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Review Article

Shelf Life of Extra Virgin Olive Oil and Its Prediction Models

Xueqi Li [1] **and Selina C. Wang** [1,2]

[1] *University of California Davis Olive Center, Davis, CA 95616, USA*
[2] *Department of Food Science and Technology, University of California, Davis, Davis, CA 95616, USA*

Correspondence should be addressed to Selina C. Wang; scwang@ucdavis.edu

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Extra virgin olive oil (EVOO), with high unsaturation degree (oleic acid, linoleic acid, and linolenic acid), is prone to oxidation during production and storage even with the presence of abundant antioxidants (e.g., phenolic compounds, alpha-tocopherol, and chlorophyll). The level of oxidation degradation is greatly affected by the EVOO chemical composition (free fatty acids, saturated and unsaturated fat ratio, total phenol content, etc.) and storage conditions (packaging material, oxygen, temperature, and light). With the increasing demand on qualitative acceptability and food safety of an EVOO product, consumers rely heavily on "shelf life" as a good indicator. Hence, it is critical for olive oil producers to provide accurate and practical information on shelf-life prediction. This review analyzes ten shelf-life prediction models that used various parameters and approaches for model establishment. Due to the complexity of chemical interactions between oil phase and environment under real-time storage and rapid accelerated testing conditions, further investigation is needed to scrutinize and minimize the discrepancies between real-time shelf life and predicted shelf life of EVOO products.

1. Introduction

Known as a key component in the Mediterranean diet for centuries, extra virgin olive oil (EVOO) has become globally recognized and appreciated by consumers due to its unique sensory characteristics and high nutritional values. In recent years, there has been considerable interests in correlating monounsaturated fatty acids (mainly oleic acid) and minor components (phenolic compounds, alpha-tocopherol and carotenoids, squalene, simple triterpenes, and volatile compounds) in EVOO with health benefits {e.g., antihypertensive activity [1], chemopreventive activity [2], tumor-inhibitory activity [3], and anti-inflammatory activity [4]} and positive sensory attributes [5–7]. However, due to high levels of unsaturated fatty acids and the presence of endogenous enzymes such as lipase, polyphenol oxidase, and peroxidase, EVOO is also prone to lipid oxidation and enzymatic hydrolysis which favors autoxidation [8–10]. EVOO oxidation is highly dependent on factors including the storage of olive fruit prior to processing [11], the techniques of oil extraction [12], the exposure degree of oxygen, light, and temperature [13], and the packaging [14] and storage conditions of the final product [15], which could greatly change the chemical composition of the oil, leading to unpleasant off-flavors and eventually degrading the quality.

For consumers, one of the most important characteristics in EVOO is freshness, as freshness is typically associated with high quality and ensures food safety [16]. The term "shelf life" is commonly referred to when determining the freshness and consumer acceptability of EVOO [17]. Specifically, EVOO shelf life could be defined as the length of time under normal storage conditions within which no off-flavors or defects are developed and quality parameters are within accepted limits for this commercial category [18]. Consumers rely on shelf-life determinations to differentiate between products that are acceptable for consumption from those that are no longer acceptable. Thus, it is obligatory for the olive oil industry to monitor oil quality throughout the production line [19] and to be able to provide realistic information on shelf-life prediction considering the temperature changes and light exposure during transport and commercial activities [20].

EVOO shelf-life testing is often conducted under real-time conditions or accelerated conditions [21]. Real-time shelf-life testing allows data collection under normal storage

conditions and reflects actual changes in EVOO matrix over time [22]. On the other hand, this process requires consistent storage conditions and can be extremely time consuming when the quality depletion of EVOO proceeds fairly slowly under normal storage conditions [21]. Hence, accelerated shelf-life testing (ASLT) methods such as Rancimat, Active Oxygen Method (AOM), and Oil Stability Index (OSI) are also employed to determine EVOO shelf life under conditions which are different from normal storage conditions within a short period of time [23]. Noticeably, as convenient and rapid as the accelerated methods can be, Kaya et al. [24] reported that extrapolation from the Rancimat values led to either underprediction or overprediction of the actual shelf life of sunflower and olive oil due to drastic ASLT conditions. Nonetheless, analytical data generated from either or both conditions can be applied to the development of EVOO shelf-life prediction models.

In general, two types of shelf-life prediction models are widely used to simulate EVOO degradation: kinetic models and empirical models. Kinetic models are developed based on how reaction rates in critical chemical parameters (Table 1) are influenced by experimental conditions related to variables such as storage time, temperature, and light [20]. Data describing the changes of these parameters under conditions simulating actual storage are submitted to modeling based on the known rate of a particular reaction. The limitation of kinetic modeling is that classical kinetic equations cannot easily accommodate the complexity of oxidation reactions and oil deteriorations. Empirical models are developed based on the correlations between individual chemical parameters and experimental condition variables. Typically, advanced statistical analyses are performed on analytical data to develop regression models which enable the prediction of maximum shelf life as a function of chemical parameters [20, 25]. The limitation of empirical modeling is the difficulty to extend beyond the measured setup (e.g., storage condition) and simplification and approximation can fail when the setup is changed.

Previous studies have been done intensively on how different ratios of chemical composition, packaging systems, and storage conditions would affect the quality of EVOO [14, 26–31]. However, the olive oil industry is still in great need of practical and effective shelf-life prediction models that can be easily used or adopted after moderate modifications in order to reasonably predict EVOO shelf life and to ensure the EVOO products complying with the current regulations for its category [32].

In this review, ten shelf-life prediction models using various parameters and approaches are discussed. In addition, future directions of shelf-life prediction models are proposed aiming at minimizing the discrepancies between real-time shelf life and predicted shelf life of EVOO products.

2. Prediction Models for EVOO Shelf-Life Determination

The development process of EVOO shelf-life prediction models is streamlined in Figure 1. While ASLT provides a more rapid and less-expensive method of predicting shelf life than real-time storage condition monitoring, some accelerated conditions may lead to erroneous shelf-life predictions because of complicated chemical reaction mechanisms from real-time conditions [33]. Thus, shelf-life prediction models are best developed based on results from both real-time and accelerated storage conditions, followed by extensive evaluation and adjustment.

Table 2 provides a summary of olive oil sample size, chemical/sensory analysis, and statistical approach of the ten shelf-life prediction models discussed in this review.

2.1. Pagliarini et al. (2000) [20]. This Tuscan EVOO shelf-life prediction model used induction time, hydroxytyrosol, and tyrosol to predict the time (in days) to reach an acceptable limit of 2.1 for UV K_{232}.

The research team analyzed a total of 37 samples from five different lots which are categorized in Table 3. The samples were subjected to different bottling, transport, and storage conditions in supermarkets, although the authors found that the stability of the oil was not significantly affected. This could be due to reasons that (1) the oil was stored properly in the tanks at processing facility in Italy (OL.MA.) before getting bottled; (2) the oil did not experience extreme travel stress during transportation to either Italian supermarket or Australia supermarket; (3) while the oil was stored in supermarkets, the uncontrolled light and temperature were still in favor of maintaining the quality of olive oil.

The research team tracked the changes in oil during storage with 21 physiochemical parameters and sensory analysis and via multivariate analysis procedure, it was concluded that the most significant parameters were K_{232}, induction time, chlorophyll, carotenoid, alpha-tocopherol, hydroxytyrosol, and tyrosol. Since the only parameter that had established limit in the standards was K_{232}, three empirical models were set up to predict the time to reach a given value for K_{232} and 2.1 was chosen as a reference value:

$$\begin{aligned} &\text{(a)}\ t = 1130.84\text{Ln}\ (\text{induction time}) - 2388.13 \\ &\text{(b)}\ t = 329.02 - 38.11\,(\text{hydroxytyrosol}) \\ &\text{(c)}\ t = 580.34 - 68.11\,(\text{tyrosol}). \end{aligned} \tag{1}$$

In these equations t is the time (in days) to reach an acceptable limit of 2.1 for K_{232}. According to the authors, this model underestimates the experimental storage time by 20 days for Rancimat induction time, 10 days for hydroxytyrosol content, and 5 days for tyrosol content.

The above models could be useful for selecting new olive/oil suppliers and comparing different suppliers, olive harvest years, and storage conditions. While these three equations consist of simple calculations, the output of estimated time is when K_{232} reaches 2.1 instead of 2.50 which is the upper limit of K_{232} for EVOO category in the International Olive Council (IOC) trade standard [32]. Hence, the results may not be reflective and reliable in their current form.

2.2. Gutiérrez and Fernández (2002) [35]. The quality indices (specified in the European Union standards EC1991 Regulation 2568/91) of EVOO samples produced from two

Table 1: Critical chemical parameters used in olive oil shelf-life prediction model development.

Parameter	Determination	Indicator	Methodology
Free fatty acids (FFA)	Free fatty acids are formed by the hydrolysis of triglycerides during ripening, processing and storage	An elevated level of free fatty acid indicates hydrolyzed fruits and/or poor quality oil made from unsound fruit, improperly processed or stored oil	Analytical titration
Peroxide value (PV)	Peroxides are primary oxidation products that are formed when oils are exposed to oxygen, producing undesirable flavors and aroma	An elevated level of peroxides indicates oxidized and/or poor quality oil	Analytical titration
Ultraviolet absorbance (UV)	Conjugated double bonds are formed from natural nonconjugated unsaturation in oils upon oxidation. The K_{232} measures primary oxidation products and K_{270} measures secondary oxidation products	An elevated level of UV absorbance indicates oxidized and/or poor quality oil	UV spectrophotometry
1, 2-Diacylglycerols (DAGs)	Fresh EVOO contains a high proportion of 1,2-diacylglycerols to 1,2- and 1,3-diacylglycerols, while olive oil from poor quality fruits and refined olive oils have higher level of 1,3-DAGs than fresh EVOO	A low ratio of 1,2-diacylglycerols to 1,2- and 1,3-diacylglycerols is an indicator for oil that is hydrolyzed, oxidized, and/or of poor quality	Gas chromatography (GC)
Pyropheophytins (PPP)	Chlorophyll pigments break down to pheophytins and then pyropheophytins upon thermal degradation and aging of olive oil	An elevated ratio of pheophytin a to pyropheophytins is an indicator for oil that is oxidized and/or adulterated with refined oil	High performance liquid chromatography (HPLC)
Sensory evaluation	Sensory refers to flavor and aroma attributes	Sensory evaluation can help identify oils that are of poor quality, oxidized, and/or adulterated with other oils	A recognized panel of 8–12 people evaluates oils for sensory characteristics
Induction time	The oxidation process is accelerated by means of heating up the reaction vessel while passing air continuously through the sample	Oxidative stability (in hours) denotes the resistance of oils to oxidation. The longer the induction time, the more stable the oil	Rancimat
Total phenols	The sum of up to 30 individual phenols which have antioxidative ability	A low level of total phenols can indicate a shorter shelf life while a high level of total phenols can indicate a longer shelf life	UV spectrophotometry/High performance liquid chromatography (HPLC)
Volatiles (e.g. hexanal/nonanal, E-2-hexenal/hexanal),	Volatile compositions change during oxidation. For example, as the oil oxidizes, the concentration of hexanal decreases while concentration of nonanal increases	The ratios of hexanal/nonanal and E-2-hexenal/hexanal can indicate oxidized oil	Headspace-gas chromatography (GC)
Fatty acid profile (FAP)	Saturated and unsaturated fatty acids consist of the principal components of fats. Fatty acid profiles are distinguishable markers between olive oils and some seed/nut oils (FAPs vary slightly depending on the varieties and growing region of olives)	Analysis of the fatty acid profile provides information on the authenticity of the olive oil and can be used as an indicator for adulteration	Gas chromatography (GC)

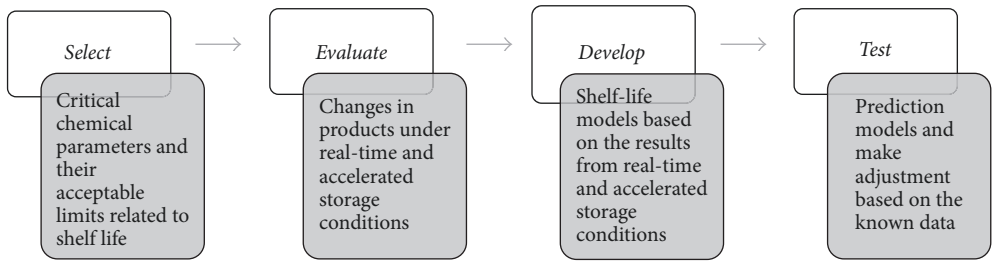

Figure 1: Shelf-life prediction model development process.

cultivars, Picual and Hojiblanca, were monitored throughout two different storage conditions, together with the evolution of the oxidative stability and sterols, polyphenols, alpha-tocopherol, chlorophyllic and carotenoid pigments, and FAP.

In this study, a total of 46 L of EVOO was extracted and packed for each cultivar in Spain. Thirty-four 1 L transparent glass bottles of each cultivar were stored inside a thermostated chamber at 30°C with illumination (800 lx; 12 h/day), which was similar to commercial storage conditions. Other twelve bottles of each cultivar were stored at 2°C in darkness. In addition, 30 L EVOO of each cultivar was purchased in a local market as commercial reference samples and stored in the thermostated room. Bottles were sampled weekly during the first 70 days and subsequently every 15 days for 6 months of storage. It is worth mentioning that the EVOO samples produced from each cultivar had similar initial values on most of the chemical parameters other than acidity (Picual: 0.44%; Hojiblanca: 0.26%), stability (Picual: 69.5 h; Hojiblanca: 43.3 h), and *o*-diphenols (Picual: 9.00 mg/kg; Hojiblanca: 14.64 mg/kg).

Overall, samples stored at 2°C in darkness remained minimal to unaltered throughout the entire storage period. Thus, the regression analysis was performed on selected chemical parameters from samples stored at 30°C with illumination for each cultivar (Table 3). Similar changes in PV of two olive cultivars were observed in a 2-fold increase during the first 21 days and followed by a linear decrease until the end of storage. The evolutions of alpha-tocopherol, chlorophyllic pigments (CP), total polyphenols (TP), and *o*-diphenols were well fitted to first-order kinetics. Most importantly, the coefficient K_{270}, which measures the accumulation of secondary oxidation products that cause off-flavors in olive oil, showed a sharp increase along the storage period in all the samples stored at 30°C with illumination in spite of cultivar and sample source. As a result, an excellent correlation between initial stability and time to reach the limit of $K_{270} = 0.25$ was established for EVOO samples bottled in glass containers regardless of olive cultivar (Table 4).

The correlation between initial stability (S) and storage time to achieve K_{270} of 0.25 has demonstrated when an EVOO no longer retains its extra virgin quality. Being a critical indicator of oxidation level, K_{270} is required by the IOC standard [32] and can be easily obtained by producers. Nonetheless, the validation of this model is in need for other cultivars with a larger sample size in an extended storage period. Storage containers other than glass type should also be taken into consideration when applying this model.

2.3. Psomiadou et al. (2003) [19]. To establish this empirical model, fifty-two Greek virgin olive oil (VOO) samples (Koroneiki *cv*) from three consecutive crops (1994–1997) were obtained as the training set for quality parameters measurement. The measured parameters included FFA, PV, UV, FAP, and the ratio of unsaturated and saturated fatty acids, alpha-tocopherol, total phenols, total chlorophylls, and OSI. Collinearity diagnostics, variable selection, and regression analysis were performed on the obtained analytical data to determine the contribution of each parameter to maintaining VOO quality.

Through statistical analyses, the research team located alpha-tocopherol, PV, total chlorophylls, and total phenols to be the most important factors that affected OSI values and yielded below model:

$$\begin{aligned}\text{OSI} = {} & 5.081 + 0.0102\ (\text{alpha-tocopherol}) \\ & - 0.364\ (\text{PV}) + 0.0477\ (\text{total chlorophylls}) \\ & + 0.0259\ (\text{total phenols}).\end{aligned} \quad (2)$$

As shown in the above model, all antioxidants contributed in a similar way to the OSI factor while PV posed clear negative impact on the oxidative stability of the oil. The predictability of this model was further examined and confirmed by a test set of 13 VOO samples of the same cultivar from 1999-2000 crop, which showed a negligible prediction bias and a low square root of the mean square error of 2.33, indicating an effective prediction of OSI was achieved in this model for VOO of Koroneiki *cv*.

In this study, the effect of many oxidative parameters on oils from different crop years was examined with comprehensive statistical analyses, yielding a simple predictive equation, and followed by validation on another 13 samples from the same cultivar. However, while this model gives useful information regarding the oil stability which impacts shelf life directly, it would require producers to incur the expense for three tests (alpha-tocopherol, total phenols, and total chlorophylls) that are not currently required in the standards [32]. Besides, producers can request OSI analysis (by Rancimat) for less of the cost than these three tests although the correlation between OSI and actual shelf life was not elaborated. Regardless, this model still has practical influence on the routine control of Koroneiki *cv* VOO in the industry and future development of prediction models for VOO made from other olive cultivars can be derived from this validated model with minor modifications.

Table 2: Summary of shelf-life prediction models discussed in the review.

Model	Sample (bottles)	Storage condition	Chemical/physical analysis	Sensory analysis	Statistical analysis	Shelf-life prediction indicator	Ref.
1	37 Tuscan EVOO from 5 Lots	(i) Dark glass (ii) In the dark (20°C)/uncontrolled light and temperature (iii) 14/16/17/21 months; sampled every 2 months	FFA, PV, UV, polyphenol, alpha-tocopherol, tyrosol and hydroxytyrosol, secoiridoid aglycons, chlorophyll absorbance, carotenoid absorbance, induction time (120°C, 20 L/h)	(i) 12 trained panelists (ii) Bitterness and astringency	(i) Sample classification: principal component analysis (PCA) and partial least-squares analysis (PLS) on Unscrambler 6.0 software package (Camo As, Trondheim, Norway) (ii) Comparison of regression lines: Statgraphics Plus 1.0 software package (Manugest KS Inc., Rockville, MD)	Time (in days) to reach K_{232} of 2.1 (t): (i) $t = 1130.84$ Ln (induction time) − 2388.13 (ii) $t = 329.02 - 38.11$ (hydroxytyrosol) (iii) $t = 580.34 - 68.11$ (tyrosol)	Pagliarini et al. (2000) [20]
2	46 experimental Spanish Picual and Hojiblanca EVOO and 30 commercial Picual and Hojiblanca EVOO	(i) Clear glass (ii) Thermostated chamber (30°C)/in the dark (2°C) (iii) 6 months; sampled weekly during the first 70 days and every 15 days afterward	FFA, PV, UV, total phenols, *o*-diphenols, tocopherols, chlorophyllic and carotenoids, FAP and sterols, induction time (100°C, 10 L/h)	(i) 12 trained panelists (ii) Highest quality (score 9) to lowest quality (score 1)	(i) Comparison of means: Duncan's test (ii) Analysis of variance and correlation: CoStat 2.10 software (CoHort Software, Berkeley, CA)	Time (in days) to reach K_{270} of 0.25(t) according to initial stability (S): $S = 1.01t - 12.84$	Gutiérrez and Fernández (2002) [35]
3	52 Greek Koroneiki virgin olive oil (VOO) from 1994 to 1997 for model development and 13 Koroneiki VOO from 1999-2000 for model validation	Stored at −22°C till analysis	FFA, PV, UV, total phenols, alpha-tocopherol, total chlorophylls, FAP and the ratio of unsaturated and saturated fatty acids (U/S), induction time (120°C, 20 L/h)	NP*	(i) Effect of the production year: linear regression, t-test and variable selection (ii) Possible collinearity among independent variables: variance inflation factor (VIF), PCA and singular value decomposition (SVD) (iii) Selection of analytical parameter affecting OSI the most: regressions, forward and backward selection, stepwise selection, Mallow's index and Akaike's information criterion (AIC) (iv) Statistical packages: SAS version 8 (SAS Institute Inc., Cary, NC), SPSS version 10 (IBM Corporation, Chicago, IL), and JMP IN version 3.1.7 (SAS Institute Inc., Cary, NC)	OSI = 5.081 + 0.0102 (alpha-tocopherol) − 0.364 (PV) + 0.0477 (total chlorophylls) + 0.0259 (total phenols)	Psomiadou et al. (2003) [19]
4	Large EVOO sample size from Mediterranean areas from 1999 to 2001 for model development and 11 EVOO from 2002 for model validation	NP	63 chemical parameters including FFA, PV, UV, minor component content, lipid oxidation status and antioxidant activity	(i) 25 trained panelists (ii) 18 sensory parameters including green olive aroma/flavor (e.g. bitterness), astringency, and pungency	(i) Fractional factorial design (FFD): Modde 8.0 software package (Umetri, Umea, Sweden) (ii) PCA and PLS: Unscrambler 7.8 software package (Camo AS, Oslo, Norway)	EVOO degradation parameter value (Y) as a function of FFA (X_1), oleic acid content (X_2) and bitterness score (X_3): $Y = c + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_1X_2 + a_5X_1X_3 + a_6X_2X_3$	Zanoni et al. (2005) [10]
5	432 Portuguese organic EVOO	(i) PET/PVC/glass bottle (ii) Covered with aluminum foil inside fiberboard boxes/under fluorescent light at 15/30/40°C with relative humidity of 60% (iii) 12 months; sampled monthly	Hexanal	NP	(i) Determination of differences between treatments for the hexanal evolution rate: SAS 8.2 (ii) Separation of the means of GC areas: Tukey test and Duncan test (iii) Model development: nonuniform finite-difference scheme with an upwinding numerical algorithm (Newton method for nonlinear systems)	Probability for the olive oil to reach the end of its shelf life during a certain period of time (P_{safe}): $P_{safe} = 1 - \frac{\int_{t_1}^{t_2} \langle C_{hexanal} \rangle (t)\, dt}{\int_{0}^{t_2} \langle C_{hexanal} \rangle (t)\, dt}$	Coutelieris and Kanavouras (2006) [34, 36]

Table 2: Continued.

Model	Sample (bottles)	Storage condition	Chemical/physical analysis	Sensory analysis	Statistical analysis	Shelf-life prediction indicator	Ref.
6	Seven Spanish Cornicabra VOO	(i) Opened amber glass (ii) In the dark at 25/40/50/60°C (iii) sampled after 93/41/34/19 weeks	PV, UV, FAP, phenolic compounds, tocopherols, induction time (100°C, 10 L/h)	NP	(i) Differences between treatments: Duncan test on SPSS version 14 (ii) Linear and nonlinear regression: GraphPad Prism 4.02 (GraphPad Software, Inc., San Diego, CA) (iii) Oxidation and antioxidant degradation rates: calculated from the slopes of respective concentration versus time curve (iv) Effect of temperature on rates of oxidation: Arrhenius equation	Time (in weeks) to reach K_{232} of 2.5 at a mild temperature ($T \leq 60^{\circ}C$): $\mathrm{TRUL} = aT^{b}$	Mancebo-Campos et al. (2008) [23]
7	Six single-cultivar VOO	(i) Amber glass (ii) In the dark at room temperature/15°C (iii) 12 months; sampled monthly	Chlorophyll pigments (pheophytin a and pyropheophytin a)	NP	(i) Differences between means: one-way ANOVA (ii) Post hoc comparison: Brown and Forsythe test [37] (iii) PCA, PLS, and nonlinear regression: Statistica 6.0 and Statgraphics Centurion XV for Windows (StatSoft Inc., Round Rock, TX)	The percentage of pyropheophytin a (% PPP) over time (t): % PPP (t) = $\left(\left(e^{(a_1-\beta_1/T)}\,[\mathrm{PP}]_0 / \left(e^{(\alpha_2-\beta_2/T)} - e^{(\alpha_{ta}-\beta_{ta}/T)}\right)\right) \cdot \left[e^{-(e^{(\alpha_{ta}-\beta_{ta}/T)}t} - e^{-(e^{(\alpha_2-\beta_2/T)}t}\right]\right) \times \left([\mathrm{PP}]_0 e^{-(e^{(\alpha_{ta}-\beta_{ta}/T)}t} + \left(e^{(a_1-\beta_1/T)}\,[\mathrm{PP}]_0 / \left(e^{(\alpha_2-\beta_2/T)} - e^{(\alpha_{ta}-\beta_{ta}/T)}\right)\right) \cdot \left[e^{-(e^{(\alpha_{ta}-\beta_{ta}/T)}t} - e^{-(e^{(\alpha_2-\beta_2/T)}t}\right]\right)^{-1}$	Aparicio-Ruiz et al. (2012) [16]
8	Nine olive oil samples	Stored at 4°C until analysis	FFA, PV, total tocopherols and total phenols, total polar compounds, conjugated diene value, ratio of mono- and poly-unsaturated fatty acids (M/P ratio), and induction time (100/110/120/130°C, 25 L/h)	NP	ANOVA and regression analyses: MStatC (Michigan State University, East Lansing, MI) and SlideWrite (Sigma Aldrich, St. Louis, MO)	Calculate shelf life at 50°C (SL_{50}) as a function of induction time (OSI): $\mathrm{SL}_{50} = 0.9985\left\{A\left(\frac{100-a_0}{100a}\right)(\mathrm{OSI}-b) + A\frac{a_1((b-\mathrm{OSI})/100a)}{1+\left((\mathrm{OSI}-b-aa_2)/aa_3\right)^2} + B\right\}$	Farhoosh and Hoseini-Yazdi (2013) [25]
9	A wide range of commercial olive oil samples for model development and 118 olive oil and 20 EVOO for model evaluation	(i) Dark glass (ii) In the dark at 18 ± 2°C (iii) 30 months; sampled when estimated best before date was reached	FFA, PV, UV, PPP, DAGs, and induction time (110°C, 20 L/h)	(i) 12 trained panelists (ii) The median values of defect, fruitiness, bitterness, and pungency	NP	Best before date (in months) from the lowest value obtained from induction time, DAGs, FFA Factor (derived from FFA) and PPP: (a) Hours of induction time at 110°C (b) $\frac{\mathrm{DAGs}-35\%}{\mathrm{FFA\ Factor}}$ FFA factor = 1.7% (if FFA < 0.4%); 2.1% (if FFA > 0.4% and <0.6%); or 2.5% (if FFA > 0.6%) (c) $\frac{17\%-\mathrm{PPPs}}{0.6\%}$	Guillaume and Ravetti (2016) [18]
10	36 EVOO	(i) Amber glass (ii) In the dark/exposed to natural and artificial light at room temperature (17–25°C) (iii) 12 months; sampled after 0/3/6/9/12 months	FFA, PV, UV, induction time; electronic tongue signal profile	(i) 4 trained panelists (ii) Olfactory sensations, gustatory-retronasal sensations, and final olfactory-gustatory sensations	See Table 10	3 best linear discriminant analysis (LDA) and simulated annealing (SA) prediction models	Rodrigues et al. (2017) [38]

*NP: not provided.

Table 3: Sample Lot information in the Pagliarini et al. (2000) model.

Lot #	Lot A (reference lot)	Lot B_1	Lot B_2	Lot C_1	Lot C_2
Time taken from freshly made batch	Immediately after processing	After 77 days of storage in tanks	After 188 days of storage in tanks	After 98 days of storage in tanks	After 188 days of storage in tanks
Bottling	100 mL dark glass, closed with screw caps	500 mL dark glass, closed with screw caps	500 mL dark glass, closed with screw caps	500 mL dark glass, closed with screw caps	500 mL dark glass, closed with screw caps
Shipping destination after bottling	Processing facility in Italy (OL.MA.)	A supermarket in Australia	A supermarket in Australia	A supermarket in Italy (close to OL.MA.)	A supermarket in Italy (close to OL.MA.)
Storage condition at destination	In the dark at 20°C	Uncontrolled light and temperature	Uncontrolled light and temperature	Uncontrolled light and temperature	Uncontrolled light and temperature
Storage period at destination	21 months	16 months	14 months	17 months	14 months

Table 4: Correlations between storage time t (in days) and selected parameters by Gutiérrez and Fernández (2002).

Cultivar	Picual	Hojiblanca
PV (mequiv/kg)	PV = $-0.04t + 7.2$; $r = 0.9532$	PV = $-0.03t + 6.6$; $r = 0.9600$
TP (mg/kg, caffeic acid)	Ln (% TP) = $-4.45\times10^{-3}t + 2.03$; $r = 0.9879$	Ln (% TP) = $-2.55\times10^{-3}t + 1.97$; $r = 0.9965$
CP (mg/kg)	Ln (CP) = $-0.11t + 12.34$; $r = 0.9848$	Ln (CP) = $-0.26t + 18.92$; $r = 0.9810$
Initial stability (S) for the achievement of $K_{270} = 0.25$ (h)	$S = 1.01t - 12.84$; $r = 0.9823$	

2.4. Zanoni et al. (2005) [10]. A phenomenological model was introduced for the first time to predict the stability of EVOO based on combined stability/instability composition indices. The experimental design comprised two steps: (1) stability/instability indices screening and (2) significant relationships between screened indices and EVOO degradation investigation and confirmation. The screening of composition indices was carried out by multivariate analysis on data derived from 63 chemical and 18 sensory parameters obtained from oils purchased from four different Mediterranean area during the 1999–2001 crops. Based on the statistical analysis, the research group proposed that acidity value was indirectly related to oil stability while oleic acid content and bitter taste were directly related to oil stability. The predictability of these most relevant indices to oil stability was then checked by measuring six major degradation parameters on eleven oil samples differing in screened indices planned by a fractional factorial design (FFD) and processed with principal component analysis (PCA) and partial least squares (PLS) regression afterward. Parameters of PV, UV, minor polar component content (oleuropein and ligstroside derivatives), oxidative status of fatty acids, antioxidant activity, and sensory evaluation were measured in this step.

Combining the results from PCA mapping and PLS modeling has proved the hypothesis that in EVOO samples (1) the more acidity the more degradation; (2) the more oleic acid content the less degradation; and (3) the more bitter the taste the less the degradation. Furthermore, PV, UV K_{232}, and lipid oxidation status (oxidized fatty acid content at 230 nm and dienoic and trienoic conjugated fatty acids content) were found to be the most critical parameters when measuring EVOO degradation. A mathematical model was established to predict EVOO degradation as a function of the combination of the three most relevant indices (acidity, oleic acid content, and bitter taste):

$$Y = c + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_1X_2 + a_5X_1X_3 + a_6X_2X_3, \quad (3)$$

where Y is the selected degradation parameter to be predicted, X_1 is the acidity, X_2 is the oleic acid content, and X_3 is bitter taste score. Constant values a_x are listed in Table 5. Unlike what had been found in previous studies [19, 20, 35], the antioxidant component content which consisted of antioxidant activity and minor polar component content in this study showed insignificant impact on EVOO degradation and was excluded from the proposed model as a result.

Predictive models of oil degradation degree can be obtained based off of the above proposed mathematical model, which may be useful to predict the rate of oil degradation if the oil degradation history was known. In this regard, a major limitation of this model is that it was based on constant indices without taking the composition changes under storage conditions into full consideration. That is, any changes of oil composition that occurred during lipid oxidation would require a new set of quality index values to maintain the model validation. Although this drawback may be overcome by replicating the experimental design several times, the application of this model may be limited to EVOO samples being stored under optimal conditions that have minimal effects on the change of stability/instability indices and/or samples that yield similar rate of degradation kinetics for the same stability/instability indices combination.

Table 5: Constant values of selected degradation parameters for empirical polynomial models by Zanoni et al. (2005) [10].

Degradation parameter	c	a_1	a_2	a_3	a_4	a_5	a_6
PV	−77.921	115.143	1.148	28.910	−1.411	−3.679	−0.367
K_{232}	−6.364	10.911	0.106	2.981	−0.133	−0.328	−0.037
Lipid oxidation status							
Dienoic trans-trans	−0.051	−0.103	0.002	0.136	0.002	−0.040	−0.001
Dienoic cis-trans, trans-cis	0.990	−0.510	0.006	0.054	0.023	−0.262	−0.002
Trienoic conjugated fatty acid content	−1.562	2.960	0.020	0.563	−0.034	−0.183	−0.006
Oxidized fatty acid content at 230 nm	−0.280	4.805	0.032	1.164	−0.054	−0.099	−0.020

Table 6: Sample packaging and storage conditions for a 12-month study in the Coutelieris and Kanavouras (2006) model.

Sample	Portuguese organic EVOO		
Packaging material	0.5 L PET bottle	0.5 L PVC bottle	0.5 L glass bottle
Oxygen transmission rate at 0.21 atm driving force (cc/m^2/day)	8	9.8	N/A
Storage location	Half covered with aluminum foil inside fiberboard boxes; half exposed to fluorescent light		
Storage temperature (°C)	15, 30, and 40		
Relative humidity (%)	60		

2.5. Coutelieris and Kanavouras (2006) [34, 36]. As listed in Table 1, volatile compounds are good indicators of olive oil quality as they are mainly produced through lipoxygenase pathway and chemical oxidation during processing and storage and contribute greatly to the olive oil flavor [39]. In this study, the evolution of hydroperoxide in the packaged Portuguese organic EVOO samples was monitored and the progression of hexanal, which was assumed as the most prominent volatile compound posing higher impact on the sensory attributes of olive oil, was quantified over a 12-month storage period. Table 6 shows the packaging materials and storage conditions of analyzed EVOO samples.

A mathematical model for the mass transfer taking place in the oil-package material interacting system was deduced based on four assumptions in the oil phase and two assumptions in the oil-package system. In the oil phase, the assumptions were (1) the oil quiescent; (2) all the hydroperoxides eventually transformed to hexanal during lipid oxidation; (3) at time $(t) = 0$, there was a measurable amount of oxygen, fatty acid, and hexanal in the oil phase; and (4) the packaging materials adsorbed hexanal according to Langmuir isotherm. In the oil-package system, the assumptions included the following: (1) oxygen and hexanal had constant concentration outside the bottles at spatial coordinate $(x) = 0$; and (2) at $t = 0$, oxygen and hexanal concentrations inside the packaging material were zero. The mass transfer phenomena were elaborated explicitly by using diffusion equations for diffusion of oxygen and hexanal and Langmuir-type adsorption for hexanal adsorption in the oil-package (cylinder bottle) system. A numerical algorithm, along with a nonuniform finite-difference scheme, was then applied with modifications to solve the issue of nonlinearity of the studied system for various combinations of the storage conditions mentioned in Table 6.

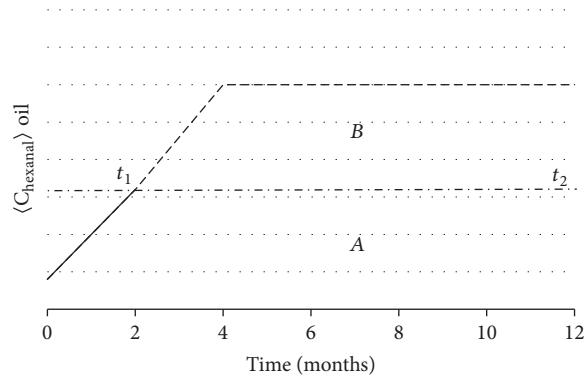

Figure 2: The graphical representation of the definition of P_{safe}. The threshold of the hexanal concentration is represented by the long dash dot line {adopted from Coutelieris and Kanavouras (2006) [34]}.

The study showed that samples kept under light had yielded much higher concentration of hexanal when compared to the samples stored in dark. In addition, the highest hexanal concentration was found in samples stored in PET bottles at 40°C with light exposure, followed by those stored in glass, and samples stored in PVC bottles had a lower hexanal concentration. As shown in Figure 2, P_{safe}, the probability for the olive oil to reach the end of its shelf life during a certain time period is comparable to the ratio of the areas below (area A) and above (area B) a roughly defined threshold of the hexanal concentration (long dash dot line). The estimation of P_{safe} was proposed in the following model during the same time period $[t_1, t_2]$:

$$P_{safe} = 1 - \frac{\int_{t_1}^{t_2} \langle C_{hexanal} \rangle (t)\, dt}{\int_{0}^{t_2} \langle C_{hexanal} \rangle (t)\, dt}, \quad (4)$$

where C_{hexanal} is the concentration of hexanal, t_1 is the time when concentration reaches the upper limit for the oil's quality acceptance, t_2 is set to 12 months in this study, and the brackets indicate spatial averaging of hexanal concentration being used.

The sensitivity of this model was tested on samples kept under different storage conditions and P_{safe} values were compared for four different thresholds (15%, 20%, 25%, and 30% over the initial hexanal concentration). One of the key findings suggested that the predictions diverged from experimental results under specific storage conditions due to the low concentrations of hexanal in oil stored in dark at any temperature. Moreover, the determination of hexanal concentration threshold was ambiguous without knowing data generated from additional chemical analyses and sensory evaluation. Most importantly, the amount of hexanal does not always allow oxidized olive oils to be distinguished from virgin ones, as this compound can come from both lipoxygenase and oxidative pathways [40]. Nonetheless, the proposed model had undertaken a comprehensive and extensive investigation on the EVOO degradation in the oil-package system by factoring in the chemical reactions and diffusion of compounds both in the oil phase and through packaging materials, granting a promising parameter for better monitoring the shelf life of packaged olive oil stored under various conditions. The validation of P_{safe} model can be further strengthened by adding sensory analysis.

2.6. Mancebo-Campos et al. (2008) [23]. During the storage of seven Cornicabra *cv* VOO samples (varied in total phenol concentrations) in dark and at mild temperatures (25, 40, 50, and 60°C), the autoxidation kinetic behavior of the main oxidation indices (PV, K_{232}, and K_{270}) and the oxidizing substrate [unsaturated fatty acids (UFA)] were reported for the first time. In addition, the extrapolated time (in weeks) required to reach the upper limit (TRUL) of each main oxidation index in the EU regulation for the VOO category was also calculated based on the experimental results from this study and a previous study conducted by the same research group [41].

According to the evolution of measurements in this study, PV did not reach its upper limit (20 meq/kg) in any samples stored at 25°C by the end of a 93-week storage, nor did it do that in some of the samples stored at higher temperatures. Stabilization of PV was reached below or slightly above the limit in all cases in spite of more harsh storage temperatures and intensive air exposure in opened bottles. This similar observation was also confirmed by other research groups as a reduction in PV would occur due to the breakdown of peroxides into secondary products [15, 42], indicating the unreliability of PV being used as a quality marker for olive oil shelf life. On the contrary, the upper limit of K_{232} ($2.5\,\text{K}^{1\%}{}_{1\,\text{cm}}$) was reached in samples stored at any conditions although K_{232} and PV tended to stabilize at a similar value in each sample stored at higher temperatures, following pseudo zero-order kinetics before reaching the plateau. On the other hand, the upper limit of K_{270} ($0.22\,\text{K}^{1\%}{}_{1\,\text{cm}}$) was reached in all samples with only two exceptions at 25°C, yielding pseudo

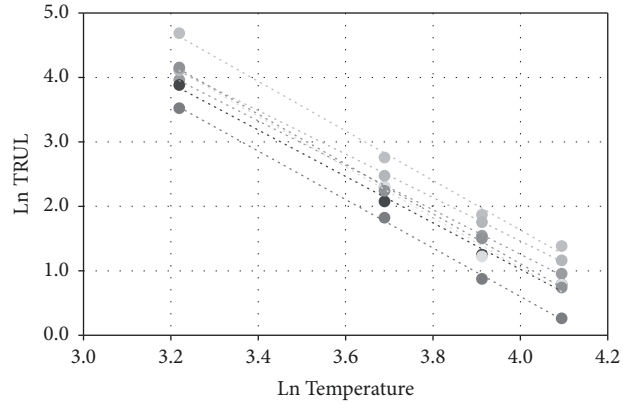

Figure 3: Correlation between TRUL and temperature for K_{232} (TRUL = aT^b). Seven samples denoted in seven shades {adopted from Mancebo-Campos et al. (2008) [23]}.

first-order kinetics. Furthermore, the polyunsaturated fatty acids (PUFA) linoleic and linolenic acids showed a linear decrease at a rate increasing with storage temperature, and the best correlation was drawn between loss of PUFA and increase of K_{232} at all temperatures as described by the linear Arrhenius equation.

As a good indicator of primary oxidation level and an easy parameter to determine, K_{232} showed high linearity in the early stages of oxidation and presented excellent correlation with loss of UFA. Thus, K_{232} was selected as the best normalized oxidation index for potential shelf-life estimation of VOO, defined as TRUL, at a mild temperature (≤60°C):

$$\text{TRUL} = aT^b. \tag{5}$$

Based on the TRUL results of K_{232} generated at different temperatures, the above model can be further explained by Figure 3. As a result, the predicted TRUL at 25°C was very close to the experimental TRUL at the same temperature when applying the proposed model to accelerated storage temperatures (40, 50 and 60°C).

Unlike drastic ASLT conditions where olive oil samples are tested on oxidative stability at over 100°C [43, 44], this model conducts an accelerated stability test at mild temperatures below 60°C and allows a time-saving shelf-life prediction to reasonably estimate the actual shelf life of VOO samples stored under normal storage conditions (25°C). It is worth noting that VOO samples were stored in open bottles throughout the study with intensive oxygen exposure, which did not reflect the actual storage conditions from a commercial standpoint. Besides, VOO samples used in this study were from the same cultivar with similar initial concentrations on the majority of the measured parameters. A follow-up study focusing on the contribution of antioxidants content and fatty acids unsaturation degrees to oxidation rates is also necessary to test the applicability of the proposed model.

2.7. Aparicio-Ruiz et al. (2012) [16]. Chlorophyll pigments are sensitive to small amounts of degradation, which would eventually take place in an EVOO even under optimal storage conditions. During storage, pheophytin a (PP) degrades to PPP (Table 1). The ratio of these two compounds therefore is a useful parameter to track olive oil degradation over time. This kinetic prediction model is established based on PPP because PPP changes predictably with time under specific temperatures [45].

In developing this model, the research team stored six single-cultivar VOO samples (Blanqueta *cv*, Arbequina *cv*, Cornicabra *cv,* and Picual *cv*) in 65 mL amber glass jars with 3% (v/v) headspace, in the dark at room temperature. The monthly temperatures range from 10.4°C to 28.6°C throughout the year, with an average annual temperature of 19.3 ± 1.9°C. Chlorophyll pigments were quantified every month up to one year. The degradation of PP was found fitting first-order kinetics after applying multivariate statistical analysis to the experimental data. The statistical results also showed that time, temperature, and initial PP concentration were the main variables that affected PPP prediction for shelf life. Percent PPP (% PPP) over time was defined as the quotient of the concentration of PPP ([PPP]) and the sum of [PPP] and [PP]. A mathematical model to predict % PPP as a function of time and temperature was then developed as shown below:

$$\%\ \mathrm{PPP}\,(t) = \frac{\left(e^{(a_1-\beta_1/T)}\,[\mathrm{PP}]_0 \,/\left(e^{(\alpha_2-\beta_2/T)} - e^{(\alpha_{ta}-\beta_{ta}/T)}\right)\right)\left[e^{-(e^{(\alpha_{ta}-\beta_{ta}/T)}t} - e^{-(e^{(\alpha_2-\beta_2/T)}t}\right]}{[\mathrm{PP}]_0\, e^{-(e^{(\alpha_{ta}-\beta_{ta}/T)}t} + \left(e^{(a_1-\beta_1/T)}\,[\mathrm{PP}]_0 \,/\left(e^{(\alpha_2-\beta_2/T)} - e^{(\alpha_{ta}-\beta_{ta}/T)}\right)\right)\left[e^{-(e^{(\alpha_{ta}-\beta_{ta}/T)}t} - e^{-(e^{(\alpha_2-\beta_2/T)}t}\right]}. \quad (6)$$

In this equation, $[\mathrm{PP}]_0$ is the initial concentration of PP, T is temperature in Kelvin, t is the storage time in hour, and values α_1, β_1, α_2, and β_2 are related to kinetic constants and are protected by industrial license according to the authors. According to the proposed model, % PPP at any time point can be calculated if the initial PP and PPP concentration and storage temperature are known.

This study also compared the change of % PPP under a well-controlled storage temperature of 15°C and room temperature for six single-cultivar VOO samples. Overall, % PPP increased under both temperatures, indicating the degradation of olive oil quality occurred over time in spite of cultivars. However, it is clear that the same samples stored at room temperature had a significant increase in % PPP from 0 to above 8%, especially during summer time (6–8 storage months) when room temperature was typically higher. The development of this parameter tended to be linear with a smaller slope (from 0 to 2%) throughout the entire storage period at 15°C. This finding confirms the temperature impact on PPP generation over time which should be taken into consideration when developing the kinetic model.

After being validated on and compared with another set of empirical data calculated from chlorophyll pigment experimental data obtained by Gallardo-Guerrero, et al. [46], the model was adopted to develop a % PPP prediction graph between 15°C and 35°C as shown in Figure 4. The authors suggested that the % PPP acceptable limit could be set at 14%, which would allow VOO to have one year of shelf life if stored under 22°C. However, this value seems arbitrary as it did take into account any other chemical parameters and/or sensory results.

In a follow-up study published in 2014 [47], the same research team applied this % PPP prediction model to single-cultivar olive oils (Arbequina *cv*) with various levels of initial % PPP at bottling. The samples were stored at different average annual temperatures, ranging from 10°C to 16°C. The authors concluded that the initial value of % PPP is of great importance to be included for a better monitoring of the storage conditions of VOO. Table 7 shows shelf life (in months) for VOO samples stored at 10°C and 16°C before reaching the Australian/California upper limit for PPP of 17%. For instance, if % PPP is 0.64% at bottling, the oil will have more than 36 months and 21 months before it reaches the limit of 17% if stored at 10°C and 16°C, respectively. These temperatures are likely to be cooler than the actual storage temperature; thus a follow-up study with oil stored at a typical store shelf temperature is recommended.

This model only consists of two chlorophyll pigments (PP and PPP) and can be used to monitor the changes of storage temperature and to detect undesired storage conditions based on the rate of pyropheophytinization. Knowing the value of % PPP at any moment during a storage period would also allow a timely adjustment on proper storage temperature and later on provide a better shelf-life estimation. However, without knowing the values of other quality parameters of VOO samples, the % PPP alone may not reflect the storage condition correctly as light exposure can cause the complete breakdown of chlorophylls and all of its derivatives therefore yield a zero value of % PPP [59]. Hence, inclusion of other quality parameters of samples would benefit the model optimization.

2.8. Farhoosh and Hoseini-Yazdi (2013) [25]. The empirical model was developed based on the relationship between oxidative stability measurements (OSI) taken at high temperatures (100–130°C) and the chemical composition data obtained at a low temperature (50°C).

To study the contribution of each compositional parameter to the oxidative stability in olive oil, nine olive oil samples in 1 L glass bottles were purchased from local shops and stored at 4°C until analysis on accelerated stability at 100–130°C. And the ratios between mono- and polyunsaturated fatty acids (M/P ratio), PV and FFA, total tocopherols (TT) and total phenols (TP), total polar compounds (TPC), conjugated diene value (CDV), and induction period (IP) were tested for the storage stability on the same samples incubated at 50°C.

Table 7: Shelf life (in months) for VOO stored at 10°C and 16°C before reaching Australian/California limit of 17% summarized from Aparicio-Ruiz et al. (2014).

% PPP at bottling	Shelf life if stored at 10°C	Shelf life if stored at 16°C
0.64	>36	21
1.35	>36	20
3.26	>36	19
7.06	34	16
8.66	30	10

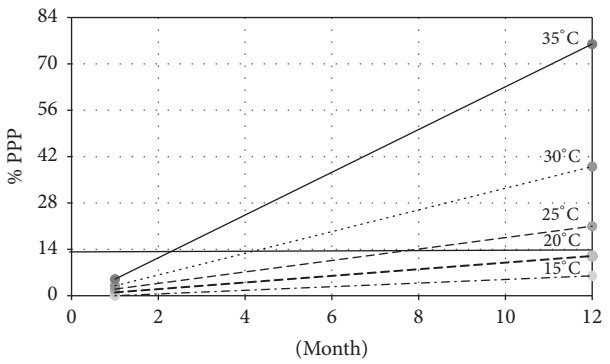

Figure 4: Predicted % PPP during one year of storage at temperatures between 15°C and 35°C {adopted from Aparicio-Ruiz et al. (2012) [16]}.

During the storage stability test conducted at 50°C, the evolution of hydroperoxides and conjugated dienes showed two pseudo zero-order kinetic curves: a gradual slope of linear stage which was considered as the initiation phase of lipid oxidation and then a steep slope of another linear stage known as the propagation phase. The storage time (in days) at intersection points of the PV and CDV curves was identified as the induction period IP_{PV} and IP_{CDV} for the olive oil sample. The level of hydroperoxides increased gradually during IP and then elevated rapidly in the propagation phase, where decomposition of hydroperoxides to aldehydes, ketones, and other secondary oxidative products occurred and off-flavors were accumulated [15]. Thus, the IP-based oxidative stability values IP_{PV} and IP_{CDV} were selected as better parameters to measure the oxidative stability and determine the shelf life of olive oil at 50°C.

Positive correlations were found between oxidative stability (IP_{CDV} at 50°C and OSI at 100–130°C) and M/P ratio, tocopherols, and phenolics. To further elucidate, the higher the M/P ratio is, the less prone to rancidity the olive oil is; the higher the content of tocopherols and/or phenolics of the oil is, the better the antioxidative ability the oil has. It is worth mentioning that the order of the IP-based oxidative stability of olive oil samples at 50°C was sample 7 > 2 > 6 ≈ 3 > 9 > 4 ≈ 1 > 8 > 5, whereas the order of that determined by the OSI from the accelerated stability test at 100–130°C followed sample 7 > 9 > 3 > 8 > 6 ≈ 2 ≈ 1 > 5 > 4. The difference may be indicative of the fact that the extrapolation from the OSI obtained at accelerated temperature to ambient conditions could lead to over- or underprediction of the actual shelf life due to complicated kinetics involved at higher temperature [24, 33].

Regression models developed under low- (model (a)) and high-temperature (model (b)) were also provided based on the analytical data generated from either condition. By incorporating the chemical composition data collected at 50°C into the OSI measurement at 100–130°C, an empirical model (c) of shelf-life prediction (SL_{50}) was derived from model (a) and model (b):

$$\text{(a)}\ \ SL_{50} = 24.0639\left(\sum_{i=1}^{3} C_i * S_i\right) + 104.7369, \tag{7}$$

where C_i and S_i are regression coefficients and standardized compositional variables.

$$\text{(b)}\ \ SL_{50} = 10^{(50s+i-1.2272)}, \tag{8}$$

where s and i values are slopes and intercept of the linear equation to the log OSI versus accelerated temperature.

$$\text{(c)}\ \ SL_{50} = 0.9985\left\{A\left(\frac{100-a_0}{100a}\right)(\text{OSI}-b) + A\frac{a_1\left((b-\text{OSI})/100a\right)}{1+\left((\text{OSI}-b-aa_2)/aa_3\right)^2} + B\right\}, \tag{9}$$

where a, b, A, and B are the values of the linear regression models developed at high and low temperatures, respectively. The values of a_0, a_1, a_2, and a_3 were calculated and shown in Table 8. According to the conclusion of Q_{10} factor from Mancebo-Campos et al. [23], which is that a decrease of 10°C in the storage temperature increases the shelf life of olive oil more than two folds, a value of 2.1 of Q_{10} was used to estimate the oil shelf life at 25°C (normal storage temperature) by using the regression model (a) and promising estimation was obtained (13.1–22.2 months) which was considered to be representative of the typical shelf life claimed by olive oil producers (12–18 months after production).

Model (c) permitted the estimation of olive oil shelf life to be achieved within acceptable errors less than ±10% by using only one measurement, OSI, at accelerated temperatures. The interrelated mathematical equation of the low- and high-temperature regression models also allows real-time shelf-life prediction from the accelerated testing results to be done rapidly. A limitation of this model is that only two EVOO samples were analyzed; without performing further validation on the empirical model on a larger size of EVOO samples, the calculated values provided in Table 8 and the correction coefficient of 0.9985 may considerably deviate and not reflect the actual situation of EVOO category.

2.9. Guillaume and Ravetti (2016) [18]. This empirical model uses four quality parameters, induction time, DAGs, FFA Factor (derived from FFA), and PPP, to identify a best before

Table 8: The values of a_0, a_1, a_2, and a_3 in the SL_{50} prediction model calculated at 100°C and 130°C by Farhoosh and Hoseini-Yazdi (2013).

Temperature (°C)	a_0	a_1	a_2	a_3
100	−174.4761	−201.4675	32898.6507	19757.9412
130	0.0108	0.0230	−0.0106	0.0190

date (BBD, in months) using the lowest value obtained from the following three equations:

$$\begin{aligned} &\text{(a) Hours of induction time at } 110^{\circ}\text{C} \\ &\text{(b) } \frac{\text{DAGs} - 35\%}{\text{FFA Factor}} \end{aligned} \tag{10}$$

FFA factor = 1.7% (if FFA < 0.4%); 2.1% (if FFA > 0.4% and <0.6%); or 2.5% (if FFA > 0.6%):

$$\text{(c) } \frac{17\% - \text{PPPs}}{0.6\%} \tag{11}$$

This model recognizes that induction time generally correlates with olive oil FAPs and antioxidant content. DAGs and PPP have been shown to be predictable and change linearly with time whereas FFA provides a value for the initial oil quality and does not change significantly under proper storage conditions. These four quality parameters represent factors that can affect olive oil shelf life over time.

To evaluate this empirical model, the research team analyzed 118 samples for FFA, PV, UV, PPP, DAGs, and sensory evaluation during a 30-month storage period. The samples were stored in a dark environment at 18°C ± 2°C, and tested immediately after reaching their estimated best before date. Of the 118 samples, only one sample (0.8% of total samples) exceeded the Australian limit of 0.8% for FFA; no sample failed the Australian limit for PV (20 meq O_2/kg) or K_{232} (2.50 $K^{1\%}_{1\,cm}$); two samples (1.7%) failed K_{270} limit (0.22 $K^{1\%}_{1\,cm}$); twelve samples (10.2%) failed the Australian limit of 17% for PPP; six samples (5.1%) failed the Australian limit of 35% for DAGs; and ten samples (8.5%) failed sensory evaluation. In addition to testing 118 samples at the end of shelf life under controlled storage condition, 20 samples with predicted shelf life were randomly collected from different retailers every three months during a 30-month storage period to validate the model from retailers' standpoint (200 samples in total). Only one sample (0.5% out of 200 samples) exceeded the limit for K_{270} and two samples (1%) exceeded the limit for DAGs at their predicted BBD. By recalculating and comparing the actual and predicted BBD, the data suggested that producers may want to deduct 1-2 months from the BBD given from the model to compensate for the potential exposure to heat and light during transportation, handling, storage, and display on the retail shelves.

This model was validated on a total of 318 samples, including 200 commercial samples from real-time storage conditions on the market, with simple and straightforward calculations and yielded clear output. Modifications to the predicted BBD are necessary when storage condition is not ideal; however, this would be true for any models that are designed for the ideal packaging and storage conditions for olive oil shelf life (Table 9).

Table 9: Recommended packaging and storage conditions for olive oil shelf life.

Packaging	Temperature	Light
Dark glass, aluminum cans with food-grade enamel coating, coated paperboard, and bag-in-box provide protection from light and oxygen. Bag-in-box also has the advantage of maintaining minimum oxygen in headspace [14]	Stored at a reduced temperature of 15°C [29]	Stored in the dark to minimize light exposure

2.10. Rodrigues et al. (2017) [38]. Coupled with powerful statistical linear discriminant analysis (LDA) [49, 50] and simulated annealing (SA) variable selection algorithm approach [51–53], a most recent study on the evaluation of EVOO shelf life was conducted by applying a potentiometric electronic tongue (E-tongue) with nonspecific cross-sensitivity lipid membranes to assess the commercial storage conditions including light exposure and storage time.

The research group had analyzed 36 amber glass-bottled EVOO samples on sensory attributors (conducted by four trained panelists to classify samples based on olfactory sensations, gustatory-retronasal sensations, and final olfactory-gustatory sensations), physicochemical parameters (FFA, UV, and PV) and oxidative stability (OSI), and electrochemical signal profiles (E-tongue device with two print-screen potentiometric arrays containing 20 sensors on each one). To further elucidate the sample storage and testing conditions, four fresh samples were analyzed immediately after processing at T0 (0 month) while 32 samples were kept under room temperature (17–25°C) for one year in the lab, with 16 samples being stored in dark and 16 samples being exposed to natural light and artificial light (14 h/day from eight fluorescent lamps) to create a 2 × 4 × 4 experimental factorial design. During the one-year storage period, four samples were taken out and analyzed every three months at time points of T3, T6, T9, and T12. As a result, the quality parameters and oxidative stability of the tested EVOO samples were indeed affected by both the storage time and light conditions. It was inferred by the authors that, being stored in amber bottles, light conditions played less significant role on the olive oil quality deterioration during the storage period. In addition, not all the positive attributors of EVOO samples were affected by the storage conditions after one-year storage period, although samples exposed to light showed the strongest correlations among the respective sensory attributors (R-Pearson ≥ 0.80).

To evaluate the possibility of correctly categorizing olive oil samples based on storage time and/or light conditions (dark/light), the Kennard-Stone selection algorithm (a uniform mapping algorithm that generates a flat distribution of data suitable for regression model development) [56]

Table 10: Summary of statistical analysis performed by Rodrigues et al. (2017).

Objective	Statistical analysis*	Statistical analysis ref.
Compare the impact of dark/light storage conditions on olive oils for each storage time	Student's t-test	[48]
Assess the effect of the storage time on olive oils stored in dark/light	One-way ANOVA, Tukey's post hoc multicomparison test	[48]
Evaluate the existence of bivariate correlations within the olive oil's physicochemical parameters	Linear Pearson correlation coefficient (R-Pearson)	[48]
Test the capability of the E-tongue to correctly classify the EVOO based on storage time or storage conditions as a supervised pattern recognition method	Linear discriminant analysis (LDA)	[49, 50]
Evaluate the qualitative classification capability of physicochemical and sensory data	LDA	[49, 50]
Select the best subsets of K independent predictors among 40 E-tongue potentiometric signals	Metaheuristic simulated annealing (SA) variable selection algorithm	[51–53]
Compare the current and the new subsets of k ($\subseteq K$) variables	Tau2 quality criterion	[51]
Evaluate the LDA classification models	Leave-one-out cross-validation (LOO-CV)	[54, 55]
Minimize the risk of overfitting from LOO-CV when sample size is large and generate a flat distribution of data for regression model development	24 olive oil samples used as "training set" for LOO-CV	[54, 55]
	12 olive oil samples used as "testing set" using Kennard-Stone algorithm	[56]

* All statistical analyses were performed using Subselect [51, 57] and MASS [58] packages of the statistical program R (version 2.15.1) at a significant level of 5%.

was adopted by splitting 36 bottled olive oil samples into two subsets (24 for internal validation and 12 for external validation). By applying the metaheuristic SA variable selection algorithm, the best subset to be included in each LDA model was selected from physicochemical parameters, sensory attributors, and E-tongue signal profiles for the determination of the effect of different storage conditions on the quality of EVOO samples. The internal validation statistical data showed that E-tongue signal profiles yielded an overall better predictive discrimination performance, enabling the establishment of three best LDA-SA prediction models (from 5 to 8 sensor/sensor-replicas as independent variables) without redundant variables. The external validation further justified the predictive capability of E-tongue by giving a representative fingerprint of the polar compounds in olive oil samples.

As a promising chemometric approach, combining E-tongue measurement and comprehensive statistical analysis (Table 10) could successfully determine the freshness of EVOO samples during normal commercial storage conditions (stored in dark or exposed to light for one year) and provide accurate shelf-life prediction. Nonetheless, it is important and necessary that at least eight trained panelists were presented to provide sensory data as the lack of sensory data could significantly influence the statistical analysis results.

3. Conclusion

The global production and consumption of olive oil has escalated significantly in the past decade [60]. According to the IOC Market Newsletter released in September, 2017, the producer prices of EVOO have increased by more than 15% (in euros) in Spain, Italy, Tunisia, and Greece compared to the same period in the previous year [61]. Thus, to maintain the high quality of EVOO products during commercial activities has become an urgent matter to olive oil producers and being able to accurately predict the shelf life of EVOO products would greatly benefit both producers and consumers.

EVOO quality can be safeguarded by using proper packaging, ideal storage conditions (cool and dark), and having an accurate best before date. Currently in literature, common parameters that are being used to track the changes in olive oil include FFA, PV, UV, DAGs, PPP, sensory evaluation, induction time, FAP, total tocopherols and total phenols, and volatiles. A mathematical model for tracking deterioration using sensitive and accurate quality parameters can be a powerful and affordable tool for accurately predicting olive oil shelf life.

In this review, ten practical mathematical models that have potential to be adopted and utilized by olive oil producers are summarized. Nonetheless, each of the models can benefit from further study with a large set of samples under real-life transport and storage conditions, monitoring both compositional and environmental variables. To establish a robust and systematic model for shelf life assessment, the most urgent tasks are (1) to remove unnecessary parameters and to confirm the acceptable limits without losing the predictability and accuracy and (2) to continue developing and fine-tuning accelerated methods to minimize their tendency for overprediction or underprediction of actual shelf life. By reducing inessential parameters used in a model, the processing time and cost of shelf life assessment are also reduced. Since sensory evaluation remains to be one

of the most sensitive methods for olive oil quality and freshness, a working model should be calibrated with sensory evaluation and complement sensory evaluation for olive oil freshness assessment in the future. Temperature, airflow rate, and oil sample size have significant impacts on shelf life prediction when using accelerated methods. It is critical to adjust and optimize the operational settings to minimize the discrepancy between the real-time shelf life and accelerated prediction of an EVOO product.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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