Food Research International 78 (2015) 388–395

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Simulating shelf life determination by two simultaneous criteria

Micha Peleg *, Mark D. Normand

Department of Food Science, University of Massachusetts, Amherst, MA 01003, United States

ARTICLE INFO

Article history:
Received 20 July 2015
Received in revised form 26 August 2015
Accepted 5 September 2015
Available online 11 September 2015

Keywords:
Shelf life criteria
Accelerated storage
Vitamins degradation
Chemical markers
Dietary supplements
Non-enzymatic browning

ABSTRACT

The shelf life of food and pharmaceutical products is frequently determined by a marker's concentration or quality index falling below or surpassing an assigned threshold level. Naturally, different chosen markers would indicate different shelf life for the same storage temperature history. We demonstrate that if there are two markers, such as two labile vitamins, the *order* in which their concentrations cross their respective thresholds may depend not only on their degradation kinetic parameters but also on the particular storage temperature profile, be it isothermal or non-isothermal. Thus, at least theoretically, the order observed in accelerated storage need not be always indicative of the actual order at colder temperatures, except where the two degradation reactions follow the same kinetic order and their temperature-dependence rate parameter is also the same. This is shown with simulated hypothetical degradation reactions that follow first or zero order kinetics and whose rate constant's temperature-dependence obeys the exponential model. It is also demonstrated with simulated hypothetical Maillard reaction's products whose synthesis rather than their degradation follows pseudo zero order kinetics. The software developed to do the simulations and calculate the thresholds crossing points has been posted on the Internet as a freely downloadable interactive Wolfram Demonstration, which can be used as a tool in storage studies and shelf life prediction. In principle, the methodology can be extended from two to any number of markers.

1. Introduction

Assuring adequate levels of nutrients in processed foods and maintaining their quality during long manned space flights is of major concern to space travel programs. Therefore, there has been a renewed interest in the kinetics of nutrient degradation and quality loss and how they can be effectively monitored, predicted and, where possibly, reduced. Understanding and quantifying the deterioration kinetics is also a key to the development and testing of new technologies and packages that minimize the damage and prolong the shelf life of processed foods, regardless of whether they are intended for consumption in space or on earth. The same can be said about dietary supplements. Shelf life of foods and of pharmaceutical products has been an active research area for many years. There is a large body of accumulated theoretical and practical knowledge on how to determine and predict a product's shelf life based on accelerated storage and organoleptic, physical, chemical and other criteria (e.g., Labuza & Schmidtl, 1985; Institute of Food Science and Technology (UK), 1993; Yoshikoa, Aso, Isutsu, & Terao, 1994; Taoukis, Labuza, & Saguy, 1997; Duyvesteyn, Shimoni, & Labusa, 2001; Reid, Kotte, Kilmartin, & Young, 2003; Mizrahi, 2004; Waterman & Adami, 2005; Corradini & Peleg, 2007; Leake, 2007), including consumers' complaints rate (Fu & Labuza, 1993; Saguy & Peleg, 2009). There are also many publications that focus on the statistical aspects of shelf life. Since deterioration can be viewed as a failure phenomenon, one should expect that individual units of any given food, even when stored under the same conditions, would reach the end of their shelf life at different times. Therefore, the emphasis of such studies is on the *distribution* of the times to reach the unacceptable quality level, see Fu and Labuza (1993) and Cardelli and Labuza (2001), for example.

In this work, we only address certain theoretical aspects of using nutrients' degradation *kinetics* in shelf life estimation. In other words, we'll be looking at the characteristic or mean times to deterioration as defined by threshold-based criteria, with full acknowledgment that individual units of the product would deviate from these times. The deviations' amplitude and pattern, e.g., symmetric or asymmetric distribution, would depend on factors that ought to be studied separately and hence will not be included in the discussion. Also left out is the deterioration of fresh commodities caused by microbial growth and/or metabolic enzymatic processes. Unlike in chemical degradation of nutrients and pigments, such processes' kinetics is primarily ruled by the effect of temperature on organisms and/or enzymes and not on the substrate itself.

Critical labile vitamins, for example, can be considered indicators of whether a particular stored food product still retains its nutritive value. But they can also be used as a marker to be followed during a product's actual, parallel and/or accelerated storage. Also, since different vitamins follow different degradation kinetics, see below, it is important to learn how different temperature histories could affect their relative retention

* Corresponding author.
E-mail address: micha.peleg@foodsci.umass.edu (M. Peleg).

http://dx.doi.org/10.1016/j.foodres.2015.09.003
0963-9969/

and which of them will cross its assigned threshold first. This could have implications in the design of foods fortified with several vitamins and other nutrients. When it comes to chemical stability, however, a product's shelf life can be determined by the loss of *any* desirable ingredient, including a pigment or compounds that impart the appealing flavor. But shelf life can also be determined by the synthesis of an undesirable compound or compounds. Examples are the Maillard reaction's products in non-enzymatic browning, or the formation of volatiles that impart off-flavor, as in rancidity. We'll refer to either kind of compound as a 'marker'. When this chosen marker's concentration falls below or surpasses its assigned threshold, the product is considered as reaching the end of its shelf life. Because different markers have different degradation or synthesis kinetics, the threshold that is crossed first must depend not only on their assigned threshold levels but also on the product's temperature history. The objectives of this work were to describe this temperature history-dependence mathematically, to develop interactive software for its simulation and visualization, and to evaluate its potential implications in the interpretation of storage and accelerated storage studies.

2. Theoretical background

Consider a hypothetical case where two vitamins (or other labile nutrients) serve as a given food's shelf life markers. We assume that these vitamins' degradation kinetics follows known or previously reported fixed order kinetics, n_1 *and* n_2, defined by the rate equations:

$$\frac{dC_1(t)}{dt} = -k_1[T(t)]C_1(t)^{n_1} \quad (1)$$

$$\frac{dC_2(t)}{dt} = -k_2[T(t)]C_2(t)^{n_2} \quad (2)$$

where $C_1(t)$ and $C_2(t)$ are their momentary concentrations in chosen units, $T(t)$ the food's temperature history and $k_1[T_1(t)]$ and $k_2[T_2(t)]$ their momentary rate constants in the particular medium. The boundary condition is that $C_1(0) = C_{01}$ and $C_2(0) = C_{02}$, the two vitamins' initial concentrations, respectively.

We also assume that the temperature-dependences of the corresponding rate constants, $k_1(T)$ and $k_2(T)$, follow the exponential model, which translates to:

$$k_1[T(t)] = k_1(T_{ref1})\,\mathrm{Exp}\left[c_1(T(t) - T_{ref1})\right] \quad (3)$$

$$k_2[T(t)] = k_2(T_{ref2})Exp\left[c_2(T(t) - T_{ref2})\right] \quad (4)$$

where $k_1(T_{ref1})$ and $k_2(T_{ref2})$ are the rate constants at the reference temperatures T_{ref1} and T_{ref2} in degrees C defined by Eqs. (1) and (2), and c_1 and c_2 characteristic constants, expressed in C^{-1}, determined by the particular food's composition, pH, etc. It can and has been shown that this simpler exponential model can be used interchangeably with the traditional Arrhenius model at temperatures pertinent to food processing and storage (Peleg, Normand, & Corradini, 2012; Peleg, Normand, & Kim, 2014; Peleg, Kim, & Normand, 2015). One can estimate the magnitude of the exponential model's c parameter from a reported "energy of activation", E_A, using the formula (Peleg et al., 2012):

$$c \approx \frac{E_A}{R(T_{ref} + 273.16)^2} \quad (5)$$

where R is the universal gas constant expressed in units commensurate with those of E_A, and T_{ref} in degrees Celsius. Or conversely, when applicable, one can estimate the Arrhenius model's E_A from the exponential model's c with formula:

$$E_A \approx cR(T_{ref} + 273.16)^2 \quad (6)$$

Eq. (1) or (2) has well known analytical solutions for constant temperatures, i.e., $T(t) = T$, which can be used to calculate and plot the two vitamins' degradation curves. A problem may arise when either or both n's $= 0$, in which case, theoretically, the concentration can become negative after a certain time. Or, when either or both n's are between zero and one, the concentration can become a complex number from a certain time onward. Although a situation of either kind is rarely if ever encountered in an actual storage study, we have eliminated the two potential problems by setting the concentration to zero whenever they occurs, see Peleg et al. (2014). For visualizing the modified degradation curves, use the freely downloadable interactive Wolfram Demonstration:http://demonstrations.wolfram.com/KineticOrderOfDegradationReactions/.

When the n's, $k(T_{ref})$'s and c's are known, one can generate any isothermal degradation curves of the two nutrients using the appropriate analytical solutions of Eq. (1) and Eq. (2). For non-isothermal degradation, Eq. (1) and Eq. (2) have analytical solutions only for certain simple temperature profiles, such as a linearly rising or falling temperature. Nevertheless, being ordinary differential equations (ODE), these two equations can be easily and rapidly solved numerically with Mathematica® (Wolfram Research, Champaign, IL), the program used in this work, and other advanced mathematical software. Therefore, we used the numerical solution for all non-isothermal profiles without searching for an analytical solution. Mathemtica's numerical solution, rendered by its NDSolve function, is in the form of an Interpolation Function, which is calculated and plotted by the program as a regular algebraic function within its specified range.

According to the described models, the times t_{c1} and t_{c2}, where the degradation curves cross their corresponding threshold concentrations, can be calculated from the equations:

$$C_1(t_{c1}) = C_{c1} \quad (7)$$

and

$$C_2(t_{c2}) = C_{c2} \quad (8)$$

where $C_1(t)$ and $C_2(t)$ are the isothermal or non-isothermal degradation curves' equations defined by Eqs. (1) & (3) and Eqs. (2) & (4), and C_{c1} and C_{c2} are the threshold concentrations of the two vitamins.

Eqs. (7) and (8) can be solved numerically by Mathematica's FindRoot function to extract the values of t_{c1} and t_{c2} and to determine which vitamin crosses its threshold concentration ratio first. The crossover is also revealed visually as the intersection of the decay curves $C_1(t)$ and $C_2(t)$ vs. t with the horizontal lines C_{c1} and C_{c2} which mark the two nutrients' thresholds – see below.

3. Methodology

A program was written to simulate and plot isothermal and non-isothermal degradation curves of a pair of vitamins or other markers whose kinetics follows Eqs. (1)–(4). For simplicity, the concentrations and threshold concentrations are all expressed as concentration ratios by setting $C_{01} = C_{02} = 1$. The program has been posted on the Internet as a freely downloadable interactive Wolfram Demonstration, use:

http://demonstrations.wolfram.com/DeterminingShelfLifeByTwoCriteria/. The Wolfram Demonstration's screen display is shown in Fig. 1. To use it, the user chooses the storage mode, isothermal or non-isothermal, and then enters the two markers' degradation kinetics parameters, their threshold concentration ratios and the axes ranges, all with sliders on the screen – see figure. The program plots the chosen temperature profile (top), and then calculates and plots the two corresponding degradation curves (bottom). Superimposed on the two degradation curves are the two thresholds marked as horizontal dashed lines. The program also calculates and displays the numerical values at the times t_{c1} and t_{c2} where the two