

Shelf life assessment of food undergoing oxidation - a review

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Shelf life assessment of food undergoing oxidation - a review

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Abstract

Oxidation is the most common event leading to the end of shelf life of microbiologically stable foods. Thus, a reliable shelf life assessment is crucial to verify how long the product will last before it becomes oxidized to an unacceptable level to the consumers.

Shelf life assessment strategies of foods and beverages suffering oxidation are critically discussed focusing on definition of the acceptability limit, as well as the choice of the proper oxidative indicators, and methodologies for shelf life testing. Testing methodologies for shelf life determination under actual and accelerated storage conditions are considered, highlighting possible uncertainties, pitfalls and future research needs.

Keywords: shelf life, oxidation, acceptability limit, kinetic modelling, accelerated test

19 **Shelf life assessment process**

20 Shelf life is an important feature of all foods, including raw materials, ingredients and semi-
21 manufactured products. Every product has its own shelf life and all the subjects involved in the food
22 chain should be aware of it. In general terms, shelf life can be defined as a finite length of time after
23 production, during which the food product retains a required level of quality under well-defined
24 storage conditions (Nicoli, 2012). This quality level discriminates products which are still
25 acceptable for consumption from those no longer acceptable. Shelf life assessment of foods has
26 always represented an exciting challenge for food scientists, but it is also a vital process for food
27 companies to maintain their brand reputation on the market. To get reliable shelf life data, the
28 adoption of a systematic approach is necessary.

29 A shelf life study can be divided into three fundamental steps, as schematically shown in Figure 1.
30 The preliminary steps imply the identification of the most critical chemical, physical or biological
31 event leading to the product quality depletion followed by the definition of the relevant
32 acceptability limit. The next step is the evaluation of the changes of the selected quality indicator as
33 a function of time under storage conditions mimicking the foreseeable storage conditions (real-time
34 shelf-life testing) or under environmental conditions able to accelerate deteriorative reactions
35 (accelerated shelf life testing - ASLT). Finally, data should be modelled to obtain a shelf life
36 estimation or prediction, respectively.

37 Real time shelf life testing is a procedure theoretically applicable for shelf life estimation of any
38 food category. However, it becomes profitable in case of perishable foods, for which quality decay
39 occurs in rather short time. On the contrary, the prediction of long term shelf life is traditionally
40 obtained by accelerating shelf life experiments performing tests under environmental conditions
41 able to speed up quality deterioration. This is the case of many microbiologically stable foods, such
42 as ambient stable and frozen products. In these wide food category, quality depletion during storage
43 is in most cases attributable to oxidation reactions. Table 1 is a list of foods whose shelf life is
44 expected to be limited by oxidative reaction development.

45 **Quality and safety issue in shelf life studies of food undergoing oxidation**

46 Oxidation in foods is a complex set of reactions involving firstly molecules belonging to the lipid
47 family and oxygen and leading to the formation of a number of radical and highly reactive species.
48 When lipid oxidation takes place in foods during storage, it causes the formation of undesirable
49 flavour and/or colour, making foods less acceptable or totally unacceptable to consumers
50 determining the end of their life on shelves. Beside quality depletion, oxidative reactions cause the
51 loss of biological activity of lipophilic bioactives (e.g. carotenoids, α -tocopherol, phytosterols, and
52 polyunsaturated fatty acids) that can be naturally present or voluntarily incorporated into a food.
53 Surprisingly, despite the growing number of new functional foods claiming on the label -after FDA
54 and EFSA approval- their beneficial effects, there are few evidences of their oxidative status during
55 product shelf-life.

56 At last but not least, oxidative reactions can cause the formation of toxic compounds. For instance,
57 the oxidation of polyunsaturated fatty acids results in significant generation of dietary advanced
58 lipid oxidation end-products (ALEs), which are cytotoxic and genotoxic compounds (Kanner, 2007;
59 Awada et al., 2012). On the basis of these considerations, a shelf life study of food undergoing
60 oxidation is not only a quality issue but also a safety one due to the development of oxidation
61 toxicants in foods.

62 In this context it can be noted that the unique compulsory indication relevant to the development of
63 oxidation in foods is that of olive oils (Commision Directive 1991/2568/EC). Based on this
64 directive, olive oils are subdivided in different categories according to their quality requirements,
65 such as oxidation indices (e.g. peroxide value, acidity, conjugated dienes) and sensory attributes.
66 Even if not compulsory, recommendations on the oxidation/rancidity level corresponding to a
67 certain quality standard for other fats and oils could also be found in the relevant Official Codex
68 Standards. However, these indications only refer to bulk oils whereas no advices for complex and
69 processed food systems are available. Moreover, compulsory acceptability limits can derive from

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3 70 voluntary label claims, such as the concentration of bioactive molecules included in the
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5 71 formulation.

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10 73 **Shelf life test vs stability test**

11 74 As extensively revised in many books and papers, the rate of lipid oxidation in foods during storage
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13 75 depends on intrinsic food characteristics, packaging related factors and environmental factors
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16 76 (Table 2). The complex interplay among these factors determines the oxidation rate and thus
17
18 77 product shelf life. It is noteworthy that a shelf-life study is addressed to finished packed products.
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20 78 This means that the possible strategies (i.e. formulation, packaging) that can be applied as tools to
21
22 79 reduce the development of oxidative reactions during storage have to be defined before shelf life
23
24 80 assessment. Thus, in principle compositional and packaging variables can be considered constant
25
26 81 during a shelf life study. When these factors are voluntarily varied with the goal to understand the
27
28 82 effect of such changes on quality decay, a stability test rather than a shelf life study is required.
29
30 83 Stability tests are generally set up to evaluate the susceptibility of a sample to oxidation with the
31
32 84 aim to predict the deteriorative reaction kinetics as a function of different variables. On the
33
34 85 contrary, a shelf life study has the objective to correctly estimate the product shelf life under
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36 86 expected storage conditions. In other words, while a stability study is addressed to measure
37
38 87 oxidation rate; a shelf life study aims to estimate the time limit for the consumption of a food
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40 88 product. Although a wide number of studies dealing with food oxidative stability as a function of
41
42 89 different environmental factors is available in the literature, results are difficult to be interpreted in
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44 90 terms of shelf life data because of the great variability in the test conditions adopted as well as the
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46 91 lack of acceptability limits.
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3 96 **Shelf life assessment steps**

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5 97 *Definition of critical indicator and relevant acceptability limit*

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7 98 The extent of lipid oxidation in foods could be monitored during storage by using different
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9 99 indicators, measured by different methodologies. In Table 3 the most widely applied methodologies
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11 100 to continuously monitor lipid oxidation during food life are summarized. To this regard it should be
12
13 101 noted that, even if instrumental analysis is very powerful, the application of sensory analysis cannot
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15 102 be disregarded since the spoilage of foods undergoing oxidation is early appreciable by the
16
17 103 consumer senses.

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20 104 Although different quality indicators may change simultaneously in food during storage, the most
21
22 105 critical index should be chosen to effectively face a shelf life study in terms of cost and time. The
23
24 106 first and simplistic criterion of choice among possible indicators is its earliness. However, this issue
25
26 107 is more complex and requires additional considerations of the links between the critical indicator
27
28 108 and the acceptability limit. The latter is the quality level discriminating acceptable products from
29
30 109 unacceptable ones (Manzocco, 2012).

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34 110 As previously stated, compulsory shelf life indicators and relevant limits coming from national or
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36 111 international regulations are rare. When not available, the acceptability limit can be freely chosen
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38 112 according to quality industry policy. In many cases the identification of the acceptability limit can
39
40 113 be rationally made by using information on food product stability acquired from previous company
41
42 114 experience, literature data, and competitor data. Such procedures are obviously fraught with the risk
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44 115 of critical overestimation or disadvantageous underestimation of the shelf life. This hazard is much
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46 116 more probable in the case of new foods, for which no previous experience is available.

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49 117 A further possible approach to define the acceptability limit is based on the application of sensory
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51 118 analysis, since sensory perception is often the earliest indicator of product failure in food
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53 119 undergoing oxidation. The company management may decide that the product reaches the
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55 120 acceptability limit when it is recognized as significantly different from the fresh one by applying
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57 121 discriminant sensory analysis (i.e. paired comparison, triangular, duo-trio or A-no-A tests).

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3 122 Differently, descriptive sensory analysis carried out with expert panels could be applied to describe
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5 123 the evolution of sensory attributes potentially responsible for consumer rejection. Although
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7 124 providing extensive information about the changes of quality attributes, results achieved with an
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9 125 expert panel could be not related with consumer's decision. For this reason, the hazard should not
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11 126 be focused on the properties of the product undergoing oxidation, rather on the attitude of consumer
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13 127 to accept or reject it (Hough et al., 2006).

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15 128 Consumer sensory dissatisfaction can be identified using survival analysis methodology (Hough
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17 129 and Garitta, 2012). Following this methodology, the product is analysed during storage by asking
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19 130 the consumers a response of acceptability/unacceptability and data are elaborated by survival
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21 131 analysis obtaining a risk function of consumer rejection of the product over storage time. The
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23 132 application of survival analysis for the estimation of consumer dissatisfaction of foods undergoing
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25 133 oxidation has been applied on minced meat (Hough et al., 2006), on roasted and ground coffee
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27 134 (Cardelli and Labuza, 2001), on sunflower oil (Ramirez et al., 2001) and on biscuits and bread
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29 135 sticks (Calligaris et al., 2007a and 2008). When applying this methodology, the food company can
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31 136 choose to be exposed to more or less risk of product failure by selecting, as an acceptability limit,
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33 137 the proper percentage of consumers rejecting the product. In other words, the acceptability limit
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35 138 becomes the maximum percentage of consumers that the company can tolerate to dissatisfy. In most
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37 139 shelf life studies a medium risk level (50% consumer rejection) is chosen as a reasonable
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39 140 acceptability limit but it has been suggested that lower percentages of consumer rejection could be
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41 141 much more reliable.

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43 142 Despite being powerful and accurate, survival analysis of consumer data is a time consuming and
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45 143 expensive process because it requires a wide testing plan assembling consumer panels. To
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47 144 overcome these pitfalls and find out methods that can be applied in the daily management of the
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49 145 shelf life issue, food operators could define internal quality levels, described by proper instrumental
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51 146 or sensory quality indicators, accounting for the risk of consumer rejection. It means that
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53 147 instrumental or sensory attributes, whose evolution is correlated to sensory dissatisfaction expressed
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3 148 by consumers, should be identified and used to monitor the evolution of product quality changes
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5 149 during storage. Once the risk function is obtained and the percentage of consumers rejecting the
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7 150 product is selected as acceptability limit, this value is used to identify the corresponding limit
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9 151 expressed by the analytical indicator. In this way, further *routine* shelf life studies can be done by
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11 152 monitoring only the instrumental indicator. For instance, a good correlation among peroxide
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13 153 number and consumer rejection was found in biscuits and bread-sticks (Calligaris et al., 2007a and
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15 154 2008).

18 155 *Testing and data modelling*

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21 156 After the identification of the appropriate oxidative indicator and the relevant acceptability limit, it
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23 157 is necessary to estimate the length of time needed to reach such a critical value. This step, generally
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25 158 defined as shelf life testing, implies the monitoring of the changes of the oxidative indicator during
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27 159 food storage under well-defined storage conditions. Data obtained are then modelled to obtain
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29 160 proper parameters describing/predicting the oxidation kinetics.

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32 161 To get shelf life data, two different strategies can be pursued; namely real-time and accelerated
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34 162 shelf life testing.

36 163 *Real-time shelf life testing*

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39 164 During real-time shelf life testing, experiments are performed under storage conditions that
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41 165 reasonably foresee the situation expected on the market shelf. The basic requirement to perform a
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43 166 reliable real-time shelf life test is that the environmental factors during storage are kept constant. It
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45 167 is appropriate to store the product under its normal storage conditions controlling not only
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47 168 temperature but also keeping constant other environmental conditions, e.g. humidity and light, since
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49 169 they are likely to significantly impact the shelf life of food undergoing oxidation. Since temperature
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51 170 oscillation is very frequent during food storage, it could be profitable to perform the shelf life test
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53 171 under the worst situation that one could expect during storage. In addition, if the package is a see-
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55 172 through container, the light exposure suffered by the product on the shelf could become a critical

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3 173 factor in determining its shelf life. For this reason, the light intensity commonly found on the
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5 174 market shelves (600-800 lux) should be also considered when planning the shelf life test.

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7 175 Data describing the changes of the oxidative indicator under conditions simulating actual storage
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9 176 are submitted to modelling according to the fundamental kinetic principles or by exploiting
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11 177 descriptive mathematical models. According to the well-known fundamental kinetic principles, the
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13 178 rate of changes of an oxidative indicator (I_{ox}) can be calculated by integrating the general kinetic
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15 179 equation:

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$$\int_{I_{ox_0}}^{I_{ox}} \frac{dI_{ox}}{I_{ox}^n} = \int_0^t k dt \quad (1)$$

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23 182 where k is the rate constant and n the reaction order. The general rate law can be integrated to obtain
24
25 183 the equations of the pseudo zero, first, second or n order. Since oxidation reactions are highly
26
27 184 complex and a huge number of factors might affect the reaction rate, it should be stressed that the
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29 185 evolution of any oxidation indicator versus time can be frequently the result of different reactions
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31 186 taking place simultaneously or consecutively. Thus, the reaction order n does not give any
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33 187 indications on the true reaction mechanisms involved and k is therefore considered as an “apparent”
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35 188 rate constant.

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38 189 Once the reaction rate constant has been calculated, the shelf life can be computed by solving the
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40 190 integrated forms of equation 1 as a function of time:

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$$SL = \frac{1}{k} \int_{I_o}^{I_{lim}} \frac{dI}{I^n} \quad (2)$$

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47 192 where I_o is the value of the critical indicator just after food production, I_{lim} is the critical indicator
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49 193 value corresponding to the previously defined acceptability limit.

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51 194 Papers dealing with this well recognized procedure have produced huge amounts of data on the
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53 195 oxidation rates of several foods in different environmental conditions. Zero and first order are
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55 196 frequently applied to describe the changes of oxidation indicators (Table 4).

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3 197 Unfortunately, due to the complex pathway of oxidative reactions, the application of a defined
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5 198 universal model may be precluded. The evolution of peroxide index as a function of storage time is
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7 199 a case in point since it is expected to follow the typical bell-shaped curve. After an induction period,
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9 200 during which very low peroxide value changes are expected, the progressive increase of peroxide
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11 201 value occurs until a maximum is reached, indicating that the oxidative reactions approach to the
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13 202 termination step.

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16 203 In terms of shelf life assessment two strategies could be applied depending on the level of peroxide
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18 204 value chosen as acceptability limit: i) first detectable changes approach that is when the shelf-life is
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20 205 defined as the time at which an increase of peroxide value is measured; ii) fixed change level
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22 206 approach that is when a selected value of peroxide is chosen as acceptability limit.

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25 207 When the first approach is used, the computation of the induction period length allows by itself the
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27 208 shelf life definition. Contrarily, when a fixed limit is defined, it is necessary to engage a modelling
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29 209 step. Assuming that all intermediate reactions follow fixed order reaction kinetics, each having its
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31 210 characteristic apparent rate constant, it is possible to model the exponential increase phase by
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33 211 considering this part of the curve separately from the others. Zero order kinetic is frequently applied
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35 212 in this step. Alternatively, the entire evolution of the peroxide value during the overall product life
36
37 213 can be modelled by identifying the empirical mathematical model best fitting the peroxide value
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39 214 curves. Different mathematical models have been applied in literature. For instance, Aragao et al.
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41 215 (2009) proposed a phenomenological mathematical model, comprising a decay factor superimposed
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43 216 on an accumulation term, to describe peroxide changes during lipid oxidation. Additional models
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45 217 (i.e. sigmoidal model, Weibull distribution function, and logistic model) are also frequently used
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47 218 (Özilgen and Özilgen, 1990; Cunha et al., 1998; Corradini and Peleg, 2007; Calligaris et al., 2008;
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49 219 Imai et al., 2008; Odriozola-Serrano et al., 2009). These strategies can be also applied to oxidation
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52 220 indexes other than the peroxide value.

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223 *Accelerated shelf life testing*

224 As aforementioned, oxidation advances fairly slowly under actual storage conditions. For this
225 reason, shelf life testing can be performed under environmental conditions that speed up oxidative
226 reactions and the results extrapolated to conditions usually experienced by the product. This
227 procedure is worldwide called accelerated shelf life test (ASLT) (Labuza and Schmidl, 1985).

228 *Temperature as accelerating factor.* Among all environmental factors that may be used to
229 accelerate oxidative reactions, temperature is certainly the most widely used. This is not only due to
230 the fact that temperature is one of the most critical factors affecting reaction kinetics in food, but
231 also to the availability of a theoretical basis for the development of a mathematical description of
232 the temperature sensitivity of quality loss rates. Indeed, the Arrhenius equation (3) (Arrhenius,
233 1901), developed theoretically on the molecular basis for reversible chemical reactions, has been
234 shown to hold empirically for a wide range of complex chemical, physical and sensory changes
235 occurring in foods (Labuza and Riboh, 1982):

$$236 \quad k = k_o \cdot e^{-\frac{E_a}{RT}} \quad (3)$$

237 in which k is the reaction rate constant; R is the molar gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the
238 absolute temperature (K); E_a is the apparent activation energy (J mol^{-1}) and k_o is the so called pre-
239 exponential factor. If the Arrhenius behaviour is fulfilled, the reaction rate at a desired temperature
240 can be extrapolated by measuring the rate of quality depletion at least at three different
241 temperatures.

242 The Arrhenius equation has been successfully used to estimate the temperature dependence of
243 oxidation rate for bulk fats and oils as well as bioactive compounds and complex foods. A number
244 data can be found in the literature relevant to the application of the Arrhenius equation to describe
245 the temperature dependence of oxidative reactions by using different oxidation indices (Table 5). E_a
246 values for different oxidative indicators greatly vary from 9 up to about 200 kJ mol^{-1} . This can be

247 attributed to differences in compositional and environmental factors taken into account in the
248 studies.

249 *Possible pitfalls in the use of temperature as accelerating factor.* The successful application of the
250 Arrhenius model requires that food is able to withstand the increase in temperature without leading
251 to dramatic development of phenomena other than the event responsible for product unacceptability
252 at usual storage temperatures. Although the Arrhenius equation is frequently applied, unfortunately
253 many pitfalls could arise in practice leading to deviations from the Arrhenius equation potentially
254 causing errors in shelf life prediction. As shown in Figure 2, in some circumstances an abrupt
255 change in the temperature dependence of the reaction rate can be observed causing positive or
256 negative deviations from the Arrhenius behaviour. The choice of the temperature interval for ASLT
257 is crucial to avoid deviations from linearity of the Arrhenius equation. Different factors can be
258 responsible for deviations from the Arrhenius behaviour of the temperature dependence of oxidation
259 rate:

260 - Changes in reaction pathway. For complex reactions, such as oxidation, the overall reaction
261 rate is directly dependent on the slowest step which is obviously the rate-determining one.
262 As temperature changes, different activation energies and pre-exponential terms for these
263 steps can lead to non-Arrhenius behaviour. Moreover, a switch in the rate determining steps
264 or a shift in the reaction pathway can occur. When a pathway dominates at lower
265 temperatures while another dominates at higher temperature, the prediction based on high
266 temperature behaviour could underestimate or overestimate the instability. As stated by
267 Frankel (2005) for food lipids, the use of temperatures higher than 100 °C in ASLT is
268 questionable, because samples develop excessive levels of rancidity, which are not relevant
269 to what happens under normal storage conditions. The more polyunsaturated the oils, the
270 lower the temperatures that should be used to test their oxidative stability; for instance,
271 vegetable oils should be tested at temperatures lower than 60 °C while fish oils only below
272 40 °C (Frankel, 2005).

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3 273 - Changes in pro-oxidant and antioxidant concentration. As temperature increases, the
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5 274 eventual thermal degradation of minor compounds with pro- or antioxidant activity could
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7 275 become critical since they can modify the temperature dependence of the overall oxidation
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9 276 rate of lipids. In addition, in multi-component foods, in which lipids, carbohydrates and
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11 277 proteins could react generating novel compounds, additional complications could arise. A
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13 278 case in point is the development of Maillard reaction that could lead, depending on the
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15 279 reaction step involved, the formation of compounds with pro-oxidant or antioxidant capacity
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17 280 These substances could greatly affect the kinetics of oxidation (Zamora and Hidalgo, 2007;
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19 281 Echavarria et al., 2012).
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23 282 - Changes in gas solubility. As well-known from the thermodynamic laws, the solubility of
24
25 283 gasses in solvents decreases with increasing temperature. This is the case of oxygen in food
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27 284 matrices. When the main driving force involved in the alternative reaction is the oxygen
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29 285 availability, deviations from the Arrhenius equation can be observed. For example, the rate
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31 286 of peroxide formation in oil-in-water emulsions stored at -30 °C resulted higher than that
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33 287 expected on the basis of the Arrhenius equation (Calligaris et al., 2007b). The latter was
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35 288 fulfilled at temperatures from 60 to -18 °C. It was hypothesized that at -30 °C the role of
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37 289 oxygen concentration becomes critical in affecting the formation of primary oxidation
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39 290 products. Similarly, oxygen concentration was found to be critical in determining the rate of
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41 291 carotenoid bleaching in tomato derivatives stored at temperatures below 0 °C (Manzocco et
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43 292 al., 2006).
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47 293 - Changes in physical structure. Physical structure modifications occurring in the temperature
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49 294 range considered for ASLT may be responsible for unexpected changes in the temperature
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51 295 dependence of oxidation rate (Parker and Ring, 1995; Calligaris et al., 2004, 2006; 2007b
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53 296 and 2008; Manzocco et al., 2006). Deviations from the Arrhenius behaviour may be the
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55 297 result of the occurrence of a cascade of temperature-dependent events, such as reactant
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57 298 concentration (i.e. unsaturated TAGs, O₂, antioxidants and pro-oxidants) and changes in
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3 299 physico-chemical properties (i.e. reactant solubility, pH, ionic strength, water activity,
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5 300 viscosity) in the liquid phases surrounding crystals (Parker and Ring 1995; Champion et al.,
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7 301 1997). These compositional modifications could counterbalance and/or even oppose the
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9 302 direct effect of temperature on the reaction rate, giving reason to the observed deviations.
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11 303 Examples of Arrhenius deviations of peroxide formation rate as a function of the reciprocal
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13 304 of temperature are reported in Figure 3.

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16 305 Due to the huge number of pitfalls potentially arising during ASLT of products undergoing
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18 306 oxidation, the extrapolation of oxidation rates at usual storage temperatures from accelerated data
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20 307 shall be performed only within the temperature range experimentally proven to conform to the
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22 308 Arrhenius model. In other words, the Arrhenius methodology requires being adapted to the specific
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24 309 circumstances of the product being considered.

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27 310 When the Arrhenius equation is not applicable, other models should be identified. Such models may
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29 311 be simply descriptive or built up starting from the understanding of the physicochemical
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31 312 phenomena leading to the Arrhenius deviation. The Williams-Landel-Ferry (WLF) model (1955)
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33 313 has been stated as appropriate to describe the rate-temperature relation for diffusion limited
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35 314 reactions. This approach was used with satisfactory results to model the kinetics of enzymatic
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37 315 browning in dried foods and model systems, flowability of fructose and melted cheese, kinetics of
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39 316 microbial and enzymatic inactivation (Roos, 1995). On the contrary, it resulted quite difficult to
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41 317 find out literature examples on the exploitability of WLF equation to describe the temperature
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43 318 dependence of oxidative reactions. For instance, Giannakourou and Taoukis (2003) reported that
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45 319 both Arrhenius and WLF models are adequate to represent temperature-dependence of ascorbic acid
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47 320 degradation within the rubbery state of a frozen vegetable matrix.

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50 321 Moreover, a modified Arrhenius equation was successfully applied to describe the temperature
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52 322 dependence of oxidation in different food systems. The common feature of these systems was that
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54 323 phase transitions of lipids or water occurred in the ASLT temperature range. The model proposed
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3 324 included a corrective factor into the Arrhenius equation to take into account the influence of the
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5 325 compositional changes caused by the temperature changes on oxidation rate:
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$$k = k_0 \cdot \Delta k \cdot e^{-\frac{E_a}{RT}} \quad (4)$$

9

10 327 where Δk is the corrective factor. Since at a given temperature the rate at which any reaction
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12 328 develops can be considered as the result of the ratio between driving forces and resistances, Δk can
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15 329 be defined by the identification of the proper forces and resistances responsible for the Arrhenius
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17 330 deviation. The application of this approach requires a deep understanding of the complex
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19 331 phenomena involved and the analytical possibility to quantify the changes occurring in the matrix as
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21 332 a consequence of temperature changes. Table 6 shows examples of factors used to compute Δk in
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23 333 different systems, such as sunflower oil, extra virgin olive oil, emulsions, biscuits, bread sticks and
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25 334 tomato derivatives (Calligaris et al., 2004; 2006; 2007a and b, 2008; Manzocco et al., 2006). The
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27 335 advantage of this approach is the possibility to perform accelerated shelf life tests even in the
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29 336 temperature range precluded due to Arrhenius deviations.
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33 337 Additional cautions should be taken in performing ASLT base on the accelerating effect of
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35 338 temperature. In fact, it may happen that the use of temperature does not allow the time necessary for
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37 339 the shelf life test to be sufficiently saved, causing the uselessness of the test. Since quality depletion
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39 340 phenomena can be differently accelerated by the increase in temperature, the time saved when
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41 341 performing the shelf life test under temperature accelerated conditions may be considerably
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43 342 different. Table 7 shows the percentage of time which can be saved when the temperature of the
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45 343 shelf life test is increased by 10 °C as a function of the activation energy of the critical phenomena.
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47 344 It is evident that about 50 kJ mol⁻¹ activation energy is required to save 50 % of the time needed to
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49 345 perform the shelf life test. From a practical point of view this means that, for oxidative reactions
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51 346 characterized by E_a values lower than 30-40 kJ mol⁻¹, the acceleration obtained by a 10 °C increase
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53 347 could be too low to be of interest in the attempt to save time during shelf life assessment. The worst
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348 possible case is when no temperature dependence of the alternative phenomena reaction rate (E_a
349 approaching 0) is observed (Calligaris et al., 2012).

350 *Other acceleration factors*

351 Low values of activation energies based on temperature changes are frequently observed monitoring
352 light induced oxidative reactions. For instance, the oxidation rate of some lipids, pigments and
353 flavors under dark may be slow, even at temperatures higher than the ambient one. By contrast
354 when the product is exposed to the light, oxidation quickly goes on showing, in any case, slight
355 temperature dependence (Kristensen et al., 2001; Manzocco et al., 2008; Manzocco et al., 2012). In
356 these conditions, light can be regarded as unconventional acceleration factor in shelf life studies.
357 Thus, the accelerated shelf life testing can be conducted by exposing the samples to increasing light
358 intensity levels instead of different storage temperatures. The basic requirement for the successful
359 exploitation of light as accelerating factor is the availability of a robust and validated mathematical
360 model correctly predicting the effect of the selected accelerating factor on the reaction rate leading
361 to quality depletion. To our knowledge, there are few examples of the use of light as accelerating
362 factor and thus predictive mathematical models. To this regard, Manzocco et al. (2012) developed a
363 mathematical model predicting the effect of light intensity on oxidation rate of soybean and
364 sunflower oil. The light dependence of the rate constants of peroxide formation (PV) resulted to be
365 well described by a power law equation:

$$366 \quad k = k_d + E_{l_1} \cdot L^{E_{l_2}} \quad (4)$$

367 where L is light intensity (lx), k_d is the reaction rate under dark and E_{l_1} and E_{l_2} are the experimental
368 parameters of the model, namely the electromagnetic energy required to activate the reaction.
369 Similarly to thermal activation energy (E_a) in the Arrhenius equation, these parameters account for
370 the electromagnetic energy required to activate the oxidative reaction.

371 By keeping constant the temperature during the test, the Authors performed ASLT of oils exploiting
372 the light as accelerating factor and predicted the shelf-life under foreseeable enlighten conditions

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3 373 (i.e. 600-800 lux on market shelves; dark). Considering that peroxide formation (PV) was well
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5 374 described by the zero order reaction order, the shelf life equation used was:
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$$SL = \frac{PV_{\text{lim}} - PV_o}{k_d + E_{l_1} \cdot L^{E_{l_2}}} \quad (5)$$

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11 376 This equation represents actually a model allowing prediction of shelf life by changing the light
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13 377 intensity at a given temperature T . The only independent variables of the proposed model is the
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15 378 light intensity (L), which is the enlighten condition experienced by the product on the retail shelves,
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17 379 and the acceptability limit. A similar approach was also efficaciously used to study the stability of
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19 380 carotenoid containing beverages exposed to different light intensity levels (Manzocco et al., 2008).
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22 381 The exploitation of light as accelerating factor appears interesting since it may allow solving the
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24 382 difficult task of predicting shelf life of photosensitive food usually marketed in the presence of
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26 383 light. Further advantages could be the possibility to use light instead of temperature to quickly
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28 384 predict shelf life of foods that cannot withstand high temperature during shelf life testing.
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31 385 Theoretically, the aforementioned approach can be applied also by using other environmental
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33 386 factors able to accelerate the oxidation. Since the oxidative reactions are strongly dependent on
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35 387 oxygen concentration, this parameter could represent a potentially exploitable accelerating factor to
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37 388 develop proper shelf life assessment methodologies and relevant predictive models. However, to
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39 389 our knowledge, until now little effort has been made on this topic. This is an open research field
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41 390 which will certainly require more attention from researchers in the future.
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3 392 **Conclusion**

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5 393 Shelf life assessment of food undergoing oxidation has always represented a challenge for food
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7 394 scientists and industry managers. Actual literature information provides limited help to solve the
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9 395 problem of shelf-life determination, which can only be faced by adopting rigorous, systematic, and
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11 396 well-designed shelf-life assessment. The most urgent open issues appear to be i) the identification
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13 397 of acceptability limits and ii) the possibility to reduce testing time as much as possible without
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15 398 losing in predictive capability. The former issue could be faced by implementing rational
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17 399 procedures merging consumer and marketing aspects and thus supporting the decision process
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19 400 leading to the identification of the acceptability limit. The second problem for food industries facing
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21 401 the oxidation development during food storage is linked to the need to apply accelerated shelf-life
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23 402 tests that can effectively speed up the shelf life assessment process. However, the generation of
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25 403 predictive models for product suffering oxidative reactions could be an arduous task due to the huge
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27 404 number of environmental and compositional factors affecting the oxidation rate.
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3 531 **Figure caption**
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5 532 Figure 1. Fundamental steps in shelf life assessment process
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7 533 Figure 2. Schematic representation of possible positive and negative deviations from the Arrhenius
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9 equation
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11 535 Figure 3. Example of Arrhenius deviations of zero order rate constant of peroxide formation as a
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13 function of temperature in biscuits and bread-sticks (modified from Calligaris et al., 2007a; 2008)
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3 538 Table 1. Foods whose quality depletion during storage is mainly attributed to oxidative reaction
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5 539 development.
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Food category	Examples
Ambient stable	Oils and fats Dried and freeze-dried foods and ingredients Coffee products Bakery products Breakfast cereals Canned products Fried snacks Soft drinks containing colorants and flavours Functional foods containing lipophilic bioactives
Frozen	Ready meals (e.g. pasta, lasagna, pizza) Meat and fish Fried foods Blanched fruit and vegetables

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3 542 Table 2. Main food characteristics, environmental and packaging related factors affecting oxidative
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5 543 reactions in foods.
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Food characteristics	Environmental factors	Packaging related factors
Fatty acid unsaturation degree	Oxygen partial pressure	Packaging barrier
Redox potential	Temperature	properties to moisture, light
Presence of antioxidants and pro-oxidants	Relative humidity	and oxygen
Surface area	Light	Active packaging
Food component physical state		

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546 Table 3. Oxidative reaction indicators and relevant analytical methodologies

Indicator	Methodology
Peroxide value	Titration, spectroscopic methods
Conjugated dienes (CD)	Spectroscopic methods
Acidity	Titration
Volatile carbonyl compounds	GC-MS
Anisidine value	Spectroscopic methods
Thiobarbituric acid index (TBA)	Spectroscopic methods
Hydrocarbons and fluorescent products	Fluorescent spectroscopy
Sensory attributes (off flavour, off odours)	Discriminant and descriptive methods, consumer acceptance
Colour	Colour analysis, image analysis, spectrophotometry
Selected compound concentration	HPLC, GC-MS

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550 Table 4. Apparent zero and first reaction orders used to describe the evolution of oxidation indices
 551 (modified from Manzocco et al., 2010)

Apparent reaction order	Index	Product	Reference
Zero	Peroxide value	Potato chips	Houhoula and Oreopolou, 2004
		Biscuits	Calligaris et al., 2007
		Extra virgin olive oil	Calligaris et al., 2006; Mancebo-Campos et al., 2008
		Salmon oil	Huang and Sathivel, 2008
		Perilla oil	Shim and Lee, 2011
		Soybean oil	Manzocco et al., 2012
		K232	Extra virgin olive oil
First	Vitamin C degradation	Frozen vegetables	Giannakourou and Taoukis, 2003
		Orange juice	Polyedra et al., 2003; Tiwari et al., 2009
		Fresh-cut strawberries	Odriozola-Serrano et al., 2009
	K270	Extra virgin olive oil	Gutierrez and Fernandez, 2002; Mancebo-Campos et al., 2008
	Oxygen consumption	Soybean oil	Colakoglu, 2007
	Free fatty acids	California almond	Lin et al., 2012

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Table 5. Temperature range of application of Arrhenius equation to estimate oxidation of different foods by using different indices

Oxidation index	Product	Temperature range (°C)	Reference
Induction period	Perilla oil	25/75	Shim and Lee, 2012
Peroxide value	Sunflower oil	4/60	Calligaris et al., 2004
	Extra virgin olive oil	25/60	Calligaris et al., 2006
	Salmon oil	10/35	Huang and Sathivel, 2008
	Bread sticks	20/45	Calligaris et al., 2008
	Soybean oil	10/30	Manzocco et al., 2012
Coniugated dienes	Almond-based products	5/40	Tazi et al., 2009
TBARS	Almond-based products	5/40	Tazi et al., 2009
Volatiles	Sunflower oil	460	Calligaris et al., 2004a
	Extra virgin olive oil	25/60	Calligaris et al. 2006
	Milk powder	37/55	Thomsen et al., 2005
Free fatty acids	California almonds	4/38	Lin et al., 2012
Carotenoids	Osmo-dehydrofrozen tomatoes	-20/-5	Dermesonlouoglou et al., 2007
	Frozen vegetables	-15/-5	Giannakourou and Taoukis, 2003
Vitamin C	Orange juice	20/45	Manso et al., 2001
	Osmo-dehydrofrozen tomatoes	-20/-5	Dermesonlouoglou et al., 2007
	Frozen pumpkin	-25/-7	Goncalves et al., 2011

554 Table 6. Examples of factors used to effectively compute Δk

Sample	Indicator	Factors affecting Δk
Sunflower oil	Hexanal in the headspace	Liquid fraction of oil
		Viscosity
Extra virgin olive oil	Peroxide value	Liquid fraction of oil
		Polyphenol concentration in liquid phase
Oil-in-water emulsion	Peroxide value	Oxygen concentration
		Hexanal in the headspace
	Hexanal in the headspace	Liquid fraction of oil
		Freeze concentration
Tomato derivatives	Colour (a* value)	Oil viscosity
		Oxygen concentration
		Freeze-concentration
Biscuits	Peroxide value	Liquid fraction of oil
Bread-sticks	Peroxide value	Liquid fraction of oil

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3 557 Table 7. Percentage of expected time saved by 10 °C temperature increase as a function of
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5 558 activation energy values.
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Activation energy (kJ/mol)	Estimated saved time % by 10 °C increase
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30	30
40	38
50	45
60	51
70	56
80	61
100	69

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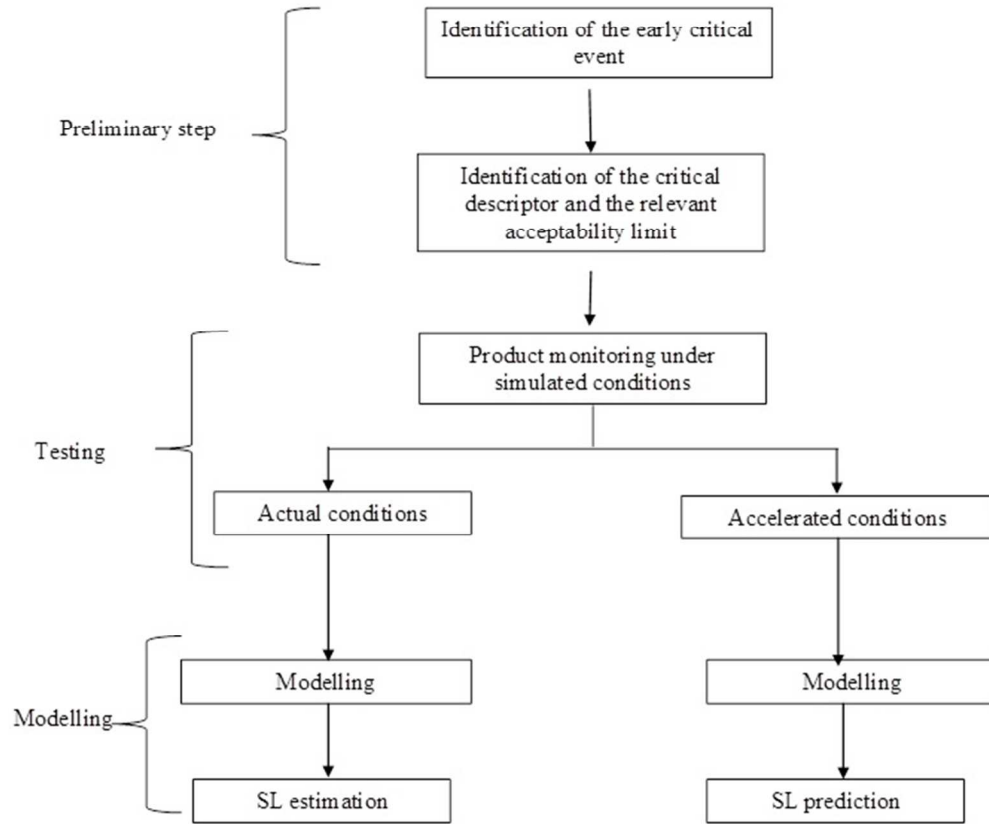


Figure 1. Fundamental steps in shelf life assessment process
178x180mm (96 x 96 DPI)

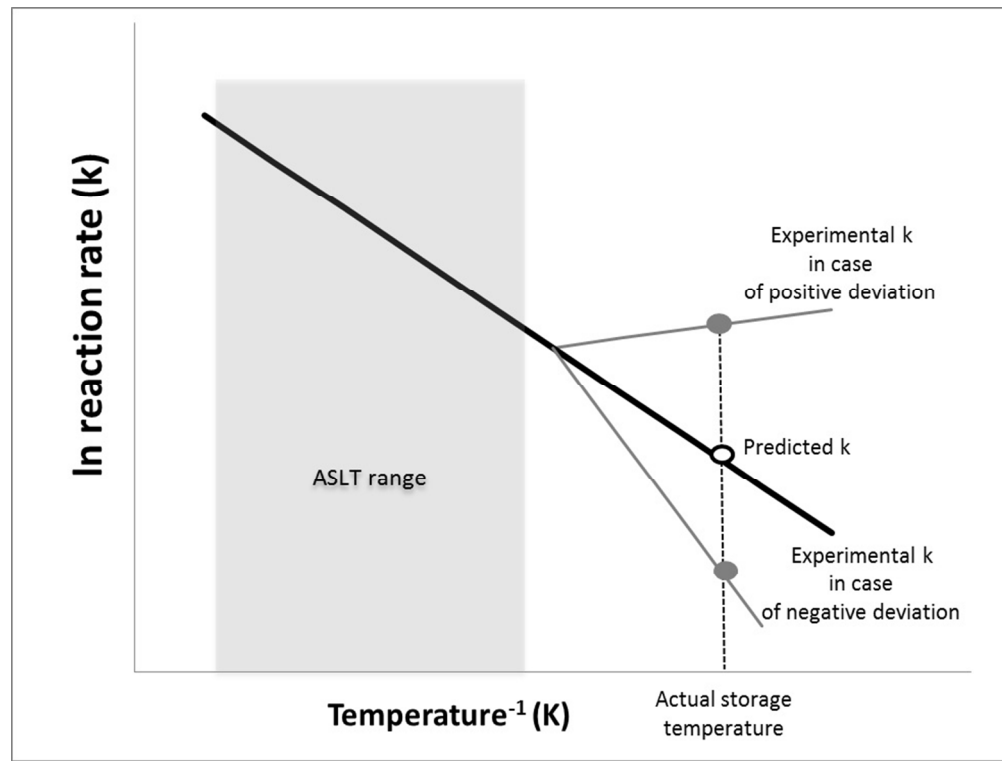


Figure 2. Schematic representation of possible positive and negative deviations from the Arrhenius equation
259x196mm (96 x 96 DPI)

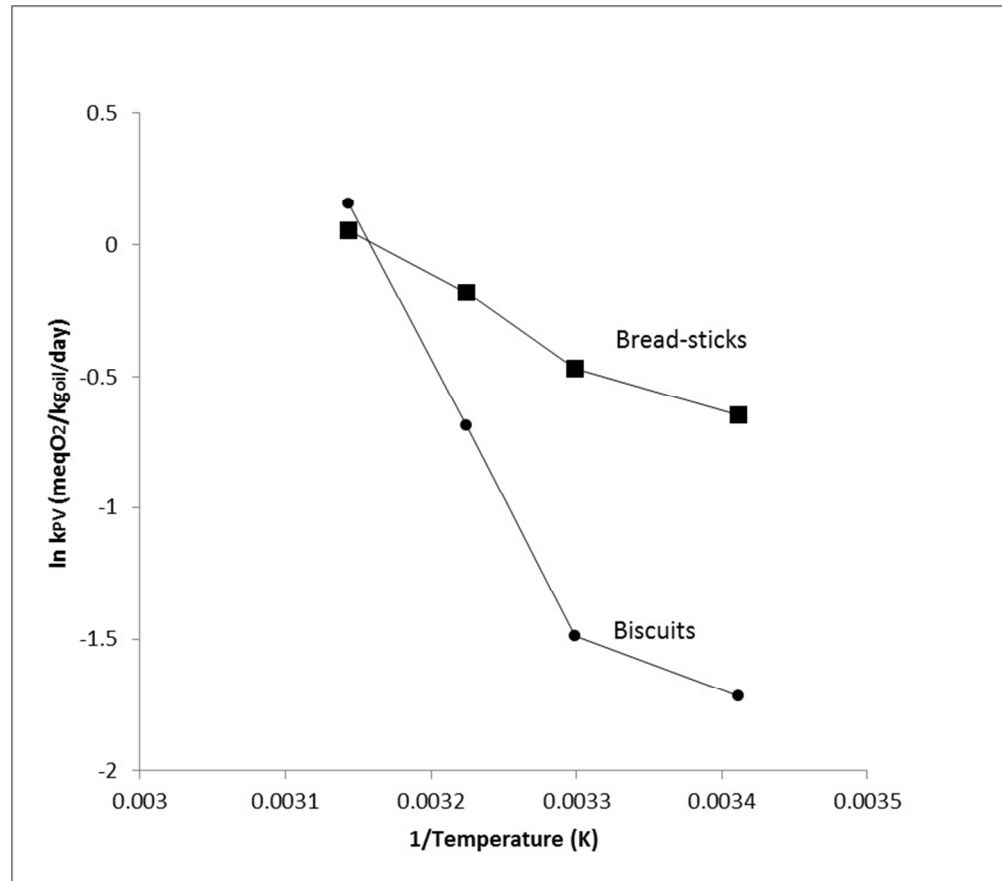


Figure 3. Example of Arrhenius deviations of zero order rate constant of peroxide formation as a function of temperature in biscuits and bread-sticks (modified from Calligaris et al., 2007a; 2008)
227x199mm (96 x 96 DPI)