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Predicting the shelf-life of extra virgin olive oil during storage at 22 and 50ºC, using a kinetic modelling approach

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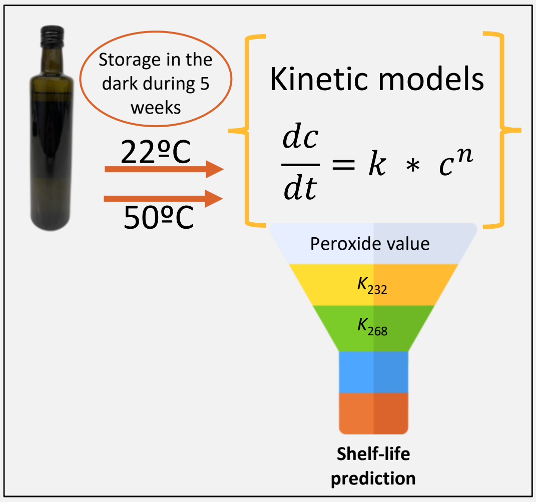

Olive oil (OO) is a high-value food due to its appreciated sensory attributes and health benefits. The shelf life (SL) of an OO is a key parameter, being influenced by the olive cultivar, agro-climatic, extraction and storage conditions. So, kinetic models were developed for 3 physicochemical quality parameters (peroxide value and the extinction coefficients at 232 and 268 nm), to estimate the SL, based on a Time to Reach the legal Upper Limit (TRUL) approach. For that, a ripe EVOO, stored in amber glass bottles, in the dark and during 5 weeks, at 22 and 50ºC, was used. Zero-, first-, and second-order kinetic models were evaluated, and the best correlations were achieved for the zero-order model. Based on this model, the SL of the stored EVOOs were predicted to be 47-210 days and 35-80 days at 22 and 50ºC, respectively. As expected, the SL decreased for the higher storage temperature, being the lowest values predicted for K_{232} and K_{268}, data, for 22 and 50ºC, respectively.

Introduction

Only extra virgin or virgin olive oils (EVOOs or VOOs), can be commercialized, being their classification dependent on the fulfillment of a set of legal thresholds [1]. EVOO is a key ingredient of the Mediterranean cuisine [2] and its intake was associated to several health benefits recognized by nutritional and health claims [3,4]. However, olive oil is prone to lipid oxidation due to its richness in unsaturated fatty acids, which is responsible for degrading the chemical and sensory quality of EVOO leading to the appearance of unpleasant off-flavors, obliging a quality grade re-classification to VOO or even lampante oil, which cannot be commercialized.

Thus, besides monitoring the oil quality through the extraction line, the olive oil industry is urged to guarantee the label information authenticity from packaging, during storage and transportation, until purchased by the end-consumer. Several strategies have been proposed aiming to establish accurate models for predicting the olive oil shelf-life (SL) [5], which can be defined as the time-period under normal storage conditions within which no off-flavors are developed and the quality parameters are within the legal limits [6]. Two types of shelf-life prediction models are available: kinetic and empirical [5,7-11].

In this study, classical kinetic models were applied aiming to describe in a straightforward way the complexity of the oxidation reactions and related oil quality degradation.

Materials and Methods

Ripe EVOO samples, from the crop year of 2022, were collected and further used. The oil was stored in amber glass bottles (100 mL) with a plastic cap. In total, 40 bottles were used, being 20 stored at 22ºC and the other 20 bottles stored at 50ºC, all of them protected from light exposure. Bottles were stored during 5 weeks, being 4 bottles picked from each storage condition, each week for analysis. Before storage, the quality parameters of the olive oil (free acidity, peroxide value and extinction coefficients at 232 and 268 nm) were assessed, following the procedures described in the Commission Delegated Regulation (EU) 2022/2104, allowing confirming the EVOO classification (FA = 0.28%; PV = 5.8 mEqO_2/kg oil; K_{232} = 1.87, and K_{268} = 0.13). The total phenols content (TPC) and total carotenoids content (TCC) of the initial EVOO were also determined, by spectrophotometry, being equal to 245 ± 24 mg GAE/kg and 8.0 ± 0.2 mg/kg. At each sampling date (7, 14, 21, 28, and 35 days) the quality parameters of the stored oils were evaluated following the EU guidelines, being further used to establish the kinetic models, which were then applied to estimate the SL of the olive oils in terms of commercial grade.

The evolution of the PV, K_{232} and K_{268} data at each storage temperature studied (22 and 50ºC), were used to calculate the thermal rate constants due to the oxidation process that took place during the storage time-period. Since the FA was almost constant along the storage time, this parameter was not considered, in terms of kinetic modelling. Three reaction orders were considered (zero-, first- and second-order kinetic models, Equation (1)), being selected the kinetic model that allowed the best mathematical fit of the experimental data:

$$\frac{dP}{dt} = k \times P^n \qquad \text{(Eq. 1)}$$

where, P refers to the parameter under study (PV, K_{232}, or K_{268}), t is the storage time-period (in days), and k is the rate constant and n is the reaction order (equal to 0, 1 or 2 for zero-, first- and second-order kinetic models, respectively).

Results and Discussion

The results showed that the zero-order kinetic model allowed the best fitting of the experimental data for the three quality parameters, which was slightly superior compared to the first- and second-order kinetic models. Table 1 shows the rate constants (k ± standard error [SE]) and the correlation coefficients (R) obtained assuming the zero-order kinetic mechanism for the thermal degradation of the EVOO quality due to the natural oxidation process at 22 and 50ºC, during the 5 weeks of storage.

Table 1. Rate constants (k ± standard error [SE]) and correlation coefficient (R) for olive oils stored during 5 weeks at 22 or 50ºC, obtained assuming a zero-order kinetic model.

Variable	22ºC		50ºC	
	k ± SE	**R**	**k ± SE**	**R**
PV	0.14±0.03*	0.928	0.18±0.04*	0.945
K_{232}	0.013±0.003*	0.935	0.011±0.003*	0.920
K_{268}	0.0004±0.0002*	0.866	0.0026±0.0002*	0.994

* k units for PV: mEq.O_2 × kg^{-1} × day^{-1}; k units for K_{232} and K_{232}: day^{-1}

Taking into account the maximum legal limits [1] for EVOO grade classification (PV ≤ 20 mEq.O_2/kg oil; K_{232} ≤ 2.50, and K_{268} ≤ 0.22) and using the zero-order kinetic models previously established, based on the experimental data collected during the 5 weeks of storage at 22 or 50ºC, it was possible to estimate the SL (i.e., the Time required to Reach the Upper Legal Limit, TRUL) for the studied oil, considering the initial values determined for the oil before storage. Table 2 shows the SL determined according to each parameter and storage temperature, predicted using the zero-order fitting. The SL values were slightly greater than those reported by Gomez-Alonso et al. [12], based on the time to reach the upper limit of PV or of the extinction coefficients, for purified olive oil, stored at 25 and 50ºC (48-104 days, and 5-24 days, respectively). However, the predicted SL were lower than those reported for monovarietal EVOO from cv. Cornicabra stored at 25ºC (238-686 days) and of the same order of magnitude of those determined at 50ºC (15-59 days) [13], which were estimated using zero- or first-order kinetic models developed for the same three quality parameters. On the other hand, for monovarietal EVOO from cv. Coratina, significantly greater SLs were reported in the literature (377 and 61 months for 25 and 50ºC, respectively) [9]. This variability may be tentatively attributed to the expected differences in the chemical composition of each olive oil, which greatly depend on the cultivar, agro-climatic conditions, olive maturation index t harvest, and extraction conditions.

Table 2. Shelf-life (SL, in days) calculated using the zero-order kinetic model.

Variable	Shelf-life (days)	
	22ºC	**50ºC**
PV	100	80
K_{232}	47	56
K_{268}	210	35

As can be inferred from Table 2, in general, the SL decreases when the storage temperature increases (with the exception of the results for K_{232}). Moreover, the correctness of the EVOO label for the studied olive oil, stored at 22ºC, mimicking the usual temperature of oil's storage, could only be ensured for 47 days, which is a rather low SL, taking into account that olive oils are often stored for 10-12 months.

Conclusions

The study performed allowed confirming that zero-order kinetic models can be used to estimate the SL of olive oils, based on the TRUL of three quality parameters (PV, K_{232}, and K_{268}) used to establish the commercial grade of olive oil, in-line with the literature. Moreover, it also highlighted that, from the referred parameters, the extinction coefficients were those that would suffer a faster raise, being those that should be used to estimate the SL of olive oils. Finally, from our results and those previous reported, it is clear that the SL prediction is greatly dependent of the olive oil under study. Besides, the study also points out that the classical kinetic models alone can hardly describe the complexity of the oxidation reactions and related oil chemical-sensory degradation.

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