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## Shelf-life Assessment of Food Undergoing Oxidation–A Review

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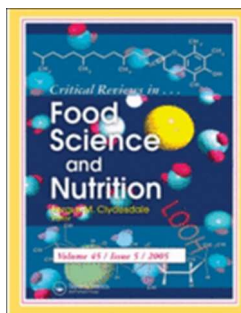
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## Shelf life assessment of food undergoing oxidation - a review

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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.

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

Oxidation in foods is a complex set of reactions involving firstly molecules belonging to the lipid family and oxygen and leading to the formation of a number of radical and highly reactive species. When lipid oxidation takes place in foods during storage, it causes the formation of undesirable flavour and/or colour, making foods less acceptable or totally unacceptable to consumers determining the end of their life on shelves. Beside quality depletion, oxidative reactions cause the loss of biological activity of lipophilic bioactives (e.g. carotenoids,  $\alpha$ -tocopherol, phytosterols, and polyunsaturated fatty acids) that can be naturally present or voluntarily incorporated into a food. Surprisingly, despite the growing number of new functional foods claiming on the label -after FDA and EFSA approval- their beneficial effects, there are few evidences of their oxidative status during product shelf-life. At last but not least, oxidative reactions can cause the formation of toxic compounds. For instance, the oxidation of polyunsaturated fatty acids results in significant generation of dietary advanced lipid oxidation end-products (ALEs), which are cytotoxic and genotoxic compounds (Kanner, 2007; Awada et al., 2012). On the basis of these considerations, a shelf life study of food undergoing oxidation is not only a quality issue but also a safety one due to the development of oxidation toxicants in foods. In this context it can be noted that the unique compulsory indication relevant to the development of oxidation in foods is that of olive oils (Commision Directive 1991/2568/EC). Based on this directive, olive oils are subdivided in different categories according to their quality requirements, such as oxidation indices (e.g. peroxide value, acidity, conjugated dienes) and sensory attributes. Even if not compulsory, recommendations on the oxidation/rancidity level corresponding to a certain quality standard for other fats and oils could also be found in the relevant Official Codex Standards. However, these indications only refer to bulk oils whereas no advices for complex and processed food systems are available. Moreover, compulsory acceptability limits can derive from

voluntary label claims, such as the concentration of bioactive molecules included in the formulation.

### **Shelf life test vs stability test**

As extensively revised in many books and papers, the rate of lipid oxidation in foods during storage depends on intrinsic food characteristics, packaging related factors and environmental factors (Table 2). The complex interplay among these factors determines the oxidation rate and thus product shelf life. It is noteworthy that a shelf-life study is addressed to finished packed products. This means that the possible strategies (i.e. formulation, packaging) that can be applied as tools to reduce the development of oxidative reactions during storage have to be defined before shelf life assessment. Thus, in principle compositional and packaging variables can be considered constant during a shelf life study. When these factors are voluntarily varied with the goal to understand the effect of such changes on quality decay, a stability test rather than a shelf life study is required. Stability tests are generally set up to evaluate the susceptibility of a sample to oxidation with the aim to predict the deteriorative reaction kinetics as a function of different variables. On the contrary, a shelf life study has the objective to correctly estimate the product shelf life under expected storage conditions. In other words, while a stability study is addressed to measure oxidation rate; a shelf life study aims to estimate the time limit for the consumption of a food product. Although a wide number of studies dealing with food oxidative stability as a function of different environmental factors is available in the literature, results are difficult to be interpreted in terms of shelf life data because of the great variability in the test conditions adopted as well as the 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  
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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  
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17 103 consumer senses.

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

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33 110 As previously stated, compulsory shelf life indicators and relevant limits coming from national or  
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35 111 international regulations are rare. When not available, the acceptability limit can be freely chosen  
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37 112 according to quality industry policy. In many cases the identification of the acceptability limit can  
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39 113 be rationally made by using information on food product stability acquired from previous company  
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41 114 experience, literature data, and competitor data. Such procedures are obviously fraught with the risk  
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43 115 of critical overestimation or disadvantageous underestimation of the shelf life. This hazard is much  
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45 116 more probable in the case of new foods, for which no previous experience is available.

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48 117 A further possible approach to define the acceptability limit is based on the application of sensory  
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50 118 analysis, since sensory perception is often the earliest indicator of product failure in food  
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52 119 undergoing oxidation. The company management may decide that the product reaches the  
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54 120 acceptability limit when it is recognized as significantly different from the fresh one by applying  
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56 121 discriminant sensory analysis (i.e. paired comparison, triangular, duo-trio or A-no-A tests).

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

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

Despite being powerful and accurate, survival analysis of consumer data is a time consuming and expensive process because it requires a wide testing plan assembling consumer panels. To overcome these pitfalls and find out methods that can be applied in the daily management of the shelf life issue, food operators could define internal quality levels, described by proper instrumental or sensory quality indicators, accounting for the risk of consumer rejection. It means that 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).  
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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.  
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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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factor in determining its shelf life. For this reason, the light intensity commonly found on the market shelves (600-800 lux) should be also considered when planning the shelf life test.

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

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

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

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

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

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

Papers dealing with this well recognized procedure have produced huge amounts of data on the oxidation rates of several foods in different environmental conditions. Zero and first order are 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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15 203 In terms of shelf life assessment two strategies could be applied depending on the level of peroxide  
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17 204 value chosen as acceptability limit: i) first detectable changes approach that is when the shelf-life is  
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19 205 defined as the time at which an increase of peroxide value is measured; ii) fixed change level  
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21 206 approach that is when a selected value of peroxide is chosen as acceptability limit.  
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23 207 When the first approach is used, the computation of the induction period length allows by itself the  
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25 208 shelf life definition. Contrarily, when a fixed limit is defined, it is necessary to engage a modelling  
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27 209 step. Assuming that all intermediate reactions follow fixed order reaction kinetics, each having its  
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29 210 characteristic apparent rate constant, it is possible to model the exponential increase phase by  
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31 211 considering this part of the curve separately from the others. Zero order kinetic is frequently applied  
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33 212 in this step. Alternatively, the entire evolution of the peroxide value during the overall product life  
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35 213 can be modelled by identifying the empirical mathematical model best fitting the peroxide value  
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37 214 curves. Different mathematical models have been applied in literature. For instance, Aragao et al.  
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39 215 (2009) proposed a phenomenological mathematical model, comprising a decay factor superimposed  
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41 216 on an accumulation term, to describe peroxide changes during lipid oxidation. Additional models  
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43 217 (i.e. sigmoidal model, Weibull distribution function, and logistic model) are also frequently used  
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45 218 (Özilgen and Özilgen, 1990; Cunha et al., 1998; Corradini and Peleg, 2007; Calligaris et al., 2008;  
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47 219 Imai et al., 2008; Odriozola-Serrano et al., 2009). These strategies can be also applied to oxidation  
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49 220 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 ( $\text{J mol}^{-1}$ ) 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  $200 \text{ kJ mol}^{-1}$ . This can be

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3 247 attributed to differences in compositional and environmental factors taken into account in the  
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5 248 studies.  
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7 249 *Possible pitfalls in the use of temperature as accelerating factor.* The successful application of the  
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9 250 Arrhenius model requires that food is able to withstand the increase in temperature without leading  
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11 251 to dramatic development of phenomena other than the event responsible for product unacceptability  
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13 252 at usual storage temperatures. Although the Arrhenius equation is frequently applied, unfortunately  
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15 253 many pitfalls could arise in practice leading to deviations from the Arrhenius equation potentially  
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17 254 causing errors in shelf life prediction. As shown in Figure 2, in some circumstances an abrupt  
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19 255 change in the temperature dependence of the reaction rate can be observed causing positive or  
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21 256 negative deviations from the Arrhenius behaviour. The choice of the temperature interval for ASLT  
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23 257 is crucial to avoid deviations from linearity of the Arrhenius equation. Different factors can be  
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25 258 responsible for deviations from the Arrhenius behaviour of the temperature dependence of oxidation  
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27 259 rate:  
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31 260 - Changes in reaction pathway. For complex reactions, such as oxidation, the overall reaction  
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33 261 rate is directly dependent on the slowest step which is obviously the rate-determining one.  
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35 262 As temperature changes, different activation energies and pre-exponential terms for these  
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37 263 steps can lead to non-Arrhenius behaviour. Moreover, a switch in the rate determining steps  
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39 264 or a shift in the reaction pathway can occur. When a pathway dominates at lower  
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41 265 temperatures while another dominates at higher temperature, the prediction based on high  
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43 266 temperature behaviour could underestimate or overestimate the instability. As stated by  
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45 267 Frankel (2005) for food lipids, the use of temperatures higher than 100 °C in ASLT is  
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47 268 questionable, because samples develop excessive levels of rancidity, which are not relevant  
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49 269 to what happens under normal storage conditions. The more polyunsaturated the oils, the  
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51 270 lower the temperatures that should be used to test their oxidative stability; for instance,  
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53 271 vegetable oils should be tested at temperatures lower than 60 °C while fish oils only below  
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55 272 40 °C (Frankel, 2005).  
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- 273 - Changes in pro-oxidant and antioxidant concentration. As temperature increases, the  
274 eventual thermal degradation of minor compounds with pro- or antioxidant activity could  
275 become critical since they can modify the temperature dependence of the overall oxidation  
276 rate of lipids. In addition, in multi-component foods, in which lipids, carbohydrates and  
277 proteins could react generating novel compounds, additional complications could arise. A  
278 case in point is the development of Maillard reaction that could lead, depending on the  
279 reaction step involved, the formation of compounds with pro-oxidant or antioxidant capacity  
280 These substances could greatly affect the kinetics of oxidation (Zamora and Hidalgo, 2007;  
281 Echavarria et al., 2012).
- 282 - Changes in gas solubility. As well-known from the thermodynamic laws, the solubility of  
283 gasses in solvents decreases with increasing temperature. This is the case of oxygen in food  
284 matrices. When the main driving force involved in the alternative reaction is the oxygen  
285 availability, deviations from the Arrhenius equation can be observed. For example, the rate  
286 of peroxide formation in oil-in-water emulsions stored at -30 °C resulted higher than that  
287 expected on the basis of the Arrhenius equation (Calligaris et al., 2007b). The latter was  
288 fulfilled at temperatures from 60 to -18 °C. It was hypothesized that at -30 °C the role of  
289 oxygen concentration becomes critical in affecting the formation of primary oxidation  
290 products. Similarly, oxygen concentration was found to be critical in determining the rate of  
291 carotenoid bleaching in tomato derivatives stored at temperatures below 0 °C (Manzocco et  
292 al., 2006).
- 293 - Changes in physical structure. Physical structure modifications occurring in the temperature  
294 range considered for ASLT may be responsible for unexpected changes in the temperature  
295 dependence of oxidation rate (Parker and Ring, 1995; Calligaris et al., 2004, 2006; 2007b  
296 and 2008; Manzocco et al., 2006). Deviations from the Arrhenius behaviour may be the  
297 result of the occurrence of a cascade of temperature-dependent events, such as reactant  
298 concentration (i.e. unsaturated TAGs, O<sub>2</sub>, antioxidants and pro-oxidants) and changes in

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299 physico-chemical properties (i.e. reactant solubility, pH, ionic strength, water activity,  
300 viscosity) in the liquid phases surrounding crystals (Parker and Ring 1995; Champion et al.,  
301 1997). These compositional modifications could counterbalance and/or even oppose the  
302 direct effect of temperature on the reaction rate, giving reason to the observed deviations.  
303 Examples of Arrhenius deviations of peroxide formation rate as a function of the reciprocal  
304 of temperature are reported in Figure 3.

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

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

321 Moreover, a modified Arrhenius equation was successfully applied to describe the temperature  
322 dependence of oxidation in different food systems. The common feature of these systems was that  
323 phase transitions of lipids or water occurred in the ASLT temperature range. The model proposed



324 included a corrective factor into the Arrhenius equation to take into account the influence of the  
325 compositional changes caused by the temperature changes on oxidation rate:

$$326 \quad k = k_0 \cdot \Delta k \cdot e^{-\frac{E_a}{RT}} \quad (4)$$

327 where  $\Delta k$  is the corrective factor. Since at a given temperature the rate at which any reaction  
328 develops can be considered as the result of the ratio between driving forces and resistances,  $\Delta k$  can  
329 be defined by the identification of the proper forces and resistances responsible for the Arrhenius  
330 deviation. The application of this approach requires a deep understanding of the complex  
331 phenomena involved and the analytical possibility to quantify the changes occurring in the matrix as  
332 a consequence of temperature changes. Table 6 shows examples of factors used to compute  $\Delta k$  in  
333 different systems, such as sunflower oil, extra virgin olive oil, emulsions, biscuits, bread sticks and  
334 tomato derivatives (Calligaris et al., 2004; 2006; 2007a and b, 2008; Manzocco et al., 2006). The  
335 advantage of this approach is the possibility to perform accelerated shelf life tests even in the  
336 temperature range precluded due to Arrhenius deviations.

337 Additional cautions should be taken in performing ASLT base on the accelerating effect of  
338 temperature. In fact, it may happen that the use of temperature does not allow the time necessary for  
339 the shelf life test to be sufficiently saved, causing the uselessness of the test. Since quality depletion  
340 phenomena can be differently accelerated by the increase in temperature, the time saved when  
341 performing the shelf life test under temperature accelerated conditions may be considerably  
342 different. Table 7 shows the percentage of time which can be saved when the temperature of the  
343 shelf life test is increased by 10 °C as a function of the activation energy of the critical phenomena.  
344 It is evident that about 50 kJ mol<sup>-1</sup> activation energy is required to save 50 % of the time needed to  
345 perform the shelf life test. From a practical point of view this means that, for oxidative reactions  
346 characterized by  $E_a$  values lower than 30-40 kJ mol<sup>-1</sup>, the acceleration obtained by a 10 °C increase  
347 could be too low to be of interest in the attempt to save time during shelf life assessment. The worst



possible case is when no temperature dependence of the alternative phenomena reaction rate ( $E_a$  approaching 0) is observed (Calligaris et al., 2012).

#### *Other acceleration factors*

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

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

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 parameters of the model, namely the electromagnetic energy required to activate the reaction. Similarly to thermal activation energy ( $E_a$ ) in the Arrhenius equation, these parameters account for the electromagnetic energy required to activate the oxidative reaction.

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

(i.e. 600-800 lux on market shelves; dark). Considering that peroxide formation (PV) was well described by the zero order reaction order, the shelf life equation used was:

$$SL = \frac{PV_{\text{lim}} - PV_o}{k_d + E_{l_1} \cdot L^{E_{l_2}}} \quad (5)$$

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

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**Conclusion**

Shelf life assessment of food undergoing oxidation has always represented a challenge for food scientists and industry managers. Actual literature information provides limited help to solve the problem of shelf-life determination, which can only be faced by adopting rigorous, systematic, and well-designed shelf-life assessment. The most urgent open issues appear to be i) the identification of acceptability limits and ii) the possibility to reduce testing time as much as possible without losing in predictive capability. The former issue could be faced by implementing rational procedures merging consumer and marketing aspects and thus supporting the decision process leading to the identification of the acceptability limit. The second problem for food industries facing the oxidation development during food storage is linked to the need to apply accelerated shelf-life tests that can effectively speed up the shelf life assessment process. However, the generation of predictive models for product suffering oxidative reactions could be an arduous task due to the huge number of environmental and compositional factors affecting the oxidation rate.

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531 **Figure caption**  
532 Figure 1. Fundamental steps in shelf life assessment process  
533 Figure 2. Schematic representation of possible positive and negative deviations from the Arrhenius  
534 equation  
535 Figure 3. Example of Arrhenius deviations of zero order rate constant of peroxide formation as a  
536 function of temperature in biscuits and bread-sticks (modified from Calligaris et al., 2007a; 2008)  
537

538 Table 1. Foods whose quality depletion during storage is mainly attributed to oxidative reaction  
539 development.

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

Table 2. Main food characteristics, environmental and packaging related factors affecting oxidative reactions in foods.

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		

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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Table 4. Apparent zero and first reaction orders used to describe the evolution of oxidation indices (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	Mancebo-Campos et al., 2008
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
		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

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

Table 6. Examples of factors used to effectively compute  $\Delta k$

Sample	Indicator	Factors affecting $\Delta k$
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

557 Table 7. Percentage of expected time saved by 10 °C temperature increase as a function of  
558 activation energy values.

Activation energy (kJ/mol)	Estimated saved time % by 10 °C increase
10	11
20	21
30	30
40	38
50	45
60	51
70	56
80	61
100	69

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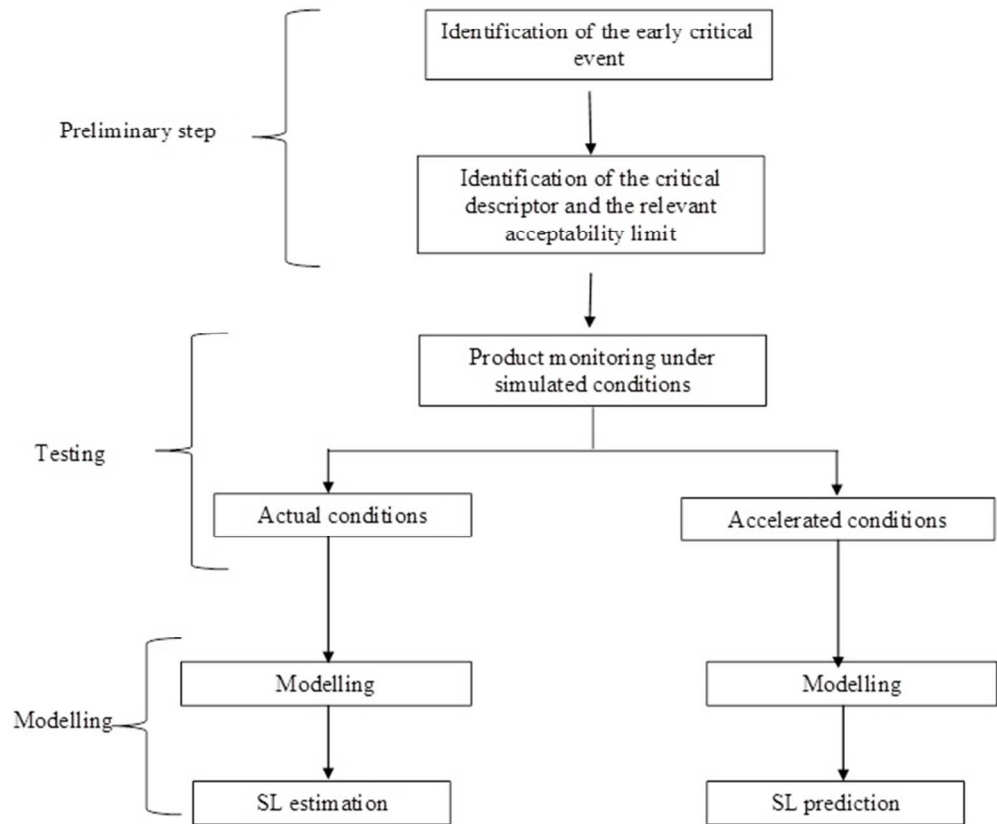


Figure 1. Fundamental steps in shelf life assessment process  
178x180mm (96 x 96 DPI)

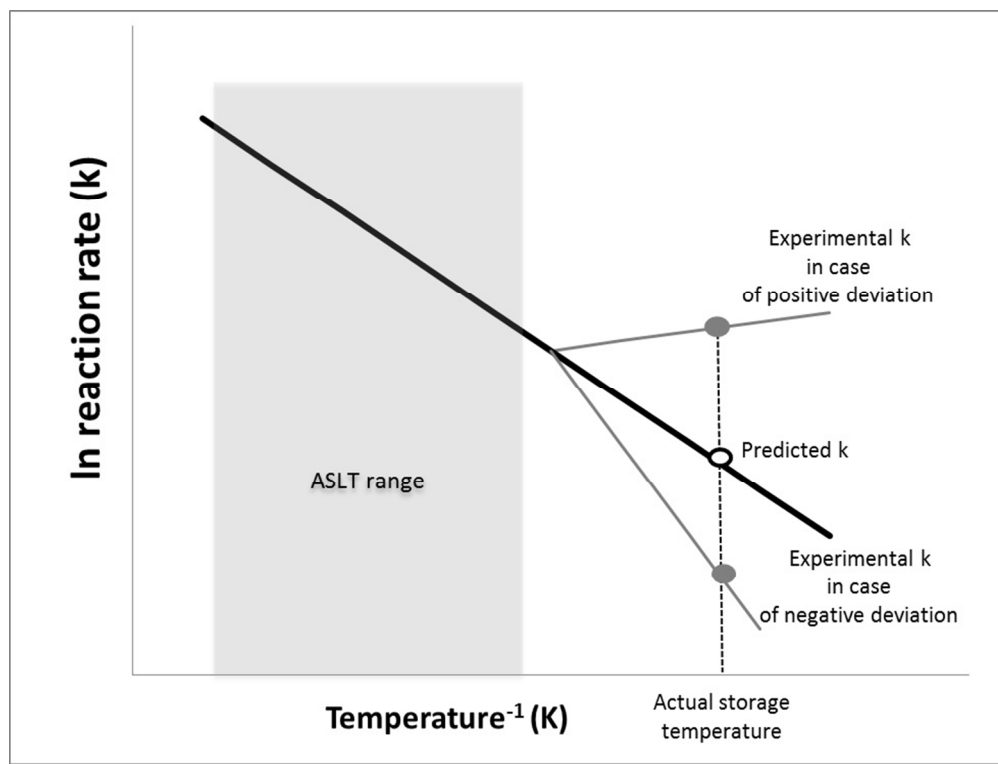


Figure 2. Schematic representation of possible positive and negative deviations from the Arrhenius equation  
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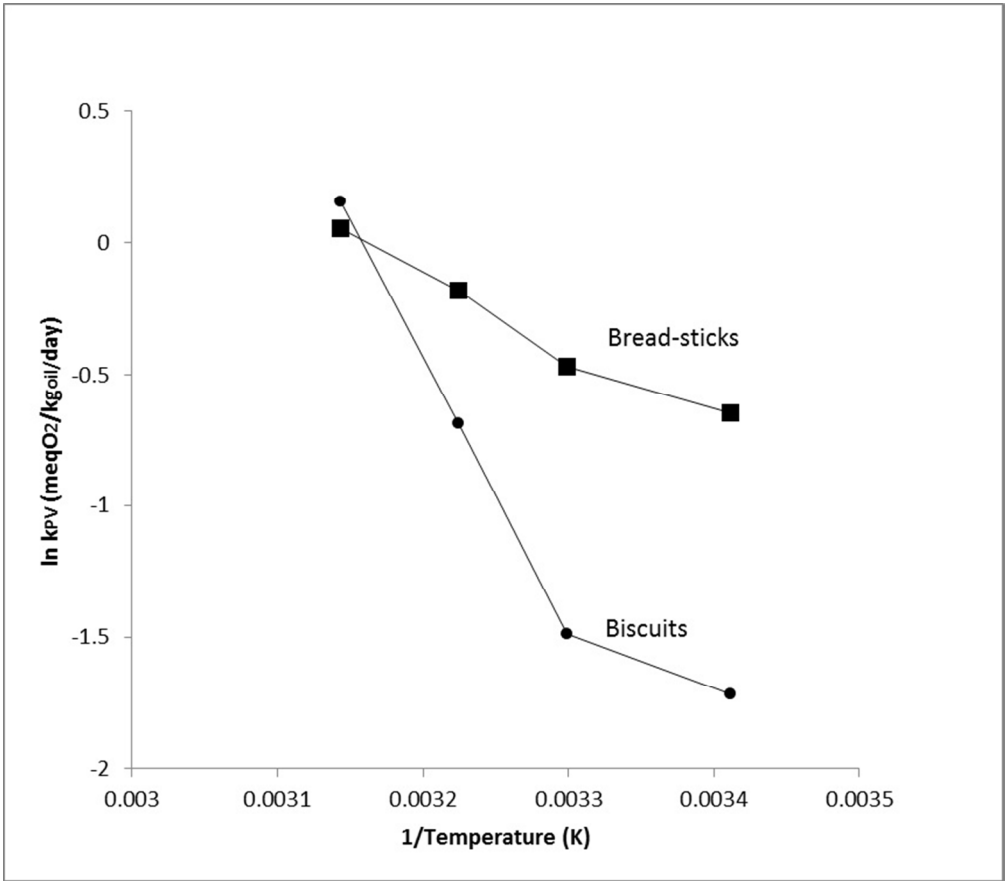


Figure 3. Example of Arrhenius deviations of zero order rate constant of peroxide formation as a function of temperature in biscuits and bread-sticks (modified from Calligaris et al., 2007a; 2008)  
227x199mm (96 x 96 DPI)