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MICHIGAN STATE UNIVERSITY

Sequential estimation of kinetic parameters for nutraceutical degradation using the Arrhenius model

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Nutraceuticals

- Nutraceutical compounds are food components having health promoting, disease preventing or medicinal properties
- Nutraceuticals found in grains, oils, fruits, vegetables, and animal products
- Anthocyanins are a nutraceutical
- Anthocyanins are sensitive and unstable at high temperatures

Objectives

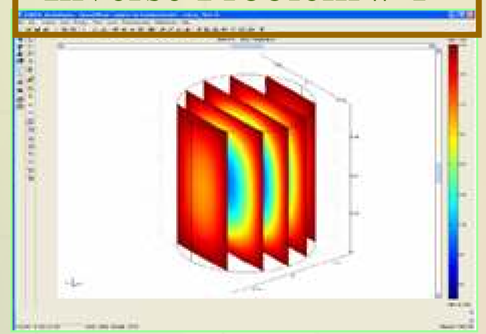
- Simultaneous estimation of kinetic degradation parameters of anthocyanins in grape pomace
- Sensitivity analysis and sequential estimation of thermal and kinetic parameter

Overview of the process

Can Sealing

Retorting at
different times

Thermal parameter
Estimation
Inverse Problem # 1



Extraction of
anthocyanins

HPLC analysis

Kinetic parameter
Estimation
Inverse Problem # 2

Inverse Problem # 1
Estimation of thermal parameter

Two-dimensional axi-symmetric heat conduction

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

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

$$\alpha(\mathrm{T})=\left(\frac{(\mathrm{T}_2\text{-}\mathrm{T})}{(\mathrm{T}_2\text{-}\mathrm{T}_1)}\times\alpha_1\right)+\left(\frac{(\mathrm{T}\text{-}\mathrm{T}_1)}{(\mathrm{T}_2\text{-}\mathrm{T}_1)}\times\alpha_2\right)$$

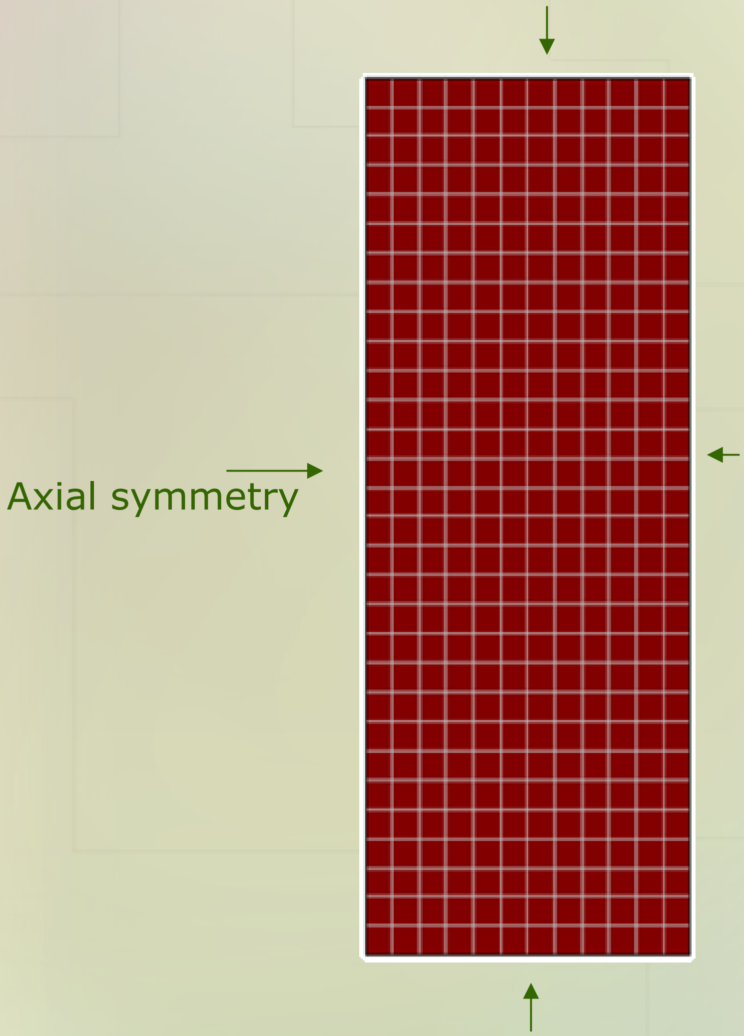
Boundary Conditions

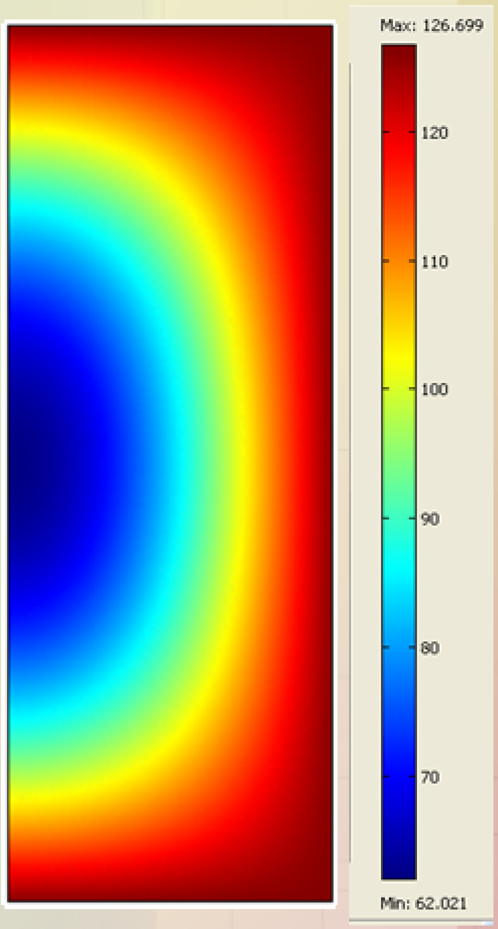
$$\frac{\partial T}{\partial r}(0,z,t)=0 \qquad T(r,z,0)=T_i \qquad \frac{\partial T}{\partial z}(r,H,t)=0$$

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

$$-k\frac{\partial T}{\partial z}(r,0,t)=h(T(r,0,t)-T_\infty)$$

Temperature Profile of the can





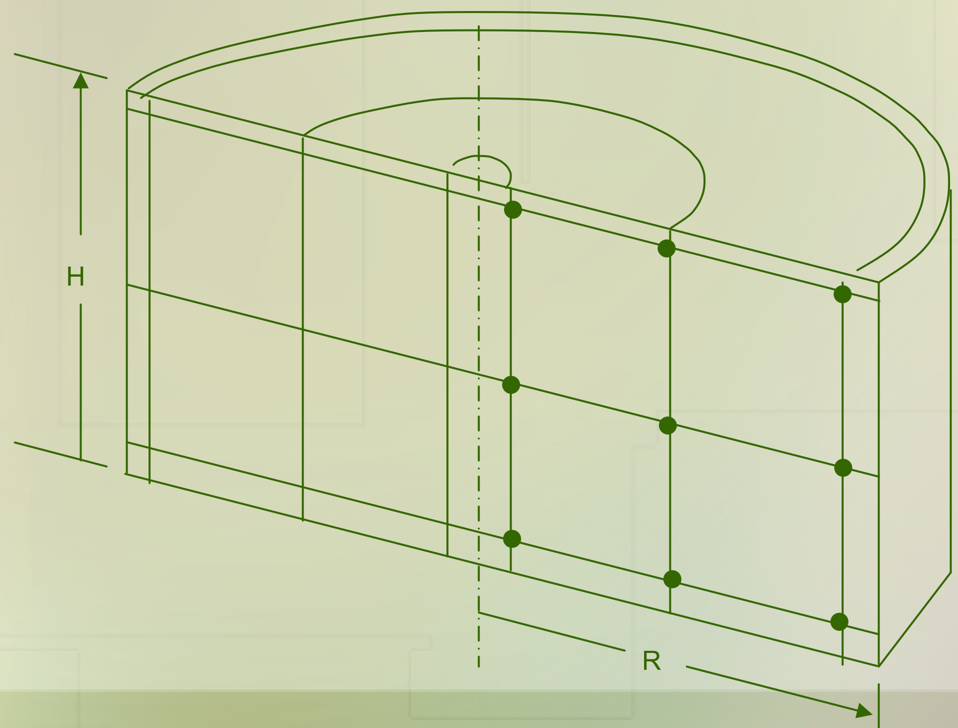
Mass Average Anthocyanin

Inverse Problem # 2

$$C_{pred} = 2C_o \iint e^{-k_r \int_0^t e^{\frac{-E_a}{R}\left(\frac{1}{T(r,z,t)} - \frac{1}{T_r}\right)} dt} \, r\,dr\,dz$$

Estimation of Kinetic Parameters

- Trapezoidal method for Integral over time
- 3-point Gauss method for integral over space



Estimation of Kinetic Parameters

Inverse Problem # 2

Nlinfit
(K_r, E_a)

⟷

$$SSQ = \sum_{i=1}^{n} \left[\overline{C}_{obs,\, i} - \overline{C}_{pred,\, i} \right]^2$$

Inverse Problem # 1

Nlinfit
(α)

⟷

$$SSQ = \sum_{i=1}^{n} \left[T_{obs,\, i} - T_{pred,\, i} \right]^2$$

Scaled Sensitivity

- A scaled sensitivity for parameter can be represented as

$$X_{p_i} \equiv p_i \frac{\partial y}{\partial p_i}$$

Finite difference method

$$X_{p_i} \equiv p_i \frac{y\left(p_i + \delta b\right) - y\left(p_i\right)}{\delta b}$$

- Useful when comparing several parameters in a model

Sequential Estimation

Updating parameters as the new observations are added

"On-line" method of parameter estimation for dynamic processes

The mathematic form is derived from MAP estimation

$$S_{MAP} = (Y - \tilde{Y})^T \psi^{-1} (Y - \tilde{Y}) + (\beta - \mu_\beta)^T V_\beta^{\;-1} (\beta - \mu_\beta)$$

If V_β is diagonal with large diagonal components, ML and OLS estimates can be approximated.

Sequential Estimation

Original Data

$$\begin{pmatrix} t_1 & Y_1 \\ t_2 & Y_2 \\ t_3 & Y_3 \\ t_4 & Y_4 \\ \vdots & \vdots \\ t_n & Y_n \end{pmatrix}$$

$$\begin{pmatrix} E_a & k_r \end{pmatrix}$$

Algorithm

$$e(b^{*})\quad X(b^{*})$$

$$K_{i+1} = P_i X_{i+1}^T (X_{i+1} P_i X_{i+1}^T + \phi_{i+1})^{-1}$$

$$e_{i+1} = (Y_{i+1} - X_{i+1} b_i)$$

$$b_{i+1}^{*} = b_i^{*} + K_{i+1}\left\{e_{i+1} - X_{i+1}(b_i^{*} - b)\right\}$$

$$P_{i+1} = P_i - K_{i+1} X_{i+1} P_i$$

Sequential Cont'd

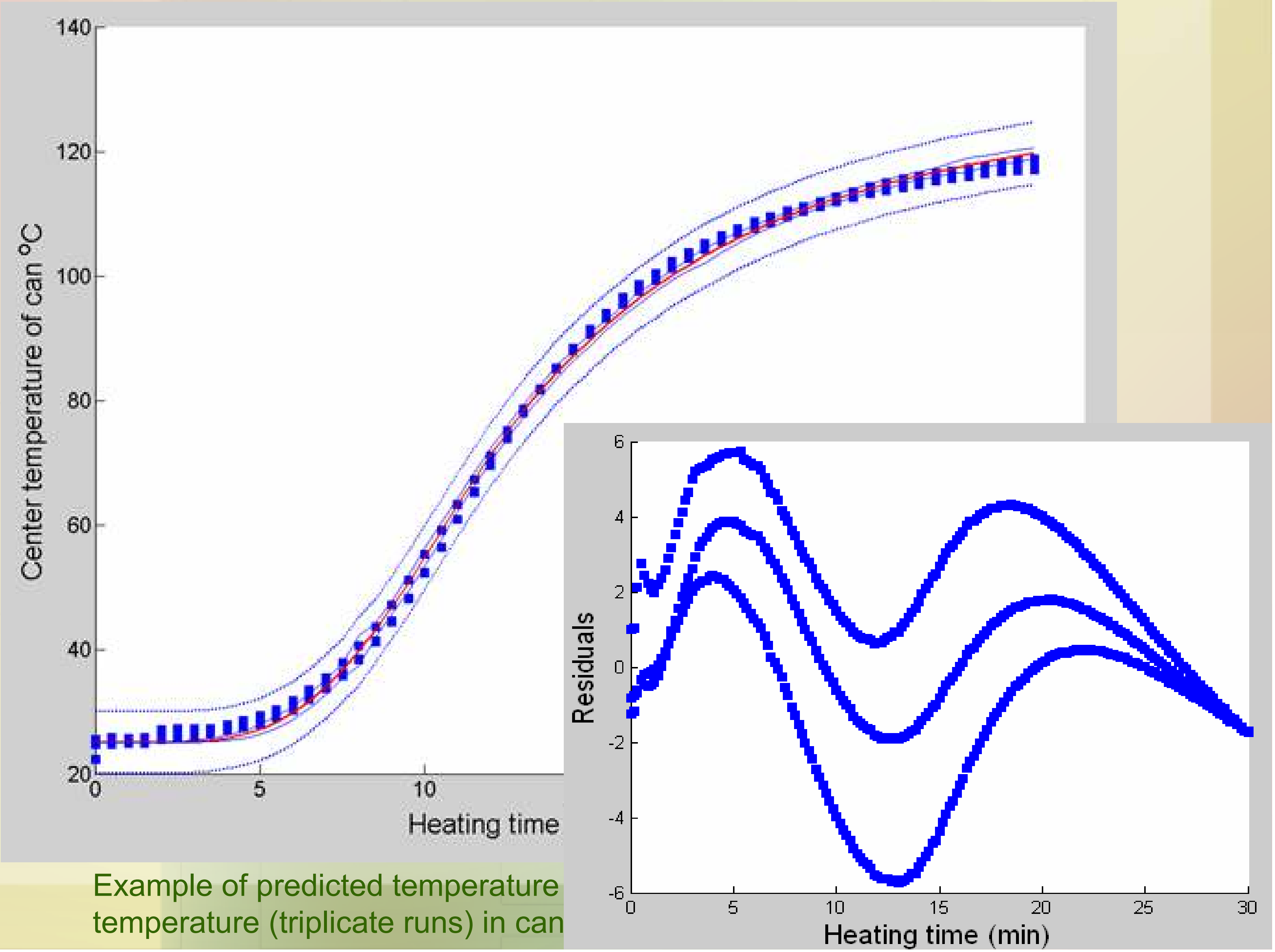
- If there is prior information, iteration starts with

$$b = \mu \text{ and } P(0) = V_\beta$$

- If there is no prior information, P can be diagonal matrix with large diagonal terms

- Model building tool

Result - Thermal Parameters

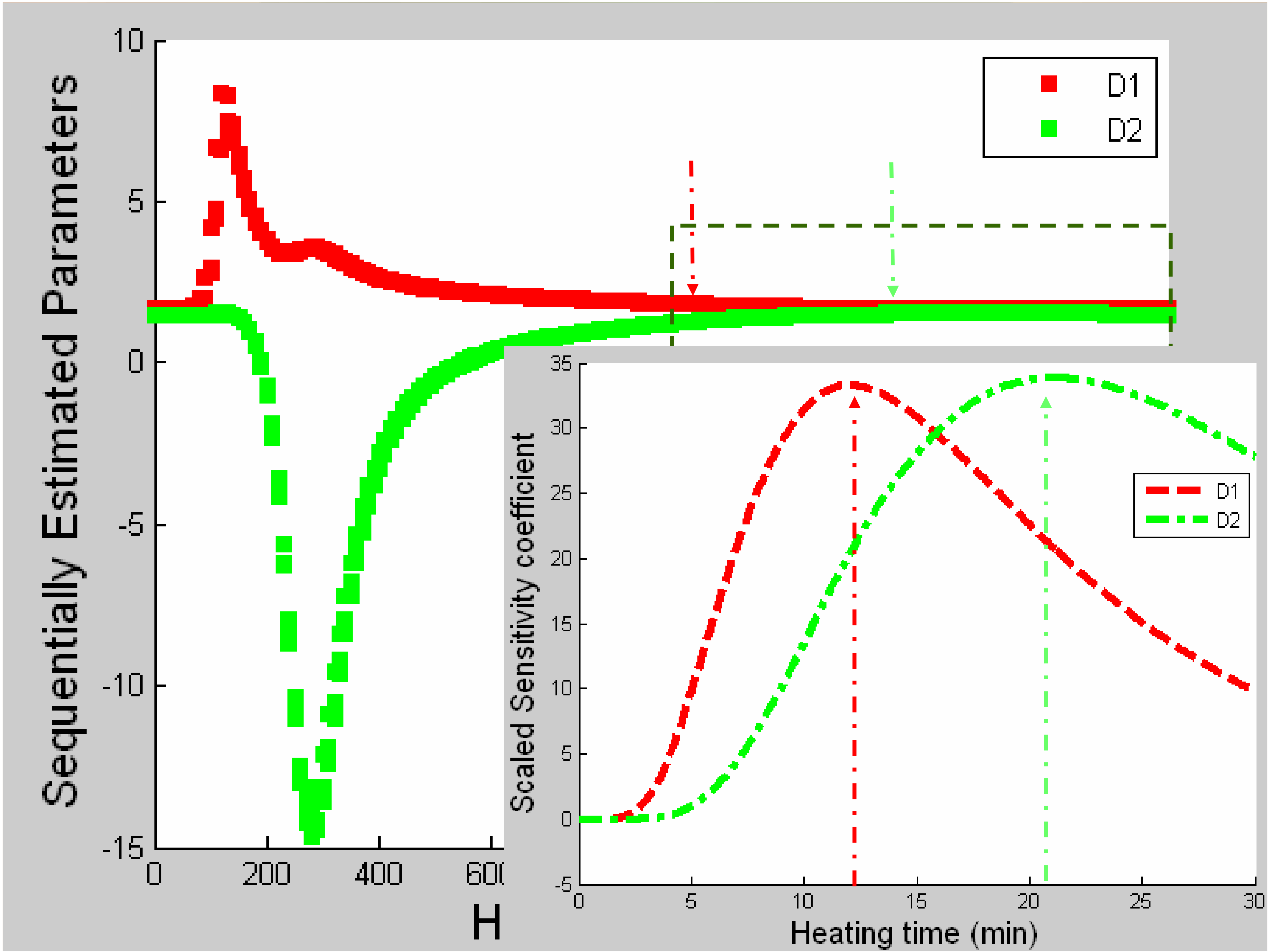


Example of predicted temperature

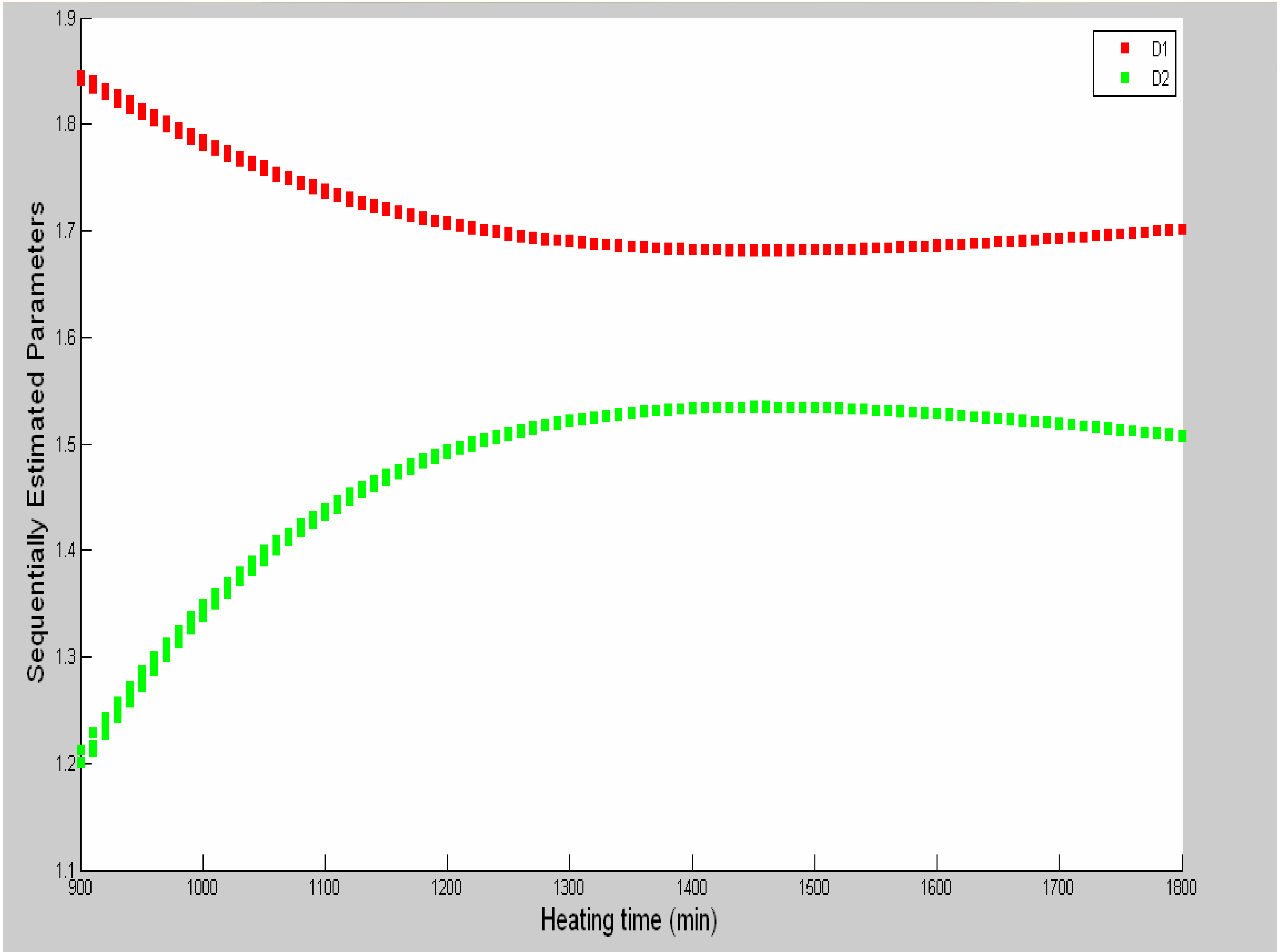
temperature (triplicate runs) in can

Estimates of thermal diffusivity parameters

Parameter	Parameter Estimates	Standard Error	Correlation coefficient	95% asymptotic confidence interval	RMSE
α_1 at 80 °C	2.32×10^{-7}	0.0054×10^{-7}	0.260	2.31×10^{-7}, 2.33×10^{-7}	2.21
α_2 at 120 °C	2.51×10^{-7}	0.014×10^{-7}		2.49×10^{-7}, 2.54×10^{-7}	

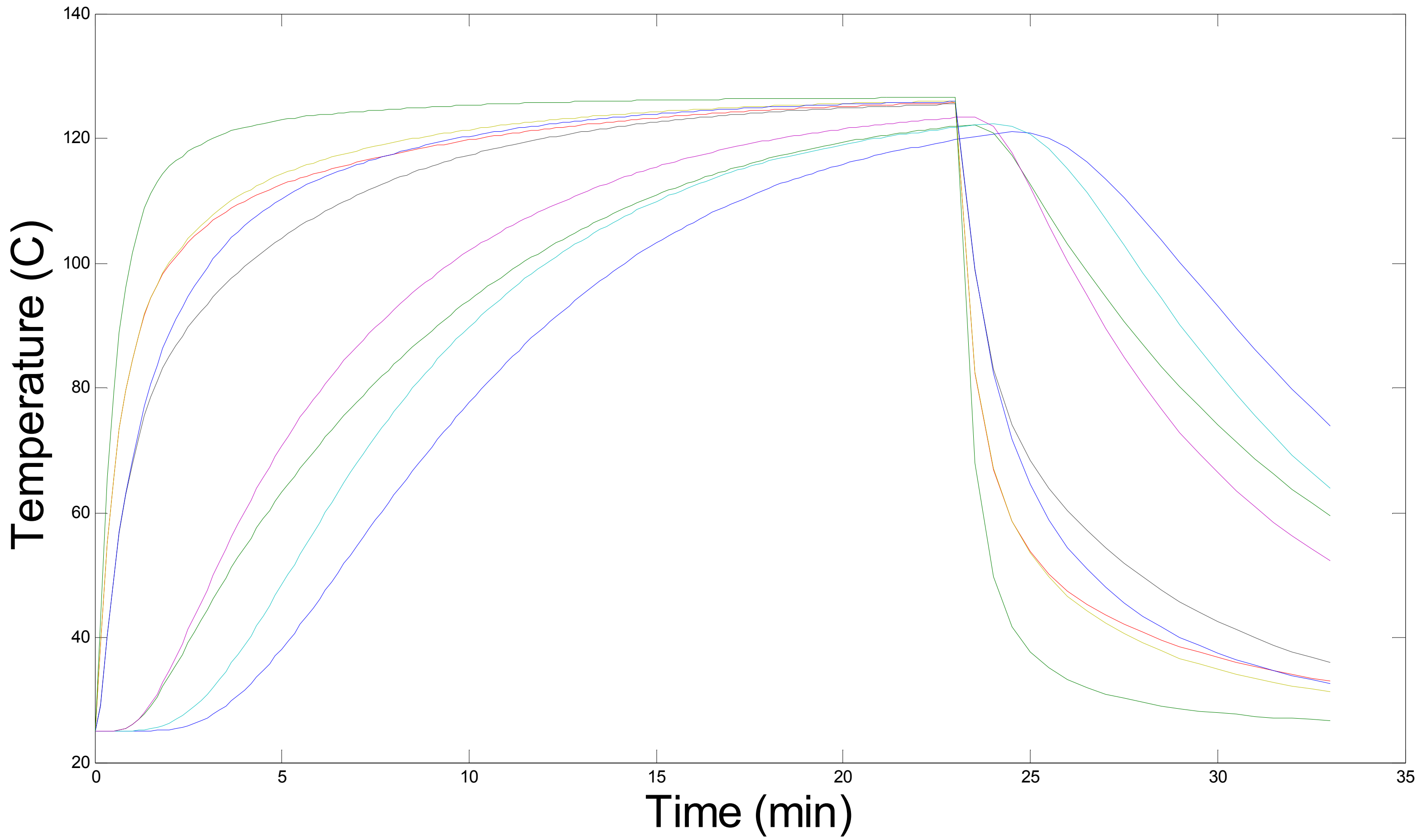


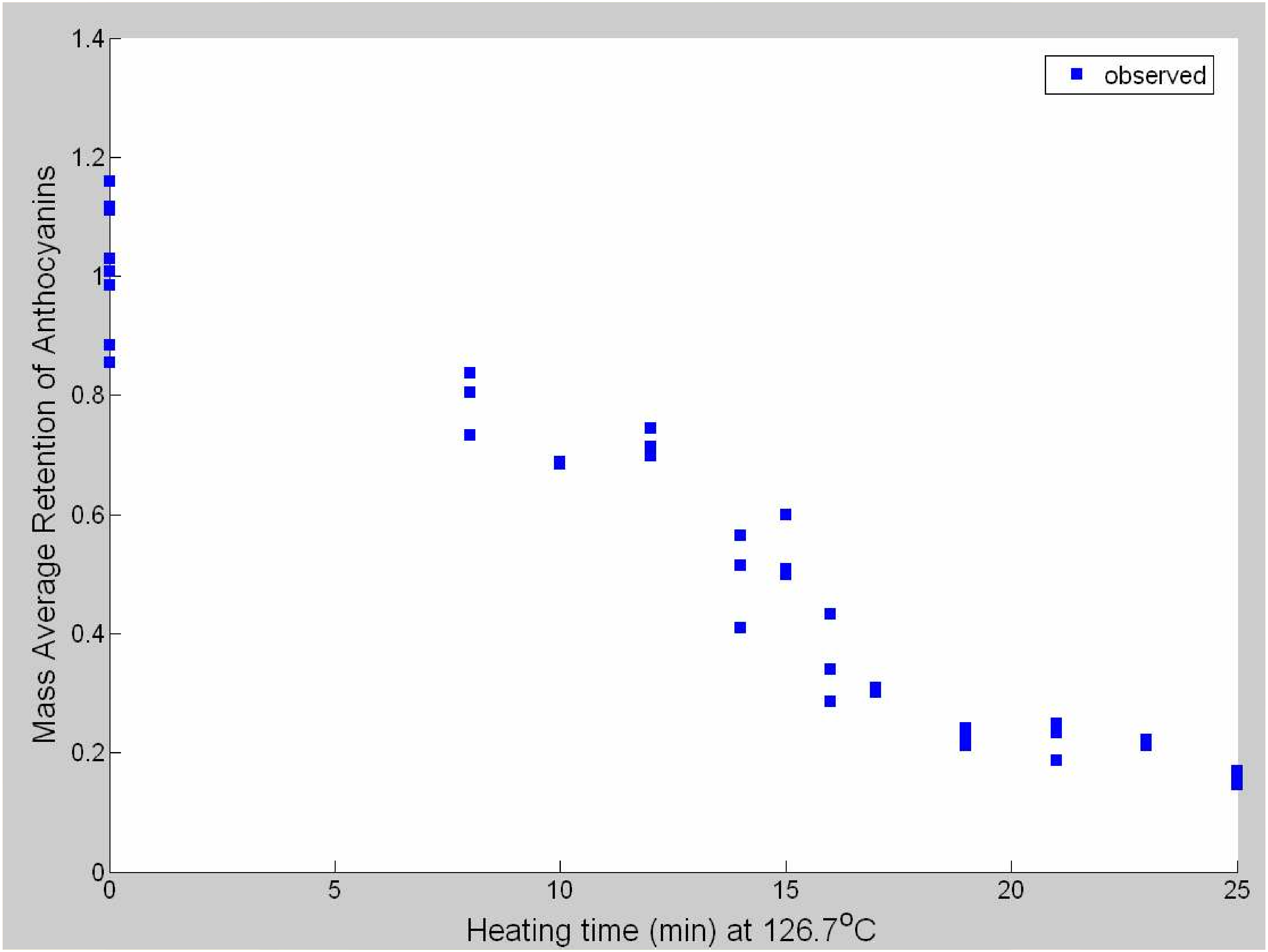
Sequentially Estimated Parameters
10
5
0
-5
-10
-15
0
200
400
D1
D2
Scaled Sensitivity coefficient
35
30
25
20
15
10
5
0
-5
0
5
10
15
20
25
30
Heating time (min)
D1
D2

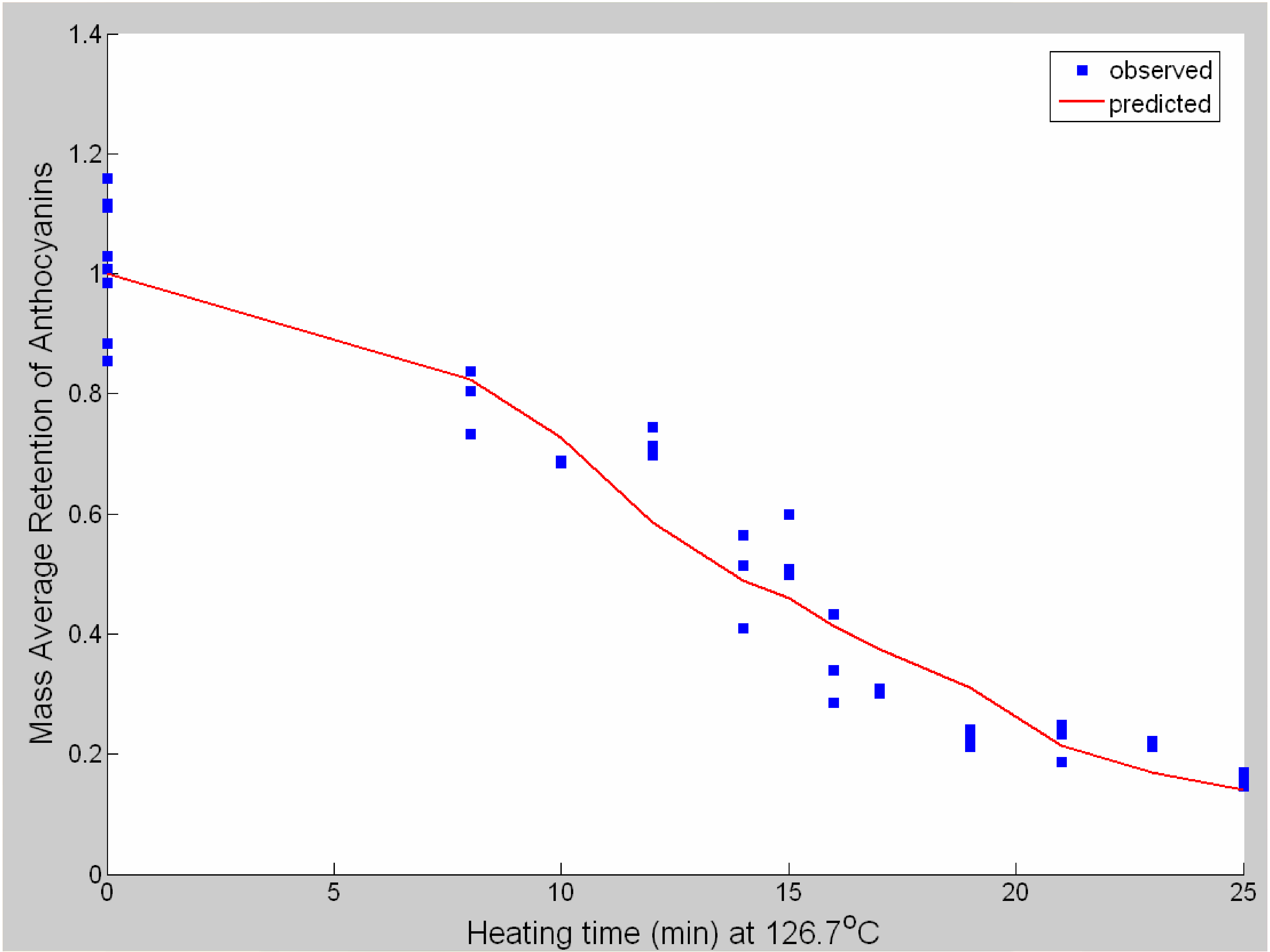

D1
D2
Sequentially Estimated Parameters
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
Heating time (min)

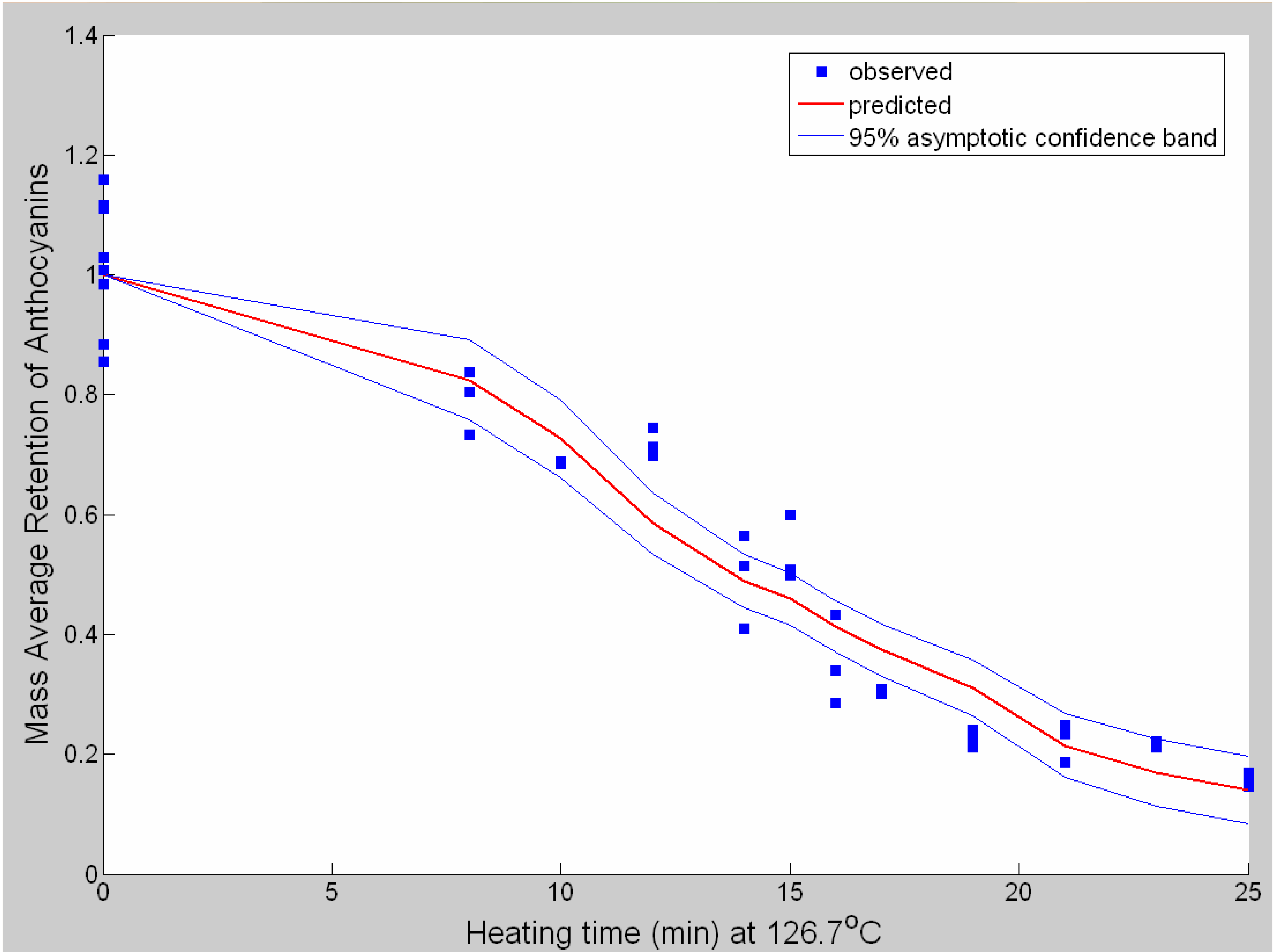
Result - Kinetic Parameters

Temperature Profile at 9 Gauss Points Inside Can

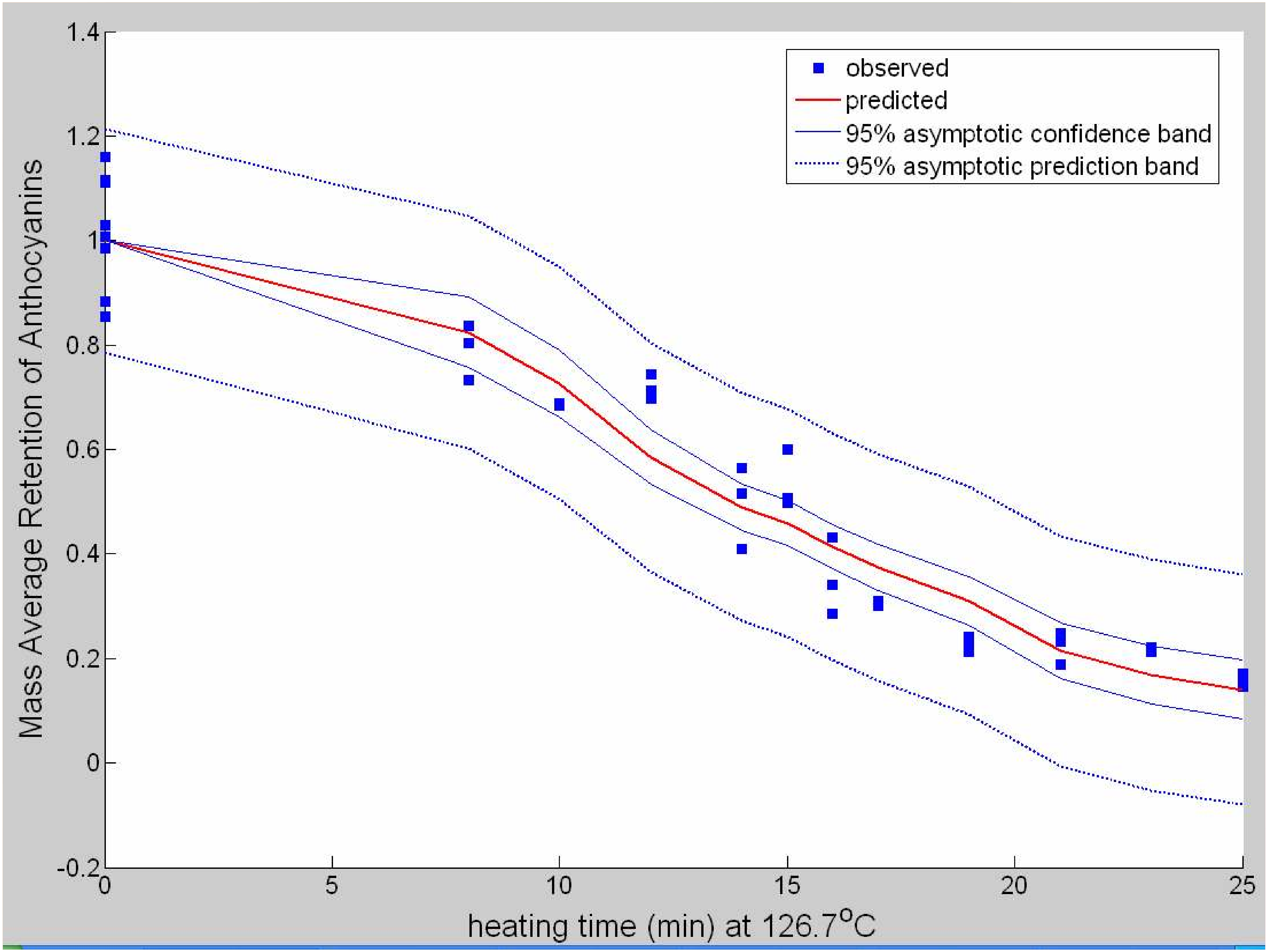



observed
Mass Average Retention of Anthocyanins
Heating time (min) at 126.7°C
0
0.2
0.4
0.6
0.8
1
1.2
1.4
0
5
10
15
20
25

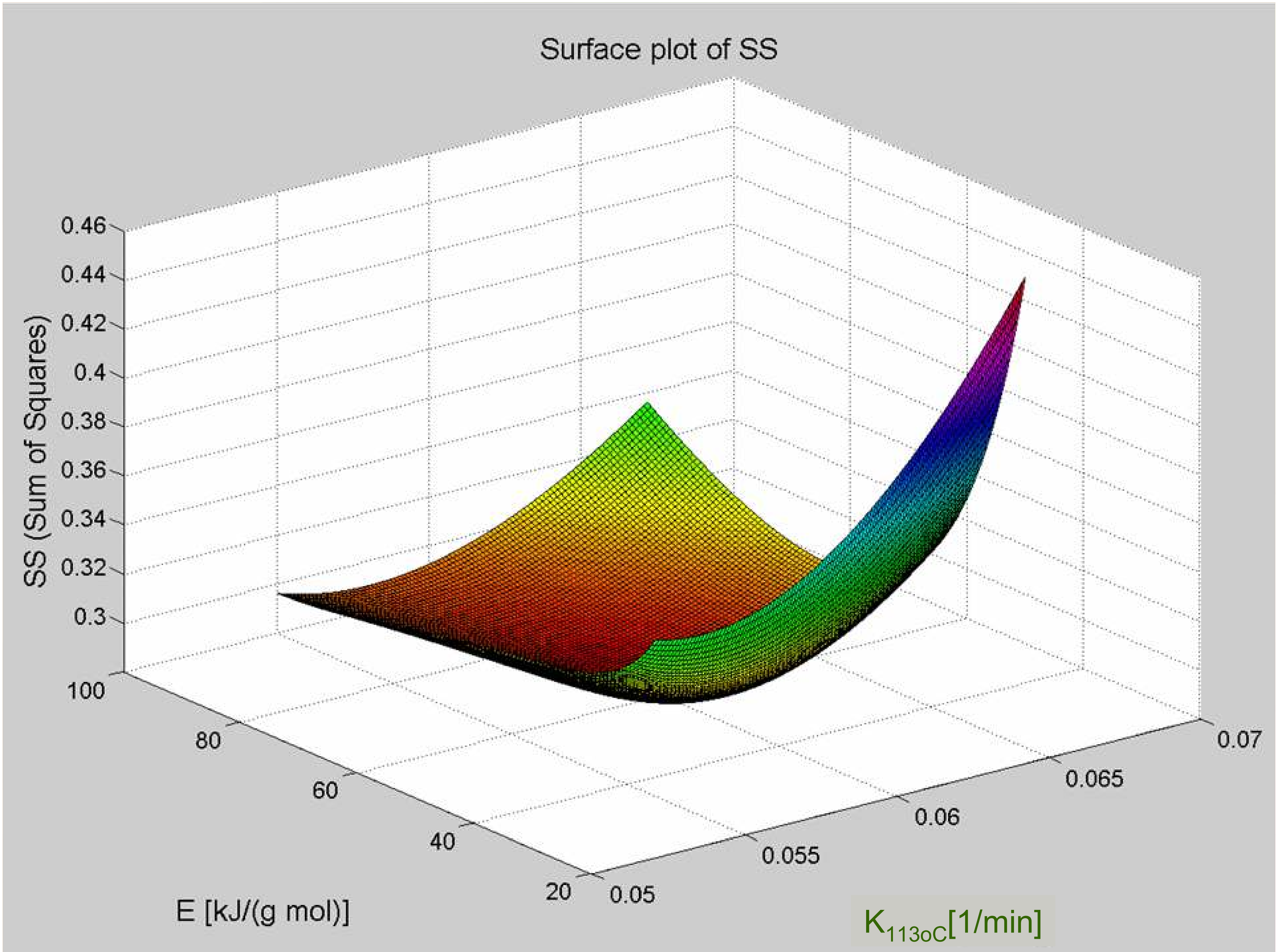

1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
5
10
15
20
25
Mass Average Retention of Anthocyanins
Heating time (min) at 126.7°C
observed
predicted



1.4
1.2
1
0.8
0.6
0.4
0.2
0
Mass Average Retention of Anthocyanins
0
5
10
15
20
25
Heating time (min) at 126.7°C
observed
predicted
95% asymptotic confidence band



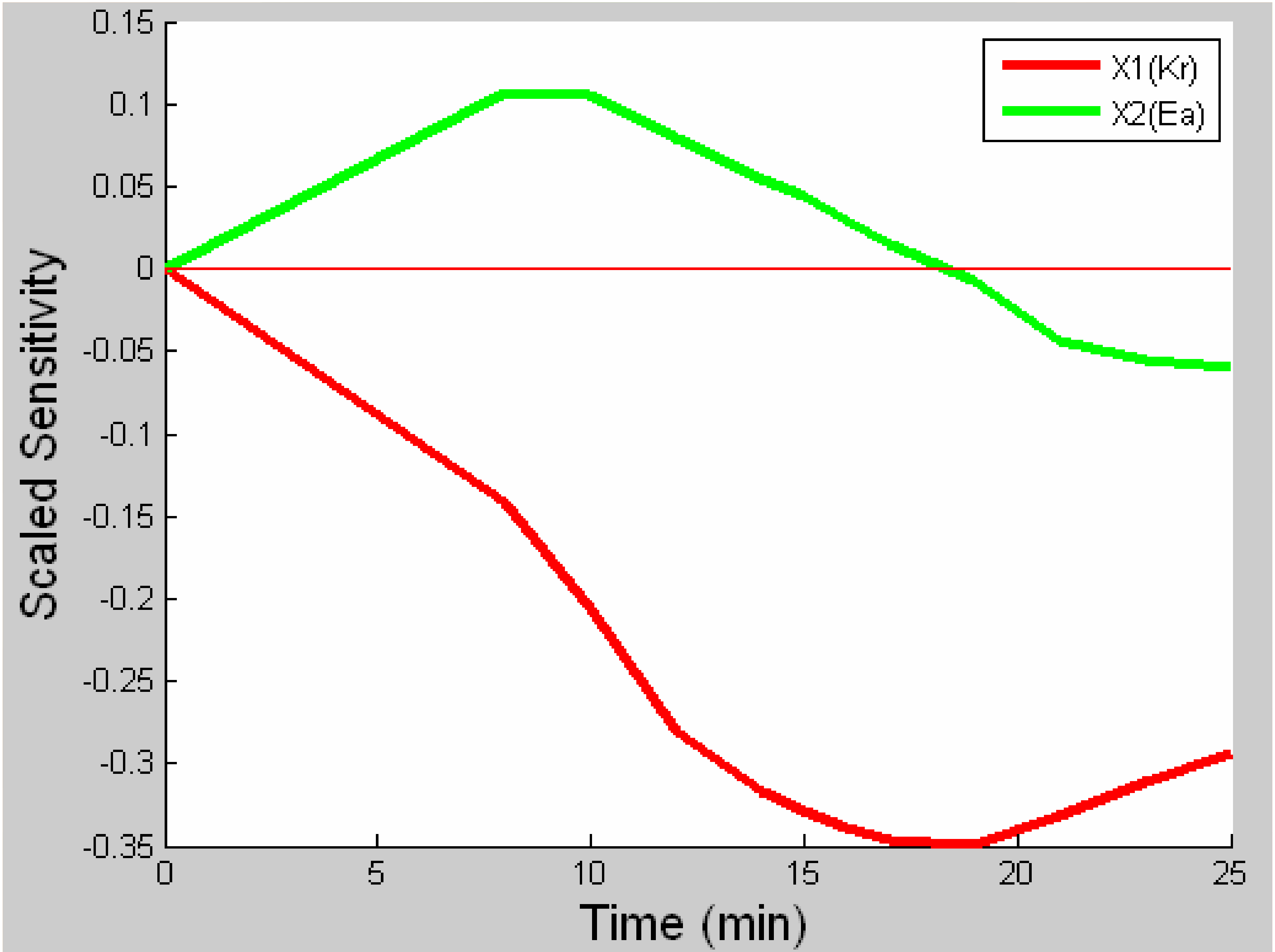
observed
predicted
95% asymptotic confidence band
95% asymptotic prediction band
Mass Average Retention of Anthocyanins
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
5
10
15
20
25
heating time (min) at 126.7°C


Surface plot of SS
SS (Sum of Squares)
0.46
0.44
0.42
0.4
0.38
0.36
0.34
0.32
0.3
100
80
60
40
20
E [kJ/(g mol)]
0.05
0.055
0.06
0.065
0.07
K113oC[1/min]

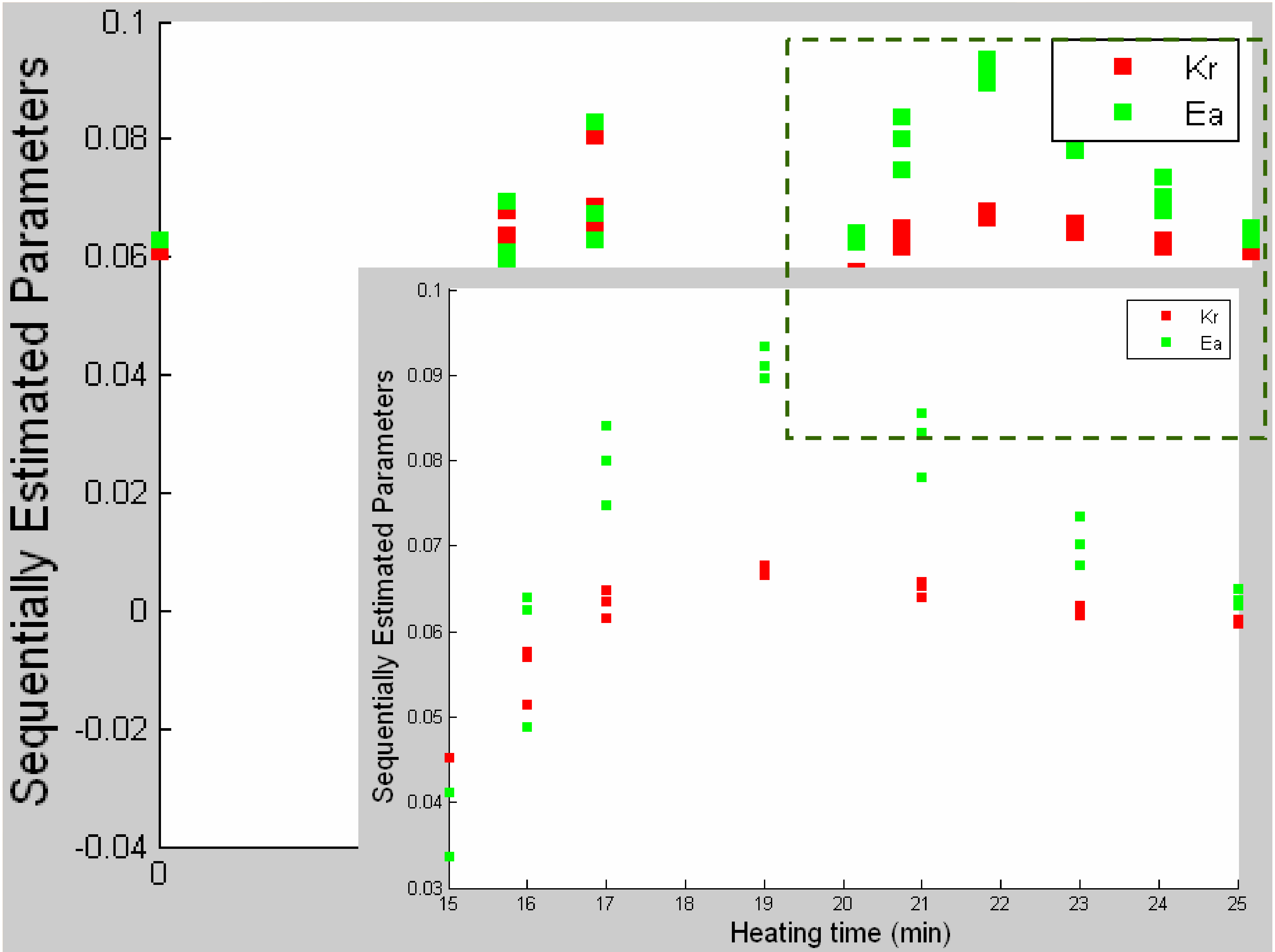
Result - Kinetic Parameters

Parameter	No. of Data	Parameter Estimates	Standard Error	Correlation coefficient	95% asymptotic confidence interval	RMSE
$k_{113.9^oC}$	42	0.0611 min^{-1}	0.0059	$\rho_{k_r E_a}$ =6.49e-5 ρ_{C_o, E_a} =-0.44 ρ_{k_r, C_o} = 0.66	0.0515, 0.0707	4.136
E_a		62.23 kJ/g mol	22.16		17.40, 107.0	
C_o		37.63 µg/ml	1.361		34.88, 40.38	

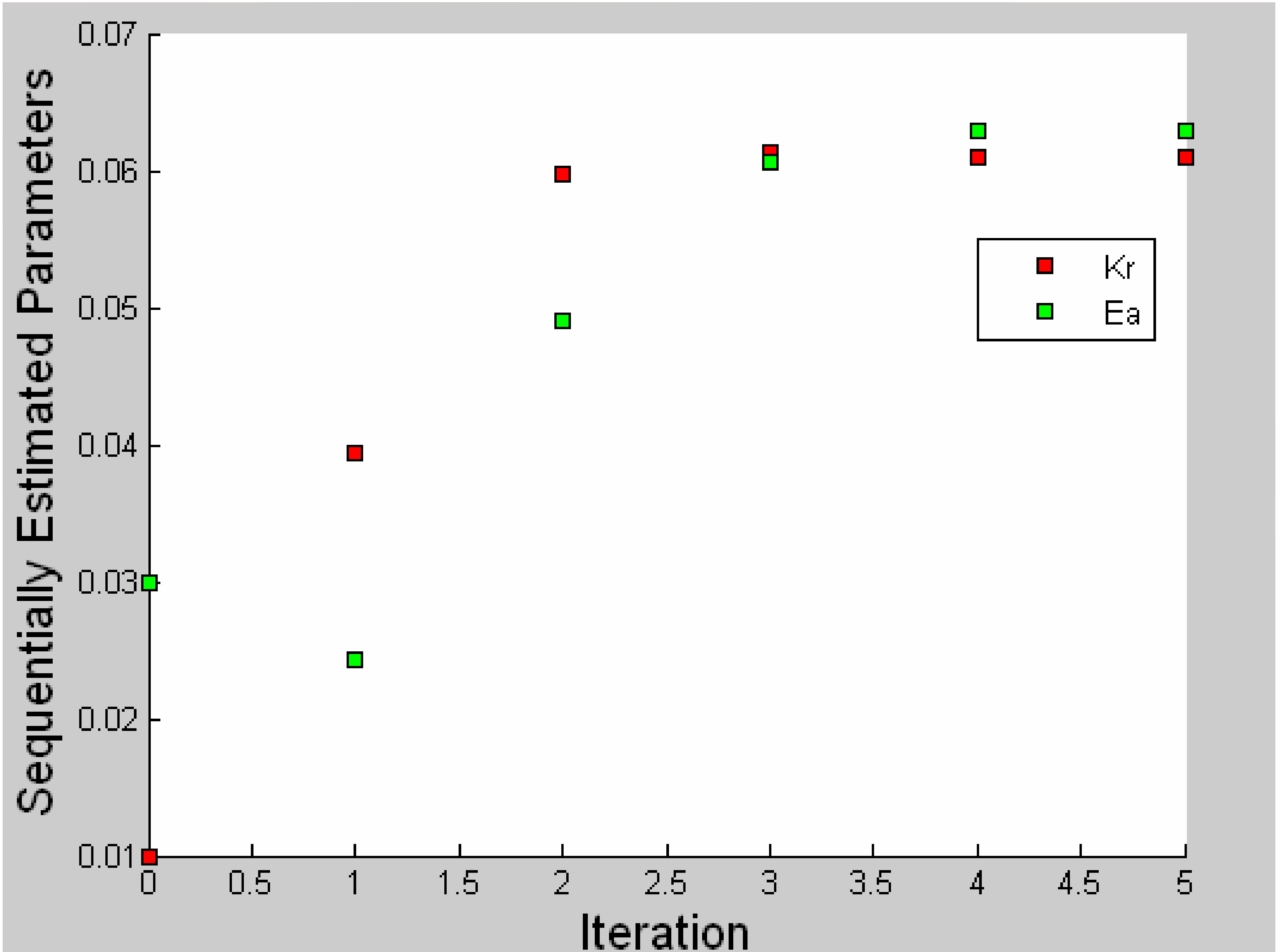
The estimated reference temperature was 113.9 ^oC (confidence interval 96.5,129.6)



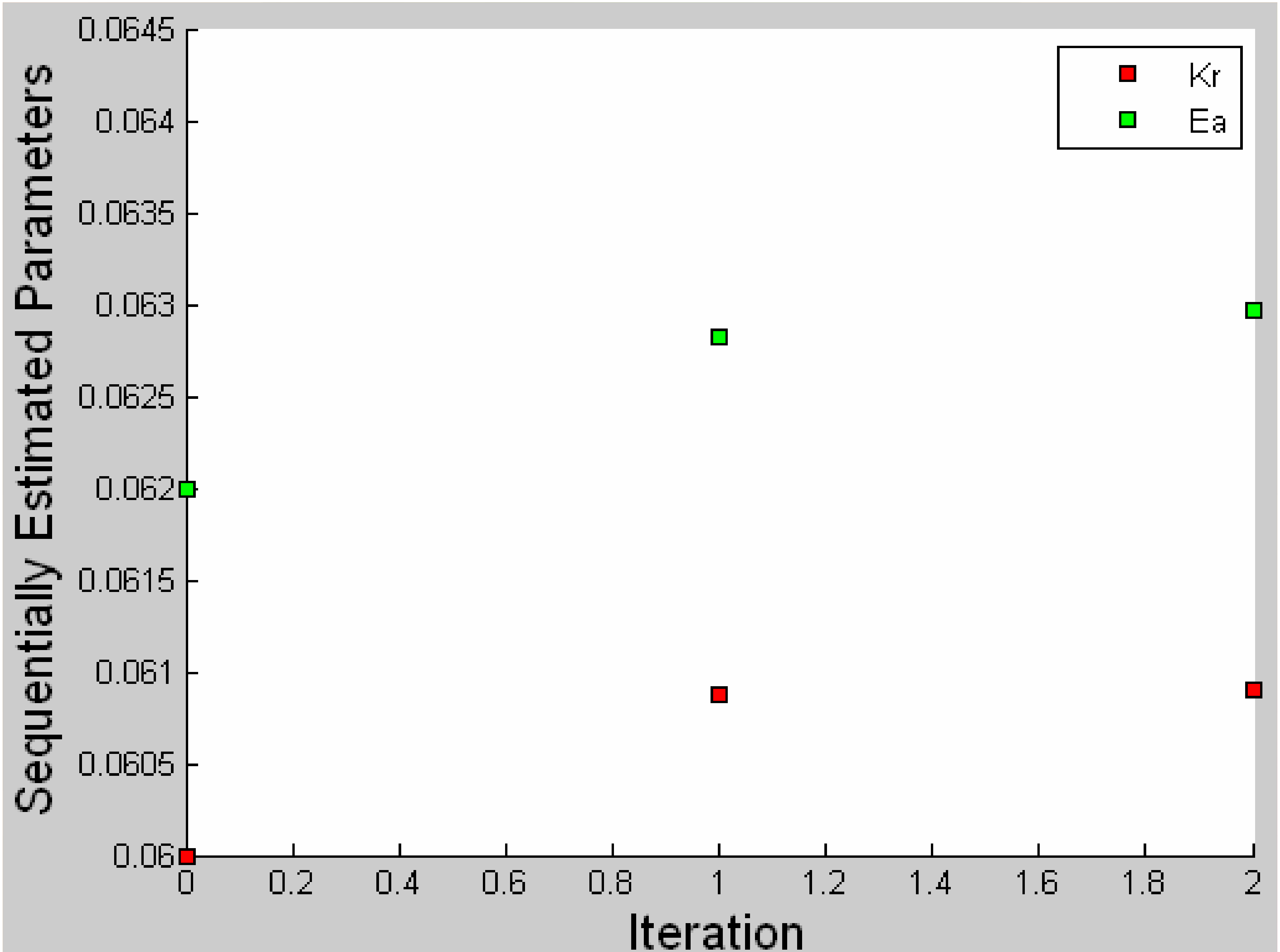
X1(Kr)
X2(Ea)
Scaled Sensitivity
Time (min)
0.15
0.1
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
-0.35
0
5
10
15
20
25



Sequentially Estimated Parameters
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
0
Kr
Ea
Sequentially Estimated Parameters
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
15
16
17
18
19
20
21
22
23
24
25
Heating time (min)
Kr
Ea



0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Iteration
Sequentially Estimated Parameters
Kr
Ea



Sequentially Estimated Parameters
0.0645
0.064
0.0635
0.063
0.0625
0.062
0.0615
0.061
0.0605
0.06
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Iteration
Kr
Ea

Conclusions

Sensitivity coefficient analysis is helpful in determining whether all the parameters are estimable in the model

Sequential estimation provides insight into the parameter estimation process