MODELING THE DEGRADATION KINETICS OF ASCORBIC ACID

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Abstract

Most published reports on ascorbic acid (AA) degradation during food storage and heat preservation suggest that it follows first-order kinetics. Deviations from this pattern include Weibullian decay, and exponential drop approaching finite non-zero retention. Almost invariably, the degradation rate constant's temperature-dependence followed the Arrhenius equation, and hence the simpler exponential model too. A formula and freely downloadable interactive Wolfram Demonstration to convert the Arrhenius model's energy of activation, E_a, to the exponential model's *c* parameter, or vice versa, are provided. The AA's isothermal and non-isothermal degradation can be simulated with freely downloadable interactive Wolfram Demonstrations in which the model's parameters can be entered and modified by moving sliders on the screen. Where the degradation is known *a priori* to follow first or other fixed order kinetics, one can use the endpoints method, and in principle the successive points method too, to estimate the reaction's kinetic parameters from considerably fewer AA concentration determinations than in the traditional manner. Freeware to do the calculations by either method

has been recently made available on the Internet. Once obtained in this way, the kinetic parameters can be used to reconstruct the entire degradation curves and predict those at different temperature profiles, isothermal or dynamic. Comparison of the predicted concentration ratios with experimental ones offers a way to validate or refute the kinetic model and the assumptions on which it is based.

Keywords

Vitamin C, kinetics, storage, chemical stability, endpoints method, exponential model.

INTRODUCTION

The chemical mechanisms and kinetics of vitamins degradation during food processing and storage has been thoroughly investigated for decades and there is a large body of literature on the subject. Recently, interest in vitamins loss kinetics has been revived due to NASA's preparations for long interplanetary human flights, and vitamin C has been prominent among them. The degradation of ascorbic acid follows two major pathways (Yan and Chen 1998, Vieira et al, 2000, Manso et al, 2001, Verbeyst et al 2013). In one, known as the 'aerobic pathway' the L-ascorbic acid (AA) is oxidized to dehydroascorbic acid (DHAA or DHA), which then can disintegrate in different ways. In the other, known as the 'anaerobic pathway', the ascorbic acid disintegrates without being oxidized first so the intermediate degradation products do not include DHAA. However, the two degradation mechanisms can operate simultaneously albeit at different rates. Thus whenever the aerobic pathway plays a role, the DHAA concentration first rise and then drops as it too disintegrates and forms other compounds. Also, since DHAA is functionally a vitamin, modeling the nutritional loss of vitamin C in foods is not as straightforward as that of other vitamins where only their intact molecule has the desired biological activity. In this article, we'll only address the degradation kinetics of the original AA molecules, which is frequently the only form of the vitamin that is monitored in industrial food processing and storage studies.

Since ascorbic acid is an antioxidant, the roles of oxygen, oxidative agents and catalysts presence in its degradation mechanisms and kinetics have also received considerable attention (e.g., Zerdin et al, 2003, Odriozola-Serrano et al, 2009, Fustier et al, 2011,Van Bree et al, 2012),

including in non-food model systems (Curtin et al, 2014). These recent publications contain extensive reference lists of pertinent earlier studies of the subject (see also Leskova, et al, 2006).

This review does not address the nutritional aspects of vitamin C and its loss in processed and stored foods, the chemistry of its degradation, or the analytical methods of its determination in foods. Its central topic is published kinetic models of ascorbic acid degradation in foods and their mathematical properties. The focus is on interactive software recently posted on the Internet with which these models can be used in simulations and visualization, and on the possibility of exploiting the models' mathematical properties to reduce the number of chemical determinations in storage studies.

THEORETICAL KINTERIC MODELS OF ASCORBIIC ACID DEGRADTION

Fixed Order Kinetics

Fixed order degradation kinetics is described by the rate equation (van Boekel, 2008; 2009):

$$\frac{\mathrm{d}C(t)}{\mathrm{d}t} = -k\left[T(t)\right]C(t)^n \quad (1)$$

where in our case $C(t)$ is the momentary AA concentration at time t, $T(t)$ the momentary temperature, $k[T(t)]$ the momentary rate constant and n the reaction's order.

For first order kinetics ($n = 1$) and for constant temperature $T(t) = T$, and for the boundary condition $C(0) = C_0$, the AA's initial concentration, Eq. 1 has an analytical solution having the form

$$C(t)/C_0 = Exp\left[-k(T)t\right] \quad (2)$$

For n^{th} order kinetics ($n \neq 1$) the isothermal solution of Eq. 1 is

$$C(t)/C_0 = 1-k(T)\ (n-1)t)^{1/(1-n)} \quad (3)\ (3)$$

Although rarely if ever encountered in practice, Eq. 3 implies that where $n = 0$, the concentration ratio becomes negative at $t > 1/k(T)$, and where $0 < n < 1$, it becomes a complex number at $t > 1/C_0/k(T)^{1-n}$. To avoid the occurrence of such situations, any general program for simulating and predicting a vitamin's degradation pattern, based on Eq. 1 as a model, has to automatically replace any negative or complex value of the concentration ratio by zero, which can be done with 'If' statements (Peleg et al, 2014). To visualize the effect, the interested reader can generate isothermal degradation patterns using the modified model with the freely downloadable interactive Wolfram Demonstration http://demonstrations.wolfram.com/KineticOrderOfDegradationReactions/. [The free Wolfram CDF Player, which runs the Demonstration (and over 10900 other Demonstrations to date), can be downloaded following the instructions on the screen.]

Zero Order Kinetics

When the decay rate is very low, and the experimental concentration measurements have a scatter, the degradation curve may appear linear at least visually. Also, if such data are submitted to linear regression, the regression coefficient r^2 is likely to be high. Thus for all practical purposes the degradation can be treated as following zero order kinetics on the pertinent time scale, but probably not for long range extrapolation. Examples of what appears as zero order

kinetic degradation of AA can be found in Tiwary et al (2009) who studied the relatively marginal effect of sonification and others, e.g., Robertson and Samaniego, 1986, Van Bree et al, 2012). However, zero order degradation kinetics has also been reported for a substantial loss of AA exposed to high temperatures and various levels of water activity (Laing et al, 1978).

First Order Kinetics

Most of the publications on AA degradation report that it followed first order kinetics, regardless of the food or medium, the temperature range and time scale (e.g., Laing et al, 1986, Johnson et al, 1995, Lee and Coats, 1999, Uddin et al, 2002, Giannakourou and Taoukis, 2003, Polydera et al, 2003, 2005, Poschet et al, 2005, Burdurlu et al, 2006, Cruz et al, 2008, Van Bree et al, 2012, Bosch et al, 2013, Li et al, 2016).

Combined First Order Kinetics Models

Ascorbic acid has two degradation mechanisms that can occur simultaneously: the already mentioned aerobic and anaerobic pathways. Consequently, the AA's diminishing concentration in a particular food or medium is governed by two temperature-dependent rate constants, $k_{\text{aerobic}}(T)$ and $k_{\text{anaerobic}}(T)$. Thus if both degradation pathways follow first order kinetics, then the AA's isothermal disappearance is described by the model (Verbeyst et al 2013):

$$C(t) = C_{aerobic} Exp(-k_{aerobic} t) + (1 - C_{aerobic}) Exp(-k_{anaerobic} t) \quad (4)$$

where $C(t)$ is the momentary fraction of the original AA and C_{aerobic} the fraction of the original AA concentration, which is degraded by the aerobic mechanism, i.e., by being oxidized to DHAA first. Also, according to these authors, when the non-oxidative mechanism's contribution

is very small, i.e., $k_{anaerobic} << k_{aerobic}$ or ~ 0, the fraction 1 - $C_{aerobic}$ is practically a constant. If so, Eq. 4 becomes (Vieira et al 2000 and ibid):

$$C(t) = C_{asymp} + \left(1 - C_{asymp}\right) Exp\left(-k_{aerobic} t\right) \quad (5)$$

where C_{asymp} is the asymptotic concentration fraction of the original AA. In other words, the degradation curve initially follows the exponential decay pattern expected from first order kinetics but then instead of the AA decaying asymptotically to zero it decays to a residual nonzero value, at least on a pertinent time scale. To simulate this isothermal degradation pattern open the Wolfram Demonstration Simulating Ascorbic Acid Degradation at http://demonstrations.wolfram.com/SimulatingAscorbicAcidDegradation/. Examples of this Demonstration's screen displays are given in Fig. 1. The left side of the figure shows a degradation curve that follows first order kinetics (C_{asymp} = 0), and the right side a curve that follows Eq. 5 as a model (C_{asymp} > 0). Notice that Eqs. 4 and 5 are akin to the biphasic exponential model (van Boekel 2008), which for our purpose can be written in the form (Corradini et al 2007):

$$\mathrm{Log}\, C(t) = -k_{aerobic} t \text{ if } t \le t_c \text{ and } -k_{anaerobic} t \text{ if } t > t_c \quad (6)$$

where t_c marks the time when the change in slope occurs and $k_{aerobic} > k_{anaerobic}$. If $k_{anaerobic} \sim 0$, it will approximate the curve produced by Eq. 5. To simulate and visualize degradation curves with Eq. 6 as a model open the freely downloadable Wolfram Demonstration at http://demonstrations.wolfram.com/BiphasicExponentialDecayAndGrowth/. Although some published data suggest the existence a biphasic degradation pattern (Polydera et al, 2003,

Verbeyst et al, 2013), whether the biphasic model (Eq. 6) has ever been tried in the study of AA degradation is unknown to the authors.

Weibullian Kinetics

Chemical and thermal degradation can be viewed as a failure phenomenon, i.e., a manifestation of the molecules' inability to remain intact in the particular environment. Thus the degradation curve, depicting the diminishing concentration vs. time relationship, is basically a survival curve, the cumulative form of the disintegration events' temporal distribution. When the degradation curve's is expressed in terms of a concentration ratio, its local slope, having time reciprocal units, is the process's *rate*. In many diverse and unrelated physical breakage and disintegration phenomena the disintegration events have a Weibull temporal distribution, which has been known as the Rosin-Rammler distribution in particulates size reduction. When adapted for isothermal chemical degradation it can be written in the form known as the stretched exponential:

$$C(t) = \mathrm{Exp}\left[-\left(\frac{t}{t_c(T)}\right)^{m(T)}\right] \text{or } \mathrm{Exp}[-b(T)t^{m(T)} \quad (7)$$

where $C(t)$ is the momentary concentration ratio, $t_c(T)$ a temperature-dependent characteristic time ("scale factor"), or $b(T)$ a temperature-dependent rate parameter, and $m(T)$ a power (known as the "shape factor"). The power $m(T)$ in Eq. 7 is usually a weak function of temperature and can be treated as a constant, i.e., $m(T) \sim m$ in many applications. Notice that where $m(T) = 1$, Eq. 7 describes first order degradation kinetics. Also, depending on the degradation data scatter, the

fixed order kinetics (Eq. 2) and the Weibullian model (Eq. 7) can be used interchangeably when *m* or *n* is between about 0.8 and 1.2. This can be seen in the interactive Wolfram Demonstration http://demonstrations.wolfram.com/FitOfFirstOrderKineticModelInDegradationProcesses/

Application of the Weibullian model to AA degradation has been reported by Manso et al (2001), Corradini and Peleg (2004, 2006), Odriozola-Serrano et al, (2009), Tiwari et al (2009), Derossi et al (2010), Zheng and Lu (2011), and others.

THE ROLE OF TEMPERATURE

The Arrhenius equation and exponential model

The temperature-dependence of the rate constant, however defined, has been traditionally described by the Arrhenius equation, which can be written in the form:

$$k(T) = k(T_{ref})\,\mathrm{Exp}\left[\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \quad (8)$$

where $k(T)$ is the rate constant in the pertinent concentration per time units at temperature T in °K, $k(T_{\mathrm{ref}})$ the rate constant at a reference temperature T_{ref} in °K. E_{a} according to this model is the "energy of activation", usually expressed as kJ or kcal per mole, and R the Universal Gas Constant in commensurate units.

It has been demonstrated (Peleg et al, 2012, 2014, 2015) that without sacrificing the fit, the Arrhenius equation can be replaced by the simpler exponential model:

$$k(T) = k(T_{ref})\ \mathrm{Exp}\left[c\left(T - T_{ref}\right)\right] \quad (9)$$

where T and T_{ref} are in°C and c is a constant having°C^{-1} units. Demonstration of the interchangeability of the two models can be viewed in the Wolfram Demonstration http://demonstrations.wolfram.com/ArrheniusVersusExponentialModelForChemicalReactions/. The advantage of the exponential model over the Arrhenius equation, apart from its obvious simplicity, is that it does not require one to assume that the activation energy of chemical reactions and biological processes in foods is universally temperature-independent, an assumption yet to be confirmed experimentally. The interchangeability of the two models should not come as a surprise. This is revealed by the Taylor series expansion of $k(T)$ when expressed by the two models at T_{ref}. It shows that the first two terms are identical and that at temperatures pertinent to food storage and processing, the series converges very rapidly (Peleg et al, 2012). Consequently, one can convert published E_a values into c values and vice versa using the formula:

$$c \approx \frac{E_a}{R\left(T_{ref}+273.16\right)^2} \text{ or } E_a \approx cR\left(T_{ref}+273.16\right)^2 \quad (10)$$

To do the conversion online one can use the Wolfram Demonstration http://demonstrations.wolfram.com/ExponentialModelForArrheniusActivationEnergy/.

Examples of the interchangeability of the two models when applied to ascorbic acid's published degradation data in different foods at different temperatures are given in Fig. 2. These examples demonstrate that as long as the reference temperature is in a pertinent temperature range, its choice has no discernible effect on the two models' fit.

Reported E_a values for ascorbic acid degradation in various foods are mostly in the range of 10-80 kJ/mole (or about 2 -18 kcal/mole) which for T_{ref} = 25°C correspond to c values of 0.0135-0.081°C^{-1}. The reported values in frozen vegetables (Cruz et al, 2008) were 130-150 kJ/mole (or 31-36 kcal/mole) which for T_{ref} = -5°C correspond to c values of 0.217-0.250°C^{-1}. Notice that the physical meaning of any reported E_a value obtained from an Arrhenius plot's slope is unclear, unless confirmed by independent experimental determination or compelling theoretical arguments that the Arrhenius model indeed applies. It is most likely that the same experimental $k(T)$ vs. T data fitted by the Arrhenius equation could also be successfully fitted with the Eyring-Polanyi model (Cisse et al, 2009), and most probably by several empirical models as well -- see below. To view the almost perfect interchangeability of the Arrhenius and Eyring-Polanyi models open http://demonstrations.wolfram.com/ArrheniusVersusEyringPolanyiModel/.

Alternative temperature-dependence models

The Arrhenius equation has been by far the most widely used model to describe the temperature-dependence of the degradation rate constant of ascorbic acid. Other models, adapted from microbial inactivation, have been the log-linear relationship, which has produce the D and z values (Johnson et al, 1995, Castro et al, 2004), variants of the Belerādek's also known as Ratkowsky's 'square root' model (Valdramidis et al, 2010) and the logarithmic-exponential model (Corradini et al, 2004, 2006, Derossi et al, 2010). The WLF equation imported form the polymer science literature has also been considered (Giannakourou and Taoukis, 2003). This model implies that the rate of chemical degradation reactions in a food is primarily determined by how far the food is from its 'glass transition temperature', T_g, which is rarely uniquely

defined.

To visualize the simplest version of the 'square root' model open http://demonstrations.wolfram.com/SquareRootModelForRatesOfMicrobialGrowthOrInactivation/, to visualize the logarithmic-exponential model, open http://demonstrations.wolfram.com/WeibullianInactivationRateAsAFunctionOfTemperature/, and to visualize the WLF equation), open http://demonstrations.wolfram.com/WilliamsLandelAndFerryEquationComparedWithActualAndUniversal/. A discussion of the merits and limitations of these and other temperature-dependency models can be found in Peleg et al (2012).

Non-isothermal degradation

In heat processing or dynamic storage of foods, where the temperature varies with time, i.e., $T(t) \neq$ constant, Eq. 1 has an analytic (algebraic) solution only for a few combinations of the values of n and the temperature history's profile. When the temperature-dependence of the rate constant's follows the exponential model (and hence the Arrhenius equation) it assumes the form:

$$\frac{\mathrm{d}C(t)}{\mathrm{d}t} = -k_{Tref}\, Exp\left[c\left[\left(T(t) - T_{ref}\right)\right]C(t)^{n}\right. \quad (11)$$

where $C(t)$ is the momentary concentration ratio, and $C(0) = 1$ is the boundary condition. Regardless of the value of n, Eq. 11 is an ordinary differential equation (ODE) and can be rapidly solved numerically with Mathematica® and other advanced mathematical programs, even for elaborate temperature profiles that might include "if" statements (Peleg et al, 2014).

Examples of dynamic degradation curves of reactions that follow fixed order kinetics can be generated with the Wolfram Demonstration

http://demonstrations.wolfram.com/NonisothermalDegradationKinetics/ whose screen display is shown in Fig. 3.

When it comes to non-isothermal degradation curves of ascorbic acid, which under isothermal conditions are governed by Eq. 5 as a model, i.e., where there is an asymptotic retention ratio C_{asympt}, Eq. 11 no more applies and needs to be replaced. In principle at least, the isothermal Eq. 5 can be converted into a general dynamic rate equation by assuming the following:

1. The asymptotic concentration ratio, C_{asympt}, is actually or practically temperature-independent.

2. In a pertinent temperature range, the temperature-dependence of the rate constant $k(T)$ still follows the exponential model (and therefore the Arrhenius equation), and

3. The momentary dynamic degradation rate, $dC(t)/dt$, is the isothermal rate at the momentary temperature, $T(t)$, at a time $t^*(t)$, which corresponds to the momentary concentration, $C(t)$. If all three assumptions hold, then

$$\frac{dC(t)}{dt} = -k_{T_{ref}} \left(1 - C_{asympt}\right) Exp\left[-Exp\left[c\left(T(t) - T_{ref}\right) k_{T_{ref}} t^*(t) + c\left(T(t) - T_{ref}\right)\right] \quad (12)$$

where

$$t^*(t) = -Ln\left[C(t) - C_{asympt}\right) / \left(1 - C_{asympt}\right)\right] / \left(k_{T_{ref}}\, Exp\left[c\left(T(t) - T_{ref}\right)\right]\right) \quad (13)$$

Despite its cumbersome mathematical appearance, this model too is an ordinary differential equation (ODE). Consequently, this model equation can be solved numerically to describe degradation patterns under almost any conceivable temperature history using Mathematica® and other advanced mathematical programs. Eqs. 12's validity as a model of AA's dynamic degradation kinetics is yet to be confirmed experimentally. Also, notice that Eq. 11 is a special case of Eqs. 12 and 13 where $C_{asympt} = 0$. The issue of whether and how the value of C_{asympt} can be assessed a priori is yet to be fully resolved, see below. However, whenever C_{asympt} is known, or can be assumed on the basis of published data, the model expressed in Eqs. 12 and 13 can be used to simulate both isothermal and dynamic degradation curves of ascorbic acid including in scenarios where it has no residual retention. An interactive Wolfram Demonstration that simulates isothermal and dynamic AA degradation can be found at http://demonstrations.wolfram.com/SimulatingAscorbicAcidDegradation/. Examples of its screen displays are given in Fig. 4.

In principle, similar assumptions can be made for the AA's dynamic degradation patterns that follow the Weibullian model (Eq. 7). In that case, however, there is no asymptotic residual concentration ratio, but as before, the rate parameter, $b(T)$, is expected to follow the exponential model (and hence the Arrhenius equation). For convenience, the resulting rate equation can be written in the form:

$$\frac{dy(t)}{dt} = -b_{Tref}\,Exp[c\left(T(t) - T_{ref}\right)]m\left[\frac{y(t)}{b_{Tref}\,Exp\left[c\left(T(t) - T_{ref}\right)\right]}\right]^{\frac{m-1}{m}} \quad (14)$$

where $y(t)$ = Ln[$C(t)$], i.e., the natural logarithm of the residual concentration ratio, $T(t)$ is the temperature profile's equation, and $y(0) = 0$ the boundary condition. The actual dynamic degradation curve expressed in terms of the concentration ratio $C(t)$ vs. t would then be described by:

$$C(t) = Exp\left[y(t)\right] \quad (15)$$

where $y(t)$ is the solution of Eq. 14. A Wolfram Demonstration that generates isothermal and dynamic Weibullian degradation patterns using the above model has been posted on the Internet, open http://demonstrations.wolfram.com/WeibullianChemicalDegradation/. Again, to the best of our knowledge, application of this dynamic version of the Weibullian model to ascorbic acid degradation has not yet been reported. One can only find a similar version of the model where $b(T)$ is described by the logistic-exponential model (Corradini and Peleg, 2006, Derossi et al, 2010). Since the Arrhenius equation, and hence the exponential model, and the log-exponential modes have a substantial region of practical overlap (Peleg el al, 2002), one can expect that these three models will produce similar dynamic degradation patterns in cases where the AA shows no asymptotic retention on the pertinent time scale.

THE ENDPOINTS METHOD TO DETERMINE AA'S KINETIC PARAMETERS

The conventional method to determine kinetic degradation parameters

Traditionally, the kinetics of ascorbic acid degradation during thermal processing or storage, as that as that of other vitamins, has been determined from a series of experimental isothermal concentration or concentration ratio vs. time relationships at a pertinent temperature range (e.g.,

Van den Broeck et al, 1998); Viera et al, 2000; Manso et al 2001, Giannakourou and Taoukis, 2003; Burdurlu et al, 2006). Plots of the data on linear, semi-logarithmic, or other coordinates and/or linear or nonlinear regression have been used to establish the degradation reaction's kinetic order, *n*, and to determine the corresponding rate constant's temperature-dependence. Almost invariably, as stated in previous sections, this dependence has been described mathematically by the Arrhenius equation, which has been employed to predict the degradation patterns at different temperature histories, isothermal or dynamic. Although mostly successful, this methodology raises two issues. At high temperature-short time processing (HTST), especially well above 100°C as in UHT processing, obtaining isothermal temperature profiles, even approximately, is extremely difficult if not utterly impossible. (Peleg et al, 2008). This problem hardly if ever exists in storage studies where the come-up and/or cooling times are almost always negligible relative to the "holding time." The main issue in storage studies is that the conventional procedure requires a relatively large number of samples to be stored and tested periodically, which creates a logistic issue (Peleg et al, 2014, 2015, 2016). For example, in a conventional setup of 4 storage temperatures with 4 samples pulled for analysis at each temperature, the number of concentration determinations is 16. If each analysis is performed in triplicates, the total number of samples to be actually analyzed is 48. The question that arises is whether the kinetic parameters can be estimated, from a smaller number of storage temperatures and a considerably smaller of number of determinations and chemical analyses. For instance, if the needed kinetic information could be extracted from the same food stored at only 3 storage temperatures and the AA concentration is determination in triplicates *only once at each temperature* (after a sufficient time to detect the degradation), the number of tested samples

would be reduced to 9. Thus if a method to calculate the kinetic parameters from a smaller number of experimental data is found, its implementation would result in considerable savings, especially in studies where a large number of food products are investigated.

The endpoints method

The endpoints method is based on the tenet that when the general kinetics is known a priori or can be assumed, and the food's temperature history accurately recorded, one can use the final concentrations after two or three different heat treatments or storage temperature histories to extract the unknown kinetic parameters -- see Fig. 5. In principle, if the kinetic model has two unknown parameters, at least two temperature histories are required, and if there are three unknown parameters, then at least three temperature histories are needed. The method was originally developed for nonlinear microbial inactivation and chemical degradation reactions at very high temperatures and short times such as encountered in UHT preservation (Peleg et al, 2008; Corradini et al, 2008, 2009). The initial assumption has been that the spores or cells survival follows Weibullian kinetics (Eq. 7) and that the temperature-dependence of the rate parameter, $b(T)$, follow the Log-Exponential model (ibid), which has a marker of the lethal temperature's onset. In contrast, the degradation of many nutrients and pigments in foods follows linear fixed order kinetics, which in many cases can facilitate the calculation (Peleg et al, 2014). When a nutrient is lost during storage, as already mentioned, the roles of the come-up and cooling times, or vice versa, are rarely if ever an issue and hence the endpoints method's advantage in this case is primarily logistic. Recent works showed that the endpoints method could be used to estimate vitamins degradation kinetic parameters, including the reaction's

kinetic order if unknown, from isothermal or non-isothermal data (Peleg et al, 2014; 2015; Peleg and Normand, 2015). The endpoints method's validation came from its ability to predict correctly residual concentrations at temperature histories not used in the kinetic parameters determination. The method is considerably simplified when the reaction's kinetic order is known a priori, or can be assumed based on reports in the literature (ibid). It is further simplified when the kinetic order is known and all the storage temperatures are constant, see next section.

The isothermal case

Consider a scenario where there are two food samples having a known initial concentration of ascorbic acid stored at two constant temperatures T_1 and T_2 for times t_1 and t_2, respectively, which resulted in their having corresponding concentration ratios C_1 and C_2. When the heating and cooling times are negligible relative to the storage duration, the temperature profile can be considered isothermal for all practical purposes. There are reports in the literature which suggest that the AA's degradation follows first order kinetics and we'll address this case first. Scenarios where it does not will be discussed separately later.

Fixed order degradation kinetics, as already stated, follows Eq. 1 as a model and its isothermal solutions for $n = 1$ and $n \neq 1$ are Eq. 2 or 3, respectively. We assume that the temperature-dependence of the rate constant $k(T)$ defined by these equations follows the Arrhenius equation and hence the simpler exponential model (Eq. 9) too.

When the exponential model holds, one can insert $k(T)$ as described by Eq. 9 into Eq. 2 or 3 to produce an algebraic isothermal degradation model for any temperature T in a pertinent range.

[One can also replace $k(T)$ with $k[T(t)]$ and T by $T(t)$ and insert them into Eq. 1 to produce a general kinetic model of which isothermal degradation is a special case (Peleg et al, 2015).]

As shown in Fig. 6 - Left, the two endpoints, $\{t_1,C_1\}$ and $\{t_2,C_2\}$, ought to be on two yet unknown degradation curves of their respective temperatures T_1, and T_2. To reconstruct these curves, see Fig. 6 - Right, we start by picking an arbitrary reference temperature T_{ref}, preferably between or in the neighborhood of T_1 or T_2. If the degradation indeed follows first order kinetics and the rate constant temperature-dependence the exponential model as assumed, then insertion of Eq. 9 into Eq. 2 implies that:

$$C_1 = \text{Exp}\left[-k\left(T_{ref}\right)\ \text{Exp}\left[c\left(T_1 - T_{ref}\right)\right]t_1\right] \quad (16)$$

and

$$C_2 = \text{Exp}\left[-k\left(T_{ref}\right)\ \text{Exp}\left[c\left(T_2 - T_{ref}\right)\right]t_2\right] \quad (17)$$

We can do the same with Eq. 3 if we know or want to try $n \neq 1$.

Eqs. 16 and 17 are two simultaneous nonlinear algebraic equations with two unknowns, namely $k(T_{\text{ref}})$ and c. The two equations can be solved numerically with the FindRoot function of Mathematica® (Wolfram Research, Champaign IL), the program used to test the concept for ascorbic acid in this article, to extract the numerical values of these two unknown parameters. This can be also be done with similar equation solving functions of other commercial mathematical software.

Once $k(T_{ref})$ and c have been calculated in this way, they can be inserted back into the isothermal degradation model equation to reconstruct the two degradation curves shown in the figure, and to predict and plot the degradation curve at any other storage temperature T_3 in a pertinent range.

The validity of the endpoints method and its underlying assumptions can be tested by comparing experimental concentration ratios *at temperatures not used in the parameters calculation* with those predicted by the described procedure. An agreement between the experimental and predicted concentration ratios, especially when observed at several temperatures, will validate the method. Failure to render close predictions can have several interpretations. It can be due to an experimental error or errors in the data and/or to that one or more of the underlying assumptions are invalid. Examples are that the degradation in the particular food follows nonlinear kinetics, or a fixed kinetic order that is substantially different from that assumed. In extreme cases, violation of the assumptions may result in failure of the iterations to converge, or if they do converge, the rendered parameter values can be unrealistic or absurd.

It ought to be stated that two endpoints are the *smallest theoretical number* of temperatures, times and corresponding final concentration ratios triplets, which are needed to extract the values of the parameters $k(T_{ref})$ and c when the kinetic order n is known a priori. This should not be confused with the *number of measurements or chemical analyses*. These should always include several replicates to assure that the method renders reliable parameters values and make correct predictions. Also, wherever feasible, one should determine and use more than two experimental endpoints, the theoretical minimal number, at least three. This will enable to validate the method and increase its predictions accuracy by averaging, see below.

To solve simultaneous nonlinear equations numerically requires close initial guesses of the sought kinetic parameters, which can be a daunting task. The development of an interactive version of the calculation procedure has eliminated this problem (see Peleg et al, 2016, and below). The program is available in the form of two Wolfram Demonstrations one for temperature above the freezing mark (http://demonstrations.wolfram.com/PredictionOfIsothermalDegradationByTheEndpointsMethod/) and the other for temperatures below (http://demonstrations.wolfram.com/EndpointsMethodForPredictingChemicalDegradationInFrozenFoods/).

Averaging the kinetic parameters obtained by the endpoints method

Suppose there are three experimental endpoints available for analysis, i.e., T_1, t_1 & C_1, T_2, t_2 & C_2, and T_3, t_3 & C_3, which we can call A, B and C for convenience. Applying the method to the three pair combinations A&B, A&C and B&C will render three values of $k(T_{ref})$: $k(T_{ref})_{A\&B}$, $k(T_{ref})_{A\&C}$ and $k(T_{ref})_{B\&C}$, and three values of c: $c_{A\&B}$, $c_{A\&C}$ and $c_{B\&C}$. These $k(T_{ref})$'s and c's values can be averaged to improve the parameters' reliability and consequently the quality of any fourth concentration ratio, c_4, at a temperature T_4, different from T_1, T_2 and T_3, which had been used in the parameters calculation. With four experimental endpoints available, the number of pair combinations for averaging is six, i.e., A&B, A&C, A&D, B&C, B&D and C&D, and with five the number rises to ten, i.e., A&B, B&C, B&D, B&E, B&C B&D, B&E, C&D, C&E and D&E, which can boost the kinetic parameters' reliability dramatically, albeit at an added logistic cost. Also, when there are six or more values, one can identify outliers by statistical criteria and

eliminate them from the average calculations (Corradini et al, 2008). In what follows in the next sections we identified suspected outliers by the two sided Iglewicz and Hoag test (Anon, 2102) with z = 3.5 using a free online program (http://contchart.com/outliers.aspx).

TESTING THE ISOTHERMAL VERSION OF THE ENDPOINTS METHOD WITH PUBLISHED ASCORBIC ACID DEGRADATION DATA

The interchangeability of the Arrhenius and Exponential models in ascorbic acid degradation

The examples of reported $k(T)$ vs. T data of AA fitted with both the Arrhenius and exponential models given in Fig. 2 are in agreement with previous observations in different nutrients and other chemical systems (Peleg et al, 2012; 2014; 2015). They demonstrate that the two models are indeed interchangeable at temperatures that are relevant to food processing and storage. The examples also demonstrate that as long as the reference temperature is in a pertinent range, its choice has no discernible effect on the two models' fit as expected.

Comparison of the endpoints' method predictions with reported data

As already explained, not all the available published data on ascorbic acid degradation are suitable for testing the applicability of the described version of the endpoints method, which was developed exclusively for degradation patterns that follow conventional first order kinetics. Since many of the original publications that we have surveyed reported the entire isothermal degradation dataset at different temperatures and the first order kinetic model's fit, we could identify several which were suitable for testing the method. Examples of Wolfram's Demonstration's screen displays that were used to calculate the AA's degradation kinetic

parameters from endpoints extracted from published isothermal data and to predict the concentration ratios at a third temperature are shown in Figs. 7-11. The figures show the reconstructed degradation curves passing through the two entered endpoints (left), and the predicted degradation curve at a third temperature (right), using the $k(T_{ref})$ and c values obtained by matching the reported experimental endpoints with the generated (reconstructed) curves. In the right plot, the two reconstructed curves are plotted in blue and the predicted curve in red.

Tables 1 and 3 summarize the endpoint combinations used to determine the AA's degradation kinetic parameters in frozen peas and spinach, and in strawberry and orange juices stored at constant ambient temperatures. Table 1 shows that with only a few exceptions, where outliers were suspected and consequently removed, the magnitude of the calculated $k(T_{ref})$'s and c's did not vary by much as a result of choosing different endpoints combinations. The table also shows that the suspected outliers removal did not have a dramatic effect on these kinetic parameters magnitudes. Tables 3 shows no suspected outliers and here too the $k(T_{ref})$'s and c's calculated with the different endpoint combinations also did not vary dramatically. Considering that in none of the original studies from which the data were obtained had given the endpoints any special consideration, i.e., the concentrations were determined with only 2 or 3 replicates, this constancy indicates that the method is fairly robust and that the assumptions on which it is based are not unrealistic.

The crucial test of the endpoints method applicability to ascorbic acid, however, is whether and how its predicted concentration ratios agreed with those reported in the original publications. Tables 2 and 4 list the predicted and reported values for comparison. In the case of the two

frozen vegetables, see table 2, the agreement was consistently reasonable at least as judged by informal criteria, i.e., the difference between the predicted and reported percent retention is mostly on the order of 1-3% (absolute), with three notable exceptions where the discrepancies were on the order of 7-9% (absolute). As shown in Table 4, the agreement between the predicted and reported values in the stored juices was inconsistent. In most trials the discrepancies varied between fairly small, i.e., absolute difference of 0-5% in the retention level, and substantial that is as high as 9-12% (absolute). Since in none of the original studies from which the data were obtained had the endpoints received special attention, as already stated, the magnitude of discrepancies suggest that the endpoints method could have been more robust had special effort been made to determine the last concentration ratios more accurately. We suspect that the shown discrepancies were most probably, or at least partly, due to the quality of the individual data points and not to a systemic failure of the method. Had this been the case, it would be very difficult to explain why none of discrepancies was of an order of magnitude and why they showed no discernible trend or pattern. Also, all the original publications from which the data shown in the tables were extracted gave no indication of asymptotic approach to a residual, i.e., nonzero, retention level. Consequently, it is very unlikely that the discrepancies were due to an inappropriate model. Because the endpoints received no special attention in the original studies, the occasional observed discrepancies and their magnitudes should have actually been expected rather than come as a surprise. All this re-emphasizes that if and when the endpoints method is implemented in storage studies, the endpoints concentration ratios should always be determined in a sufficient number of replicates.

Potential applications of the endpoints method with non-isothermal data

Consider two temperature profiles $T_1(t)$ and $T_2(t)$, at least one of them not isothermal, with corresponding endpoint concentration ratios C_1 and C_2, respectively. We assume that the degradation follows known fixed order kinetics, and that the rate constant's temperature-dependence obeys by the exponential model (or Arrhenius equation). If so, then the two endpoint concentration ratios C_1 and C_2 are the solutions of Eq. 11 for the two temperature profiles $T_1(t)$ and $T_2(t)$ for times t_1 and t_2, respectively. Or mathematically:

$$The\ solution\ for\ t_1\ of\ \frac{\mathrm{d}C(t)}{\mathrm{d}t} = -k\left(T_{ref}\right)Exp\left[c\left(T_1(t)-T_{ref}\right)\right]C(t)^n = C_1 \quad (18)$$

$$The\ solution\ for\ t_2\ of\ \frac{\mathrm{d}C(t)}{\mathrm{d}t} = -k\left(T_{ref}\right)Exp\left[c\left(T_2(t)-T_{ref}\right)\right]C(t)^n = C_2 \quad (19)$$

These two simultaneous equations can be solved numerically with Mathematica® to extract the values of the two unknown $k(T_{\mathrm{ref}})$ and c. Once obtained, these parameters values can be used to reconstruct the entire degradation curves of the two temperature profiles $T_1(t)$ and $T_2(t)$ and predict concentration ratios at different times along them or at different temperature profiles to test the method. The concept and calculation procedure have been validated with computer simulations and published data on anthocyanins degradation (Peleg et al, 2015) but are yet to be tested with AA data. A freely downloadable interactive Mathematica® program that demonstrates the concept and calculation procedure method can be found at

http://people.umass.edu/aew2000/nutrient_degradation/InterpolatedDegradation.html.

The program solves the two simultaneous equations by moving the $k(T_{ref})$ and c sliders on the screen until the two reconstructed degradation curves at $T_1(t)$ and $T_2(t)$ pass through their corresponding endpoints $\{t_1,C_1\}$ and $\{t_2,C_2\}$. The program has one version particularly suitable for heat processing temperature and another for storage temperatures. Also, both versions offer the options to enter the two temperature profiles $T_1(t)$ and $T_2(t)$ in the form of algebraic expressions or digitized time-temperature files, which it automatically converts into smooth Interpolation Functions for use in the parameters calculation.

The successive points method

In principle, the parameters of a degradation reaction following a known kinetic order can be extracted from successive concentration ratios determined during a *single non-isothermal temperature history*. The method is based on a special case of Eqs. 18 and 19 where $T_1(t) = T_2(t) = T(t)$. Hence, for first or other fixed order kinetics degradation where the rate constant's temperature-dependence follows the exponential model, $k(T_{ref})$ and c are the numerical solutions of the two simultaneous equations (Peleg and Normand, 2015):

$$The\ solution\ for\ t_1\ of\ \frac{\mathrm{d}C(t)}{\mathrm{d}t} = -k\left(T_{ref}\right)Exp\left[c\left(T\left(t\right)-T_{ref}\right)\right]C\left(t\right)^n = C_1 \qquad (20)$$

$$The\ solution\ for\ t_2\ of\ \frac{\mathrm{d}C(t)}{\mathrm{d}t} = -k\left(T_{ref}\right)Exp\left[c\left(T\left(t\right)-T_{ref}\right)\right]C\left(t\right)^n = C_2 \qquad (21)$$

A freely downloadable interactive program that demonstrates the successive method can found at

http://demonstrations.wolfram.com/DegradationParametersFromConcentrationRatios/.

A freely downloadable Mathematica® version of the program that allows the user to use any entered temperature profile equation or actual digitized time-temperature data can be found at

http://people.umass.edu/aew2000/nutrient_degradation/NutrientDegradation.html.

In both versions, the program finds a numerical solution to the two equations by moving the $k(T_{ref})$ and c sliders until the (single) reconstructed degradation curve passes through the two entered (experimental) points $\{t_1,C_1\}$ and $\{t_2,C_2\}$. The second and more elaborate version of the program also offers the option to make predictions, which can be tested against entered experimental data (Programs A to C). The successive points method has been tested with computers simulations and published data on vitamin A. It might well apply to AA degradation, but only in scenarios where it follows first or other fixed order kinetics.

Non-linear kinetics

When the AA's isothermal degradation approaches an asymptotic residual retention level (Eq. 5) or follows the Weibullian model, its kinetics is defined by *three* kinetic parameters instead of two. In principle, the endpoints and successive points methods can be used to extract these models' parameters by numerically solving three instead of two simultaneous equations. Indeed, this can and has been done with simulated data that had no or very small scatter. Increasing the scatter to levels encountered in experimental concentration measurements almost invariably results in failure of the iterations to converge or unrealistic and frequently absurd parameter values (e.g., negative or complex numbers). The problem can be circumvented by solving only two equations iteratively with one of the sought parameters rising by small increments, or falling by small decrements. At each step, the calculated intermediate parameters are used to predict the

third endpoint concentration and the iterations stop when the discrepancy between the predicted and actual concentration ratios becomes smaller than the user's specified tolerance (Peleg et al, 2008). Such a program already exists for the Weibullian model (Eq. 7) for cases where the power *m* is unknown, assuming that it is practically temperature-independent. Since that model was written (and tested) for microbial inactivation, the temperature-dependence term is not the exponential model. If needed, the program could be easily modified to accommodate the exponential model. Obviously, where the exponent *m* is known or can be assumed, the need for the iterative procedure is eliminated. Thus assuming that $b(T)$ in Eq. 7 follows the exponential model, one can determine the kinetic parameters *c* and $k(T_{ref})$ by the non-isothermal version of the two endpoints method, that is by solving a pair of simultaneous equations numerically. A freely downloadable Mathematica® program that does it for Weibullian degradation can be found at http://people.umass.edu/aew2000/Weibullian_degradation/WeibullianDegradation.html.

The main issue, however, would still be how to know in advance whether there is an asymptotic residual concentration in which case this program will not work -- see below.

CONCLUDING REMARKS

The literature on ascorbic acid degradation during thermal processing and storage suggests the existence of at least three possible main patterns: conventional first order kinetics, initial exponential decay changing to an asymptotic approach to a residual retention level, and nonlinear kinetics, e.g., Weibullian, decay all the way. The three patterns might be practically indistinguishable initially, and in particularly slow degradation could even be indistinguishable from zero order kinetics. But if the corresponding models are used for extrapolation in order to

predict the AA retention in foods stored for long times, i.e., well beyond the experiment time scale, they could lead to very different results. In light of the inherent scatter in AA's concentration determinations in foods, it is unlikely that statistical considerations alone would be helpful to identify the degradation pattern unambiguously from short-term experimental data. It would therefore be a challenge to researchers to find *a chemical marker or markers*, if they exist, which would indicate whether the degradation tends to be complete (e.g., first order or Weibullian kinetics), or if it will end up with residual retention or a transition to a slower rate regime (e.g., the asymptotic residual or biphasic model). Although not discussed in this review, the roles of oxygen tension and perhaps catalysts presence might provide the key in certain foods.

Where applicable, the endpoints method's advantage over the traditional ways to estimate kinetic parameters from storage data is primarily logistic. It could eliminate the need to monitor the AA's concentration periodically resulting in significant saving. In addition, the two freely downloadable interactive Wolfram Demonstrations, for foods at ambient temperatures and cold or frozen storage, enable the extraction of the kinetic parameter in a matter of minutes, eliminating the need to plot the experimental data and/or subject them to linear or nonlinear regression. In thermal processing, the endpoints method could eliminate the problem of how to account for the come-up and cooling times' roles when withdrawing samples for the analysis.

In the endpoints method versions for which there is free software on the Internet, the main underlying assumption is that the AA's degradation follows kinetic patterns that have been described in the literature. This assumption is testable. If wrong, then either the method would

not work at all, i.e., no match between the endpoints and reconstructed curves could be achieved, or its predictions would be consistently off mark. In the first order kinetic case, one could assume a different kinetic order and move the *n*-slider to a contemplated new *n* value. The two Wolfram Demonstrations allow the user to move the *n*-slider to the right or left, retrieve the new $k(T_{ref})$ and *c* values, recalculate the predicted concentration ratio, and compare it with the actually observed in a few minutes. Actually doing this revealed that with $n = 1.00 \pm 0.05$, the retrieved parameters and predicted retention values are only very slightly affected. In other words the method seems to be robust against, or insensitive to slight deviations from the assumed first kinetic order, if indeed they are real.

The endpoints method, as already mentioned, was originally developed for UHT sterilization where the processing time is too short for retrieving samples for analysis. Such a process only allows to examine the product after its completion, which includes the cooling stage, and hence the method's name. In storage, if there is a suspicion that the AA's degradation might not follow the assumed kinetics, one can test samples *early during the storage* to confirm or refute the hypothesis. Obviously, this will add to the number of concentration measurements, but their total number will still be smaller than in systematic concentration determinations at fixed intervals. If the suspicion is confirmed, then one could test a different *n*, for example, or any of the available alternative models. In the worst case, one could always resort to the traditional method of recording the entire degradation curves and search for a totally new degradation kinetic model. In case where two or more of the presented models render similar predictions of the AA's retention, it would be prudent to use the one that predicts the lowest retention in order to be on the safe side from a nutritional viewpoint.

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Table 1. Kinetic degradation parameters of vitamin C in two frozen vegetables[1.]

Food	T_1 (°C)	t_1 (days)	T_2 (°C)	t_2 (days)	Pair	k_{Tref} (t^{-1})	c (T^{-1})
Frozen Peas	-16	111	-12	94	AB	0.022	0.140
	-16	111	-8	104	AC	0.027	0.160
	-16	111	-3	80	AD	0.019	0.127
	-16	111	-1	42	AE	0.028	0.160
	-12	94	-12	94	BC	0.028	0.172
	-12	94	-3	80	BD	0.020	0.120
	-12	94	-1	42	BE	0.027	0.168
	-8	104	-3	80	CD	0.021	0.070 *
	-8	104	-1	42	CE	0.027	0.160
	-3	80	-1	42	DE	0.012	0.380 *
	T_{ref} = -5°C				Mean ± SD	0.023 ± 0.005	0.166 ± 0.081
					Revised Mean ± SD	0.025 ± 0.004	0.151 ± 0.019
Frozen Spinach	-20	149	-12	78	AB	0.100	0.205
	-20	149	-8	41	AC	0.082 *	0.192
	-20	149	-3	13	AD	0.100	0.205
	-12	78	-8	41	BC	0.080 *	0.170
	-12	78	-3	13	BD	0.100	0.198
	-8	41	-3	13	CD	0.098	0.240 *

	T_{ref} = -5°C	Mean ± SD	0.093 ± 0.010	0.202 ± 0.023
		Revised Mean ± SD	0.100 ± 0.000	0.203 ± 0.004

[1] The original data are from Giannakourou & Taoukis (2003).

[*] Suspected outliers identified by the Iglewicz and Hoag test.

Table 2. Comparison of concentration ratios of vitamin C in two frozen vegetables predicted with the isothermal version of the endpoints method and those reported[1.]

							% Retention	
Food	**Predicting**	**T_{ref} (°C)**	**k_{Tref}/Mean k_{Tref}**	**c/Mean c**	**T (°C)**	**t (days)**	**Predicted**	**Reported**
Frozen Peas	A	-5	0.025	0.155	-16	111	60	60
	B		0.025	0.152	-12	94	44	46
	C		0.023	0.143	-8	104	21	18
	D		0.026	0.160	-3	80	5	14
	E		0.023	0.144	-1	42	18	11
Frozen Spinach	A	-5	0.099	0.219	-20	149	57	50
	B		0.100	0.205	-12	78	16	15
	C		0.100	0.203	-8	41	11	14
	D		0.100	0.205	-3	13	14	13

[1] The original data are from Giannakourou & Taoukis (2003).

Table 3. Kinetic degradation parameters of vitamin C in stored fruit juices.

Food	T_1 (°C)	t_1 (days)	T_2 (°C)	t_2 (days)	Pair	k_{Tref} (t^{-1})	c (T^{-1})
Strawberry Juice[1]	5	14	10	10	AB	0.060	0.093
	5	14	25	7	AC	0.065	0.110
	10	10	25	7	BC	0.060	0.115
	T_{ref} = 10°C				Mean ± SD	0.062 ± 0.003	0.106 ± 0.012
Pressurized Orange Juice[2]	65	385[a]	70	354[a]	AB	0.004	0.080
	65	385[a]	80	290[a]	AC	0.004	0.084
	70	354[a]	80	290[a]	BC	0.004	0.084
	T_{ref} = 70°C				Mean ± SD	0.004 ± 0.000	0.083 ± 0.002
HPP Orange Juice[3]	0	40	5	40	AB	0.015	0.060
	0	40	10	40	AC	0.016	0.075
	0	40	15	40	AD	0.018	0.104
	5	40	10	40	BC	0.015	0.088
	5	40	15	40	BD	0.018	0.106
	10	40	15	40	CD	0.010	0.165
	T_{ref} = 5°C				Mean ± SD	0.015 ± 0.003	0.100 ± 0.036
Pasteurized Orange	0	40	5	40	AB	0.021	0.040
	0	40	10	40	AC	0.021	0.034

Juice[3]	0	40	15	40	AD	0.025 *	0.073
	5	40	10	40	BC	0.021	0.036
	5	40	15	40	BD	0.021	0.093
	10	40	15	40	CD	0.011 *	0.150
	T_{ref} = 5°C				Mean & SD (±)	0.020 ± 0.004	0.071 ± 0.045
					Revised Mean ± SD	0.0210 ± .0.000	0.051 ± 0.028
HPP Orange Juice[4]	0	109	5	91	AB	0.006	0.047
	0	109	10	64	AC	0.006	0.067
	0	109	15	46	AD	0.001 *	0.118
	0	109	30	15	AE	0.007	0.090
	5	91	10	64	BC	0.006	0.086
	5	91	15	46	BD	0.006	0.150
	5	91	30	15	BE	0.006	0.098
	10	64	15	46	CD	0.003 *	0.220
	10	64	30	15	CE	0.005	0.100
	15	46	30	15	DE	0.014 *	0.062
	T_{ref} = 5°C				Mean ± SD	0.006 ± 0.003	0.104 ± 0.050
					Revised Mean ± SD	0.006 ± 0.001	0.091 ± 0.032
Pasteurized	0	90	5	90	AB	0.013	0.088

Orange Juice[4]	0	90	10	59	AC	0.013	0.086
	0	90	15	41	AD	0.013	0.081
	0	90	30	9	AE	0.013	0.085
	5	90	10	59	BC	0.013	0.085
	5	90	15	41	BD	0.013	0.079
	5	90	30	9	BE	0.013	0.085
	10	59	15	41	CD	0.015 *	0.066 *
	10	59	30	9	CE	0.013	0.085
	15	41	30	9	DE	0.012 *	0.088
	T_{ref} = 5°C				Mean ± SD	0.013 ± 0.001	0.083 ± 0.007
					Revised Mean ± SD	0.013 ± 0.000	0.084 ± 0.003

[1] The original data are from Derossi et al. (2010)

[2] The original data are from Van den Broeck et al. (1998).

[3] The original data are from Polydera et al. (2003)

[4] The original data are from Polydera et al. (2005)

[a] time is in minutes

[*] Suspected outliers identified by the Iglewicz and Hoag test.

Table 4. Comparison of concentration ratios of vitamin C in stored fruit juices predicted with the isothermal version of the endpoints method and those reported.

							% Retention	
Food	**Predicting**	**T_{ref} (°C)**	**k_{Tref}/Mean k_{Tref}**	**c/Mean c**	**T (°C)**	**t (days)**	**Predicted**	**Reported**
Strawberry Juice[1]	A	10	0.060	0.115	5	14	62	59
	B		0.065	0.110	10	10	52	55
	C		0.060	0.093	25	7	18	9
Pressurized Oranges[2]	A	70	0.004	0.084	65	385[a]	34	33
	B		0.004	0.084	70	354[a]	22	22
	C		0.004	0.080	80	290[a]	7	6
HPP Orange Juice[3]	A	5	0.014	0.120	0	40	73	65
	B		0.015	0.115	5	40	55	56
	C		0.017	0.090	10	40	34	40
	D		0.015	0.074	15	40	28	12
Pasteurized Orange Juice[3]	A	5	0.021	0.065	0	40	54	50
	B		0.021	0.034	5	40	44	43
	C		0.021	0.067	10	40	31	37
	D		0.021	0.037	15	40	30	12
HPP Orange Juice[4]	A	5	0.006	0.109	0	109	70	62
	B		0.006	0.086	5	91	57	60
	C		0.006	0.096	10	64	54	57

	D		0.006	0.081	15	46	54	30
	E		0.006	0.088	30	15	45	37
Pasteurized Orange Juice[4]	A	5	0.013	0.081	0	90	46	46
	B		0.013	0.082	5	90	31	31
	C		0.013	0.084	10	59	31	31
	D		0.013	0.086	15	41	29	30
	E		0.013	0.081	30	9	37	37

[1] The original data are from Derossi et al. (2010)

[2] The original data are from Van den Broeck et al. (1998).

[3] The original data are from Polydera et al. (2003)

[4] The original data are from Polydera et al. (2005)

[a] time is in minutes

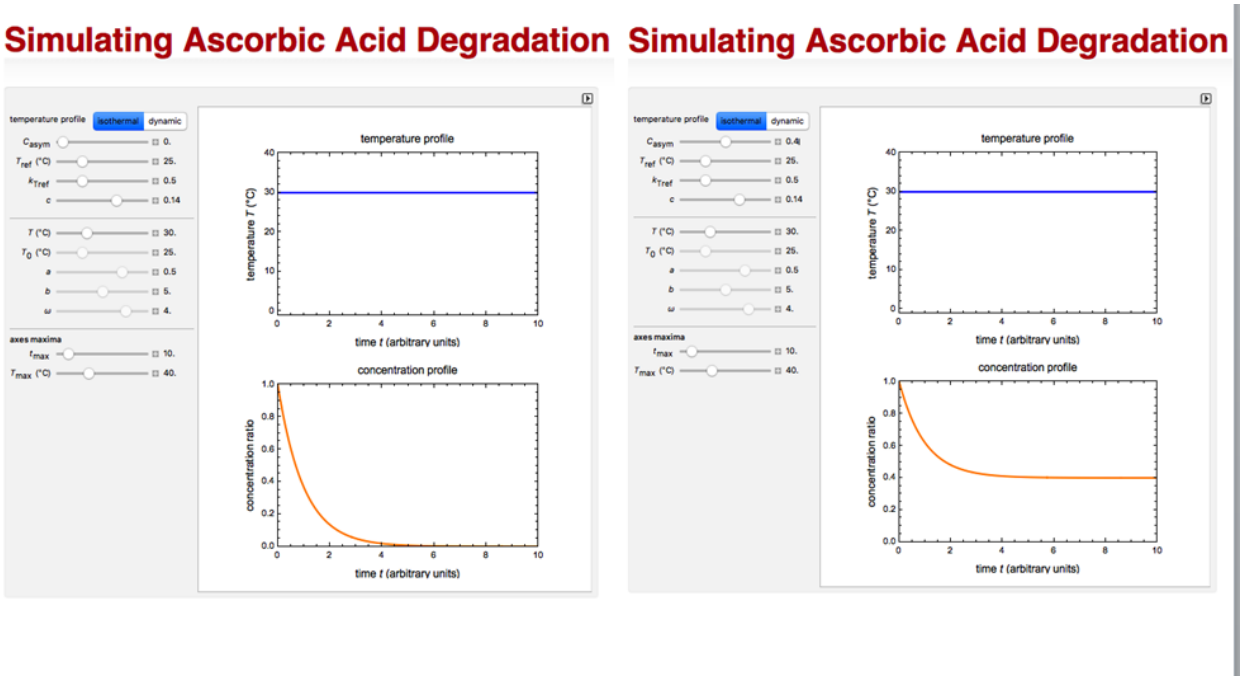

Fig. 1. Screen displays of the Wolfram Demonstration that simulates isothermal ascorbic acid degradation. Left -- Conventional first order kinetics, right -- Exponential decay approaching asymptotic residual retention.

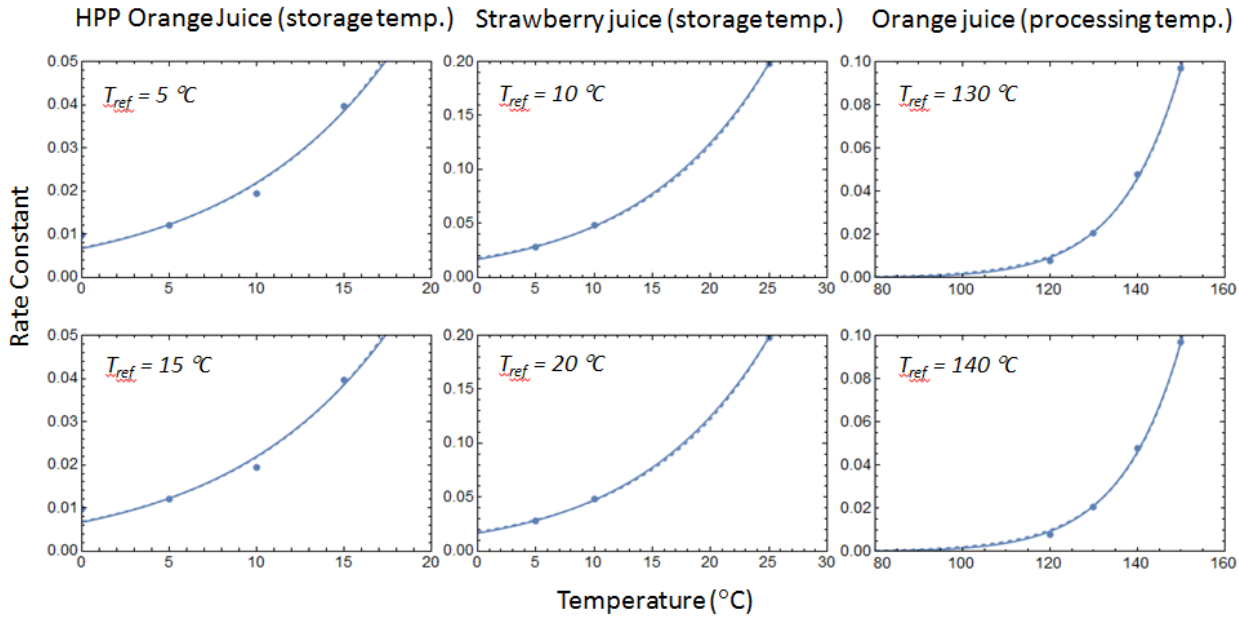

Fig. 2. The interchangeability of the Arrhenius equation (Eq. 6 -- solid curve) and exponential model (Eq. 7- dashed curve) for describing ascorbic acid degradation. The experimental data, left to right, are from Polydera et al. (2003), Derossi et al. (2010), and Polydera et al. (2005), respectively.

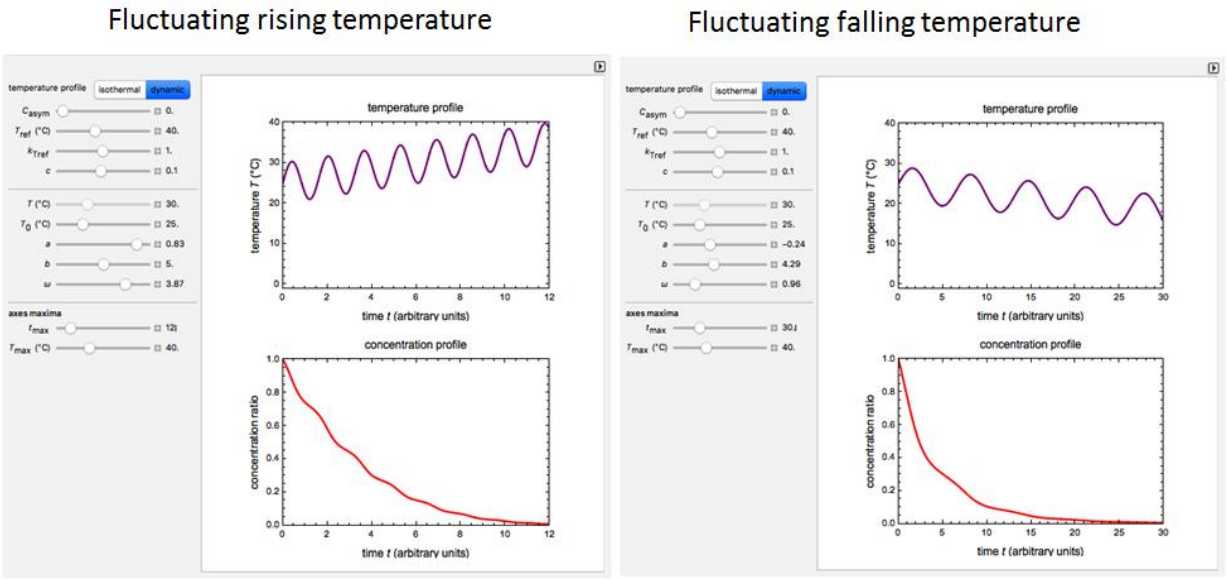

Fig. 3. Simulated non-isothermal (dynamic) degradation curves that follow fixed order kinetics using Eq. 9 as a model.

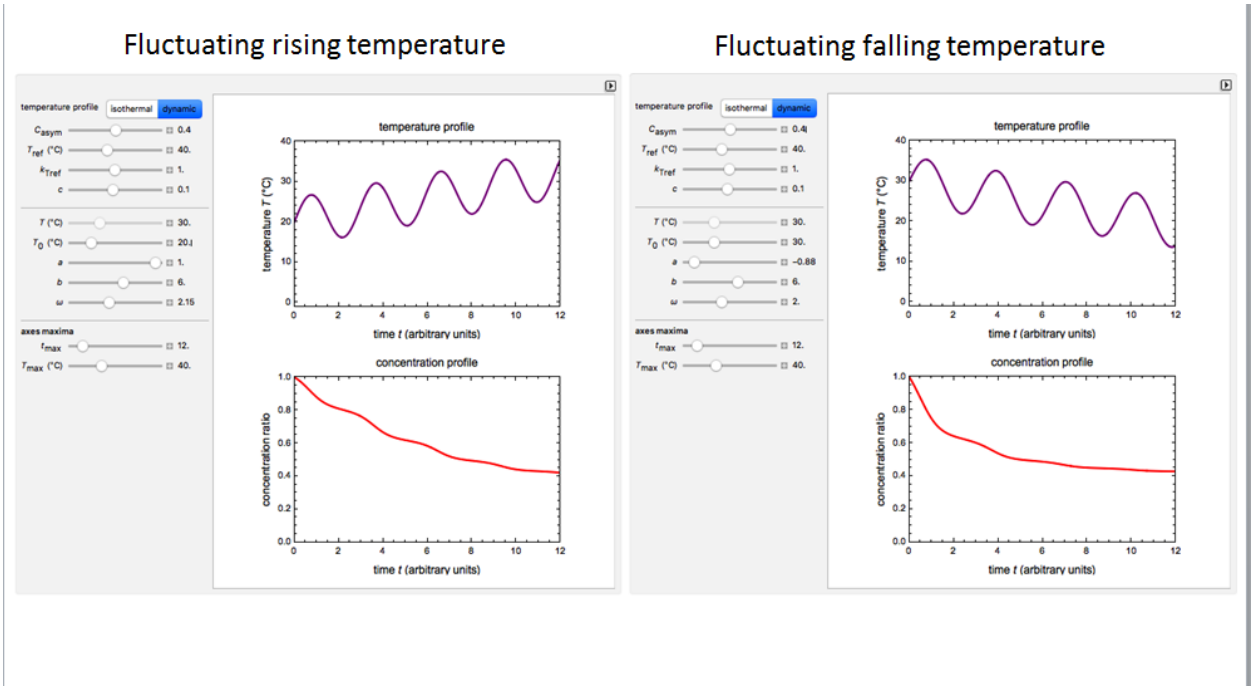

Fig. 4. Simulated non-isothermal (dynamic) degradation curves that approach asymptotic residual retention using Eq. 10 as a model.

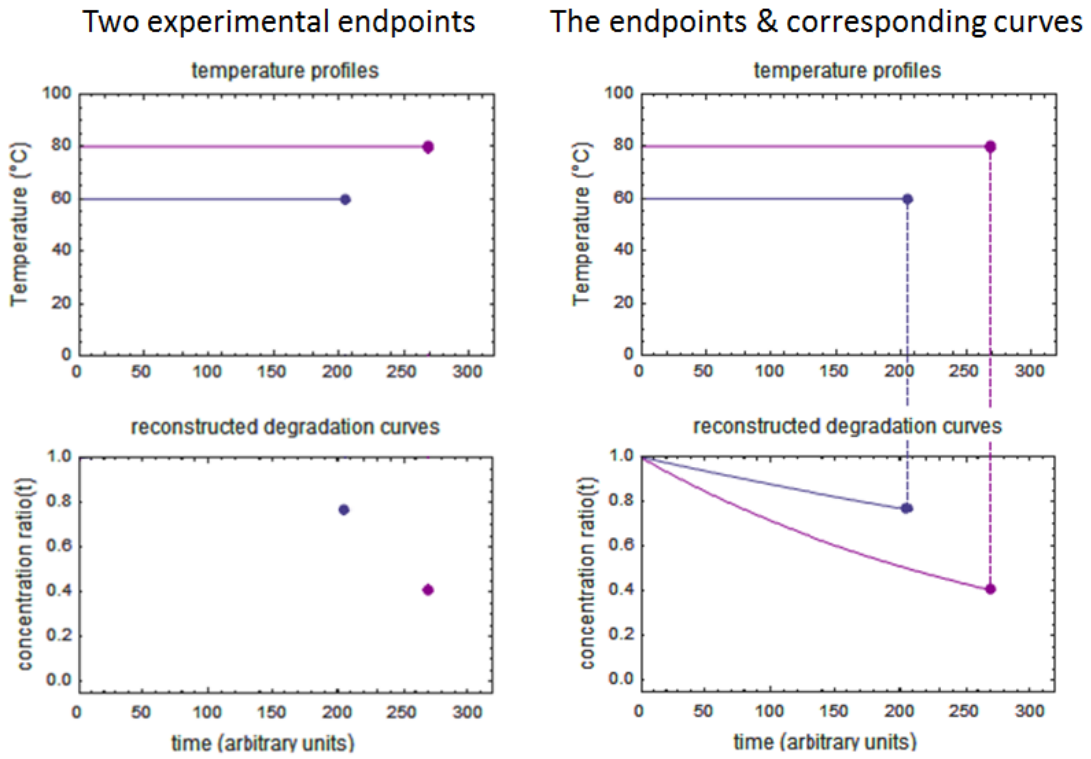

Fig. 5. The principle of the endpoints method: Left -- Two experimentally determined AA concentration ratios C_1 and C_2 at two temperatures, T_1 and T_2 at times t_1 and t_2, respectively, Right -- these two endpoints ought to lie on the two corresponding degradation curves, which follow the kinetic model's equation.

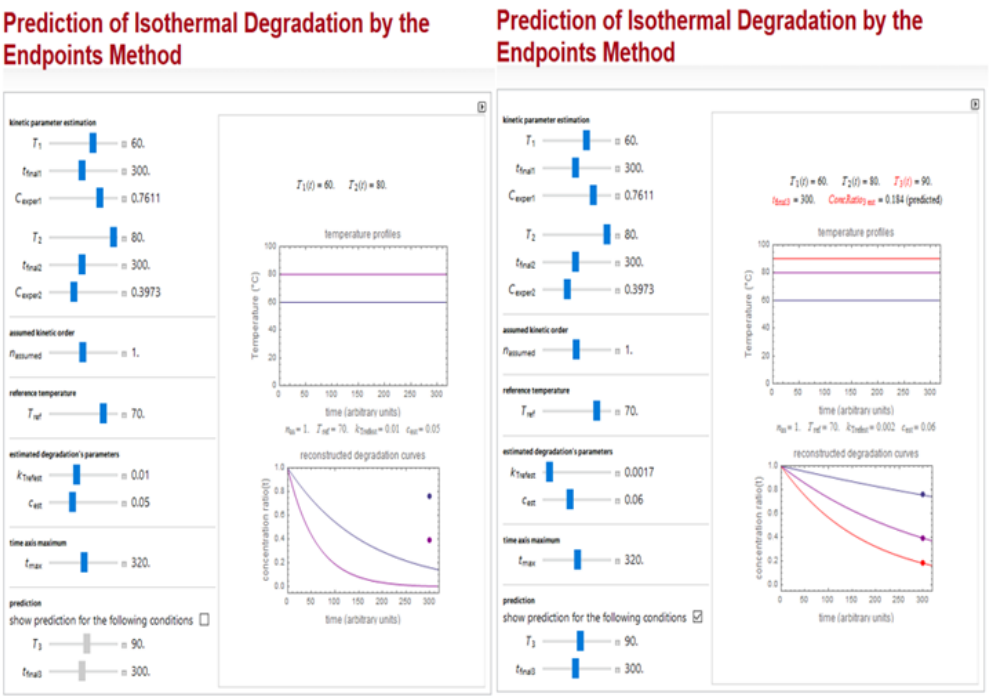

Fig. 6. Screen displays of the Wolfram Demonstration that extracts the degradation kinetic parameters by the isothermal version of the endpoints method in the default and prediction modes: Left --The two endpoints before being matched by the reconstructed degradation curves. Right -- The matched reconstructed curves obtained by moving the k_{Tref} and c_{esi} sliders and a predicted degradation curve at a third temperature T_3 not used in the parameters calculation (marked in red). Notice the positions of T_3 and t_{final3} sliders.

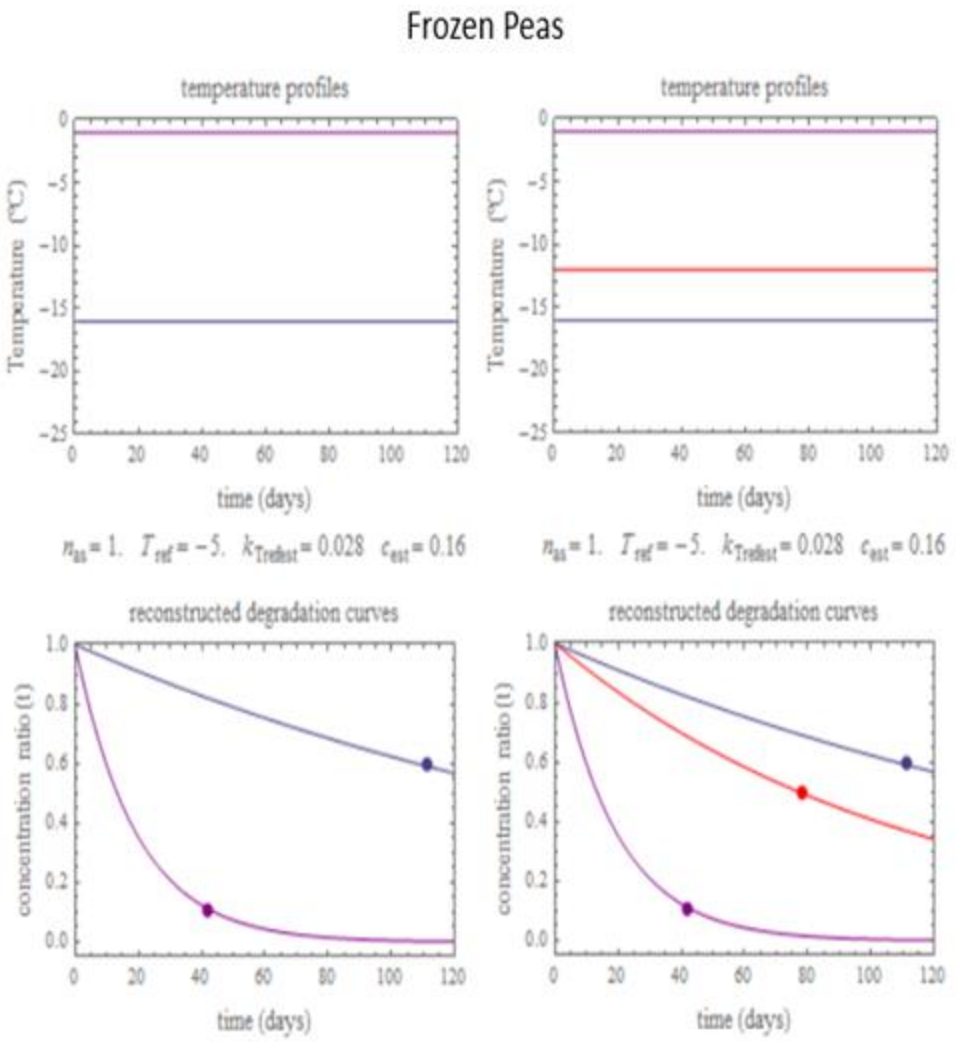

Fig. 7. The endpoints method applied to ascorbic acid loss in frozen peas. The reconstructed curves are in blue and purple, and the predicted is in red. The numerical values of the retrieved parameters and predicted retentions are listed in Tables 1 and 2. The experimental data are from Giannakourou and Taoukis (2003).

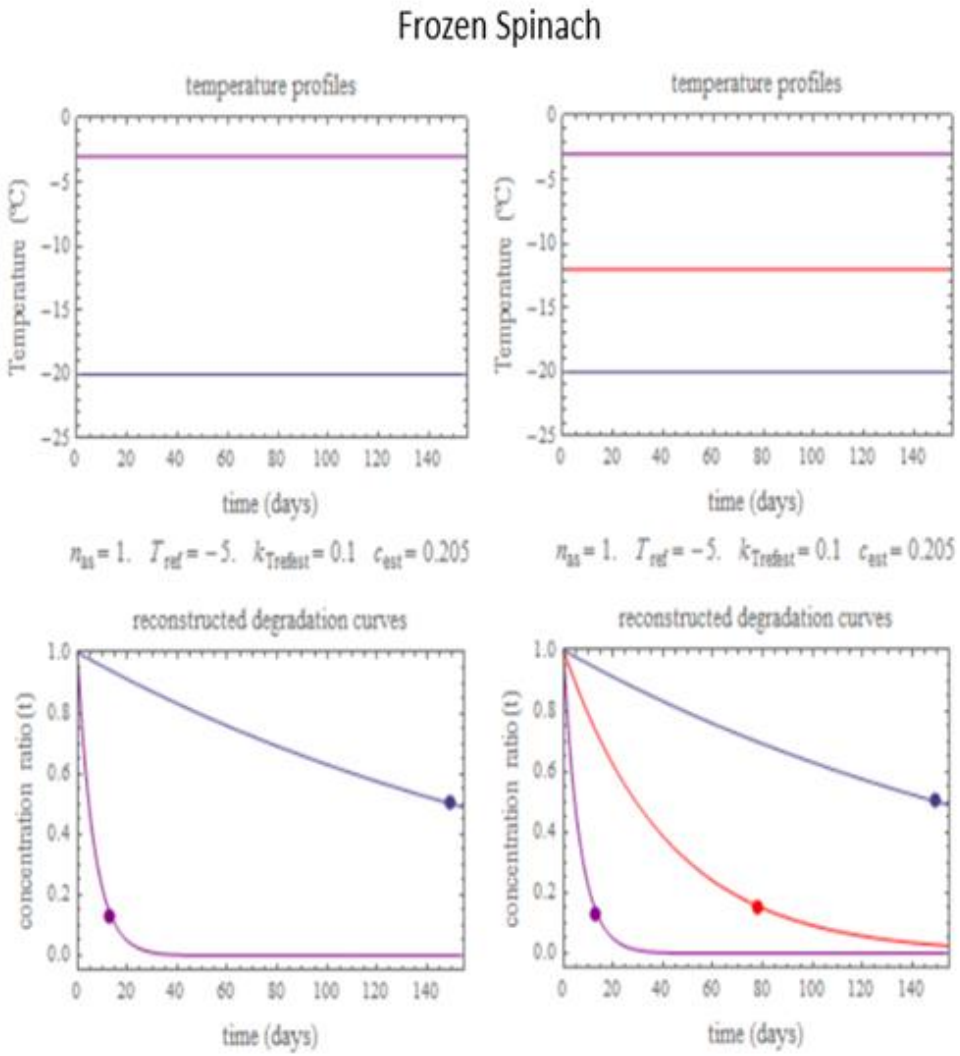

Fig. 8. The endpoints method applied method to ascorbic acid loss in frozen spinach. The reconstructed curves are in blue and purple, and the predicted is in red. The numerical values of the retrieved parameters and predicted retentions are listed in Tables 1 and 2. The experimental data are from Giannakourou and Taoukis (2003).

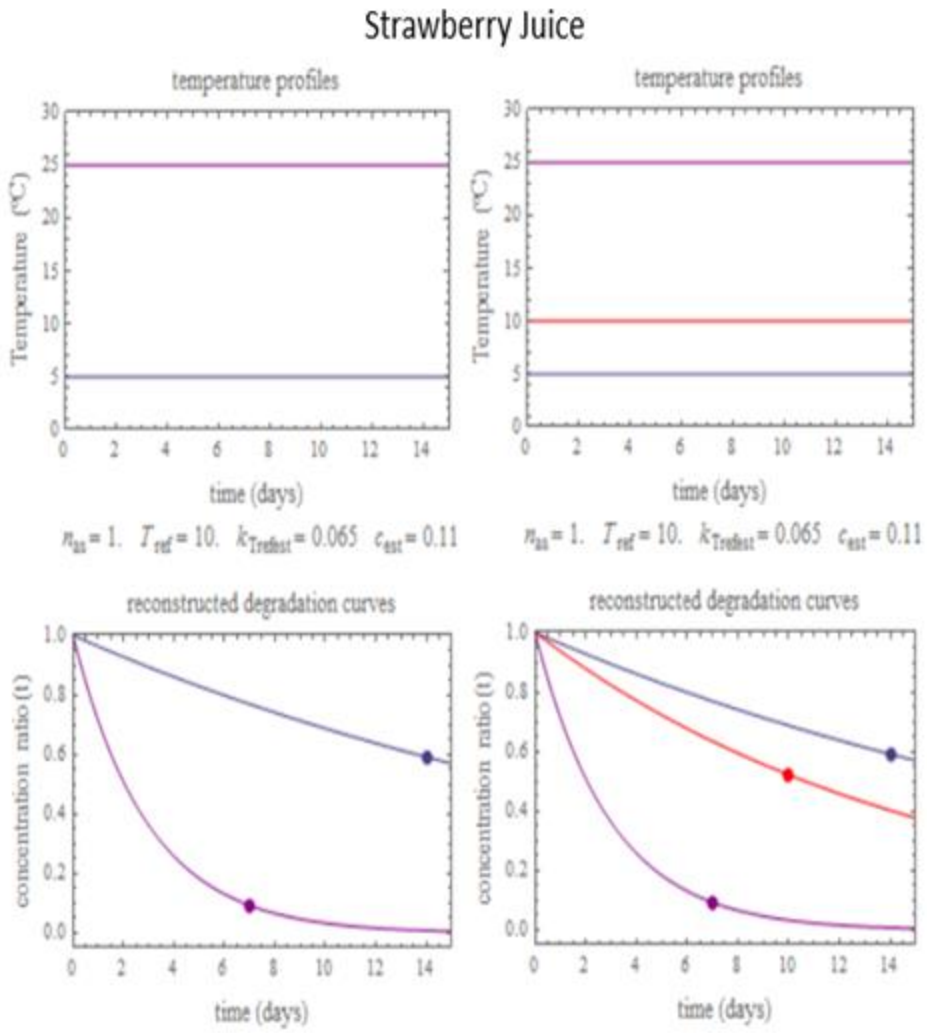

Fig. 9. The endpoints method applied method to ascorbic acid loss in strawberry juice. The reconstructed curves are in blue and purple, and the predicted is in red. The numerical values of the retrieved parameters and predicted retentions are listed in Tables 3 and 4. The experimental data are from Derossi et al. (2010).

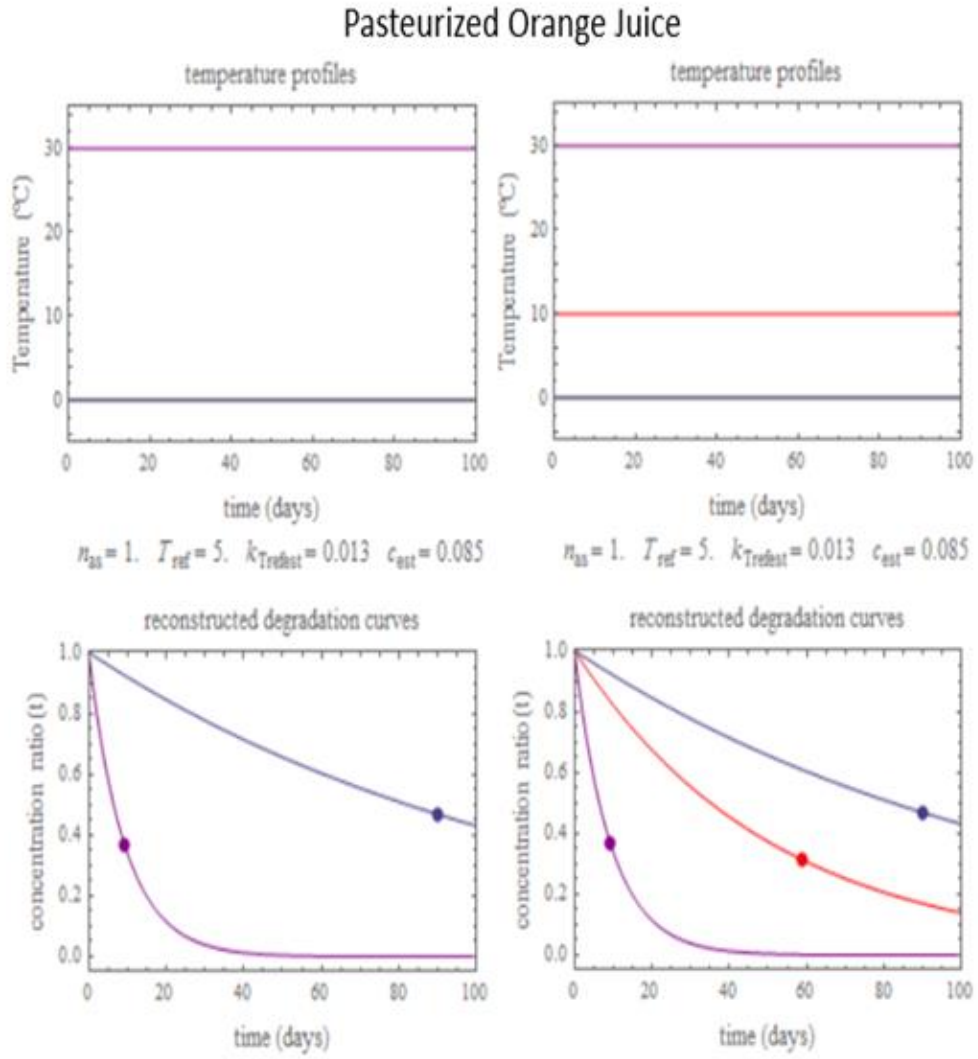

Fig. 10. The endpoints method applied method to ascorbic acid loss in pasteurized orange juice. The reconstructed curves are in blue and purple, and the predicted is in red. The numerical values of the retrieved parameters and predicted retentions are listed in Tables 3 and 4. The experimental data are from Polydera et al. (2003).

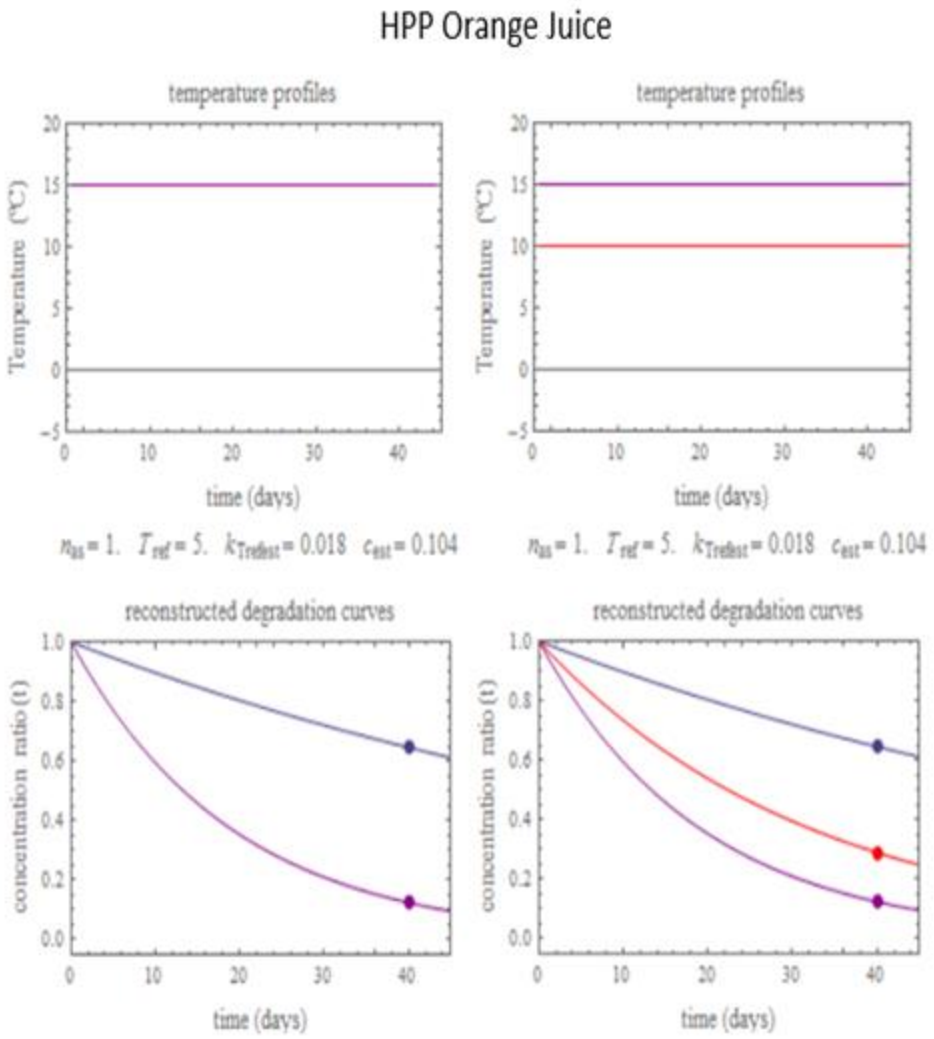

Fig. 11. The endpoints method applied method to ascorbic acid loss in ultra high-pressure treated orange juice. The reconstructed curves are in blue and purple, and the predicted is in red. The numerical values of the retrieved parameters and predicted retentions are listed in Tables 3 and 4. The experimental data are from Polydera et al. (2003).