorbance spectra of native (non-diluted) olive oil samples showed several maxima above 400 nm (up to 670 nm). These absorbancies associated also with chlorophyll pigments

showed strong mutual correlations; however, no correlations were seen with a strong absorbance at around 210 nm determined in diluted cyclohexane solutions. Results of a Principal Component and Classification Analysis suggested that fluorescence emissions of chlorophyll pigments and components C1 and C3 have a potential to differentiate between "commercial" and some location-specific samples; light absorbance at 210 and 670 nm also has this capability. When the classification tree technique was applied to concentration scores of the fluorescent components, two groups of samples were identified as one class non-overlapping with others, and the other three groups of samples were essentially differentiated.

When all the oil samples were considered, no statistically significant correlations were found between concentration scores of fluorescent components and organoleptic panel-derived characteristics such as fruitiness, bitterness and pungency. Yet, weak, albeit statistically significant, positive relations were found between absorbance at 414 nm and bitterness and pungency. When examined correlations in separate sample groups, some statistically significant relations were noted (at p 0.05). For example, in commercial sample series, pungency and bitterness were correlated with the C3 concentration scores (r 0.72 and 0.6, respectively), and fluorescence of chlorophyll-associated component C2 was correlated with fruitiness (r 0.41) and pungency (r 0.40). However, when statistically significant correlations within the same pair of variables were compared between different sample series, they were found in some cases to show opposite trends. For example, the C3 concentration scores showed positive association with pungency in commercial samples (r 0.72), and negative association in musty-humid samples (r -0.57). At the same time, positive correlations were obtained between the C3 concentration scores and the content of free fatty acids in both musty-humid and fusty-infested olive oil sample sets. In part, some inconsistency in the observed associations could be explained by variable and different histories of sample damage in different groups. It could be also contributed by a relatively low degree of oil degradation, expressed in generally high oil quality based on panel evaluations. Nevertheless, the PARAFAC-analyzed fluorescence seems to justify sample separation into groups originally associated with their sources and locations, and may further be linked to oil quality indicators. Therefore, it may be proposed, that fluorescence could serve, alone or in combination with other spectroscopic or analytical techniques, as a monitoring tool for quantifying olive oil quality and authenticity.

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