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SHELF LIFE MANAGEMENT USING MULTIPLE COMPONENT TIME-TEMPERATURE INTEGRATORS

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ABSTRACT

Prerequisite of TTI application is that the TTI response and the food quality loss reaction have the same activation energy (E_A). Estimating the effect of this "error" in quality prediction, this requirement can be overcome by the use of multiple-component TTI systems. Such systems, with time range at 5°C from 2d to few weeks were experimentally studied in the temperature range 0 to 15° C and the established kinetic models were validated under dynamic conditions.
Key words: shelf life prediction, TTI, multiple response, temperature profiles

INTRODUCTION

Practice and industrial studies have shown that temperature conditions in chill distribution, handling, transport and storage often deviate from the recommended ones. Thus, monitoring, recording and controlling them becomes crucial for product's safety and quality as well as for shelf life predictions and expiration date labeling [1]. A cost-effective way would be the application of suitable Time Temperature Indicators (TTI). TTI are small, inexpensive devices that show an easily measurable, time-temperature dependent change that reflects the full, or partial temperature history of a food product to which it is attached. The principle of TTI operation is a mechanical, chemical, electrochemical, enzymatic or microbiological irreversible change, usually expressed as a visible response, in the form of a mechanical deformation, color development or color movement [2]. Since the rate of change depends on temperature, TTI response offers an integrated representation of the storage conditions. Prerequisite for application of TTI is the development of a correlation scheme, which would translate TTI response to the quality status of the food at any point of the distribution chain. Basic structural elements of this scheme are validated kinetic models of TTI response and kinetics of the degradation indices of the food, such as predictive models of microbial growth. By translating their response to the respective temperature handling throughout the chill chain, TTI can serve as temperature monitors and tools for the optimization of stock management [3,4].
In the present study, enzymatic TTI were kinetically studied in a wide range of chill temperature conditions and the established kinetic models were validated in dynamic storage conditions. The importance of the (E_{Afood}-E_{ATTI}) difference in the accurate prediction of food status and remaining shelf-life was assessed. An objective of this work was to develop a procedure for using multiple-component TTI systems, with different kinetic characteristics.

MATERIALS AND METHODS

Enzymatic TTI (VITSAB AB, Malmö, Sweden), Type M and L were kinetically studied in the range between 0 and 15°C, in isothermal incubators (Sanyo MIR 153, Sanyo electric Co., Ora-Gun, Japan), with temperature being constantly monitored by type T thermocouples and a multichannel datalogger (CR10X, Campbell Scientific, Leicestershire, U.K.). For the validation of the established models, experiments under non-isothermal conditions were also performed in the aforementioned programmable incubators, applying different dynamic time-temperature cycles. These TTI are based on a color change caused by a pH decrease, due to a controlled enzymatic hydrolysis of a lipid substrate. Before the activation, the lipase and the lipid substrate are in two separate minipouches. The activation is realized by mechanically breaking the barrier that separates them, and the enzyme is mixed with the substrate, leading to the initialization of the enzymatic reaction. The progression of this chemical phenomenon is visualized by a gradual color change from deep green to bright yellow, via a transparent window. Tested TTI were of Type M4-5, M4-10 and M4-20, with different enzyme concentration. Similarly, Type L10-1, L10-3 and L10-5, with different expiration times, were kinetically studied at the same temperature range.

TTI response measurement

Color change can be visually graded on a 6-point reference scale constructed from TTI inactivated at a certain level or quantitavely measured on the CIELab scale, with the Minolta CR-200, Chromameter. The TTI response, X_c (normalized chroma) was then calculated from eq. (1):

$$X_c = \frac{C - C_{min}}{C_{max} - C_{min}}, \text{ where } C = \sqrt{a^2 + b^2} \quad (1)$$

where C_{min} is the minimum measured chroma value at the time of TTI inactivation and C_{max} the chroma value that corresponds to the value reached after the endpoint of the TTI. When X_c is plotted as a function of time, it has a sigmoidal shape, rather similar to a Gaussian function (with general equation $X=1-\exp[-(kt)^2]$). Thus, use of the former generalized equation leads to the following form of linearized response function (eq.(2)):

$$F(X_c) = \sqrt{\ln\left(\frac{1}{1-X_c}\right)} = k_I t \quad (2)$$

where k_I is the response rate of the tested TTI.

TTI application scheme

An algorithm, illustrated in Fig.1, is introduced that allows the correlation of the TTI response to a characteristic quality or safety index A of the food. Assuming the applicability of the Arrhenius law for describing the temperature dependence of the response rate of TTI, eq. (2) becomes (eq3):

$$F(X_c)_t = k_I t = k_{I_o} \exp\left(\frac{-E_{A_I}}{RT}\right) t \quad (3)$$

where the constant k_{Io} and the activation energy E_{Ai} are the Arrhenius parameters. For a non-isothermal temperature distribution T(t), the term of the effective temperature T_{eff}, which is the constant temperature that causes the same response (or change) as the variable profile T(t), is introduced and the response function can be expressed as follows (eq. (4)) [5]:

$$F(X_c)_t = \int_0^t k\,dt = k_{I_o} \int_0^t \exp\left(\frac{-E_{A_I}}{RT(t)}\right) dt = k_{I_o} \exp\left(\frac{-E_{A_I}}{RT_{eff}}\right) t \quad (4)$$

Similarly, the change of the parameter A of the food needs to be modelled, following a similar methodology, in a way that a linearized model f(A)=kt, is established. For a TTI going through the same temperature distribution T(t) as the attached food in question, the value of $F(X_c)_t$ can be calculated from the measured response. The value of T_{eff} is then estimated from the second part of eq. (4), which combined to the kinetic parameters of the food spoilage model, the quality and safety status of the food, described by the corresponding $f(A)_t$ value can be assessed.

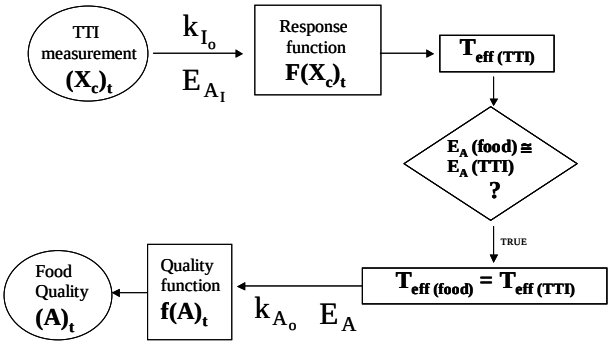

Fig.1: Schematic illustration of the correlation algorithm for the application of TTI as food quality monitor

As it is depicted in Fig. 1, the estimation of the effective temperature T_{eff} is the ultimate information obtained from the TTI response, which will be translated to food remaining shelf life. Consequently, TTI reliability is related to the error in T_{eff}. An important source of error is the uncertainty in the Arrhenius equation, statistically expressed by the confidence limits of the regression values of E_{Ai} and k_{Io}. Secondly, any difference between the activation energies of the TTI and the food poses a systematic error, that is reflected in the shelf-life remaining prediction. As it is depicted in Fig1, a significant prerequisite for successfully "mimicking" food handling and distribution with TTI, is to select a TTI with an activation E_{Ai} close to that of the food spoilage (E_A).

RESULTS AND DISCUSSION

Kinetic analysis of TTI

According to eq. (2), the response rate k_I at each experimental constant temperature can be calculated by plotting $F(X_C)_t$ vs time, by linear regression analysis (Fig2a). The temperature dependence of the response rate of TTI, Type L10-3 was modelled by the Arrhenius equation (Fig 2b). Similarly, Type M was also kinetically studied. Arrhenius results for the parameters E_{Ai}, including the 95% confidence range of all types of TTI studied are summarized in Table 1. Shelf life of all TTI is also estimated from the established models at 2 temperatures in the range of interest (Table 1).

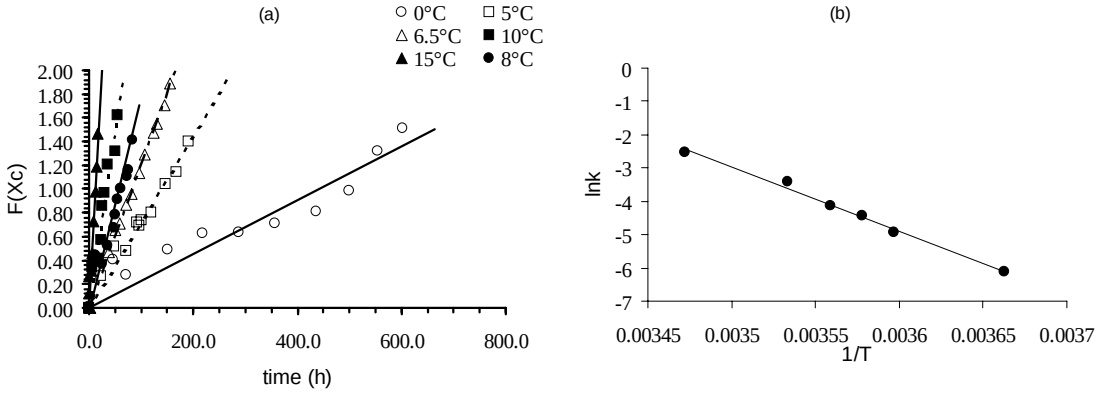

Fig 2: (a) Response vs time at 6 constant temperatures and (b) Arrhenius plot of the response rate for TTI type L10-3.

Table 1: Arrhenius kinetic parameters for enzymatic TTI, type M and L

Type of TTI	E_{Ai} (kJ/mol)	R^2	Total response time (h)	
			0°C	10°C
M4-5	69.0±13.8	0.988	181	62
M4-10	76.0±18.0	0.972	432	133
M4-20	75.2±20.2	0.964	836	260
L10-1	151.0±4.9	0.995	174	17
L10-3	160.1±21.9	0.991	646	54
L10-5	155.7±51.9	0.946	1649	146

In all cases of studied TTI, the established kinetic equations were validated at different time-temperature profiles, with stepwise temperature shifts, within the range studied. Such a profile, shown in the interior of Fig.3, with an estimated effective temperature, T_{eff}= 4.9°C represents temperature shifts, that frequently occur in the real chill chain. The agreement between prediction using the established kinetic model for TTI, Type M4-10 and experimental results was satisfactory, since closed circles lie in between the 95% confidence limits, that were estimated using SYSTAT 8.0® (CLECOM, Software specialists; Birmingham, U.K). In the case shown, the predicted rate, according to joint confidence contour analysis, was found to have an upper and lower limit of $5.32*10^{-3}$ and $8.82*10^{-3}$ (h^{-1}) respectively and the experimental value was estimated $k_{exp}=6.92*10^{-3}$ (h^{-1}), (R^2=0.953). Results for all types of TTI, Type M and L were similarly satisfactory when different temperature profiles were used, with different T_{eff} (T_{eff}≅7.5 and 11.8°C).

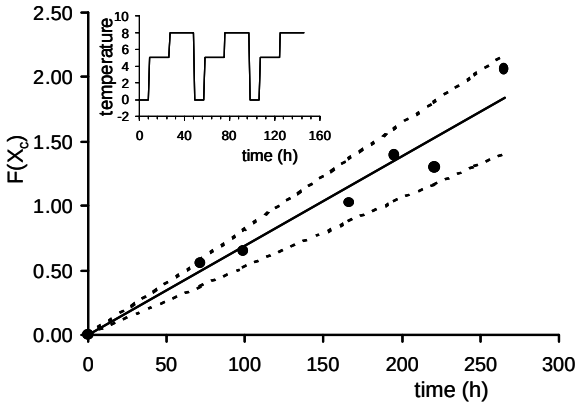

Fig. 3: Comparison of experimental (closed circles) and predicted results of Type M4-10 response for exposure at the shown variable temperature profile. The solid line represents the linear fit of the response measurements and dotted lines depict the upper and lower 95% confidence band of TTI response predicted for the estimated T_{eff}

In order to assess the significance of the difference between E_{Afood} and E_{ATTI}, an indicative temperature scenario of chill distribution for a food with $E_A \cong 70$kJ/mol was assumed and the T_{eff} was calculated based on the responses of TTI of a wide E_A range (Fig.4).

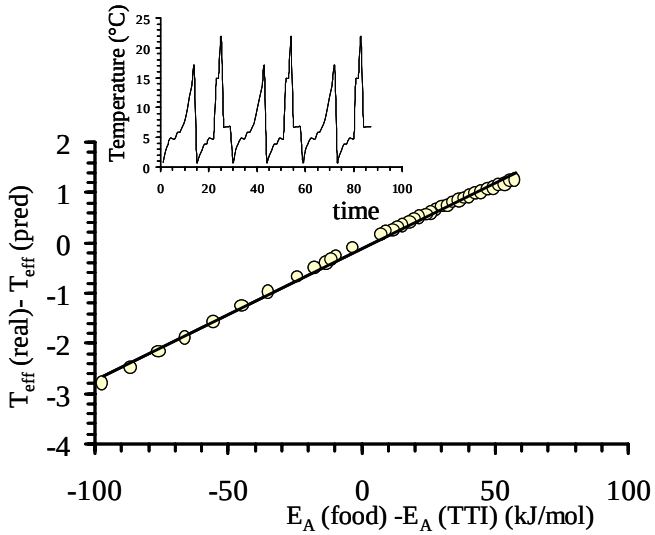

Fig. 4: Effect of the difference (E_{Afood}-E_{ATTI}) on the prediction of T_{eff} for the illustrated temperature profile.

To evaluate the effect of the error in T_{eff} estimation on quality prediction, a case study is assumed, where different TTI are attached on MAP (20% CO_2) ground lamb products. Microbial growth data were collected and studied within the SMAS project [5], and the respective Arrhenius parameters were estimated, giving a value of E_A of lactic acid growth of 70.3 kJ/mol, which is almost identical to the one calculated for the response of TTI, type M. Based on collected kinetic data i.e. initial population, $\log N_o \cong 2.5$, population at the expiration time $\log N_s \cong 8$, shelf life@0°C≅305h, exponential growth ($N=N_o e^{kt}$) and the Arrhenius law temperature dependence, one can estimate the effect of the error in T_{eff} evaluation (assessed by the attached TTI response) on the microbial population prediction and, consequently, on the remaining shelf life evaluation (Fig 5).

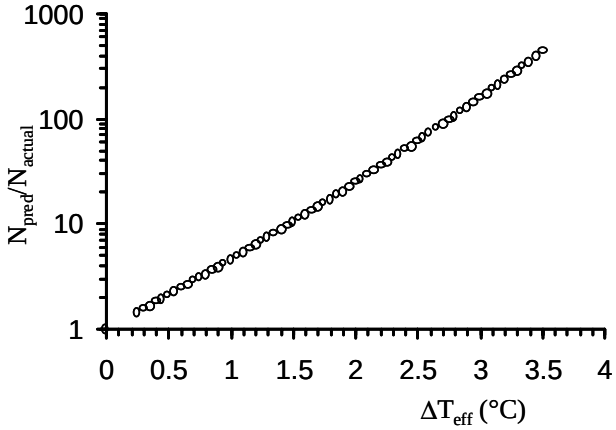

Fig.5: Effect of the error in the prediction of T_{eff} on the estimation of the microbial population

Using TTI of Type M, there would practically be no error in the estimation of the microbial population. With TTI of Type L, T_{eff} is overestimated ($\Delta T_{eff} \cong 2.2$°C), leading to an error of approximately 1.6 log cycles, which is translated to about 25h underestimation of the actual shelf life of the product, under the specific temperature conditions illustrated in Fig 4. Consequently, the necessity of minimizing this error in the prediction of T_{eff} is crucial for the systematic application of TTI as quality and safety monitors in the chill chain. In this context, the potential use of a multi-component instead of single TTI-system was tested, where the prediction was made by the appropriate combination of the response of tags of different E_A. A similar approach has been proposed for thermal process TTI [6].

According to Fig.4, for the specific food studied, ΔT_{eff} estimated is proportional to the ΔE_A between the food and the attached TTI (eq 5):

$$\Delta T_{eff} = \alpha \Delta E_A \quad (5)$$

Applying the same temperature profile for different E_{Afood} ranging from 60 to 170 kJ/mol, the same linearity between ΔT_{eff} and ΔE_A was observed, and parameter α, was found to be practically independent of the E_{Afood}. The value of α is actually a correction factor that minimizes the error in T_{eff} prediction and it can be estimated quite accurately using two TTI of different kinetic characteristics, from the following equation (eq.6):

$$\alpha = \frac{T_{eff}(TTI_1) - T_{eff}(TTI_2)}{E_A(TTI_1) - E_A(TTI_2)} \quad (6)$$

Then, the T_{eff} could be better predicted, using the following equation (eq. 7):

$$T_{eff}(\text{predicted}) = T_{eff}(TTI_1) + \alpha \bullet \left(E_A(\text{food}) - E_A(TTI_1)\right) \quad (7)$$

In Table 2, predictions of T_{eff} by single TTI (of the two types M and L available) are compared to the ones made by the double system TTI, using the temperature profile of Fig. 4, showing the significant improvement accomplished. The E_{Afood} used was approximately 83 kJ/mol, corresponding to the microbial spoilage of chilled fish (boque), studied by Taoukis et al, 1999 [7].

Table 2: Comparison of T_{eff} prediction, based on single or double TTI response, for fish boque, using TTI of Type M and L

	E_A (TTI) (kJ/mol)	**T_{eff} predicted (°C)**	**ΔT_{eff} ($T_{eff(act)}$-$T_{eff(TTI)}$)**
Single TTI	69	8.58	0.39
	151	10.76	-1.79
Double TTI	(69-151)	8.95	0.02

CONCLUSIONS

In this study, the applicability of TTI as reliable tools for chill chain monitoring was studied and their effectiveness was assessed in predicting the temperature history of food. A prerequisite for TTI use is a thorough isothermal kinetic study, followed by validation of the established kinetic model under dynamic conditions. The use of a multiple system offers a sound alternative to the single TTI, minimizing the error in the prediction of the T_{eff} of the food.

Based on TTI application, the principles of a safety management system for the optimisation of the distribution of chilled food products at the time of consumption are developed in a EE funded programme, coded “Safety Monitoring and Assurance System” (SMAS). In this system, instead of the conventional first in first out (FIFO) method a new approach based on actual risk evaluation at important points of the chill chain is used, in order to promote products to the next stage of distribution. This evaluation based on continuous product temperature monitoring by TTI, and the use of predictive models for the growth of food pathogens and quality deterioration, allow to give priority to products in such a way that risk at consumption time is minimized and quality optimally managed.

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Information on the project can be found at http://smas.chemeng.ntua.gr

REFERENCES

[1] Taoukis P.S., Labuza T.P. Applicability of Time-Temperature Indicators as Shelf Life Monitors of Food Products. Journal of Food Science, 54, 783-788, 1989.
[2] Taoukis P.S. Modelling the use of time-temperature indicators. Food process modelling. Ed. L.M.M. Tijskens, M.L.A.T.M. Hertog, B.M Nicolai, 402-431, Woodhead Publishing In Food Science and Technology, England, 2001.
[3] Giannakourou M.C., Taoukis P.S. Systematic application of Time-Temperature Indicators as tools for control of frozen vegetable quality. Journal of Food Sciencce, 67, 2221-2228, 2002.
[4] Giannakourou M.C., Taoukis P.S. Application of a TTI-based distribution management system for quality optimisation of frozen vegetables at the consumer end. Journal of Food Science, 68, 201-209, 2003.
[5] “Development and Application of a Safety Monitoring and Assurance System for Chilled Meat Products, SMAS” (2003-2006), EE funded action project, under the key action of Food, Nutrition and Health of the “Quality of Life and management of living resources” thematic programme, (QLK1-2002-02545), http://smas.chemeng.ntua.gr.
[6] Stoforos N.G., Taoukis P.S. A theoretical procedure for using multiple response time-temperature integrators for the design and evaluation of thermal processes. Food Control, 9, 279-287, 1998.
[7] Taoukis P.S., Koutsoumanis K., Nychas G.J.E. Use of time-temperature integrators and predictive modelling for shelf life control of chilled fish under dynamic storage conditions. International Journal of Food Microbiology, 53, 21-31. 1999.