Use of the Activation Energy Concept to Estimate The Quality Reduction of Packaged Olive Oil

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ABSTRACT: In the present study, the probability of packaged olive oil not reaching the end of its shelf life, P_{safe}, was used as a quality factor to evaluate the time taken for olive oils stored at various conditions to reach the end of their shelf lives. P_{safe} was used to comment on the activation energy required during the degradation process per actual or simulated case, and hexanal was used as the main quality-related indicator. Based on the month after bottling at which P_{safe} reached 70%, the activation energy of an “equivalent” chemical reaction, representative of overall quality degradation, was calculated for several storage conditions. Using the differences between activation energies estimated using the above method, we found the most important factors influencing the shelf life of the packaged olive oil to be the initial storage period in the dark, the role of elevated temperatures, and the presence of light, either continuous or in alternating patterns, in association with the packaging materials used in this study. These results were in qualitative agreement with previously reported experimental observations and simulations, indicating the validity of using P_{safe}, and of activation energies calculated from it, to predict the shelf life of packaged olive oil.

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KEY WORDS: Activation energy, flavors, olive oil, oxidation, packaging, shelf-life prediction.

The type of material (plastics, glass, tin), the storage conditions (light, temperature), and the storage period can significantly influence the quality of olive oil (1–5). Plastic bottles are used extensively for packing and bottling vegetable oils, but they are not always suitable for this purpose (6). Kiritsakis and Dugan (7) studied the relative effects of plastic and glass bottles on the oxidation of olive oil exposed to diffused light. They demonstrated the role of light and oxygen on the quality of the olive oil through the evolution of the PV. They also found that olive oil stored in colorless glass bottles and exposed to diffused light lost all of the chlorophyll and about 70% of the carotene content. Another key parameter is the oxygen permeability of the container, since olive oil kept in bottles permeable to air (e.g., polyethylene and polypropylene) should be sold within 4 wk (8–10). Poly(vinyl chloride) (PVC) bottles with lower air permeability can hold olive oil for 3 mon.

The importance of monitoring temperature during oil processing, distribution, and storage becomes evident by recognizing the effect of temperature abuse, which may result in a significant reduction of the shelf life. The time for a food product to reach the end of its shelf life (response time) could be established for a range of temperatures under isothermal conditions. These data could be applied to the Arrhenius equation, and the activation energy of the product could be determined. Among others, the activation energy approach was implemented previously to study the role of temperature on the kinetics of the spoilage process, e.g., to evaluate the application of an enzyme process-based time–temperature integrator (11) in the reduction of the L-ascorbic acid of green vegetables in the temperature range of freezing storage (12), or for the degradation of antioxidants and antioxidant activity in tomato products (pulp, puree, and paste) submitted to accelerated aging (13).

Among the applications used to monitor the quality of olive oil based on the reaction kinetics during storage were kinetic studies of the thermodegradation reaction of the oils conducted by Paz and Molero (14,15). Their results showed that the oxidizing atmosphere has a negative influence on the thermal stability of the oils. This work suggested that consumable vegetable oils could be characterized not only by their thermogravimetrical curves but also by the kinetic data deduced. The influence of a series of metals (iron, copper, tin, and lead) on the thermal stability of olive oils of different origins and refined grades was studied, and the influence of iron and tin on oil oxidation, compared with copper and lead, was demonstrated (16). Changes in the degradation rate also were compared with degradation in the absence of metals, confirming the negative influence of iron and tin on the oil oxidation process, regardless of the kind of oil tested. Furthermore, the pheophytin-A photodecomposition process, at 15, 40, and 50°C and at three different luminous energies, was developed according to a first-order reaction (16). From the Arrhenius straight lines, it appeared that the incident luminous energy did not change the activation energy but increased the reaction frequency factor.

Having recognized that data on the oxidative degradation kinetics in packaged olive oil are scarce, in the present work we applied the activation energy concept to extra virgin olive oil packaged in various packaging materials and stored under a wide range of storage conditions. A better understanding of the synergistic effects among oxidation-favoring parameters during storage would allow a valuable quality-predicting methodology to be introduced for packaged olive oil.

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EXPERIMENTAL PROCEDURES

To investigate storage conditions not attained by experiments, the hexanal concentration was estimated by using the model presented by Coutelieris and Kanavouras (17), and the data reported previously (5) were used to validate the analytical tool presented here. The probability of a packaged olive oil not reaching the end of its shelf life, P_{safe}, was selected for specific compounds ranked as quality markers for oil, i.e., hexanal (5).

The procedure developed to estimate the quality of the oil can be summarized as follows: (i) Record the evolution of hexanal in the oil phase through storage experiments. (ii) Determine and numerically solve the system of differential transport equations along with the appropriate boundary conditions (model). (iii) Verify the validity of the model by replicating the experimental measurements. (iv) Apply the simulations to other storage conditions. (v) Use the hexanal concentrations obtained in the previous simulations to estimate the probability of the packaged olive oil not reaching the end of its shelf life (P_{safe}). (vi) Use P_{safe} to calculate the activation energy from the plot of the evolution of P_{safe} vs. time (i.e., ln$k$ against $1/T$, where k is the rate constant of the "equivalent" chemical reaction representing overall quality degradation).

A detailed experimental procedure is presented elsewhere (5). In brief, organic Portuguese extra virgin olive oil was packed under nitrogen gas, without headspace, in cleaned and dried 500-mL drinking water bottles made of poly(ethylene terephthalate) (PET), PVC, or clear, fully transparent glass, all approved for food contact. The properties of the packaging materials were evaluated before use. Half of the bottles were stored in the dark and the other half were exposed to fluorescent light (four 40-W fluorescent light bulbs placed 30 cm above the bottles), all in controlled-environment chambers at 15, 30, or 40°C. The separation and identification of hexanal was done according to a previously developed methodology (5). Oil samples (3 mL) were placed in the recommended 6-mL glass vial fixed to the apparatus (Dynatherm 1000; Dynatherm Analytical Instruments Inc., Kelton, PA), preheated for 5 min at 37°C, and purged with dry nitrogen gas for 15 min at 200 mL/min. Tenax-TA traps (Supelco, Bellefonte, PA) preconditioned for 8 h at 350°C and purged for 30 min with nitrogen prior to use were used to collect the stripped volatiles. The traps were then immediately placed into a desorption unit (Model 890; Dynatherm Analytical Instruments Inc.) connected by a heated transfer line to a Hewlett-Packard 5890 Series II gas chromatograph (Hewlett-Packard, Philadelphia, PA) with a 30 m × 0.32 mm id fused-silica capillary column (SPB-5; Supelco). Helium was used as carrier at a flow of 7 mL/min and at a desorption pressure of 750 kPa to desorb the molecules. The desorption time was 8 min, and the trap was heated to 300°C. The transfer line and valve were maintained at 230°C to avoid the condensation of volatiles. The GC temperature program was as follows: initial temperature, 35°C for 5 min, increased to 80°C at a rate of 3°C/min, held for 1 min, then increased to 180°C at 10°C/min, held for 1 min, and finally increased to 220°C at 4°C/min, where it was held for 10 min. The carrier gas was maintained at a flow rate of 1.75 mL/min at 40°C. The traps were cleaned by heating at 320°C for 30 min. Statistical analyses were performed using commercial software (SAS$^{\text{TM}}$ Proprietary Software Release 8.2, TS2M0; SAS Institute Inc., Cary, NC).

Based on the main chemical reactions related to oxidative degradation inside the oil phase, we applied a representative model for the evolution of hydroperoxides in the packaged olive oil. Further details about the description and solution of the system can be found elsewhere (17). Briefly, by taking into account the chemical reactions occurring in the oil phase (5) and the reaction constant rates estimated there, the transport equations with reaction terms were formulated in the oil phase and the packaging material for hexanal and oxygen. The interfacial phenomena between the compounds under consideration and the packaging material also were incorporated into the system as boundary conditions following the Langmuir-type isotherm. In addition, the presence or absence of light was included by using a binary indicator. Values for all the parameters used (diffusivities, permeability of the materials, etc.), were either estimated experimentally or taken from the related literature. The boundary value problem described by the partial differential equations, along with the proper initial and boundary conditions, was solved numerically by using a numerical algorithm that involved a typical Newton method for nonlinear systems in conjunction with a finite differences scheme.

Given the time evolution for the concentration of any off-flavor compound in the oil phase, which is related to the oxidative degradation reactions, the probability of the olive oil not reaching the end of its shelf life during a certain time period (P_{safe}) is analogous to the ratio of the areas below and above a quality threshold that the compound in question might reach. This threshold can be defined rather arbitrarily from various production as well as depletion circumstances within the product-packaging system. Based on experimental observations reported previously (5,8), hexanal is a very suitable compound for characterizing the quality of the oil; thus, it was used as a quality indicator in this study. According to the graphical representation of the concept (see Fig. 1), the probability of the oil reaching the end of its shelf life during a time period (t_1,t_2) is analogous to the ratio of the surfaces defined by the curves CDFEC and ABFEA. The selected quality threshold depends on a certain value of the hexanal concentration, considered as an upper limit for quality acceptance. In this study, this quality threshold was adjusted so that the ratio of the areas was 30%. Since the aforementioned areas can be expressed by integrals of the spatially averaged hexanal concentration, we could then define the probability of the oil not reaching the end of its shelf life, P_{safe}, during the same time period (t_1,t_2) as

$$P_{\text{safe}} = 1 - \frac{\int_{t_1}^{t_2} C_{\text{hexanal}}^{\text{oil}}(t)dt}{\int_{0}^{t_2} C_{\text{hexanal}}^{\text{oil}}(t)dt} \qquad [1]$$

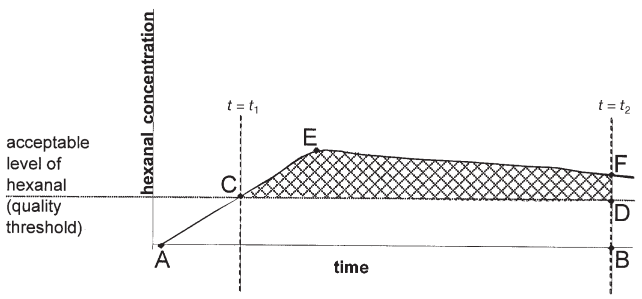

FIG. 1. Definition for the probability of stored olive oil not reaching the end of its shelf life during a certain time period.

where t_1 is the time when the hexanal concentration reaches the critical value and the upper edge of the integrals, t_2, could be any time period. In general, P_{safe} is simply an estimated quality indicator, dependent on the evolutionary history of the compound in question through a single value that allows an extensive analysis of experimental data and easy-to-make comparisons. Further on, it was used in this study for the transition from the actual concentration profiles to the activation energy concept.

The fundamental purpose for setting up the activation energy concept was to represent the overall quality degradation of the olive oil with an equivalent chemical reaction of first order or quasi-first order. The rate constant of this reaction is temperature dependent only and can be described by Arrhenius-type kinetics (18). Therefore, it is rather easy to derive equivalent activation energy values for isothermal conditions. For that application, we can define the response time as the time from the initiation of the reaction up to the time of the measurement. The plot of the value of the logarithm of the rate constant, ln$k$, against $1/T$ is a straight line whose slope defines the activation energy of the reaction. This activation energy gives us a direct estimation of the sensitivity of the product to quality degradation factors. In the current study, hexanal concentrations in the packaged olive oil were used to predict the P_{safe} values as given by the relevant model. Following that, the activation energies were calculated by plotting the evolution of P_{safe} vs. time for different storage temperatures. The outcome was then used to evaluate the effects of the various storage conditions on the preservation of olive oil and to draw conclusions on their significance.

According to the concept presented above (activation energy values based on P_{safe}, which were previously calculated from the actual concentrations of hexanal), an overall simulation period of 24 mon was considered for the following cases:

(i) Case 1A: Daily alteration of light and dark every 12 h at 15°C for 24 mon.
(ii) Case 1B: Daily alteration of light and dark every 12 h at 30°C for 24 mon.
(iii) Case 1C: Daily alteration of light and dark every 12 h at 40°C for 24 mon.
(iv) Case 2A.1: After a dark period of 1 mon, daily alteration of light and dark every 12 h at 15°C for 23 mon.
(v) Case 2A.2: After a dark period of 1 mon, daily alteration of light and dark every 12 h at 20°C for 23 mon.
(vi) Case 2A.3: After a dark period of 1 mon, daily alteration of light and dark every 12 h at 25°C for 23 mon.
(vii) Case 2A.4: After a dark period of 1 mon, daily alteration of light and dark every 12 h at 30°C for 23 mon.
(viii) Case 2A.5: After a dark period of 1 mon, daily alteration of light and dark every 12 h at 35°C for 23 mon.
(ix) Case 2A.6: After a dark period of 1 mon, daily alteration of light and dark every 12 h at 40°C for 23 mon.
(x) Case 2B.1: After a dark period of 2 mon, daily alteration of light and dark every 12 h at 15°C for 22 mon.
(xi) Case 2B.2: After a dark period of 2 mon, daily alteration of light and dark every 12 h at 20°C for 22 mon.
(xii) Case 2B.3: After a dark period of 2 mon, daily alteration of light and dark every 12 h at 25°C for 22 mon.
(xiii) Case 2B.4: After a dark period of 2 mon, daily alteration of light and dark every 12 h at 30°C for 22 mon.
(xiv) Case 2B.5: After a dark period of 2 mon, daily alteration of light and dark every 12 h at 35°C for 22 mon.
(xv) Case 2B.6: After a dark period of 2 mon, daily alteration of light and dark every 12 h at 40°C for 22 mon.
(xvi) Case 2C.1: After a dark period of 3 mon, daily alteration of light and dark every 12 h at 15°C dark for 21 mon.
(xvii) Case 2C.2: After a dark period of 3 mon, daily alteration of light and dark every 12 h at 20°C dark for 21 mon.
(xviii) Case 2C.3: After a dark period of 3 mon, daily alteration of light and dark every 12 h at 25°C dark for 21 mon.
(xix) Case 2C.4: After a dark period of 3 mon, daily alteration of light and dark every 12 h at 30°C dark for 21 mon.
(xx) Case 2C.5: After a dark period of 3 mon, daily alteration of light and dark every 12 h at 35°C dark for 21 mon.
(xxi) Case 2C.6: After a dark period of 3 mon, daily alteration of light and dark every 12 h at 40°C dark for 21 mon.

The cases presented were chosen to reflect the influence on overall oil quality of the parameters contributing most to oxidation, such as light, temperature, and initial storage period in the dark.

RESULTS AND DISCUSSION

Oxygen is one of the factors determining the volatile compounds produced in the breakdown of the alkoxy radical, whereby such compounds are formed following a specific reaction route. The domination of a particular pathway depends on the oxidative state of the oil, temperature, oxygen pressure, the presence of pro- and antioxidative catalysts, and other factors. The volatile aldehydes and vinyl ketones are mainly responsible for potent off-flavors because their threshold levels are very low. Hexanal can obtained from various unsaturated FA (i.e., linoleate and arachidonate) monohydroperoxides on the basis of the β-scission reaction (19).

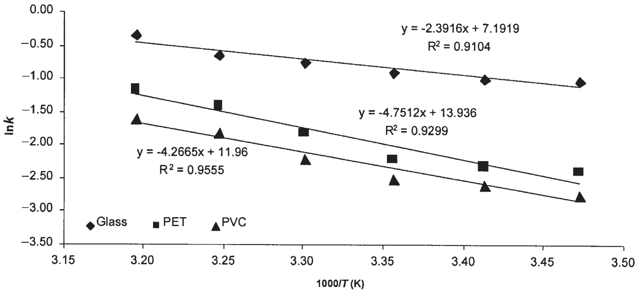

FIG. 2. Activation energies for olive oils packaged in glass, poly(ethylene terephthalate) (PET), and poly(vinyl chloride) (PVC) materials stored isothermally and under alternating light conditions.

Figure 2 shows the activation energies for olive oils packaged in glass, PET, and PVC materials stored isothermally and with light alternated according to the conditions described for Case 1. PET and PVC showed higher slopes than glass; thus, the role of temperature was clearly more important for these oxygen-permeable materials. This result may underline the synergistic role of temperature and oxygen that stimulates oxidative degradation phenomena inside the oil mass when greater energy is provided for the active oxygen species to react with the FA. In general, this observation is in accordance with previously reported results and recommendations (7,20,21). It has been reported that during the thermal oxidation of olive oil samples, hexanal could be generated by the thermal decomposition of linoleate 13-OOH, especially at lower temperatures (22,23).

Figure 3 shows the activation energies for olive oils packaged in glass, PET, and PVC materials stored isothermally and initially at 1, 2, or 3 mon in dark conditions before exposure to light (see the description of Cases 2A–C). The packaging materials showed a similar effect on P_{safe} independent of the initial dark period. The longer the initial dark period, however, the longer the time needed for P_{safe} to reach the critical value corresponding to the end of its shelf life, indicating that initial storage in the dark significantly prolonged the shelf life of the product when it was exposed to light later on. A summary of the activation energies calculated according to Figure 3 for Cases 2A–C is presented in Table 1, where the comparison among the three materials used in this study can easily be made: The lower the activation energy, the less protective the material. Thus, at the shortest storage time in the dark, glass was the least protective material, followed by PVC and then by PET. Glass seemed to be a significantly more protective material for packaged olive oil with a prolonged initial storage in the dark (2,24). In any case, PET had the best overall performance for each of the initial dark conditions without exhibiting a great difference among the three initial periods of storage in the dark. PVC had a lower performance as the initial dark period increased, becoming the least protective material at an initial storage of 2 or 3 mon in the dark.

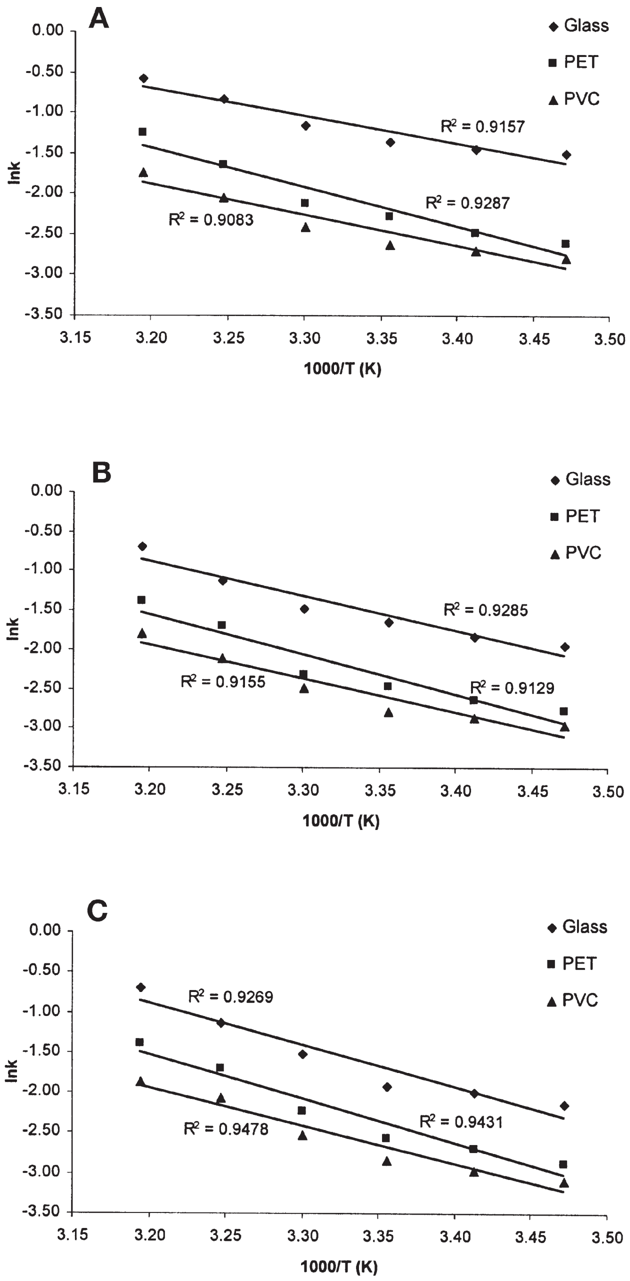

FIG. 3. Activation energies for olive oils packaged in glass, PET, and PVC materials stored isothermally for an initial (A) 1, (B) 2, and (C) 3 mon in the dark. For abbreviations see Figure 2.

This study demonstrated the value of calculating the activation energy through experimentally and theoretically predicted hexanal concentrations in packaged olive oil stored in different packaging materials and under different environmental conditions. These calculations were used to evaluate the role of storage and environmental conditions on quality reductions of the product. The overall results showed that longer initial storage periods in the dark resulted in lower concentrations of hexanal in the oil phase. This translated to higher P_{safe} values, as calculated by the model used. Initial storage of the packaged olive oil in the dark synergistically interacted with the variance in the elevated temperatures toward quality losses, as illustrated by the corresponding P_{safe} values. On the other hand, although the elevated temperatures stimulated deteriorative reactions,

TABLE 1
A Summary of the Activation Energy Values Calculated According to Figure 3[a]

Initial dark	Glass	PVC	PET
1 mon	–3.41	–3.79	–4.85
2 mon	–4.38	–4.26	–5.06
3 mon	–5.24	–4.65	–5.52

[a] PVC, poly(vinyl chloride); PET, poly(ethylene terephthalate).

they were not as significant as light, which was present either continuously or in alternating patterns. All the materials tested provided sufficient protection for packaged olive oil kept in the dark. In conclusion, even short time exposures of oils to the light should be avoided, since they could significantly stimulate oxidative degradation and be further assisted by elevated temperatures and the presence of oxygen. Although analogous findings have been reported from several experimental and simulation results elsewhere, the present study justifies the use of the P_{safe} and activation energy concepts as useful tools for further understanding and predicting the oxidative degradation of bottled olive oils with time under various storage conditions.

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