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Accelerated shelf life testing of foods

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Abstract: The food industry has a great need to obtain, in a relatively short time, the necessary information for determining the shelf life of its products. The chapter reviews the approaches available for running accelerated shelf life tests. The scientific basis behind each of these approaches is discussed as well as the problems and challenges that are involved. The chapter reviews methods that are based on the traditional linear kinetic models as well as on the recently emerging ones that are derived from non-linear ones.

Key words: accelerated shelf life tests, non-linear kinetic models, kinetic model approach, dynamic shelf life testing.


15.1 Introduction

The food industry has a great need to obtain, in a relatively short time, the necessary information for determining the shelf life of its products. It has a very important impact on handling of the products’ storage, distribution and shelf life dating. Moreover, it provides an essential tool to probe the possibilities of extending shelf life through proper product formulation and processing techniques. For practical reasons, especially when the actual storage time is long, the industry resorts to accelerated test techniques that considerably shorten the process of obtaining the necessary experimental data. In the context of this chapter, therefore, accelerated shelf life testing (ASLT) will refer to any method that is capable of evaluating product stability, based on data that are
obtained in a significantly shorter period than the actual shelf life of the product.

This chapter will discuss first the scientific basis of accelerated shelf life testing. It will indicate what tools are available for carrying out the tests and explain the problems encountered when using them. At the end, an attempt is made to suggest where this important area of accelerated shelf life testing is heading and what expectations one should have with regard to developing novel practical and reliable tools that the industry will find convenient to use.

15.2 Basic principles

ASLT is applicable to any deterioration process that can be quantitatively expressed by a valid model. This model may follow the changes in a shelf life expressing the value of a marker of deterioration or the extent of product failure under a given storage and handling history. The deterioration processes may be chemical, physical, biochemical or microbial. The principles of the ASLT will be the same in all cases. However, a larger range of different ASLT approaches are available for chemical deterioration of foods and therefore the examples in this chapter will be based on them. The following sections will discuss these approaches, all of which have a common goal of getting reliable deterioration data in a short period and selecting the proper model to use for predicting the shelf life of the product. In addition, cases of ASLT that have no need for a model will also be discussed.

15.3 Initial rate approach

Conceptually, one of the simplest techniques for obtaining useful data in a relatively short time for predicting shelf life is the ‘initial rate approach’. It may be applicable to cases where there is a shelf life determining deterioration marker that can be accurately monitored at levels well below failure. Such an approach may require an extremely accurate and sensitive analytical method. This method should be capable of measuring minute changes in the extent of deterioration after a relatively short storage time at actual conditions. The data of the initial rate of the deterioration process can serve to evaluate the parameters of a valid quantitative model. If a conventional kinetic model is used, the most important parameters to evaluate are the order of reaction \( n \) and the kinetic constant \( K \). In the case of monitoring the changes in the concentration \( C \) of a deterioration marker, the kinetic equation may be expressed as:

\[
\frac{dC}{dt} = KC^n
\]

where \( t \) is time. For sake of simplicity, let us define an index of deterioration \( D \) that has the form:
By doing that, the index of deterioration will be always linear with time and will have the following form:

\[ D - D_0 = Kt \]  

where \( D_0 \) is the initial level of the index of deterioration. Equation 15.3, if valid, is the only kinetic model that is required to employ this approach to ASLT and the extrapolation process, after evaluating the value of \( K \) from the initial rate, is obviously very simple. The product shelf life \( (t_s) \) is therefore:

\[ t_s = \frac{D - D_0}{K} \]  

Fortunately, information about the order of reactions in many food systems is available in the literature. Many of the chemical deterioration reactions in foods follow either a zero- or a first-order kinetics. The value of the index of deterioration will be in these cases:

- Zero order \((n = 0)\) \( D = C \)
- First order \((n = 1)\) \( D = \ln C \)

On a time scale it is translated to a linear or semi-logarithmic relationship, respectively (Fig. 15.1).

When the order of reaction is unknown, a simple accelerated test procedure may be used to evaluate it empirically. In that case the simplest version of the kinetic model approach, which is discussed in the following sections, may be used. Such a method uses any convenient kinetically active factor to accelerate the deterioration process.

The initial rate method, when applicable, can provide practically an ideal accelerated shelf life testing technique. It has the advantage of obtaining, in a relatively short time, the kinetic data at the actual storage conditions.

![Fig. 15.1](image-url)  
Fig. 15.1 Extent of deterioration as a function of time for zero- and first-order kinetics.
An example of using a relatively sensitive analytical method was attempted by Teixeira Neto et al. to determine the rate of oxygen uptake during oxidation of dehydrated foods.\textsuperscript{3} The commonly used manometric techniques are notorious for being insensitive to minute changes in the relatively large mass of oxygen in the headspace.\textsuperscript{4} To overcome this problem, Teixera Neto et al.\textsuperscript{3} determined the rate of oxygen uptake by analyzing the changes in the mass of the oxygen, which was adsorbed or entrapped in the product.\textsuperscript{5} Since that mass is relatively much smaller than that of the headspace, the data of the rate of oxygen uptake by the product were obtained in only a few days.

The discussion of the initial rate approach may serve also as an appropriate reminder as to why there is a need to have other accelerated shelf life testing methods for food systems having a shelf life determining marker. In the absence of a very sensitive and accurate analytical technique, the deterioration process should be allowed to progress for a longer time to enable the available method to detect the changes in a statistically significant way. The minimal time required to obtain significant data is therefore dependent on the accuracy and sensitivity of the analytical method; the worse they are the longer the time needed to obtain the data. In a way, accelerated shelf life testing is required to overcome the shortcomings of the analytical methods that are used by the industry. Therefore, the selection of the proper analytical techniques for monitoring the deterioration process is of great importance to shorten the period of the ASLT.

### 15.4 Kinetic model approach

The kinetic model approach is the most common method for accelerated shelf life testing. The basic process involves the following steps:

- Selection of the desired kinetically active factors for acceleration of the deterioration process.
- Running a kinetic study of the deterioration process at such levels of the accelerating factors that the rate of deterioration is fast enough.
- By evaluating the parameters of the kinetic model, extrapolating the data to normal storage conditions (Fig. 15.2).
- Use the extrapolated data or the kinetic model to predict shelf life at actual storage conditions.

The absolute requirement for using this procedure is to have a valid kinetic model for the deterioration process. The general and most comprehensive kinetic model for chemical reactions in foods includes all the factors that may affect their rate. These factors may be divided into two main groups, namely compositional (\(CF_i\)) and environmental factors (\(EF_j\)).\textsuperscript{6} The model may be generally expressed as follows:

\[
\frac{dD}{dt} = K(CF_i, EF_j)
\]  

15.7
This equation indicates that the kinetic constant $K$ is a function of these factors. In practice, however, one does not need a comprehensive kinetic model. For prediction of shelf life at actual storage conditions, the model should include only those factors that change during storage ($SF_i$). Therefore, the required model should only be as follows:

$$\frac{dD}{dt} = K(SF_i)$$  \hspace{1cm} (15.8)

The list of $SF_i$ should include factors such as temperature, moisture content, light intensity, composition and others, but only if they change during storage. Obviously, when one is interested in predicting the shelf life of a product at a constant temperature, it is of no interest to have a kinetic model that includes this factor. Yet, temperature can be used very effectively to accelerate the rate of the deterioration process. Therefore, the demands from a kinetic model for ASLT may be different from one that is used only to predict shelf life. The model for accelerated shelf life testing should contain two groups of factors. The first comprises those that are changing during storage ($SF_i$), as is in Eq. 15.8, and the second those that are used to accelerate the rate of reaction ($AF_j$).

The kinetic model for ASLT therefore has the form:

$$\frac{dD}{dt} = K(SF_i, AF_j)$$  \hspace{1cm} (15.9)

The kinetic model for accelerated shelf life testing may therefore be different
from the one usually used to predict product stability at normal storage conditions. Obviously, any of the factors that are changing during storage may be used to accelerate the rate of reaction.

Equation 15.9 expresses a concept of great practical importance for ASLT. It indicates that it is possible to use any desired factor to accelerate the process of deterioration regardless of whether it is active during normal storage conditions. Weissman et al.\textsuperscript{7} have suggested that one might even use compositional factors to accelerate the rate of deterioration. Corradini and Peleg\textsuperscript{8} have suggested reducing the salt concentration in order to accelerate bacterial growth. This implies that the composition of a product may be altered just for the benefit of accelerating the deterioration rate. Clearly, the information obtained is useful only if a valid kinetic model is available for these compositional factors. Such a concept can open a large number of creative avenues for conducting accelerated shelf life testing.

\section*{15.5 Single accelerating factor}

The simplest and most commonly used method of ASLT is based on employing only a single factor, mostly temperature, to expedite the deterioration process. The simplicity of such a method is related to both the experimental procedure and the availability of valid models. It should be emphasized that in ASLT, the validity of the kinetic model is crucial to obtaining accurate prediction of shelf life. Unfortunately, the validity of the model cannot be fully verified by the ASLT procedure, because the levels used for the accelerating factor do not include those of actual storage conditions. This is in contrast to the situation where the quantitative model is established and verified for actual storage conditions. Therefore, it is of great advantage if the selection of a model for ASLT is based on prior knowledge of its validity. The following sections will discuss the pros and cons of using temperature as a single accelerating factor and of the available models.

\subsection*{15.5.1 Arrhenius model}

The Arrhenius model that relates the rate of a chemical reaction to the changes in temperature is the best example of what is believed to be a generally accepted model with experimentally proven validity. It is a linear model expressing the effect of temperature on the rate constant ($K$) of different reactions in many food systems, represented by:

$$K = K_0 \exp \left( -\frac{E_a}{RT} \right)$$

where $K_0$ is a constant, $E_a$ the energy of activation, $R$ the gas constant and $T$ the absolute temperature. The Arrhenius model requires the evaluation of two parameters only, $K_0$ and $E_a$, that are supposed to be temperature independent.
Therefore, it is very convenient that these parameters can be accurately evaluated by accelerated tests at high temperatures. Moreover, since this model has been applied to many cases, a large database is available, mainly of the energy of activation of different reactions. One may conveniently use this information to get a reasonable estimate of the extent a change in temperature may affect the rate of reaction. To simplify the process further, one may avoid the need to evaluate $K_0$ by using a ratio between the rates of reaction when the temperature is changed by any arbitrary value. The most commonly used value is 10 °C and therefore the ratio between the rate of reactions is known as $Q_{10}$.

The value of $Q_{10}$ may be calculated by using Eq. 15.8 to express the rate of reaction first for a temperature of $(T + 10)$ and then for $T$ and divide the two, namely:

$$Q_{10} = \frac{\frac{dD_2}{dt}}{\frac{dD_1}{dt}} = \exp\left(\frac{E_a}{R(T + 10)}\right) = \exp\left(\frac{10E_a}{RT(T + 10)}\right)$$

The simplicity of using $Q_{10}$ has made it a very popular method for estimating shelf life. If prior knowledge or estimates of the value of the energy of activation are relied on, the accelerated tests may be run only at one elevated temperature. When choosing the maximal possible temperature, for which the Arrhenius model is still valid, the data are obtained in the shortest possible time by minimal experimental efforts. To improve the accuracy of this version of tests further, the energy of activation may also be evaluated. In that case, the rate of reaction must be obtained at a number of different temperatures below the maximal one in order to be within the range where the model is valid. Obviously, such a procedure takes a much longer time to run. The rule in accelerated stability tests is that to get more accurate data requires a longer experimental time.

The use of the Arrhenius model, as will be discussed later, is questionable when changes in the mechanism of reaction take place due to phase transition and competitive reactions. However, even if it is valid, its use, or rather any approach that is based on a single accelerating factor, may be problematic with regard to the accuracy of the extrapolated data. To demonstrate that problem, let us consider first a simple case where the kinetic constant of the reaction is linearly related to the accelerating factor (Fig. 15.3). In this figure, the solid line represents the true relationship between the kinetic constant ($y$) and the accelerating factor ($x$). The point at the top end of the line represents the true kinetic constant ($Y_e$) at the level ($X_e$), which may be estimated from the experimental data. To extrapolate the data, the slope ($a$) of the line must be evaluated by curve fitting of the accelerated test’s kinetic data. That value of the slope is used to extrapolate the line to actual storage conditions ($X_s$) where the true rate of reaction is supposed to be ($Y_s$). However, the error in the slope (Δ$a$) may cause the extrapolated line to produce a predicted kinetic constant ($Y_p$).
(high) or \( Y_p \) (low) which deviates from that true value \((Y_s)\) by \( \Delta Y \) (Fig. 15.3). For the line that has a slope of \((a - \Delta a)\), which is symmetrical to the one with a slope of \((a - \Delta a)\), the following expression should hold:

\[
\frac{Y_c - Y_p (\text{high})}{X_c - X_s} = \frac{Y_c - (Y_s + \Delta Y)}{X_c - X_s} = a - \Delta a
\]  

15.12

For the true line:

\[
\frac{Y_c - Y_s}{X_c - X_s} = a
\]  

15.13

Subtracting Eq. 15.13 from Eq. 15.12 one obtains:

\[
\frac{\Delta Y}{X_c - X_s} = \Delta a
\]  

15.14

To find how the error in evaluating slope \((a)\) affects the accuracy of the extrapolated value, one should divide Eq. 15.14 by Eq. 15.13, resulting in the following expression:

\[
\frac{\Delta a}{a} = \frac{\Delta Y}{Y_c - Y_s} = \frac{\Delta Y}{Y_s(\frac{Y_c}{Y_s} - 1)}
\]  

15.15

Therefore, the error in the extrapolated value is:

\[
\frac{\Delta Y}{Y_s} = \frac{\Delta a}{a} \left(\frac{Y_c}{Y_s} - 1\right)
\]  

15.16

Let us define the acceleration ratio \((AR)\) as the rate of the accelerated reaction in reference to that at normal storage conditions. In the case of the linear...
relationship between the kinetic constant and the accelerating factor, the value of that acceleration ratio is expressed as:

\[ AR = \frac{Y_e}{Y_s} \]  

Therefore, the relative error of the predicted value of the kinetic constant is:

\[ \frac{\Delta Y}{Y_s} = \frac{\Delta a}{a} (AR - 1) \]  

The extrapolation process multiplies the experimental error of evaluating the slope of the line by the acceleration ratio minus one. The error of the predicted kinetic constant may be extremely high, especially when a very high acceleration ratio is used and if special care is not taken to reduce the experimental error to a very low value (Fig. 15.4). The magnitude of the error changes when the relationship between the kinetic constant and the accelerating factor is no longer linear. For example, when that relationship is exponential (Arrhenius model) or a power law, the extrapolation error may be different and it can be estimated by turning these models into their linear form and then using the above equations. The only necessary step is to assign the y-axis the value of \( \ln K \). In such a case, Eq. 15.18 will read:

\[ \frac{\Delta \ln K}{\ln K_s} = \frac{\ln K_p - \ln K_s}{\ln K_s} = \frac{\ln (K_p/K_s)}{\ln K_s} = \frac{\Delta a}{a} \left( \frac{\ln K_e}{\ln K_s} - 1 \right) \]  

Therefore:

\[ \ln \frac{K_p}{K_s} = \frac{\Delta a}{a} (\ln K_e - \ln K_s) = \frac{\Delta a}{a} \left( \ln \frac{K_e}{K_s} \right) = \frac{\Delta a}{a} \ln AR \]  

![Fig. 15.4 Error in linear extrapolation.](image_url)
That results in:
\[
\frac{K_p}{K_s} = (AR)^{\Delta a/a}
\]

15.21

The error in the extrapolated data is:
\[
\frac{K_p - K_s}{K_s} = K_s \left(AR^{\Delta a/a} - 1\right) = AR^{\Delta a/a} - 1
\]

15.22

It appears, therefore, that using a model like the Arrhenius equation involves a lower error in extrapolating data (Fig. 15.5) than in the case of a simple linear model (Fig. 15.4).

15.5.2 Non-linear kinetic models

The popularity of using the Arrhenius model, especially when the order of reaction is known, has made it synonymous with ASLT and therefore temperature has been the major accelerating factor. The practical aspects and data interpretation of such tests have been recently reviewed by Saguy and Peleg.9 Most of the reported ASLTs are based on this model.10–15 However, as indicated above, this model may not be valid especially when changes in the mechanism of reaction take place due to phase transition, competitive reactions, glass transition, chemical changes in the food, etc.16 Therefore, large experimental efforts and lengthy procedures are required mainly to validate the linear Arrhenius model. In such cases a recently proposed approach of using non-linear kinetic versatile models may become attractive. This approach, developed mainly at the University of Massachusetts by Peleg and colleagues, is based on
empirical models that are relatively simple to handle and are remarkably capable of quantitatively expressing the progress of a wide range of deterioration processes including very complex ones. Moreover, their usage does not require any assumption or knowledge about the order of reaction or the nature of the mechanisms that control food spoilage. There are a number of empirical models of that kind that fit the data of the deterioration processes and thus may be considered as a possible basis for ASLT. The one that got most of the attention is the Weibullian distribution that in our context has the following form in its decay mode:

$$D = \frac{C}{C_0} = \exp\left(-Zt^\alpha\right)$$  \hspace{1cm} 15.23

where $Z$ and $\alpha$ are constants known as the ‘rate’ and the shape parameters, respectively. The kinetics of first-order decay is a special case of Eq. 15.23 where the shape parameter $\alpha = 1$. In this case the rate parameter $Z = K$. For exponential growth, the sign of the exponent is reversed. Equation 15.23 has two temperature dependent coefficients, which must be determined experimentally instead of one as in the Arrhenius model. Fortunately, in many cases, the shape parameter ($\alpha$) is much less sensitive to temperature changes and therefore can be considered constant. The determination of the temperature dependence of $Z$, and wherever needed of $\alpha$ as well, may not require any additional ASLT experiments but only different mathematical treatment. This issue was discussed by Corradini and Peleg, who suggested a number of simple versatile secondary models for this purpose. One model, for example, which they used to fit the rate parameter ($Z$) vs temperature data is the log logistic equation:

$$Z = \log_e\left\{1 + \exp[B(T - T_c)]\right\}$$  \hspace{1cm} 15.24

where $B$ and $T_c$ are constants.

Sometimes, evaluating these two constants by regression is all that is required when the shape parameter ($\alpha$) can be considered constant. However, if the shape parameter is temperature sensitive, its temperature dependence too ought to be expressed by an empirical secondary model, a power law type, for example.

In view of the available information for ASLT tests based on temperature, the non-linear kinetic approach has the potential of becoming generally accepted for many deterioration processes. Its use may become more common, especially when the deviations from constant order kinetics are large and the Arrhenius model’s validity might come into question. In such a case, validation of the model also requires carrying out experiments at temperatures close to actual storage conditions, thus requiring a lengthy procedure.

So far, the single accelerating factor that was discussed was temperature. As already indicated above, any factor that affects the deterioration process may be used in ASLT but only if it has a valid model for data extrapolation. The non-linear kinetic models apply also for other accelerating factors but need more work to establish their validity.
15.6 Glass transition models

One of the most interesting approaches to kinetic studies and their use for ASLT is based on glass transition models, which were borrowed from polymer science. Clearly, this approach may be applicable only to products that are in the physical state for which such models are valid. These models, such as the Williams, Landel and Ferry (WLF) model, relate changes in the system properties, which are connected with the polymer molecular mobility, to the temperature within the range of the transition of the product from its glassy to rubbery state. Based on the assumption that the rate of the deterioration reactions should relate to molecular mobility in much the same way, this approach yielded valuable information about processes of recrystallization, and losses of flavor and desired textural attributes caused by such structural changes. When applicable, glass transition models offer a number of very attractive features with regard to kinetic studies and ASLT. The first one is the fact that it combines both the effects of the temperature and the moisture content into one relatively simple equation. The second one, which is even more interesting, is that the rate of the deterioration is related only to the physical state of the system, which can be independently determined in a very short time by readily available physical techniques. That considerably simplifies the experimental work since one needs only the kinetic data, at one high level of temperature or moisture content, and the physical characterization of the system. Unfortunately, that kind of interesting approach to ASLT has, so far, found very limited use. In general, the glass transition model was found to correspond closely to a stability limit with respect to physical processes, such as the ones mentioned above. On the other hand, the glass transition model proved inadequate to account for different deterioration kinetics. In general, the glass transition model failed to account for diffusion of some small molecules, especially water. However, it has been proposed that the glass transition model may be applicable to predict changes in the rate of chemical reactions in food deterioration but only if proven to be diffusion limited.

15.7 Multiple accelerating factors

The use of multiple accelerating factors presents an effective approach to obtain a high acceleration ratio of the deterioration reaction at a minimal cost of prediction error. To demonstrate this fact, let us consider a simple theoretical case of a kinetic model that has the following form:

\[ K = (c_1 F_1)(c_2 F_2) = c_1 c_2 F_1 F_2 \]  

where \( c_1 \) and \( c_2 \) are the estimated parameters of the accelerating factors \( F_1 \) and \( F_2 \), respectively. In order to evaluate the error in the kinetic constant due to that of the estimated parameters, Eq. 15.25 is differentiated with regard to these parameters, resulting in:
When dividing Eq. 15.26 by Eq. 15.25 and combining it with Eq. 15.18, the estimated error is found from the following expression:

\[
\frac{\Delta K}{K} = \frac{\Delta c_1}{c_1} + \frac{\Delta c_2}{c_2} = (AR_1 - 1)RE_1 + (AR_2 - 1)RE_2
\]

where \( RE_1 \) and \( RE_2 \) are the experimental relative errors for the factors \( F_1 \) and \( F_2 \), respectively. By using multiple factors, a 100-fold acceleration of the deterioration reaction, e.g. a single one may be replaced by two factors each having an acceleration ratio of only 10. This one order of magnitude reduction in the acceleration ratio decreases considerably the extrapolation error. If, for example, the error in estimating the model parameter for each of these factors is only 1%, the extrapolated data might deviate from the real value by 99% (Eq. 15.18) for a single as compared to 18% (Eq. 15.27) for two accelerating factors. While the total acceleration effect of using two or more factors is a multiplication of their effect, the error is only the summation. Moreover, the required relatively low acceleration ratio is achieved by a much smaller change in the level of the kinetic factors and thus the system stays much closer to the actual storage conditions. Furthermore, when a narrower range of the accelerating factor is used, not only is the validity of the kinetic model better maintained but also the kinetic model may have a simpler form. The advantages of the multiple factors approach are obtained at a cost of running a more complicated experimental procedure. That is the result of the need to evaluate not only the effect of each factor on the reaction kinetics but also a possible interaction between them. The procedure, therefore, lacks the simplicity that makes such a technique more practical for the food industry.

A multiple factor acceleration of the deterioration reaction was carried out by Mizrahi et al. by combining the effect of temperature and moisture content \((m)\). It enabled a shelf life that lasts for over one year to be predicted based on an experimental study that required only 10 days. The basic kinetic equation had the following general form:

\[
K(m, T) = f(m)_{T_r} \exp \left[ \frac{E_a}{R(1/T_r - 1/T)} \right]
\]

where \( T_r \) is a reference temperature. Since moisture content in a food product is related to the water activity \((a_w)\) by the sorption isotherm, the kinetic function at the constant reference temperature \((f(m)_{T_r})\) could be expressed also in terms of that water activity.

One form of such a function for non-enzymatic browning of cabbage is:\(^{10}\)

\[
K = K_0(a_w)^s
\]
the moisture content and then keeping the latter constant at any desired level and varying the temperature. In many cases, especially when the range of temperature and moisture content changes are kept within a relatively narrow range, that procedure may be adequate. However, when that range is relatively large, a possible interaction between the two factors might play an important role in determining the accuracy of the shelf life prediction. Such was the case in the study of the non-enzymatic browning of cabbage where the energy of activation happened to be affected by the moisture content. The empirical expression that was used to describe the effect of the moisture content on the energy of activation was:

\[ E_a = c_1 \exp(-c_2m) \]

where \( c_1 \) and \( c_2 \) are constants. That interaction between the factors greatly complicates the experimental procedure since the effect of the moisture content on the energy of activation should be tested by changing both factors at the same time. That requires a much longer time and more experimental work, which may make this method very unattractive for practical use. However, as stated before, when a narrower range of accelerating factors is used, that elaborate and cumbersome procedure may not be necessary.

Another example of using two factors for accelerating the deterioration process could have been based on the data of Dattatreya et al. that quantitatively evaluated how pH and temperature affect the rate of browning of sweet whey powder (SWP). Their data enabled an ASLT procedure to be devised where very high acceleration ratio could be obtained by acidifying this product and exposing it to elevated temperatures. In this case too, the Arrhenius model may be used for expressing the effect of temperature on the rate of reaction. Other empirical equations are used for the effect of pH. In a similar way to the former case where temperature and moisture content were combined to further accelerate the deterioration process, in this case too the Arrhenius model must be modified in order to account for the effect of the pH on the value of the energy of activation. But again, this multiple-factors ASLT method facilitates changing them only within a relatively narrow range in which the Arrhenius model is practically valid.

The above discussion indicates that when using multiple accelerating factors, their interaction is complicating the deterioration models. In fact, one has to use mostly empirical models that are derived by curve fitting of data that are relevant to a specific case. Moreover, in order to establish their validity, the experimental conditions should include actual storage conditions. This requires a long experimental time that makes it impractical as an ASLT method. The same problem exists when using non-linear kinetic models. In this approach, too, the parameters of the empirical models should be expressed as a function of the accelerating factors. So far there are no such models that proved to be universal. Until this situation changes, the non-linear approach, therefore, does not look attractive when considering ASLT by multiple accelerating factors. So far, the practical use of multiple accelerating factors seems to be limited only to cases having well-established valid models.
15.8 Dynamic methods

In many ways the simplest method of accelerating the rate of reaction is by placing the product at elevated constant temperatures. Data fitting establishes the parameters of the kinetic model which in turn helps in estimating the shelf life at storage conditions. More explicitly, the latter means storage at constant temperature. Based on the evaluated model, prediction of shelf life in a dynamic situation where the temperature is changing during handling and storage, may be inaccurate in cases where history effects exist. Quast and Karel\textsuperscript{29} found such an effect in oxidation of potato chips. Similarly, Labuza and Ragnarsson\textsuperscript{30} reported a significant history effect in lipid oxidation when transferring samples from one temperature to another. This, in turn, casts doubts about using Arrhenius or any other model for dynamically changing temperatures. Therefore, one must consider the possibility that the mode of changing the storage conditions might have an extra effect on the extent of deterioration. Regular kinetic models do not account for such extra effects. Therefore, for predicting shelf life under dynamic storage conditions one has not only to establish a kinetic model but also to determine if there might be a history effect and how it might be accounted for. In cases where the kinetic experiments are carried out at constant levels of the accelerating factor, for example temperature, one must include a step where samples are transferred from one temperature to another and monitoring whether their kinetics are the same as those of the samples that are kept all the time at that constant condition. Another way of establishing the existence of history effects may be by dynamic testing as will be discussed later in this section. For sake of convenience, the following discussion will use temperature as the main example of the kinetic factor in dynamic testing. The common term for such procedures is non-isothermal testing.\textsuperscript{8,31–40}

Before getting into the discussion about dynamic testing, it may be helpful to consider first some of the pros and cons of such methods compared to the ones that are using constant conditions. When using constant temperature, for example, the effect of the come up and cooling time is assumed to be negligible due to slow kinetics. However, when the kinetics is very fast, one faces an experimental problem for which dynamic testing presents a good way to overcome such a problem. On the other hand, constant temperatures are much easier to maintain. One way, therefore, to improve the accuracy of the dynamic non-isothermal testing is to change the temperature in steps.\textsuperscript{39} Another advantage of dynamic testing is when it is possible to continuously monitor the extent of deterioration. In such a case, one needs a much smaller number of samples as compared to isothermal tests where samples are withdrawn periodically for analysis. When dynamic testing is used as an ASLT procedure, shortening of the experimental time simply means that samples are not allowed to stay at the lower range of temperature for long enough to validate the model. Most of the significant kinetic data are obtained from the higher range of temperatures.

In dynamic testing, the product is subjected to conditions where the kinetically active factor is programmed to change with time in any desired way.
That creates a situation where both the extent of deterioration and the value of the kinetic factor are changing with time (Fig. 15.6). At any given time, namely at a given level of the kinetic factor, the rate of reaction can be obtained by a numerical or graphical derivative of the deterioration curve. When running a non-isothermal ASLT procedure and following the extent of deterioration, the rate of reaction is the slope of the curve of the extent of deterioration at a momentary value of temperature and time. The obtained data may be fitted with models that have been established or believed to be valid for the deterioration processes of the tested product. In order to test for history effect, one has to run another dynamic experiment having a different pattern of how the kinetically active factor is programmed and checking for a discrepancy between the calculated results and the actual ones.

Another important way to establish the deterioration model and evaluate its parameters is to express the temperature history and the kinetics in a single rate equation. In cases where the Arrhenius model is valid, its coefficients $K_0$ and $E_a$ can be evaluated by one non-isothermal procedure. This is because the rate of reaction is dependent only on temperature. In case of the non-linear kinetic model, the rate of reaction is dependent also on time. That requires a different data analysis approach. In this case too the temperature history and the kinetics are expressed in a single rate equation. Solving this equation will result in an expression relating the extent of deterioration as a function of the model parameters that need evaluation. The technique was described by Corradini et al.\(^\text{41,42}\) In their case, the combined equation contained three adjustable parameters. Therefore, they had to have the results of four tests having four different dynamic temperature histories. They used the results of three experiments to create three equations with the three deterioration parameters ($B$, $T_c$ and $\alpha$) as the three unknown. By solving these three equations, the model parameters were determined. The model validity was thereafter tested by comparing the curve
generated with these parameters inserted into the model equation with the actual data from the fourth experiment.

Non-isothermal procedures, as well as dynamic moisture content tests have been reported in the food and in the pharmaceutical related literatures.\textsuperscript{1,8,31–41} A combination of non-isothermal tests and compressed oxygen has been reported for products that are susceptible to oxidation.\textsuperscript{39} A combination of dynamic tests involving temperature and moisture content have been successfully used for accelerating the procedure for kinetic model evaluation.\textsuperscript{43–45}

15.9 The ‘no model’ approach

The ‘no model’ approach is a term used for the accelerated shelf life testing method that assumes that a valid kinetic model exists but does not require experiments to evaluate it. This approach, which is a sort of dynamic test, may apply only to cases where the kinetically active factor ($F$) is changing during storage in a monotonically, continuous way. The ASLT technique is based on monitoring the extent of deterioration in the same product in which that factor is programmed to change in such a way that it goes through the ‘storage’ cycle in a shorter period. The obtained data are then converted into real storage conditions by a calculation that is based only on knowing how the kinetically active factor ($F$) is changing with time ($t$), namely on having the following function ($g$):

$$ F = g(t) $$ \hspace{1cm} 15.31

The inverse of that equation yields the function ($f$) of how time relates to the changing factor:

$$ t = f(F) $$ \hspace{1cm} 15.32

It should be noted that this equation might have an analytical expression, but may as well represent a numerical or graphical datum. Assuming that a valid kinetic model exists for the deterioration reaction, it will have the following form:

$$ dD = K(F)dt $$ \hspace{1cm} 15.33

The value of $dt$ may be replaced in this equation by using the derivative of Eq. 15.32, namely:

$$ dt = f'(F)dF $$ \hspace{1cm} 15.34

Thus Eq. 15.33 changes into:

$$ dD = K(F)f'(F)dF $$ \hspace{1cm} 15.35

When we have two samples of the same product, one at actual storage conditions and the other at accelerated test conditions (denoted by subscript $s$ and $a$, respectively), the ratio between their rate of deterioration is:
Thus, the rate of deterioration at actual storage conditions is related to that at accelerated ones by:

\[
\frac{(dD)_s}{(dD)_a} = \frac{(K(F)f'(F)dF)_s}{(K(F)f'(F)dF)_a} 
\]

Let us consider first a situation where the kinetic factor \((F)\) is changing linearly with time both in storage and accelerated test conditions, thus having the following respective expressions:

\[
F = F_0 + b_s t \quad 15.38 \\
F = F_0 + b_a t \quad 15.39
\]

where \(b\) is a constant. Using the inverse form of these equations, the ratio of their derivative is:

\[
\frac{f'_s(F)}{f'_a(F)} = \frac{b_a}{b_s} \quad 15.40
\]

Therefore, the ratio between the extent of deterioration in this case is:

\[
(D - D_0)_s = \frac{b_a}{b_s} \left( \int_{F_0}^{F} K(F)dF \right)_s \quad (D - D_0)_a = \frac{b_a}{b_s} (D - D_0)_a \quad 15.41
\]

Since both integrals in this equation are only functions of the factor \(F\), they have the same value and therefore cancel out. The extent of deterioration at storage conditions is therefore obtained by accelerating the change in the kinetically active factor with time and multiplying the obtained data by the ratio of the rates of change.

So far, this method is applicable only to cases where the kinetic factor is changing linearly with time. The application of this approach may be extended also to the general situation, which is expressed by Eq. 15.37. In that case, it is possible to divide the whole range of these equations into \(n\) sections, each of which may be approximated by a straight line with a slope, which can be calculated from the derivative of this equation. The basic equation in this case will be:

\[
(D - D_0)_s = \sum_{j=1}^{n} (\Delta D_j)_s = \sum_{j=1}^{n} \frac{f'_s(F_j)}{f'_a(F_j)} (\Delta D_j)_a \quad 15.43
\]

This ‘no model’ approach was developed and successfully tested for a moisture-sensitive dry product. The product was packaged in a water vapor

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permeable plastic film. Since the water activity in common storage conditions of such a product is higher than that of the packaged foods, the product will continuously absorb moisture through the film. The accelerated shelf life testing in this case was carried out by packing the same product in a film that has significantly higher water vapor permeability than the original one. In both the actual storage and the accelerated test conditions, the change in moisture content with time is not linear. In fact, the derivative of the relationship between time and moisture content for the samples that were kept at external constant water activity \( (a_e) \) can be expressed:

\[
f'(m) = [KP(a_e - h(m))]^{-1}
\]

where \( h \) denotes a function of moisture content \((m)\), \( k \) is a constant and \( P \) is the packaging film permeability to water vapor. If different films are used for storage and for accelerated tests having a permeability of \( P_s \) and \( P_a \), respectively, then:

\[
\frac{f'_s(m)}{f'_a(m)} = \frac{P_a}{P_s}
\]

In that case the extent of deterioration is given by:

\[
(D - D_0)_s = \frac{P_a}{P_s} (D - D_0)_a
\]

This is the same solution as the linear case owing to the fact that the external water activity is the same for storage and accelerated tests. Such an accelerated shelf life testing method is simple to perform, especially since it does not require the evaluation of the kinetic model. However, there is one important problem that should be considered. It has to do with the fact that the higher the rate that one programs the change of the kinetic factor, namely the moisture content in this example, the lower the extent of deterioration. That is simply the result of the fact that the deterioration reaction is given less time to develop. This approach is therefore more effective, the better the accuracy and sensitivity of the analytical method used to monitor the deterioration process. In any case, the acceleration ratio in this approach is very dependent on how small a fraction of the total acceptable extent of deterioration may be significantly determined.

### 15.10 Combination of approaches

The application of a combination of methods to accelerated shelf life testing has the same advantages as using multiple accelerating factors. Such a combination may provide an effective approach in obtaining a high acceleration ratio of the deterioration reaction at a minimal cost of prediction error by staying closer to actual storage conditions. Moreover, this approach provides potentially the largest number of avenues to ASLT. One may use a combination of multiple factors together with initial rate and ‘no model’ approaches. Mizrahi and Karel
have used a combination of the ‘no model’ approach together with elevated temperature for accelerated stability tests of moisture-sensitive products.\(^4\) This combination presents an interesting case of how to link the effect of two methods where one requires evaluation of the kinetic model and the other one does not. The assumption was that the Arrhenius equation is a valid kinetic model for the rate of deterioration at different temperatures when the moisture content is kept constant. The procedure is based on packing the product in films of different permeability and placing them in an environment of the same, or different, water activity and elevated temperatures. The temperature changes not only the rate of reaction but also the moisture gain. Therefore, in order to evaluate the parameters of the Arrhenius equation one has to separate the two processes. The technique is based on the following steps:\(^4\)

- Arbitrarily select a reference moisture gain curve. It may be, for example, the moisture gain of the product at actual storage conditions. For some cases, one may conveniently select a straight line.
- At each temperature, transform the extent of deterioration to the reference moisture gain line by using the procedure outlined in the ‘no model’ approach, namely by using Eq. 15.37 or 15.46 for the simple case where the ratio of the moisture gain is constant.
- Use the transformed data, which are now normalized to the same reference line, to obtain the parameters of the Arrhenius equation.
- Use the combination of the reference data and Arrhenius equation to extrapolate the data to actual storage conditions.

15.11 Problems in accelerated shelf life tests

The problems that are related to ASLT may be classified into three main groups. The first has to do with those cases where no valid kinetic model is believed to exist for any accelerating kinetic factor. No accelerated test procedure is available for such a case. The second kind of problem is encountered when a model does exist but it is very complicated and requires the evaluation of too large a number of parameters. The experimental procedure in such a case may prove very cumbersome to a point where the ASLT procedure may not be practical. The third group of problems relates to the application of valid ASLT methods. These problems are discussed in the following section.

15.11.1 Absence of a deterioration index

Food products may be judged on the basis of sensory evaluation that is influenced by the combined effect of a multitude of different reactions. In many cases, a measurable deterioration index, which correlates well with the sensory evaluation, is unavailable. The product may therefore be judged only on the basis of being acceptable or unacceptable and not by a continuous measurable scale, thus eliminating the possibility of using the ‘initial rate’, the ‘no model’,
or the ‘dynamic’ approaches to accelerated stability tests. However, the kinetic model approach may be used in such cases simply by assigning the kinetic constant \((K)\), at constant conditions, a value of:

\[
K = \frac{1}{t_c}
\]

where \(t_c\) is the critical time that marks the end of the shelf life of the product. This approach arbitrarily assigns the point of product failure a value of one. As in any other kinetic study, this kinetic constant is evaluated by an experimental procedure that is carried out at different constant storage conditions. The obtained data of the values of the kinetic constant as a function of these conditions provide the basis for evaluating the kinetic model and its parameters. That model can be used for predicting shelf life by integrating the kinetic equation and finding the time it takes to reach a degree of deterioration of one. This approach is exactly the same as the time–temperature tolerance (TTT) that has been extensively used to predict shelf life mainly in frozen products.\(^{48,49}\)

### 15.11.2 Statistical problems

Statistics is an essential part of designing the experimental procedures and analyzing the data both in common kinetic studies as well as in ASLT. Statistical methods have been critically evaluated, for example, for their use in data fitting of the Arrhenius model.\(^{50,51}\) In any case, it is essential that the proper statistical methods be used in ASLT. One particular subject in that respect, which relates to the validation of kinetic models, should be especially noted. The validity of the model is best established when kinetic data are available for both the actual storage and the accelerated test conditions. Obviously, the ASLT technique by itself lacks the capability of verifying the validity of the model, especially an empirical one, for actual storage. Moreover, when any model is used its parameters are evaluated only by using the data of the very high rate of reaction. That may produce a large deviation of the extrapolated data from normal conditions. One should therefore use statistical methods that test the sensitivity of the model by a cross-validation method. In principle, these methods use part of the data to verify the validity of the model. This requires a wider range of accelerated storage conditions. The closer they are to the actual storage conditions the better. Such an approach costs more both in time and in experimental effort.

### 15.12 Future trends

The subject of prime importance in ASLT and in the prediction of shelf life will continue to be the pursuit of simple-to-handle versatile kinetic models of product deterioration and establishing their validity. Such models are ideally expected to be \textit{a priori} valid for any deterioration process, regardless of how complex it is, under any handling and storage conditions. In fact, this is what the non-linear...
kinetics approach claims to offer, as discussed earlier in this chapter. As already indicated, the non-linear kinetic models’ approach is based on empirical equations that potentially cover a broad range of deterioration processes. The main difficulty with these models is that the resulting rate equation requires a numerical solution. This need not be a problem, though, because almost all modern mathematical software can handle such differential equations. Furthermore, there is a need now for secondary versatile models to correlate between the parameters of the non-linear models and the accelerating factors. Therefore, it is reasonable to believe that the major thrust in the future will be in two areas. The first is to further establish the versatility of the non-linear kinetic models. The second area is to establish the validity and versatility of secondary equations preferably having a minimal number of constants. As already indicated, such work has been done with regard to temperature as the accelerating factor. In a similar way, it is expected that future research work will provide more information about the behavior of other accelerating factors that may be considered in ASLT.

In future efforts to establish versatile secondary equations, one might expect also an attempt to reduce the number of parameters in the kinetic model. The best example so far is the shape parameter in the Weibullian model that shows little sensitivity to temperature changes. This greatly simplifies the deterioration rate model, which with a constant $\alpha$, has only two temperature-dependent terms that need to be expressed algebraically.

A practical usage of non-linear models for ASLT and shelf life prediction must obviously be based first and foremost on the validity of the models. For cases where these models are proven valid, one should expect that future efforts will be dedicated also to making the non-linear kinetics much more popular. This may not be a simple task, especially when the curve fitting model combines both the primary and the secondary equations. It may be even more complex when using such models in dynamic ASLT procedures. The group of Peleg and his colleagues at the University of Massachusetts has been handling these problems using available mathematical software. It should be expected that their work and of other people will help in formulating experimental and data analysis ASLT procedures as well as in developing software that will make their use relatively simple.

### 15.13 References


21. BUERA P and KAREL M, ‘Application of the WLF equation to describe the combined effect of moisture, temperature and physical changes on non-enzymatic browning rates in food systems’, J of Food Processing and Preservation, 1993 17 31–47.


23. CHIRIFE J and BUERA P, ‘Water activity, glass transition and microbial stability in
41. CORRADINI M G, NORMAND M D and PELEG M, ‘Prediction of an organism’s inactivation pattern from three single survival ratios determined at the end of three non-isothermal

42. CORRADINI M G, NORMAND M D, NEWCOMER C, SCHAFFNER D W and PELEG M, ‘Extracting survival parameters from isothermal, isobaric, and “iso-concentration” inactivation experiments by the “3 end point method”’, *J of Food Science*, 2009 74 R1–R11.


