BOOTSTRAP CONFIDENCE INTERVALS FOR THE KINETIC PARAMETERS OF DEGRADATION OF ANTHOCYANINS IN GRAPE POMACE

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Accepted for Publication April 23, 2009

ABSTRACT

Because of the growing interest in nutraceuticals and their health benefits, it is important to develop tools for modeling degradation of nutraceuticals in low-moisture- and high-temperature-heated foods. The objective of this study was to estimate the kinetic parameters for the degradation of anthocyanins in grape pomace and to calculate the bootstrap confidence interval (CI), which is a more realistic estimate of the true CI than the commonly used asymptotic CI. Thermal and kinetic parameters for unsteady-state conduction-heated foods (grape pomace) were estimated separately using an inverse problem technique. Rate constant (k_r) *and activation energy* (E_a) *for the degradation of anthocyanins in grape pomace were estimated, and the 95% bootstrap CIs were calculated and compared with the 95% asymptotic CIs. Grape pomace at 42% moisture content (wet basis) in steel cans (radius 0.027 m, and height 0.073 m) was heated in a steam retort at 126.7C. Anthocyanin retention was measured by high-performance liquid chromatography. The retention values were used to estimate kinetic parameters, which were* $k_{113.9C} = 0.0606$*/min and* $E_a = 65.32$ *kJ/mol. Asymptotic CIs for* $k_{113.9C}$ *and* E_a *were 0.052 and 0.068, and 23.3 and 102.7, respectively. Bootstrap 95% CIs for* $k_{113.9C}$ *and* E_a *were 0.053 and 0.066, and 49.08 and 104.9, respectively. Bootstrap confidence band and bootstrap prediction band (PB) for anthocyanin retention were smaller than asymptotic confidence and PBs, respectively.*

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Journal of Food Process Engineering **34** (2011) 1220–1233.
DOI: 10.1111/j.1745-4530.2009.00425.x

The smaller width of the bootstrap bands, which are considered more accurate than asymptotic bands, allows more accurate process design and cost-savings, potentially leading to higher-quality nutraceutical products.

PRACTICAL APPLICATIONS

Thermal and kinetic parameters for unsteady-state conduction-heated foods (grape pomace) were estimated separately using nonlinear regression techniques. This non-isothermal method of estimating thermal and kinetic parameters is fast, convenient and more accurate than the isothermal method. Also, for certain application such as low-moisture solids at high temperatures, isothermal experiments are not feasible. There is much more information gained from the type of plot presented here than from the typical plot with only one fitted line showing the mean values. The smaller width of the bootstrap bands, which are considered more accurate than asymptotic bands, allows more accurate process design and cost-savings, potentially leading to higher-quality nutraceutical products.

INTRODUCTION

Methods to estimate parameters for isothermal processes, such as degradation of nutraceutical compounds in foods with high moisture content, are well established. Isothermal experiments can be performed with high-moisture food samples because the temperature gradient is very small and isothermal heating has very short lag times. The rate of reaction and the activation energy (E_a) for the degradation of nutraceuticals can be computed by a two-step method of two semilog plots, assuming first-order reaction kinetics and a rate that follows the well-known Arrhenius equation. Conducting isothermal experiments for low- and intermediate-moisture foods is challenging because of the large temperature gradients within the sample and long lag times. Hence, non-isothermal experimentation is required for low-moisture foods like extruded products, breads, jam and jelly and vegetable pastes. For non-isothermal processes, kinetic parameters can be estimated by nonlinear regression methods.

The accuracy of an estimated parameter is not commonly reported in modeling of nutraceutical retention. Some researchers have proposed methods to calculate the asymptotic confidence interval (CI) and the joint confidence region to get good estimates of the error and correlation on estimated parameters (Bates and Watts 1988; Claeys *et al.* 2001; Dolan *et al.* 2007). The jackknife method for the estimation of the experimental error on parameters

was used for the kinetic model for thiamine destruction in pea puree (Nasri *et al.* 1993). However, CIs on predicted *Y* (microbial retention) and CIs of the parameters were not reported. The Monte Carlo method was used to estimate the CI for mass average retention of conduction-heated canned foods (Lenz and Lund 1977), but the CIs on predicted *Y* were not reported. A novel method has been proposed (Dolan *et al.* 2007) to calculate the confidence band (CB) on the predicted *Y* and prediction band (PB) on *Y*. In the literature surveyed, there were very few CIs reported for parameters, and none for predicted *Y*, which is typically the most important variable for processors.

Some researchers have applied the method of bootstrapping to get the CIs on the estimated parameters (Almonacid-Merino *et al.* 1993). However, none of the studies reviewed showed computation of CIs using bootstrap for degradation of nutraceuticals in food materials. The purpose of this study was to provide a tool to future researchers who can apply this method to report the CIs on the parameters obtained by an inverse method, thereby potentially improving safety and quality of the processed food. In the context of providing realistic estimates of error of the parameters involved in non-isothermal processing, the objectives of this study were:

(1) To compute bootstrap CIs of kinetic parameters;
(2) To compute bootstrap CBs for predicted anthocyanin retention and bootstrap PBs for anthocyanin retention; and
(3) To compare bootstrap confidence and prediction values to their asymptotic counterparts.

MATERIALS AND METHODS

Thermal Parameter Estimation

The heat transfer model for this experiment was for heat conduction in cylindrical coordinates:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(k(T)r\frac{\partial T}{\partial r}\right)+\frac{\partial}{\partial z}\left(k(T)\frac{\partial T}{\partial z}\right)=C(T)\frac{\partial T}{\partial t} \tag{1}$$

The governing boundary conditions were;

$$\frac{\partial T}{\partial r}(0,z,t)=0 \tag{2}$$

$$T(r,z,0)=T_{\mathrm{i}} \tag{3}$$

$$\frac{\partial T}{\partial z}(r,0,t)=0 \tag{4}$$

$$-\mathrm{k}(T)\frac{\partial T}{\partial r}(R,z,t)=h(T(R,z,t)-T_{\infty}) \tag{5}$$

$$-\mathrm{k}(T)\frac{\partial T}{\partial z}(r,H,t)=h(T(r,H,t)-T_{\infty}) \tag{6}$$

The term $C(T)$ was considered constant with temperature in Eq. (1). We are assuming that the $k(T)$ relation varies much more with T than does $C(T)$. In this case, Eq. (1) can be written as

$$\frac{1}{r}\frac{\partial}{\partial r}\left(\alpha(T)r\frac{\partial T}{\partial r}\right)+\frac{\partial}{\partial z}\left(\alpha(T)\frac{\partial T}{\partial z}\right)=\frac{\partial T}{\partial t} \tag{7}$$

This transient conduction heat transfer problem was solved with the finite element model using Comsol (Comsol Inc., Burlington, MA) and Matlab (The MathWorks Inc., Natick, MA). Thermal diffusivity as a function of temperature was estimated via an inverse technique by minimizing the sum of squares of measured temperature and the predicted temperature of the center of the can and $\alpha(T)$ at two different temperatures was estimated using Eq. (8).

$$\alpha(T)=\left(\frac{(T_2-T)}{(T_2-T_1)}\times\alpha_1+\frac{(T-T_1)}{(T_2-T_1)}\times\alpha_2\right) \tag{8}$$

Kinetic Parameter Estimation

A detailed discussion about the nonlinear regression technique can be found in (Mishra *et al.* 2008). The parameter estimation process is described briefly in this paper. Thermal degradation of anthocyanins has been shown to follow first-order reaction kinetics (Cemeroglu *et al.* 1994; Ahmed *et al.* 2004),

$$\frac{dC}{dt}=-kC, \tag{9}$$

The reaction rate can be quantified by the Arrhenius model:

$$k=k_{\mathrm{r}}e^{\frac{-E_{\mathrm{a}}}{R}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{r}}}\right)} \tag{10}$$

Under dynamic temperature conditions, retention of anthocyanins can be expressed by

$$\left(\bar{C}/C_o\right)_{\text{pred}} = 2\iint e^{-k_r\int_0^t e^{-\frac{E_a}{R}\left(\frac{1}{T(r,z,t)}-\frac{1}{T_r}\right)}dt}\, r\, dr\, dz \tag{11}$$

where variables r and z were normalized; hence, the limits of both integrals were from 0 to 1. The kinetic parameters E_a and k_r were estimated via an inverse method using Matlab in combination with Comsol using the following command:

$$[\text{beta, r, J}] = \text{nlinfit}(\text{X, y, @fun, beta0}) \tag{12}$$

The command "nlinfit" in Matlab returns the estimated parameters (beta), the residuals (r) and the Jacobian (J) by minimizing Eq. (13) to get the best sum
of squares for the estimated parameters.

$$SS = \sum_i \left[\left(Y_{\text{obs}}\right)_i - \left(\hat{Y}_{\text{pred}}\right)_i\right]^2 \tag{13}$$

Parameters k_r and E_a were estimated simultaneously using the nonlinear regression method. Residual plots were also plotted to check for the absence of trends or correlations.

Overview of Bootstrap Method

The bootstrap method was found to be a better tool than the jackknife method, which was proved to be a linear approximation of the bootstrap method (Efron 1979). If the distribution from which the samples are drawn is known and if the function is sufficiently tractable, the standard errors and, hence, the CIs can be constructed (Felsenstein 1985). Bootstrap procedure is most useful when the error distribution of the sample is not known. When CIs for the parameters or retention are reported, typically, they are asymptotic and symmetric, because asymptotic CIs are computationally efficient. Monte Carlo methods such as the bootstrap are known to produce more realistic CIs. Now that more sophisticated software is available for most researchers, we can take advantage of these powerful statistical techniques to improve quality and safety of foods.

The bootstrap method used in the present study is discussed in the following steps.

Step 1: For the data points $x_1, x_2, \ldots, x_n$, an estimate of parameter t can be obtained using a method T of statistical estimation (Felsenstein 1985):

$$t = T(x_1, x_2, \ldots, x_n), \tag{14}$$

For example, T can be nlinfit in Matlab which is based on the Gauss–Newton method of nonlinear regression.

Step 2: The bootstrap method allows randomized resampling of the data to construct a fictional set of data. Each of these data sets is constructed by sampling n points with replacement from the x_n data. These fictional data sets consist of $x_1^*, x_2^*, \ldots, x_n^*$ points, where each x_i^* is drawn at random from the original data set. Then, t is again estimated for the new data set as,

$$t^* = T(x_1^*, x_2^*, \ldots, x_n^*), \tag{15}$$

Step 3: The sampling process, i.e., step 2, is repeated many times to get a set of values of the estimated t^*. The distribution of this estimate approximates the distribution of the actual estimate t.

Step 4: Confidence limit on the parameter is calculated based on the upper or lower percentiles of the observed t^* values.

Application of Bootstrap to Kinetic Model

For 42 retention values of anthocyanins Y and time–temperature (tT) history, i.e., $Y_1t_1T_1$, $Y_2t_2T_2$, . . . , $Y_{42}t_{42}T_{42}$, were used to estimate k_r and E_a;

$$[E_a, k_r] = \text{nlinfit}\,(Y_1t_1T_1, Y_2t_2T_2, \ldots, Y_{42}t_{42}T_{42})] \tag{16}$$

A fictional data set was constructed by random sampling with replacement to obtain $(Y_1^*t_1^*T_1^*, Y_2^*t_2^*T_2^*, \ldots, Y_{42}^*t_{42}^*T_{42}^*)$. As the sampling was with replacement, there were chances that one data point occurred more than once, and that one data point did not occur at all. These new data sets were used to estimate the new set of parameters,

$$(E_a^*, k_r^*) = \text{nlinfit}(Y_1^*t_1^*T_1^*, Y_2^*t_2^*T_2^*, \ldots, Y_{42}^*t_{42}^*T_{42}^*) \tag{17}$$

Random sampling process was repeated many times to obtain a set of values of the estimated parameter vector (E_a^*, k_r^*).

Bootstrap CI on Parameters

The confidence limits on the parameters were calculated based on the upper and lower 95 percentiles of the observed (E_a^*, k_r^*) values. For example, the CI on E_a for the 100 $(1 - \alpha)$ percentile can be obtained by,

$$\left(E_{a_{lo}}, E_{a_{up}}\right) = \left(\hat{E}_a^{*(\alpha/2)}, \hat{E}_a^{*(1-\alpha/2)}\right) \tag{18}$$

For example, if there were 1,000 bootstrap iterations, then the pairs of (E_a^*, k_r^*) are sorted from lowest $(E_a^*, k_r^*)_1$ to highest $(E_a^*, k_r^*)_{1000}$. The lower and upper 95% confidence limits for the two parameters would be $(E_a^*, k_r^*)_{25}$ and $(E_a^*, k_r^*)_{975}$, respectively.

Bootstrap CI on Predicted Y

The bootstrap CB on predicted Y was determined by (1) computing Y for each of the 1,000 pairs of bootstrap parameter estimates; (2) sorting Ys at each of the heating times; and (3) computing the lower and upper 95% CIs by using the lower and upper percentile values, i.e., $Y(25)$ and $Y(975)$. Bootstrap PB was calculated using the equation (Montgomery and Vining 2006):

$$\text{prediction width}_i = \sqrt{(\text{confidence width}_i)^2 + \left(t_{\alpha/2,n-p} * RMSE\right)^2} \quad (19)$$

where i is the index for heating time, and "prediction width" and "confidence width" are either the upper or the lower bootstrap band width, and the upper width is computed separately from the lower width because the bootstrap band does not have to be symmetric.

Normal bivariate distribution was plotted and the 90 and 95% confidence regions were plotted for the kinetic parameters.

Experimentation

Analytical method to determine the anthocyanin content was adopted from Mishra *et al.* (2008). In short, grape pomace (42% moisture content [wet basis]) was retorted in steel cans (radius 0.027 m, and height 0.073 m) in a rotary steam retort at 126.7C. The heating time varied from 8 to 25 min to obtain different levels of retention of anthocyanins in grape pomace. Extraction solvent (50 mL of methanol + 33 mL of water + 17 mL of 37% HCL) was used to extract the anthocyanins from the raw and retorted grape pomace. The quantification of anthocyanins was done by hydrolyzing the anthocyanins to anthocyanidins and was injected in high-performance liquid chromatography system and the dual wavelength detector read the absorbance reading. The area under the peaks of chromatograms was used to calculate the anthocyanin content in the raw and retorted samples.

Results and Discussion

Data used in this study were adopted from Mishra *et al.* (2008). The heating time and retention of anthocyanins are provided in Table 1.

TABLE 1.

RETENTION ($\bar{C}/C_o$) VALUE OF ANTHOCYANINS FOR GRAPE POMACE AT 42% MOISTURE CONTENT (WET BASIS) AS MEASURED FROM HPLC

Sample number	Heating time (min.) at 126.7C	Retention of anthocyanins
1	0	0.984
2	0	0.768
3	0	0.802
4	0	0.831
5	0	0.935
6	0	0.982
7	0	1.128
8	0	1.271
9	0	1.300
10	8	0.871
11	8	0.756
12	8	0.858
13	10	0.729
14	10	0.739
15	10	0.676
16	12	0.729
17	12	0.749
18	12	0.748
19	14	0.583
20	14	0.533
21	14	0.455
22	15	0.539
23	15	0.547
24	15	0.636
25	16	0.376
26	16	0.338
27	16	0.455
28	17	0.307
29	17	0.340
30	17	0.343
31	19	0.256
32	19	0.295
33	19	0.275
34	21	0.290
35	21	0.239
36	21	0.298
37	23	0.248
38	23	0.245
39	23	0.239
40	25	0.225
41	25	0.206
42	25	0.194

HPLC, high-performance liquid chromatography.

Parameter Estimates

Thermal diffusivity was estimated at two different temperatures, i.e., α_1 at 25C and α_2 at 126C. The root mean square error (RMSE) was 2.21C and the correlation coefficient of the two parameters was –0.82. The results are shown in Table 2. Estimated value of the rate of reaction was 0.0606/min, whereas the E_a was found to be 65.32 kJ/gmol. Correlation coefficient $\rho_{k_r E_a}$ was 6.49e-5 at a reference temperature (T_r) of 113.9C. The *RMSE* was 0.10 fractional retention, which is approximately 10% of the total scale of 1.0 for *Y*, showing a good fit. Ninety-five percent bootstrap CI for $k_{113.9C}$ was very close to the 95% asymptotic CI (Table 3). The bootstrap CI width on *E*a (49.08, 104.93 kJ/g mol) was 30% narrower than the asymptotic 95% CI (23.3, 102.7 kJ/g mol) on the lower bound, but it was almost the same as that of the asymptotic CI on the upper bound (Table 3); this phenomenon clearly illustrates the flexibility of the bootstrap method, without the constraint of symmetry.

Bootstrap CI

Table 4 shows the CIs at different number of iterations for bootstrapping. From these results, it was concluded that 1,000 bootstraps (Table 4) were sufficient to get the CI on the parameters. This result was the same as the minimum recommended by Efron (1987).

TABLE 2.
ESTIMATES OF THERMAL DIFFUSIVITY PARAMETERS

Parameter	Parameter estimates m^2/s	Standard error	Correlation coefficient	95% asymptotic confidence interval	RMSE, C
α_1	2.07×10^{-7}	0.02×10^{-7}	–0.82	2.02×10^{-7}, 2.10×10^{-7}	2.21
α_2	2.55×10^{-7}	0.01×10^{-7}		2.51×10^{-7}, 2.58×10^{-7}	

RMSE, root mean square error.

TABLE 3.
KINETIC PARAMETERS FOR ANTHOCYANIN DEGRADATION IN GRAPE POMACE AT 42% (WET BASIS) MOISTURE CONTENT

Parameter	No. of data	Parameter estimates	Standard error	95% bootstrap confidence interval	95% asymptotic confidence interval	RMSE (fractional retention)
$k_{113.9C}$	42	0.0606/min	0.003	(0.053, 0.066)	(0.052, 0.068)	0.10
E_a		65.32 kJ/g mol	19.6	(49.08, 104.93)	(23.3, 102.7)	

TABLE 4.
BOOTSTRAP 95% CONFIDENCE INTERVAL FOR E_a AND k_r

Number of bootstraps	Confidence interval E_a	Confidence interval k_r
10	(54.90, 89.54)	(0.0634, 0.0710)
100	(49.04, 108.8)	(0.0604, 0.0739)
200	(48.52, 108.2)	(0.0629, 0.0742)
500	(48.86, 107.0)	(0.0621, 0.0746)
1,000	(49.08, 104.93)	(0.0531, 0.0660)
2,000	(49.60, 106.28)	(0.0533, 0.0658)
5,000	(49.31, 106.11)	(0.0532, 0.0659)

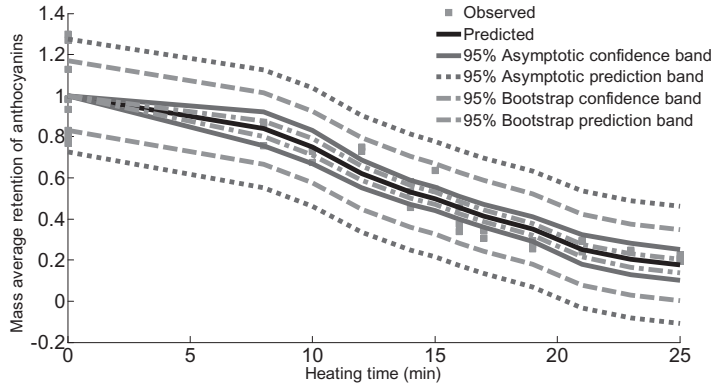

FIG. 1. 95% BOOTSTRAP CONFIDENCE BAND, 95% BOOTSTRAP PREDICTION BAND, 95% ASYMPTOTIC CONFIDENCE BAND AND 95% ASYMPTOTIC PREDICTION BAND FOR MASS AVERAGE RETENTION OF ANTHOCYANINS IN GRAPE POMACE HEATED IN 202 × 214 CANS AT RETORT TEMPERATURE OF 126.7°C

Figure 1 shows 95% bootstrap CB, 95% bootstrap PB, 95% asymptotic CB and 95% PB for mass average retention of anthocyanins. Correlation coefficient was −0.12. Many data fall outside the CB, as CB is the region where 95% of the regression lines are expected to be. The PB is the region where 95% of the data are expected to be. If more data were collected, we expect that ~5% of all the data would fall outside the PB. CB for the predicted Y is very small for the bootstrap as compared to the asymptotic (Fig. 1). PB also shows the same trend for the bootstrap, i.e., bootstrap PB is narrower than the asymptotic PB. The confidence and PBs of bootstrap are asymmetric in nature. For the bootstrap CB, the upper is varying from 60 to 30% and the lower is 41 to 49% of the total asymptotic CB. For the bootstrap PB, the upper is 61% and the lower is also 59% of the total asymptotic PB. Asymptotic PB

contains 98% of the data, while bootstrap PB contains 91% of the data. This suggests that the asymptotic PB is probably too wide.

The normal bivariate distribution (Fig. 2) for the 1,000 bootstrap parameters was plotted as a three-dimensional plot in Matlab. The contours of the confidence level of 90 and 95% were constructed out of the plotted distribution. The plot of 1,000 bootstrap estimated parameters is shown in Fig. 3. Joint confidence region was plotted on the same plot to compare confidence regions at 90 and 95% confidence levels. Ninety percent confidence level has the bigger region as expected, which covers 90% of the bootstrap estimated parameters. It can be concluded from the plot that E_a varies from 35 to 97 kJ/mol, while rate constant at 113.9C varies from 0.055 to 0.067/min. These confidence limits are in good agreement with the values obtained from asymptotic confidence and bootstrap CI for the parameters (Table 3).

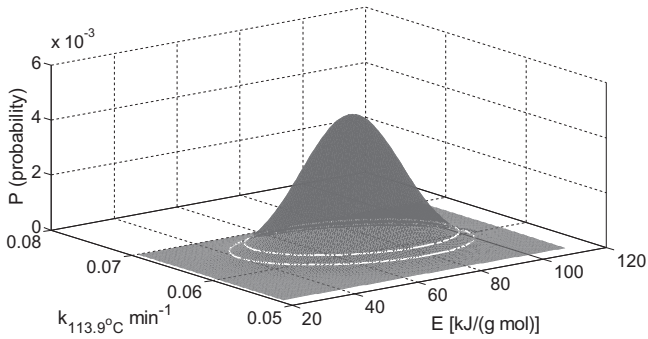

FIG. 2. 3-D PLOT OF THE BIVARIATE NORMAL DISTRIBUTION AND 90 & 95% CONTOURS OF THE CONFIDENCE LEVEL

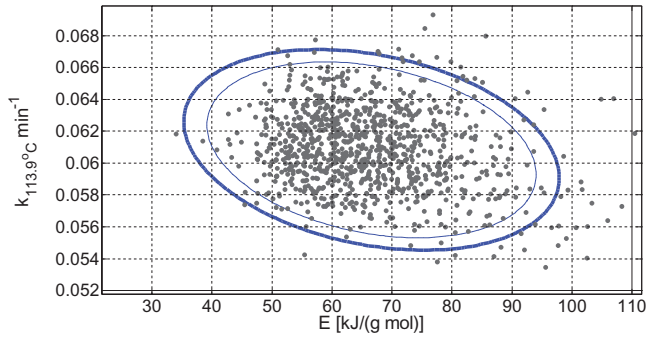

FIG. 3. SCATTER PLOT OF 1,000 BOOTSTRAP-ESTIMATED PARAMETERS AND CONFIDENCE REGIONS AT 90 AND 95% CONFIDENCE LEVELS

It is significant that although the bootstrap CIs for parameters were not greatly different from the corresponding asymptotic CIs (Table 2), the bootstrap CB for predicted *Y* was noticeably narrower (only ~50% the width) than the asymptotic band (Fig. 1).

For processors who wish to improve food quality while maintaining the same safety level, the more narrow bootstrap bands can be considered when designing a shorter heating process. The practical significance of bootstrap is to have a tighter and more realistic confidence as well as PB. For example, if a processor wishes to estimate the retention of anthocyanins after 14 min of processing time, one can look at 14 min on the *x*-axis of Fig. 1 and draw a vertical line passing through the PBs. If bootstrap PB is considered, then we would expect that 95% of the cans would have retention between 35.79 and 70.0%, whereas if the asymptotic CB is used, then we would expect 95% of the cans to have retention between 24.93 and 81.21%. Depending on the thermal treatment of the product, the prediction of the retention of anthocyanins can be quantified using the method presented in this study. Quantification of nutraceuticals in the product will enhance the value of the product and will attract consumers who are concerned about eating healthy food.

CONCLUSIONS

The bootstrap approach to determine the CIs of kinetic parameters for non-isothermal high-temperature processes for low-/intermediate-moisture foods can be a valuable tool for researchers and various food industries engaged in making functional foods. This paper presents three novel results: (1) bootstrap CI of the parameters; (2) bootstrap CB on the predicted *Y*; and (3) bootstrap PB on *Y*. This study was done with hope that future researchers will use these methods to report the error estimates and CIs, which will help in designing processing systems and in improving safety and quality of food.

NOMENCLATURE

α	thermal diffusivity, m^2/s
ρ	density, kg/m^3
σ	standard error
ρ	correlation coefficient
$\bar{C}$	mass average anthocyanins concentration within a can
C_o	initial mass average anthocyanin concentration
C_p	specific heat, J/kg C

E_a	activation energy, J/gmol
H	half height of the cylindrical can, m
k	rate constant min^{-1}
k	thermal conductivity, W/m K
k_r	rate constant at reference temperature T_r, min^{-1}
n	number of data
p	number of parameters
r	dimensionless radius
R_g	gas constant (J/g-mole K)
R	container radius, m
$RMSE$	root mean square error, g/g or C
T	temperature (K)
T_i	initial temperature, K
T_r	reference temperature = 387.05 K (113.9C)
T_∞	steam temperature in retort = 399.85 K (126.7C)
w	Gauss weights
x	time–temperature history (s, independent variable)
Y	mass average retention of anthocyanins, fractional g/g
Z	dimensionless axial position, where $z = 0$ is at the half-height point of the can

ACKNOWLEDGMENT

This research was supported in part by Michigan Agricultural Experiment Station and by NSF award DMS 0706518.

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