Reliability of Time Temperature Indicators Under Temperature Abuse

E. SHIMONI, E.M. ANDERSON, AND T.P. LABUZA

ABSTRACT: The present study systematically examined the reliability of 7 MonitorMark time temperature indicators (TTIs) in isothermal and non-isothermal scenarios simulating temperature abuse. The ‘reaction order’ (m) of the response function varies from 0.16 to −3.94. The response of the TTIs under isothermal storage agreed with both the Arrhenius and shelf life plot models, and the calculated activation energies range from 23.3 to 31.3 kcal/mol. Using m and k values from the isothermal experiments, all the TTIs reported the shelf life under temperature-abuse storage within a safe margin. Five indicators showed a positive “history effect”. Given the positive history effect in the studied TTIs and their activation energy range, it is suggested that they may be useful when microbial growth is the major deteriorative mode of the food.

Keywords: time-temperature-indicator, temperature abuse, shelf-life

Introduction

Temperature is the most important factor affecting the quality and safety of food during distribution and storage. While proper packaging can easily control other factors such as gas composition and relative humidity, the temperature of the food depends on the conditions during distribution and storage. While many manufactures and consumers desire shelf life and open date labeling, the difficulty in controlling and knowing the temperature history of the product during distribution and storage makes true shelf life difficult to predict. Non-accurate prediction of shelf life, based on erroneous assumptions of temperature history, may result in products of unacceptable quality, before the stated end of shelf life in cases of temperature abuse. On the other hand, a conservative estimate may lead to waste of good quality products. Temperature abuse of the product may become even more important for food safety. Emerging pathogens such as *Listeria monocytogenes* and *E. coli* H7:O157 may be present in sub-detectable amounts, and grow to an infectious dose after the product has left the factory. This is a major cause for concern in a growing market of ready-to-eat and chilled foods, and was a subject of proposed regulation on temperature control and monitoring in the chill chain (Federal Register. Transportation and storage requirements for potentially hazardous food, Vol. 61, November 22, 1996).

Monitoring the temperature during distribution and storage can provide the accurate and reliable information about the time left to the end of shelf life. This approach can correct the sometimes meaningless expiration dates, and lead to better control of quality and decrease food waste. A tool for achieving these goals is a time-temperature indicator (TTI). TTIs are small, inexpensive devices that show a time-temperature dependent, easily measurable and irreversible change, that can be correlated to changes of quality of a food undergoing the same time-temperature exposure (Taoukis and Labuza, 1989). A variety of TTIs based on different physicochemical principles have been described in the literature (Byrne, 1976; Wells and Singh, 1985; Taoukis and Labuza, 1989). The applicability of TTIs was evaluated for various perishable foods. These include chilled fish (Tinker and others 1985; Taoukis and others 1999), dairy products (Chen and Zall 1985; Grisius and others 1987; Shellhammer and Singh 1991), meat and poultry (Labuza and Fu 1995), frozen strawberries (Singh and Wells 1987), and frozen meats (Rodriguez and Zarizkzi 1983; Singh and Wells 1985; Yoon and others 1994).

Labuza and Taoukis (1989) developed a general approach that allows the correlation of the response of a TTI to the quality changes of a food product of known deterioration modes, without actual simultaneous testing of the indicator and the food. This approach was used to mathematically model 3 major commercial types of TTIs using the Arrhenius kinetics, based on large number of experiments at constant temperatures. This approach was later shown to be also applicable for non-isothermal conditions (Labuza and Taoukis 1989). Fu and others (1991) found this approach efficient in assessment of TTIs for monitoring microbial spoilage of milk.

The objective of this research was to test the response and reliability of a new commercial TTI under isothermal conditions as well as under non-isothermal conditions simulating a temperature abuse scenario.

Materials and Methods

Time-temperature indicators

The time-temperature indicator evaluated in this study was the MonitorMark™ (also known as Freshness Check™, 3M, St. Paul, Minn.) (Arens and others 1997). This TTI is based on a time temperature diffusion of a viscoelastic material into a light-reflective microporous matrix at a rate which varies with temperature to progressively change the light transmissivity of the porous matrix, and thereby provide a visually observable indication. As a result, the indicator changes its color from light to dark gray/black. The indicator is designed as shown in Figure 1. The color change of the center bar depends on the activation energy of the diffusion rate. The end-of-shelf-life point is the time at which the color of center bar and the circle match, therefore the end point can be changed by changing the color of the circle. The TTIs used in this study were designed for various activation energies, and to
different end of shelf life times. All tags were provided by 3M, and activated manually in 3M laboratories.

Data analysis
The data analysis was based on the kinetic approach described by Taoukis and Labuza (1989a,b). The TTI response, L, can be expressed as a function of time in equation 1 where:

\[ F(L) = kt \]  

(1)

In this equation F(L) is the response function of the TTI, t is the time, and k is the response rate constant. Since the order of the reaction for the TTI’s was unknown, their quality function was given the general form of:

\[ F(L) = \frac{1}{m-1} \left( L_f^{-m} - L_0^{-m} \right) = kt \]  

(2)

where m is the reaction order, L_0 is the quality of the TTI at t = 0, and L_t is the quality of the TTI at time t. The values of the reaction order m, and the response rate constant k were calculated by plotting L_f against using the nonlinear regression function of JMP-IN software version 3.2.1 (SAS Institute Inc.).

Given a known end of shelf life value of L_0, m, and k, the exact time to end of shelf life t_{SL} was calculated by:

\[ t_{SL} = \frac{1}{k} \left( \frac{1}{m-1} \left( L_f^{-m} - L_0^{-m} \right) \right) \]  

(3)

The activation energy E_a of the tag was calculated from a plot of ln (t_{SL}) where m is the reaction order, L_0 is the unknown, their quality function was given the general form of:

\[ F(L) = \frac{1}{m-1} \left( L_f^{-m} - L_0^{-m} \right) = kt \]  

Experimental design
In all experiments, tags were prepared fresh at the 3M Co., and transferred immediately over dry ice in an insulated case to the Dept. of Food Science and Nutrition at the Univ. of Minnesota. There were 7 different tags with slightly different molecular weight of diffusant received, labeled 1 to 7. Strips of 15 tags were taped onto aluminum plates (0.25" thick), and the plates were then placed in incubators at the different temperatures to start the experiment. The experimental setup was designed to study the reliability of the TTI's under both isothermal and nonisothermal (temperature abuse) conditions. For the isothermal experiments, 15 tags each were stored at 0, 5, 10, 15, and 22 °C. For the temperature abuse conditions, tags were initially stored at 5 °C, and then transferred for 2 or 6 h to 15 or 22 °C and then back to 5 °C (Table 1). The values of m and k were calculated for each tag separately, followed by the calculation of the exact t_{SL} for every single tag. The L value of the TTI was measured using the color parameter for the tags. A Chroma Meter CR-200 (Minolta, Osaka, Japan) measured the value of L for the center bar with a CR-221 unit, using the L, a, b, color system. Experiments were stopped after the value of L reached the value of the color of the circle (L).

Results and Discussion
The purpose of this study was to evaluate the reliability of the new MonitorMark™ TTI’s. First the response function for the TTI was determined. The MonitorMark™ TTI response is the change of light transmissivity of a porous matrix due to the diffusion of a short polymer in the matrix following Williams-Landel-Ferry kinetics. Since the quality function for this response was unknown, the general equation for an unknown reaction order was used (Eq. 2). By using this equation, the values of the reaction order and rate were calculated, thus allowing the calculation of the shelf life. As shown in Table 2, ‘reaction orders’ calculated were either negative (−2.4 to −3.9) or close to zero (−0.52 to 0.17). These values describe well the color change of the tags, that was slow in the beginning of storage and increased as the TTI was closer to the end of its self life.

Table 1—Temperature abuse conditions. Storage at 5 °C, abuse at 15 or 22 °C for different times and return to 5 °C.

<table>
<thead>
<tr>
<th>TTI No.</th>
<th>Storage temp. [ºC]</th>
<th>Abuse temp. [ºC]</th>
<th>Abuse time [h]</th>
<th>Start</th>
<th>End</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>15</td>
<td>119.75</td>
<td>125.75</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>15</td>
<td>119.75</td>
<td>125.75</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>22</td>
<td>48.12</td>
<td>50.12</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>22</td>
<td>48.08</td>
<td>50.08</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>22</td>
<td>45.72</td>
<td>47.72</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>22</td>
<td>21.4</td>
<td>23.4</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>22</td>
<td>47.68</td>
<td>49.68</td>
<td></td>
</tr>
</tbody>
</table>

The data analysis was based on the Arrhenius plot (Table 2). In Figure 4, F(L) as a function of time for 5 constant temperatures is plotted using the data from 15 tags of the same type at each temperature and time point. The values of k for the TTI’s were calculated from these plots. Plotting ln k against 1/T gave very good linear fit (Table 2), verifying the assumption that the indicators follow an Arrhenius behavior over a narrow temperature range even though the diffusion process follows the WLF equation as was established by Nelson and Labuza (1994). From the Arrhenius plot the kinetic parameters of the TTI’s were derived (Table 2). The activation energies obtained were close to the expected for spoilage microorganisms. For example 16.2 kcal/mol (76.2 kJ/mol) for Pseudomonas fragi in skim milk model system (Fu and others 1991), and 19.5 kcal/mol (81.6 kJ/mol) for Pseudomonas spp. or 19.8 kcal/mol (82.7 kJ/mol) at 5 °C, where the color of the center bar (L) is plotted against time, giving a curve that was typical for all the TTI’s that were tested. If the response function F(L) is plotted against time, as in Figure 3, a straight line is obtained. The data showed high linear fit to the response function (Eq. 2) calculated by the kinetics parameters from the Arrhenius plot (Table 2). In Figure 4, F(L) as a function of time for 5 constant temperatures is plotted using the data from 15 tags of the same type at each temperature and time point. The values of k for the TTI’s were calculated from these plots. Plotting ln k against 1/T gave very good linear fit (Table 2), verifying the assumption that the indicators follow an Arrhenius behavior over a narrow temperature range even though the diffusion process follows the WLF equation as was established by Nelson and Labuza (1994). From the Arrhenius plot the kinetic parameters of the TTI’s were derived (Table 2). The activation energies obtained were close to the expected for spoilage microorganisms. For example 16.2 kcal/mol (76.2 kJ/mol) for Pseudomonas fragi in skim milk model system (Fu and others 1991), and 19.5 kcal/mol (81.6 kJ/mol) for Pseudomonas spp. or 19.8 kcal/mol (82.7 kJ/mol)
for *Shewanella putrefaciens* in chilled fish (Taoukis and others 1999).

The shelf life plot (Figure 5) approach was also used to calculate $Q_{10}$ values for the TTI’s. The normalized $Q_{10}$ and activation energy values are shown in Table 3 using the procedure of Taoukis and others (1997). The activation energies from the shelf-life plot (Table 3) ranged from 23.4 to 30.4 kcal/mol. It was also found that the tags by changing the color of the outer circle could easily detect a range of shelf life times at the same temperature sensitivity. For example, tags 6 and 7 have similar $E_a$ values (23.59 and 23.46 respectively), however, they will ‘report’ end of shelf life at 7.43 and 14.42 d respectively. It should be noted that although $E_a$ values calculated by the shelf life plot method are generally lower than the values from the Arrhenius plot as is expected based on the method (Taoukis and others 1997), the activation energies from both methods have a good and significant correlation ($r^2 = 0.944, p < 0.0003$).

The 2nd part of this study examined the reliability of the MonitorMark™ TTI in storage, simulating a situation of a stepwise temperature abuse. Tags were stored at 5°C, transferred to an elevated temperature for a short period, and returned to storage at 5°C until end of shelf life was recorded as shown in Table 1. The calculation of the predicted shelf life under temperature abuse conditions was based on the parameters shown in Figure 6. The values of $L_1$ and $L_2$ were calculated by Eq. (4) using $L_0$ and $L_1$ as the initial L value respectively. The predicted $t_{SL}$ was calculated using Eq. (5). The experimental $t_{SL}$ was calculated for each group of 15 tags, based on Eq. (5) using the 1st value of L measured after $t_2$ as $L_2$.

$$L_i = \frac{1}{e} \left( m_L L_0 t + L_0^{1/e} \right)$$

(4)

$$t_{SL} = t_2 + \frac{1}{k_{1/2} \ln(2)} \left( \frac{1}{L_{1/2}^{1/e}} - L_2^{1/e} \right)$$

(5)

The results for the MonitorMark™ TTI’s are presented in Figure 7. The results are shown as the average of 15 shelf life points for each TTI ± the standard deviation. All of the 7 TTI’s that were tested showed a decreased time to endpoint compared to isothermal storage at 5°C. The shelf life of TTI 2 and 3 were exactly as predicted by the response function and by the kinetic parameters calculated from the isothermal experiments. The end of shelf life for the other 5 TTI’s (1,4,5,6,7) was shorter than that predicted by the kinetic model. Therefore, all the TTI’s responded exactly to the temperature abuse, or they changed color sooner. A linear correlation was found for the measured against predicted shelf life under abused storage over all tags (Fig-

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**Table 2—Kinetic parameters of the MonitorMark™ TTI’s from the Arrenius plot, and their fit to the data from isothermal storage.**

<table>
<thead>
<tr>
<th>TTI No.</th>
<th>$m \pm SD$</th>
<th>$k_0 \pm SD$ [h⁻¹]</th>
<th>$E_a \pm SD$ [kcal/mol]</th>
<th>Fit to data $r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-3.038 ± 0.755</td>
<td>4.197 ± 0.735</td>
<td>31.39 ± 1.174</td>
<td>0.965</td>
</tr>
<tr>
<td>2</td>
<td>-3.382 ± 0.207</td>
<td>4.162 ± 0.340</td>
<td>29.12 ± 0.791</td>
<td>0.990</td>
</tr>
<tr>
<td>3</td>
<td>-2.386 ± 0.310</td>
<td>3.978 ± 0.587</td>
<td>25.06 ± 1.012</td>
<td>0.959</td>
</tr>
<tr>
<td>4</td>
<td>-3.940 ± 0.370</td>
<td>4.232 ± 0.978</td>
<td>30.37 ± 1.496</td>
<td>0.976</td>
</tr>
<tr>
<td>5</td>
<td>-3.100 ± 0.759</td>
<td>4.049 ± 0.869</td>
<td>25.81 ± 1.341</td>
<td>0.971</td>
</tr>
<tr>
<td>6</td>
<td>-0.515 ± 0.697</td>
<td>3.767 ± 0.947</td>
<td>23.39 ± 1.450</td>
<td>0.988</td>
</tr>
<tr>
<td>7</td>
<td>0.166 ± 0.389</td>
<td>3.690 ± 0.901</td>
<td>23.53 ± 1.385</td>
<td>0.990</td>
</tr>
</tbody>
</table>

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**Figure 3**—$F(L)$ as compared with time for all samples of TTI #2, stored at 5°C with least square linear fit and 95% confidence limit ($r^2 = 0.995$)
ure 6, $r^2 = 0.983$), and the measured shelf life was $0.922 \times$ that predicted for these conditions. It is therefore concluded that these TTI can provide a safe margin for temperature abuse, as may occur during storage and distribution.

An interesting trend in the reaction of these TTI’s to temperature abuse is a “History effect”. Overall the TTI’s showed a positive “history effect” that is, an acceleration of their response rate at low temperature after being exposed to abusive storage conditions at elevated temperature. Although it may be a negative observation as far as the accuracy of the prediction models, Taoukis and Labuza (1989) noted that such history effect has been shown to occur for deteriorative reactions in foods, for example, in lipid oxidation (Labuza and Ragnarsson 1985) and loss of thiamin in dry foods (Kam and others 1981). Several studies of microbial growth have also shown history effects (Ng and others 1962; Powers and others 1965; Shaw 1967; Fu and others 1991; Dufrenne and others 1997). Fu and others (1991) showed a positive “history effect” on the growth rate of *Pseudomonas fragi* in a skim milk model system, and that these effects were more profound when the temperature changes were stepwise against occurring in a sine wave. It is therefor evident, that when the deterioration mode that determines the end of shelf life has a positive “history effect”, TTI’s that show similar effect may be extremely beneficial. On the other hand, it may be an economic concern since they may signal the end of shelf life before it actually occurs.

**Conclusion**

In the present study, we have systematically examined the reliability of TTI’s in isothermal and non-isothermal scenarios simulating temperature abuse. The “reaction order” ($m$) of the response function varies from one TTI to another thus it should be measured for each TTI group prior to use. Once $m$ is known the response of the TTI’s under isothermal storage agreed with both the Arrhenius and shelf life plot models. Using $m$ and $k$ values from the isothermal experiments, the shelf life under abused storage were reported with safe margin by all the TTI’s, 5 of which showed positive “history effect”. As was shown previously (Taoukis and Labuza 1989), monitoring the quality by application of TTI in food products could be achieved only when the kinetic parameters for both the food and TTI are well characterized. Given the positive history effect in the studied TTI’s and their activation energy range, it is suggested that they may be useful when microbial growth is the major deteriorative mode of the food.

**Table 3**—Activation energies, $Q_{10}$, and shelf life at $22^\circ$C of the MonitorMark™ TTI’s from the shelf-life plot.

<table>
<thead>
<tr>
<th>TTI No.</th>
<th>$Q_{10}$</th>
<th>$E_a$ [kcal/mol]</th>
<th>Fit of results to model</th>
<th>Shelf life at $22^\circ$C ± SD</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>7.0</td>
<td>29.31</td>
<td>29.72</td>
<td>28.97</td>
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<tr>
<td>2</td>
<td>6.2</td>
<td>29.31</td>
<td>29.72</td>
<td>28.97</td>
</tr>
<tr>
<td>3</td>
<td>4.7</td>
<td>24.91</td>
<td>25.27</td>
<td>24.53</td>
</tr>
<tr>
<td>4</td>
<td>5.2</td>
<td>29.12</td>
<td>28.63</td>
<td>27.78</td>
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<tr>
<td>5</td>
<td>6.2</td>
<td>26.38</td>
<td>26.90</td>
<td>25.85</td>
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<tr>
<td>6</td>
<td>4.4</td>
<td>22.59</td>
<td>24.22</td>
<td>22.95</td>
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<td>7</td>
<td>4.3</td>
<td>27.56</td>
<td>29.10</td>
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