Calculating the degradation kinetic parameters of thiamine by the isothermal version of the endpoints method

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ABSTRACT

Thiamine (vitamin B_1)'s degradation during thermal processing and storage of foods is known to follow first-order kinetics, where the rate constant's temperature-dependence can be described by the two-parameter Arrhenius equation. In agreement with previous reports, a simpler two-parameter exponential model could replace the Arrhenius equation in thiamine degradation without sacrificing the fit. Theoretically, the exponential model's two parameters can be estimated from the concentration ratios after two isothermal exposures by solving a pair of simultaneous nonlinear algebraic equations of which they are the two unknowns. Once calculated, these two parameters can be used to reconstruct the entire degradation curves to which the two endpoints belonged, and to predict those at any other exposure in a pertinent temperature range. The concept and mathematical calculation procedure were implemented in a freely downloadable interactive Wolfram Demonstration, with which the user solves the equations by moving sliders on the screen to match the reconstructed degradation curves with the experimental endpoints. The method was tested with computer simulations and with published experimental data on thiamine's degradation in a model solution, beef, pasta and salmon, over large temperature ranges and exposure times, and validated by comparing thiamine's predicted final concentration ratios with those reported at temperatures not used in the kinetic parameters calculation. The described method and interactive calculation program can facilitate and economize the study of thiamine degradation in stored foods by eliminating the need to record entire sets of isothermal degradation curves.

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1. Introduction

Maintaining adequate level of nutrients in space foods during long storage and interplanetary flights is of main concern to NASA, and most probably to other national and international space agencies. For this reason, interest in the degradation kinetics of vitamins especially thiamine (vitamin B_1) has been recently revived.

Traditionally, the degradation kinetics of thiamine and other vitamins during food processing and storage has been determined by periodically monitoring its decreasing concentration at several constant temperatures. Thus, industrial, governmental and academic research laboratories are equipped with incubators and/or refrigerators that provide constant storage temperatures. They are primarily used in shelf life assessment according to established protocols, which may involve parallel and/or accelerated storage. Different techniques are used to determine the vitamin's loss kinetics during thermal processing where the temperatures are much higher and the times much shorter. In both cases however, and regardless of the food, the experimental thiamine's isothermal concentration vs. time relationships, $C(t)$ vs. t, have been almost always a straight line when plotted on semi-logarithmic coordinates. Hence it has been

concluded that thiamine's degradation in storage and during heat processing follows first order kinetics (e.g., Kamman, Labuza, & Warthesen, 1981; Kong, Tang, Rasco, & Crapo, 2007; Kwok, Shiu, Yeung, & Niranjan, 1998; Arabshahi & Lund, 1988; Mauri, Alzamora, & Tomio, 1992; Mulley, Stumbo, & Hunting, 1975; Pachapurkar & Bell, 2005; Ramaswamy, Ghazala, & van de Voort, 1990; Nisha Rekha, Singhal & Pandit, 2004.)

Mathematically, fixed order degradation kinetics, where the stoichiometric coefficient $v = 1$, is described by the rate equation (van Boekel, 2008, 2009):

$$\frac{dC(t)}{dt} = -k[T(t)]C(t)^n \tag{1}$$

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

In first order kinetics, $n = 1$. The isothermal solution of Eq. (1), i.e., where $T(t) = T = $ constant, and the boundary condition $C(0) = C_0$, is the familiar exponential decay equation:

$$C(t) = C_0 Exp[-k(T)\,t] \tag{2}$$

where C_0 is the experimentally determined initial concentration.

Where $n \neq 1$, see below, the general isothermal solution of Eq. (1) is:

$$C(t) = \left(C_0^{1-n} + k(T)(n-1)t \right)^{\frac{1}{1-n}}. \tag{3}$$

According to Eq. (3), if $0 < n < 1$ and $t > (C_0/k(T))^{1-n}$, $C(t)$ becomes a complex number. This has no physical meaning in our context, and hence $C(t)$ ought to be set to zero when this occurs (Peleg, Normand, & Kim, 2014). Where $n \sim 1$, however, this situation would rarely, if ever, be encountered in a realistic time and hence should not worry us here.

The temperature-dependence of the rate constant $k(T)$ has been traditionally described by the Arrhenius equation or plot. The rationale for using this model in foods can be challenged on several grounds (Peleg, Normand, & Corradini, 2012). The most obvious practical shortcoming of the Arrhenius plot, Ln $[k(T)]$ vs. $1/T$, where T is the temperature in degrees Kelvin, is the needless compression and reversal of the temperature axis. But more important conceptually is that the widespread use of the Arrhenius model leaves the impression that all chemical reactions and biological processes in foods have a temperature-independent energy of activation, a tenet yet to be supported by independent experimental evidence. Suffice it to state here that almost every experimental $k(T)$ vs. T relationship that has been fitted by the Arrhenius equation can also be fitted by the much simpler exponential model (Peleg, Kim, & Normand, 2015; Peleg et al., 2012, 2014):

$$k(T) = k(T_{ref}) \, \text{Exp}\left[c(T - T_{ref}) \right] \tag{4}$$

where T is the temperature in degrees Celsius, $k(T_{ref})$ is the rate constant at a chosen reference temperature T_{ref}, and c is a characteristic constant expressed in degrees Celsius reciprocal. It can be shown that where T_{ref} is in a pertinent range, the Arrhenius and exponential models diverge only at temperatures that are either well above those encountered in thermal processing or well below those encountered in cold storage. Consequently, we have opted to use the simpler exponential model in what follows. Because the two models are interchangeable around the reference temperature, our choice should not be construed as contradicting authors who have used the Arrhenius equation to describe the same experimental data. It can be shown that the magnitude of the exponential model's c parameter can be estimated from a reported 'energy of activation', E_A, using the formula (Peleg et al., 2012):

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

where R is the Universal gas constant expressed in units commensurate with those of E_A, and T_{ref} is in degrees Celsius. If applicable, one can estimate the Arrhenius model's E_A from the exponential model's c parameter with the inverse formula, i.e.:

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

1.1. The isothermal version of the endpoints method

Consider two hypothetical isothermal degradation curves depicting a reaction known or assumed to follow first order kinetics at two constant temperatures T_1 and T_2 as shown in Fig. 1 — left. These two temperatures are assumed to be low enough and/or the exposure times long enough so that the come-up and cooling times play an insignificant role as in storage, for example. Determined experimentally are the thiamine's initial concentration and its residual concentration at the end of the two exposures. These are used to calculate the corresponding concentration ratios C_1 (C_{exper1} in the figure) at time t_{f1} (t_{final1} in the figure) and C_2 (C_{exper2} in the figure) at time t_{f2} (t_{final2} in the figure). We express the concentrations not in
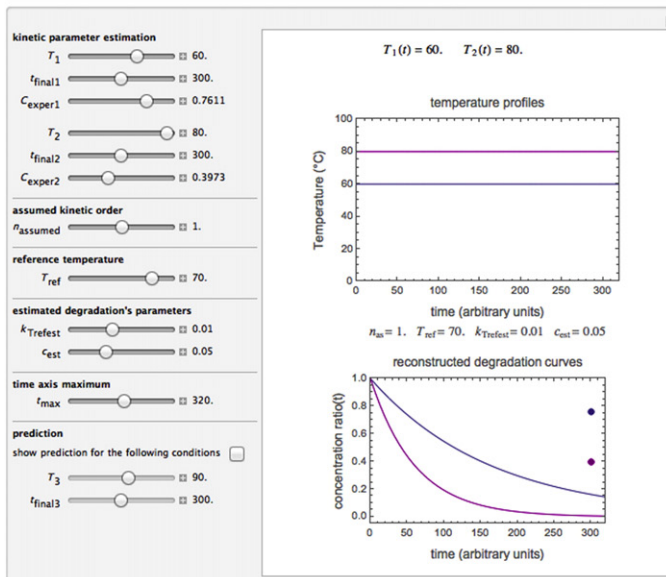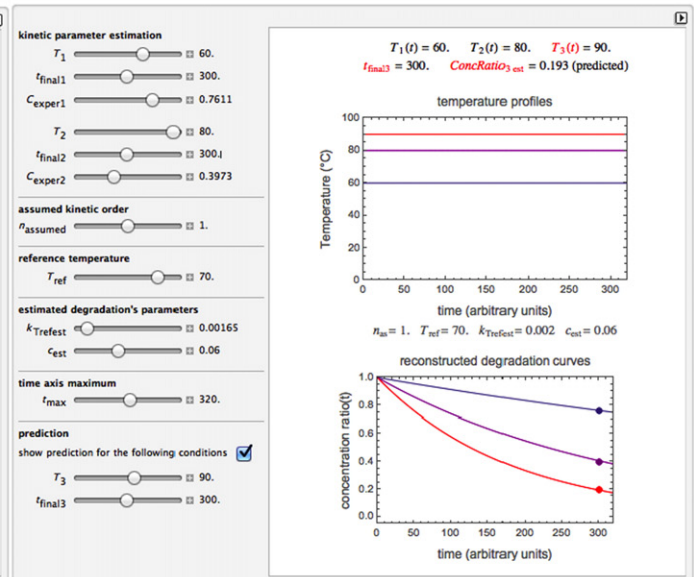

Fig. 1. Screen displays of the Wolfram Demonstration to estimate the degradation parameters of thiamine by the isothermal version of the endpoints method and to predict the vitamin's concentration ratios at temperatures not used in the kinetic parameters calculation. Left: the two entered experimental endpoints for temperatures T_1 and T_2 and times t_{final1} and t_{final2}, with the default reconstructed degradation curves. Right: the matched reconstructed degradation curves reached by moving the $k_{Trefest}$ and c_{est} parameters' sliders. The two sliders' positions mark the estimated degradation parameters. The red (lowest) curve is a predicted third isothermal degradation curve shown with its endpoint superimposed. The corresponding predicted concentration ratio is shown above the temperatures plot.