Historical review and state of the art in Time Temperature Integrator (TTI) technology for the management of the cold chain of refrigerated and frozen foods

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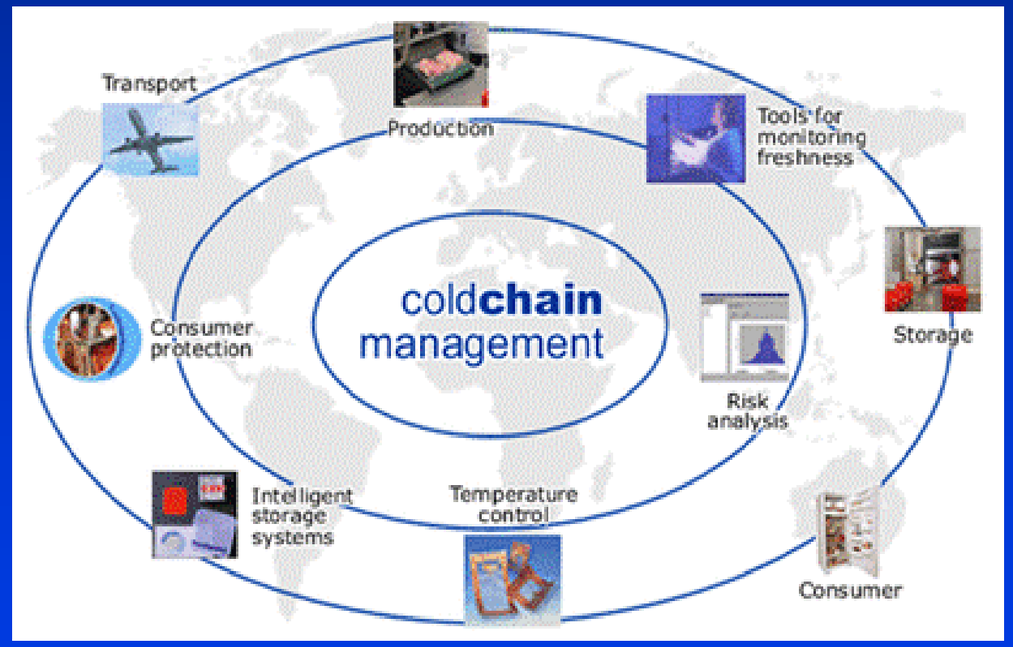


National Technical University of Athens, School of Chemical Engineering,
Laboratory of Food Chemistry & Technology

FOOD QUALITY ASSURANCE

Current philosophy :

- Decrease of focus on end product testing and verification traditional cornerstones of quality and regulatory control
- Development and application of structured quality assurance systems based on prevention by monitoring, controlling and recording of critical parameters through product's entire life cycle

Monitoring tools for chill chain

Need for development of practical systems to monitor, record and translate the effect of temperature from production to consumption.

Time Temperature Integrators (TTI)

A prerequisite for effective application of a TTI based control system is the determination and kinetic study and modeling of the food quality loss indices and of the response of the TTI.

INTRODUCTION

Active packaging
vs
Intelligent (Smart) packaging

Direct Quality Indicators vs Indirect Quality Indicators

Time Temperature Integrators (TTI)

CHARACTERISTICS OF THE ACTUAL CHILL CHAIN

Weak links in the chill chain

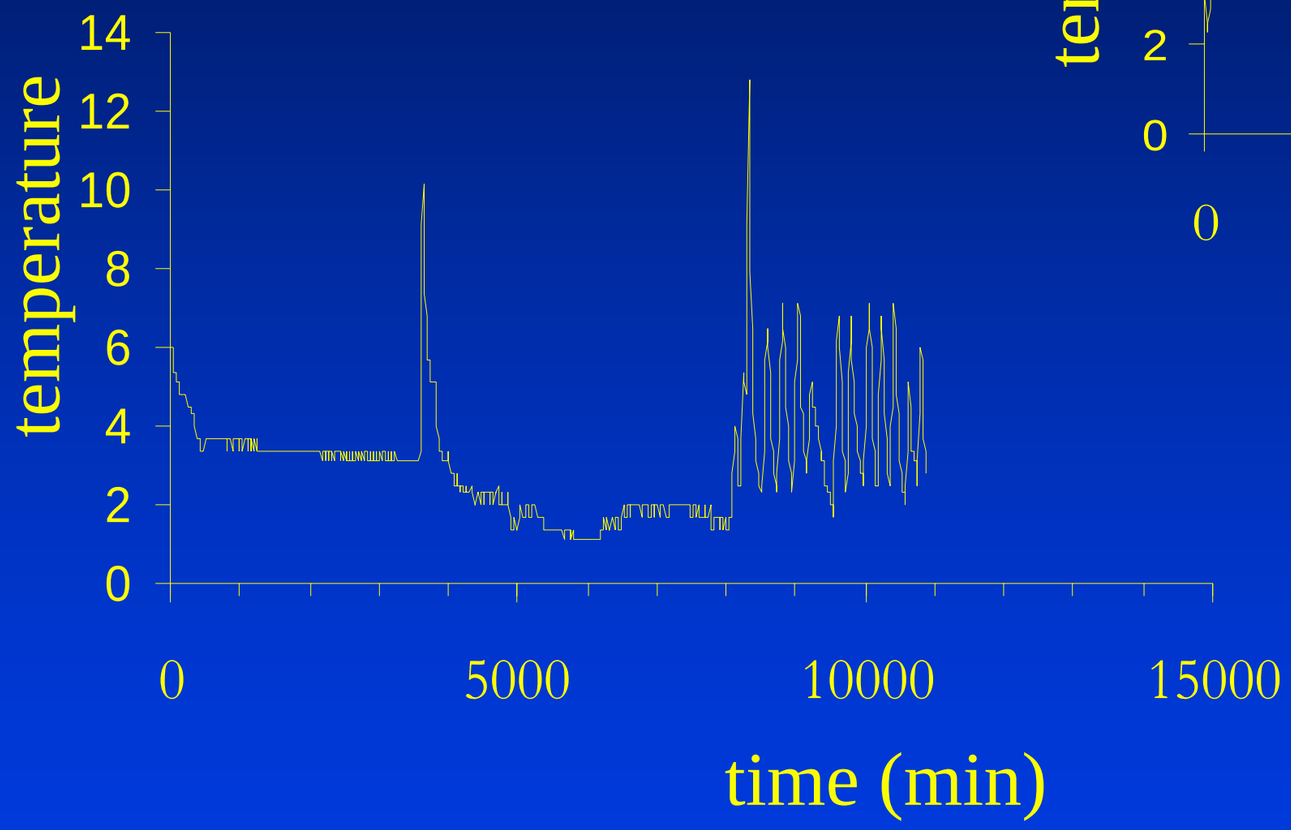
Electronic dataloggers

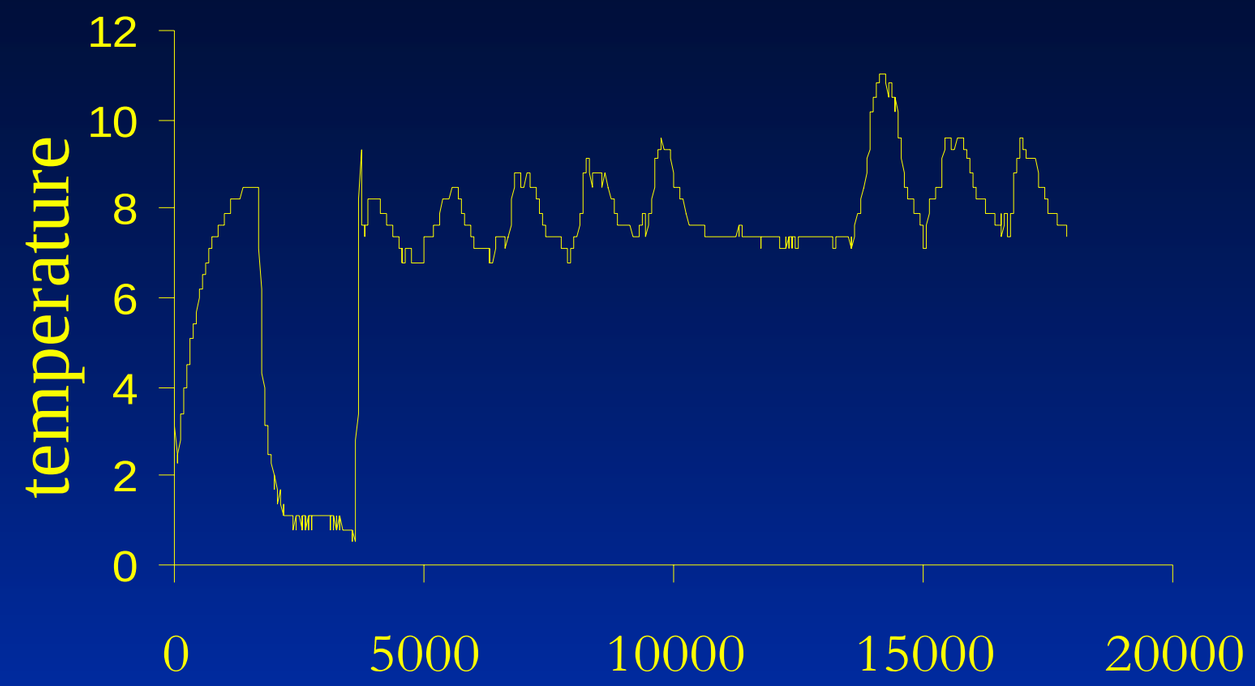
1st stage of the survey:

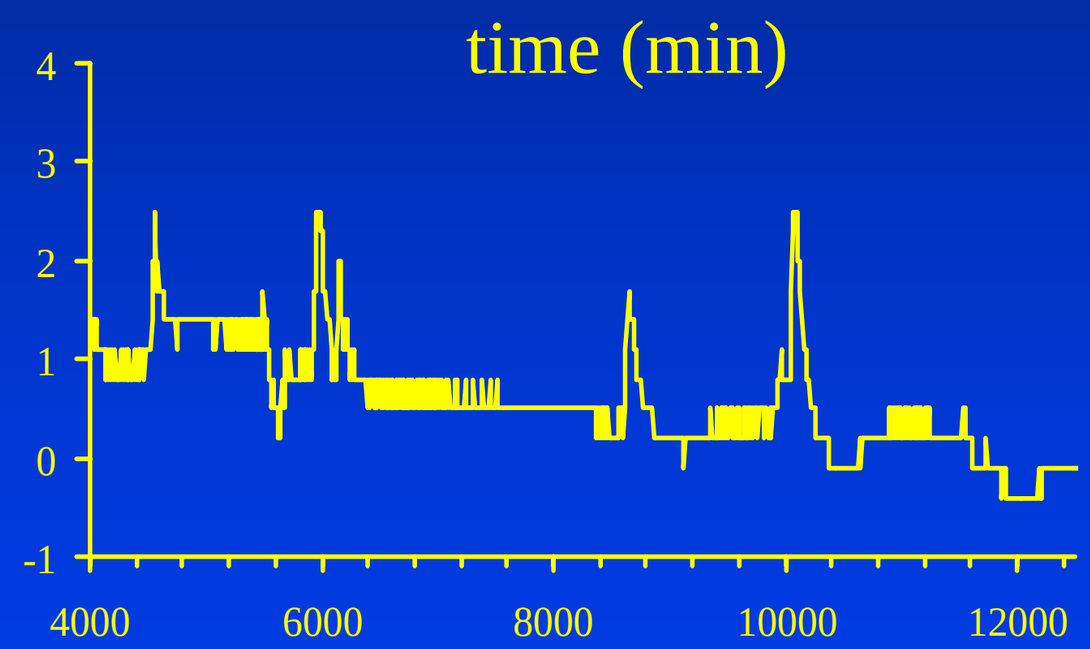
Data loggers were sealed in packages of products and monitored from processing through distribution to delivery and storage in SuperMarkets all over Greece

Survey for temperature conditions (1)

Temperature conditions FROM production TO the retail outlet





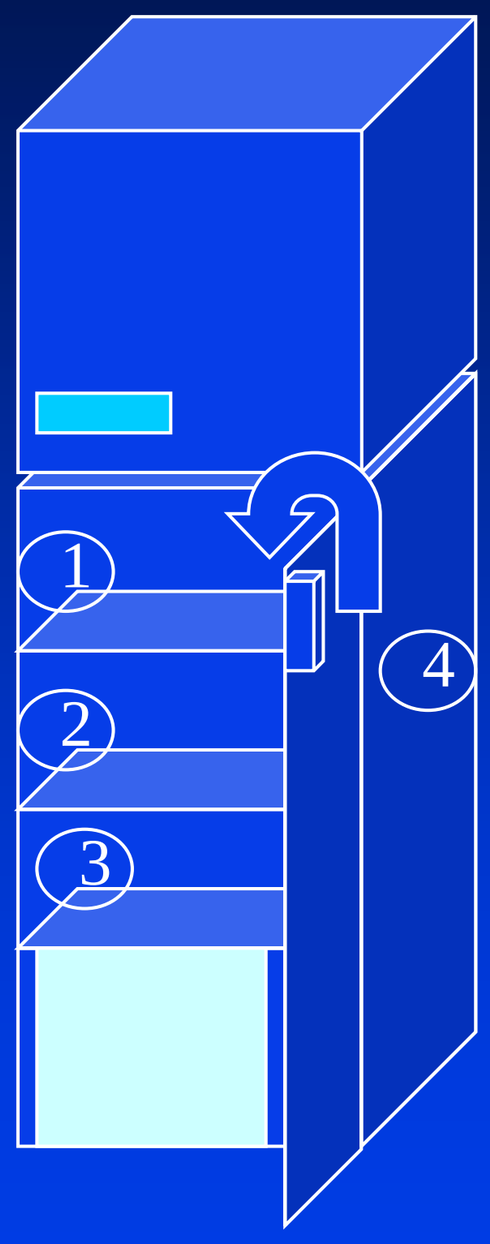


Conclusions from chill chain study

Temperature conditions FROM production TO the retail outlet

- Sharp (but short) increases of temperature (during transport)
- Cases of retail storage at temperatures > 7°C
- Significant temperature fluctuations

Survey for temperature conditions (2)
Variations WITHIN the domestic refrigerator



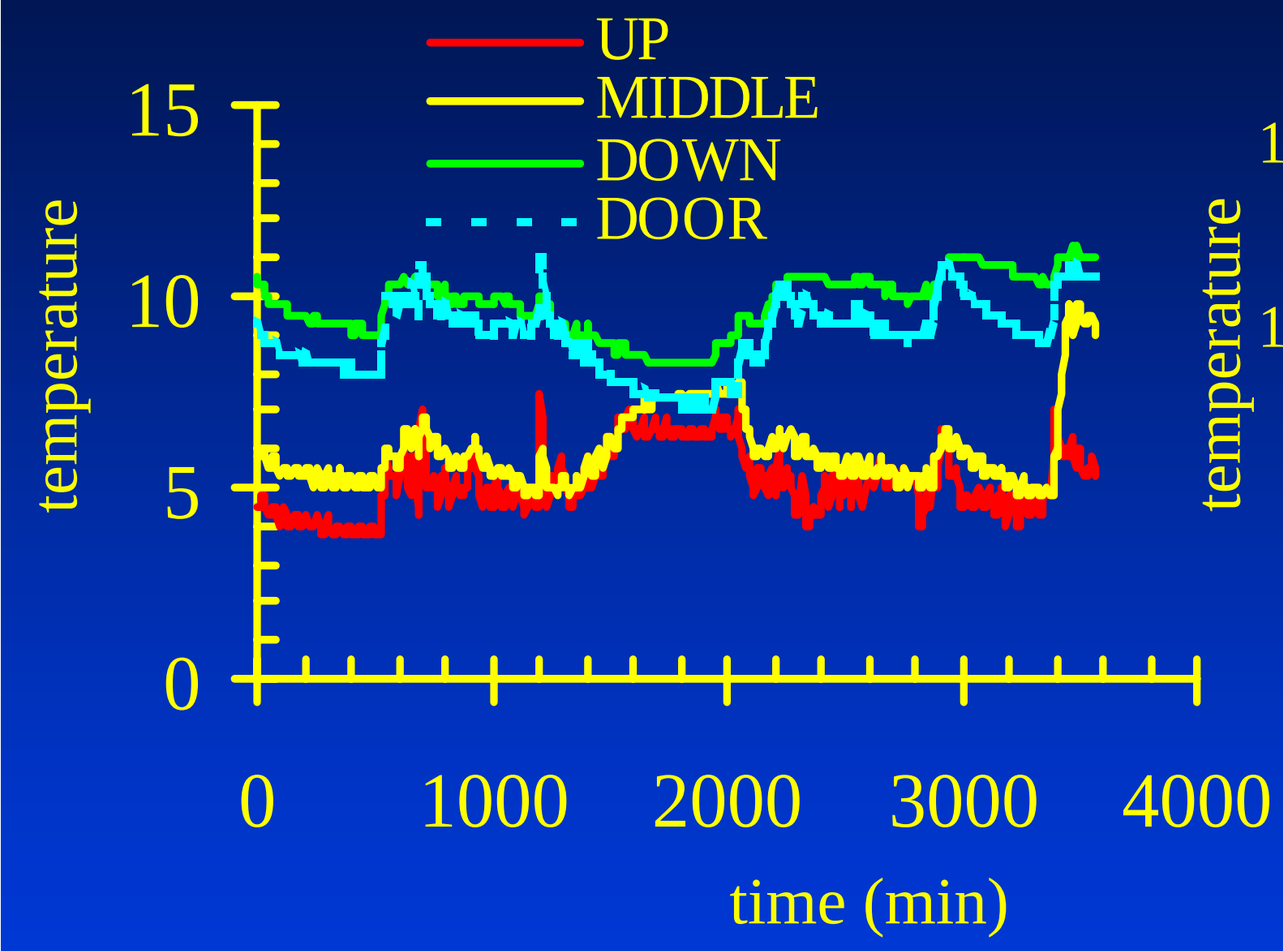
2st stage of the survey:

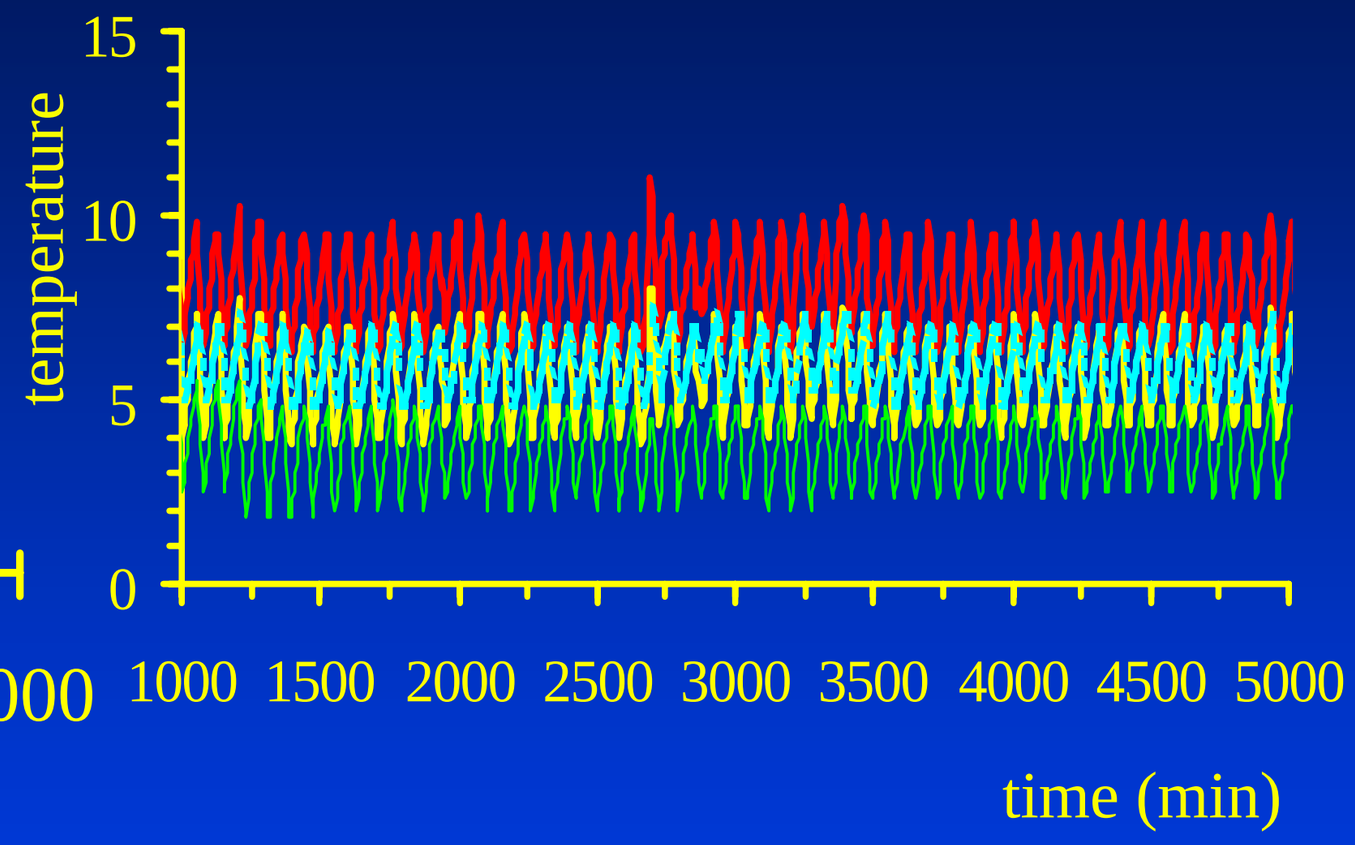
4 data loggers were distributed randomly to potential consumers to monitor variations INSIDE the refrigerator

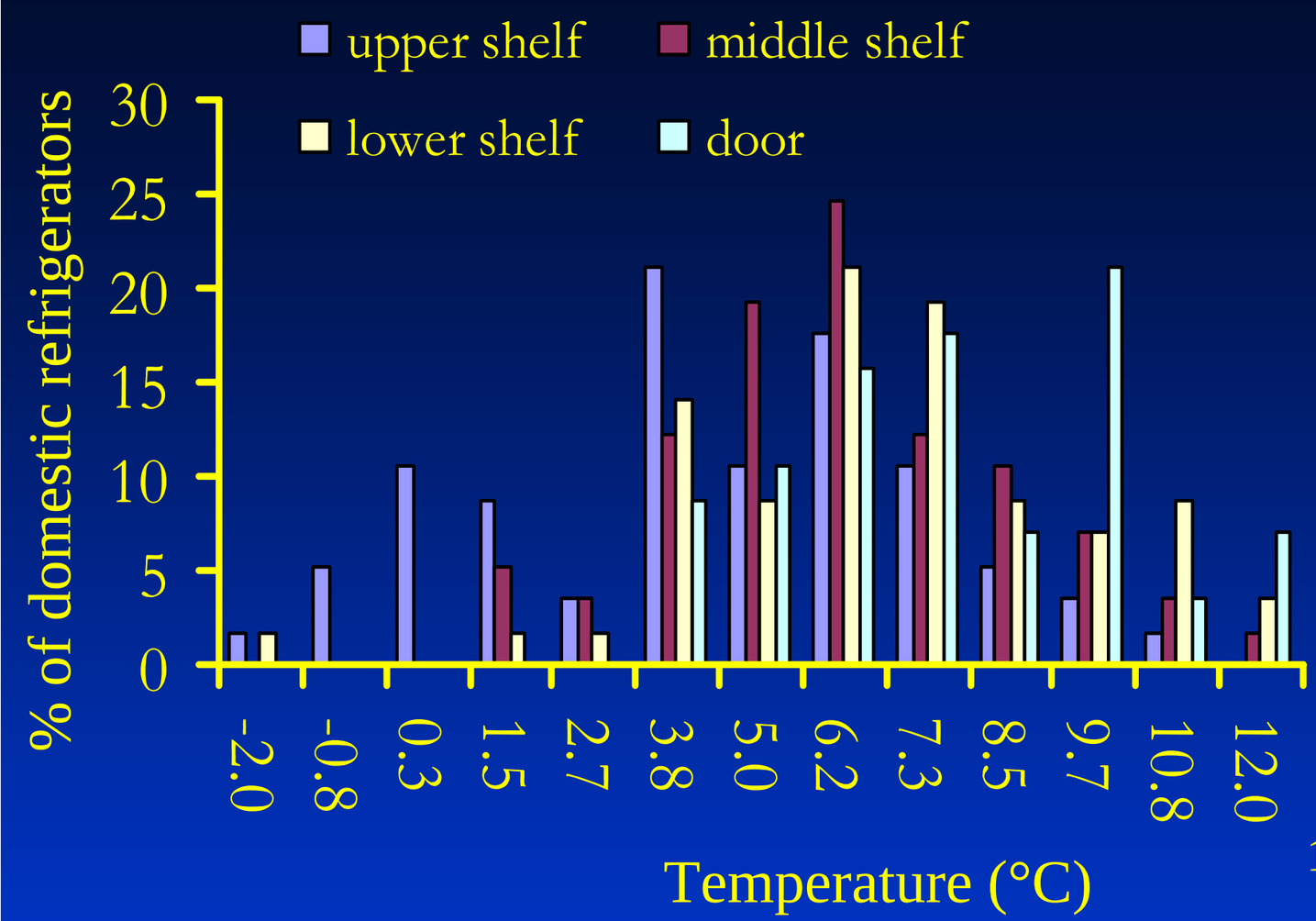
Electronic dataloggers

1: upper shelf
2: middle shelf
3: lower shelf
4: door

Temperature conditions IN the domestic refrigerator

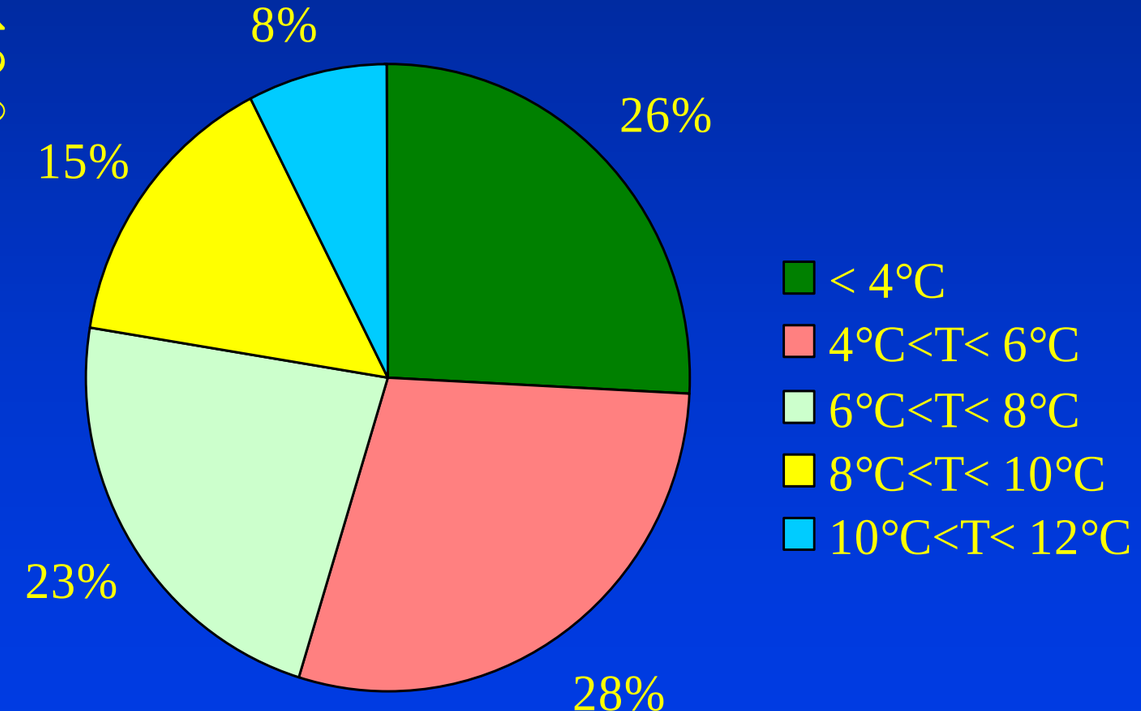






Temperature variation within domestic refrigerators

Average temperature of domestic refrigerators (~400 cases)



frisbee

Food Refrigeration Innovations for Safety, consumers Benefit, Environmental impact and Energy optimization along the cold chain in Europe.

Food Refrigeration Innovations for Safety, Consumers' Benefit, Environmental Impact and Energy Optimisation Along the Cold Chain in Europe

EC 7th Framework RTD Project Grant agreement no.: **245288**

Temperature variations in distribution and storage conditions

Justification for continuous monitoring

TTI

APPLICABILITY OF TTI FOR MONITORING THE CHILL CHAIN

TTI PRINCIPLES
&
APPLICATION

TTI: main principles

Time Temperature Indicators (TTI) are simple, inexpensive devices that can show an easily measurable, time and temperature dependent change that cumulatively indicates the time-temperature history of the product from the point of manufacture to the consumer, allowing the location and the improvement of the critical points of the chill chain

TYPES OF TTI

- **Diffusion based**
- **Microbial**
- **Enzymatic**
- **Polymer based**
- **Photochemical**

PRINCIPLES OF TTI

TTI applications

1. **Constant temperature monitoring of the chill chain-elucidation of the "problematic" distribution phases**
2. **Correlation to food quality deterioration kinetics-prediction of the remaining shelf life at ANY point of the distribution chain.**
3. **Improvement of the management and stock rotation system (FIFO) – introduction of Least Shelf life Out (LSFO)/ Shelf Life Decision system (SLDS).**

Early TTI


3M
Monitor Mark
INDEX/INDICE
A
B
C
I-POINT TTM
3M MonitorMark
Freeze Indicator 32 F
I-POINT TTM
3360
I-POINT TTM
Time Temperature Monitor
3M
Monitor Mark
INDEX/INDICE
1
2
3
4
5
I-POINT FTM FREEZER TEMPERATURE MONITOR
IDEAL
OK
Protected by Patents
Made in Sweden
2548000057
18

Enzymatic TTI

•Enzymatic TTI is based on a colour change caused by a pH decrease which is the result of a controlled enzymatic hydrolysis of a lipid substrate

Enzyme and substrate are mixed by mechanically breaking a separating barrier inside the TTI

Hydrolysis of the substrate causes acid release and the pH drop is translated in a color change of a pH indicator from deep green to bright yellow or orange red

Enzymatic TTI colourscale

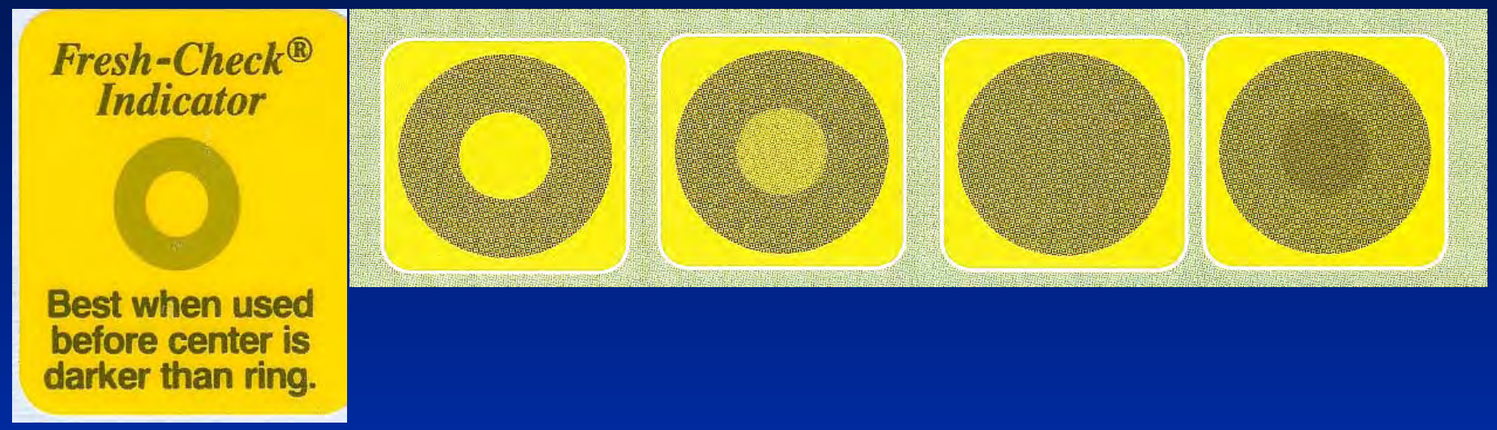
Microbial TTI

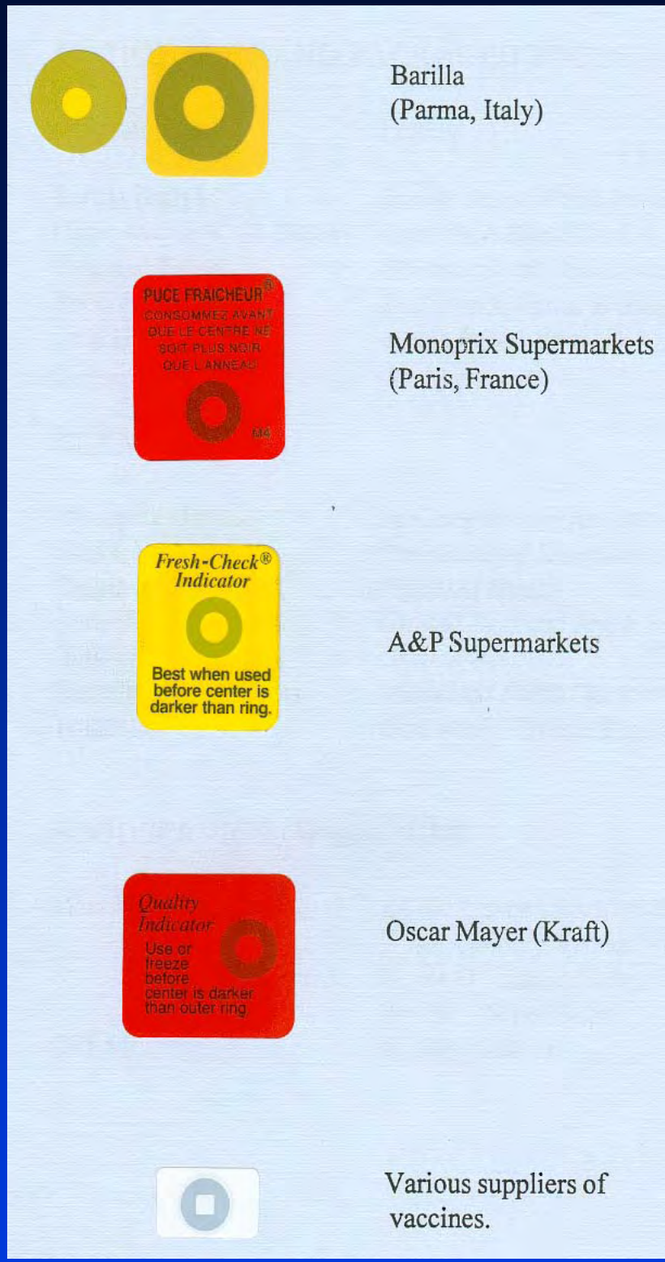
Accepted food quality

The food quality is not accepted

eO^{R} Cryolog, Gentilly, France

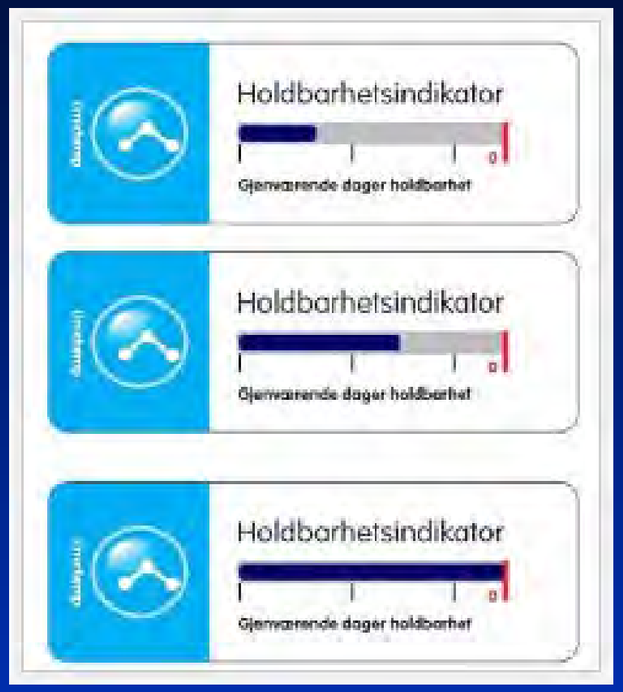
Polymer TTI





Solid state polymerization reaction.

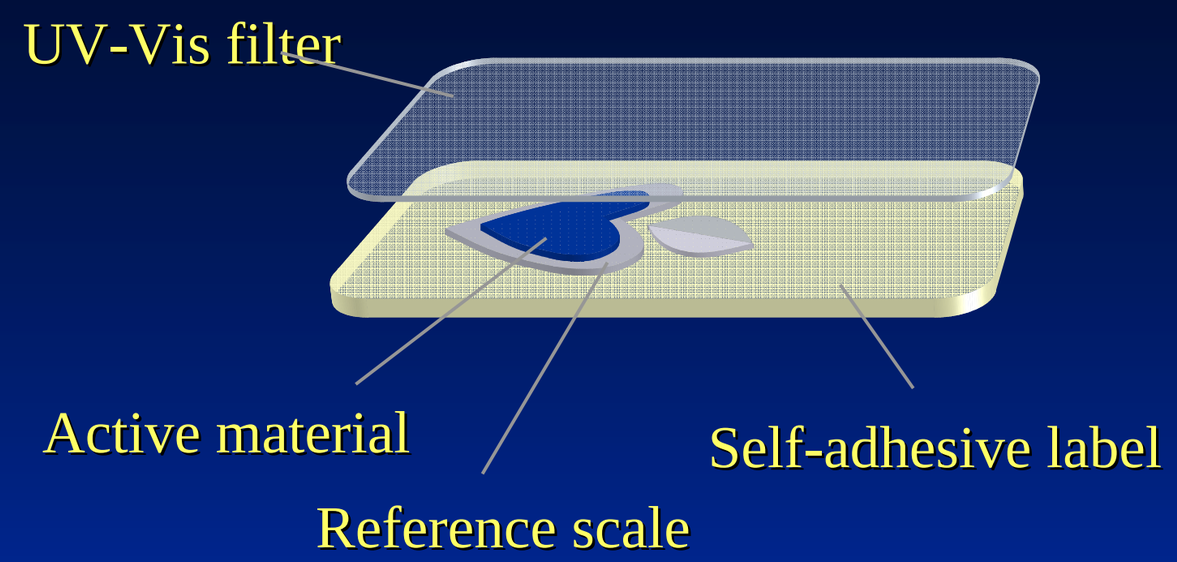
TimeTemp TTI



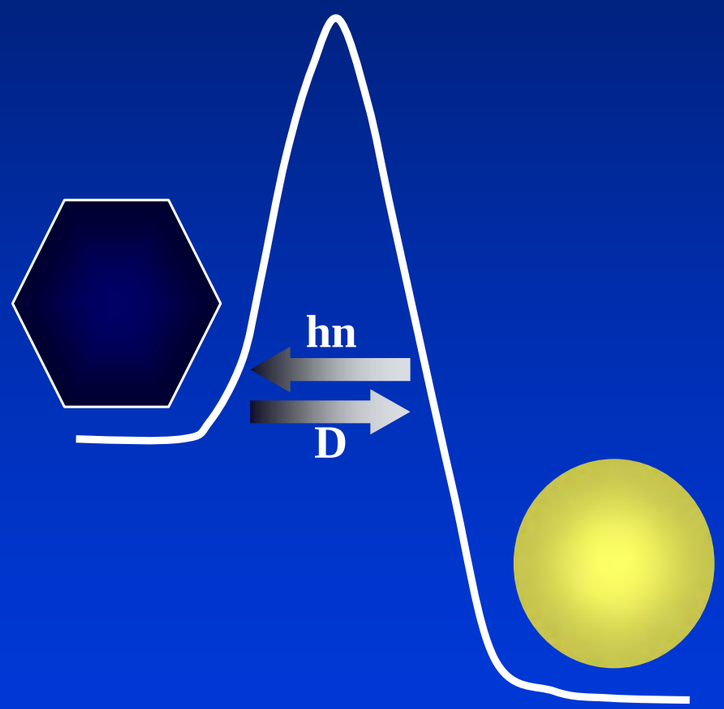
DIFFUSION REACTION SYSTEM

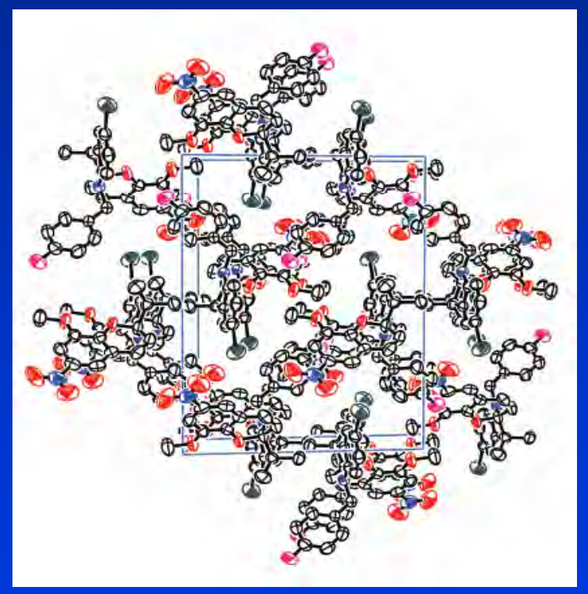
TimeTemp AS, Norway

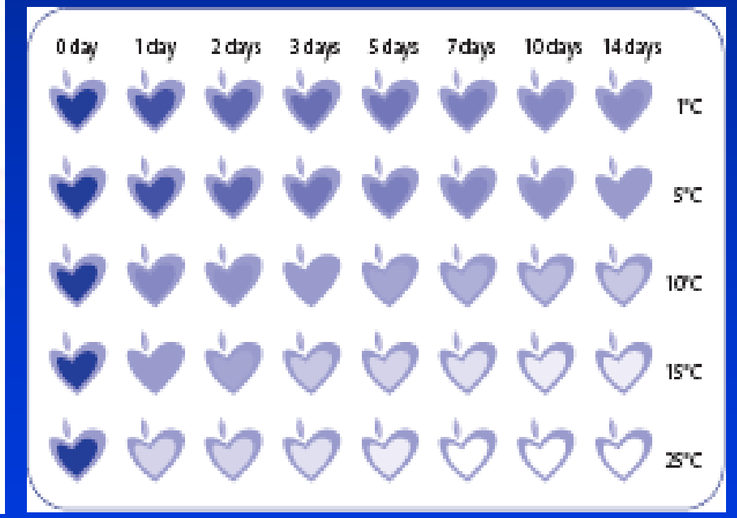
Photochemical TTI



Photosensitive compounds are excited and coloured by exposure at UV radiation

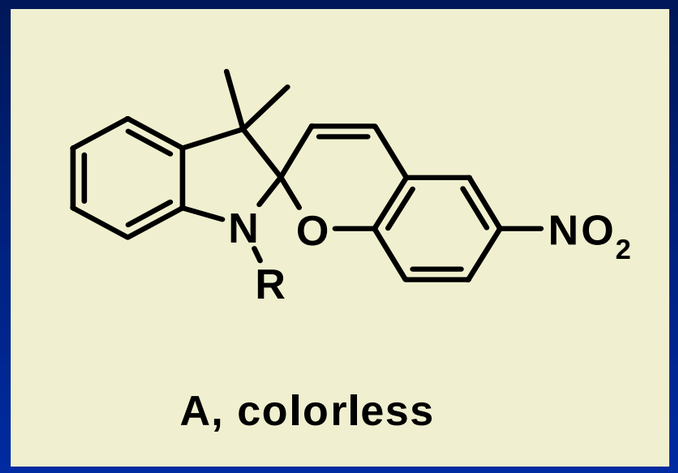






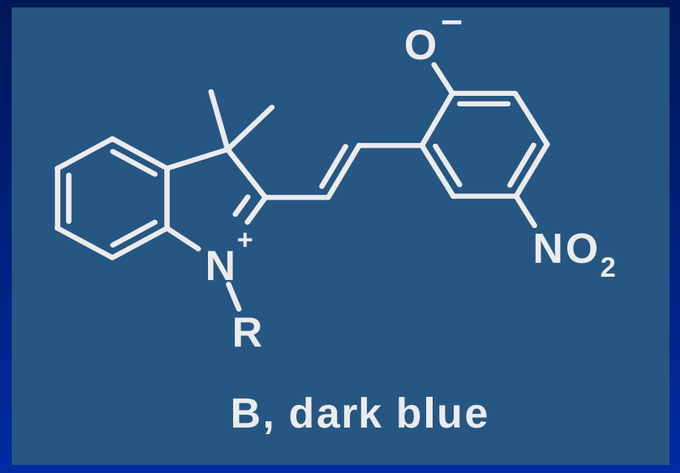
OnVu, Ciba-Freshpoint Switzerland

Photochemical TTI



Light, 365 nm
Activation

Heat
Fading



- Photochromism in **crystalline state**
- Color fading and activation energies of spiropyran crystals correspond to characteristics of food spoilage

Industrial / High speed chargers

Manual chargers

S M A S

Development and application of a TTI based Safety Monitoring and Assurance System for Chilled Meat Products

A European Commission Research and Technology Development Project

Quality of life and management of living resources

http://smas.chemeng.ntua.gr

FRESHLABEL

Integrated Approach to enable Traceability of the Cold chain of Fresh Chilled Meat and Fish Products by means of tailor-made Time/Temperature Indicators

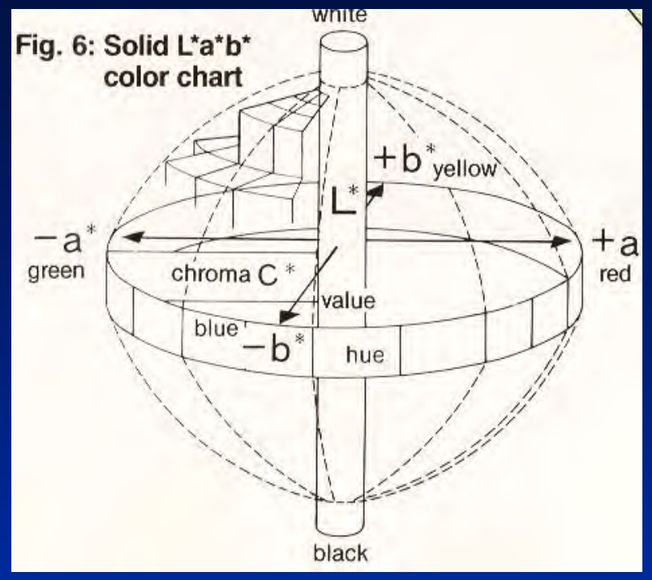
http://www.freshlabel/net

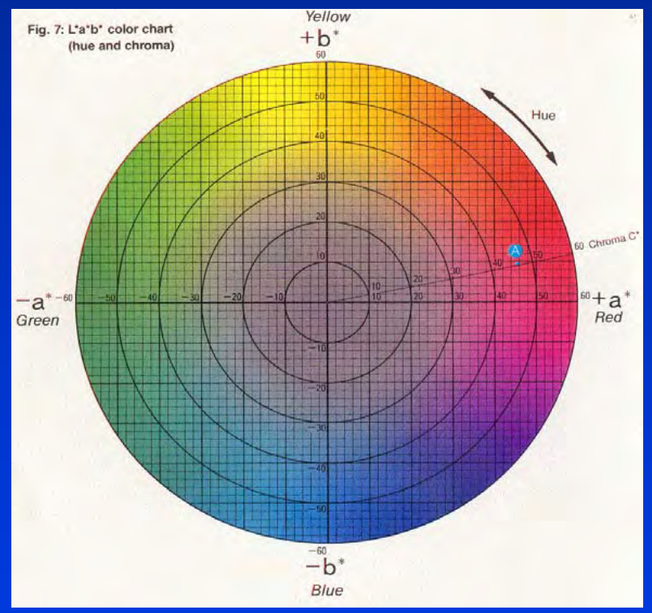
IQ-Freshlabel

Project IQ-Freshlabel

Developing novel intelligent labels for chilled and frozen food products and promoting the influence of smart labels application on waste reduction, food quality and safety in the European supply chains

Instrumental measurement of TTI colour



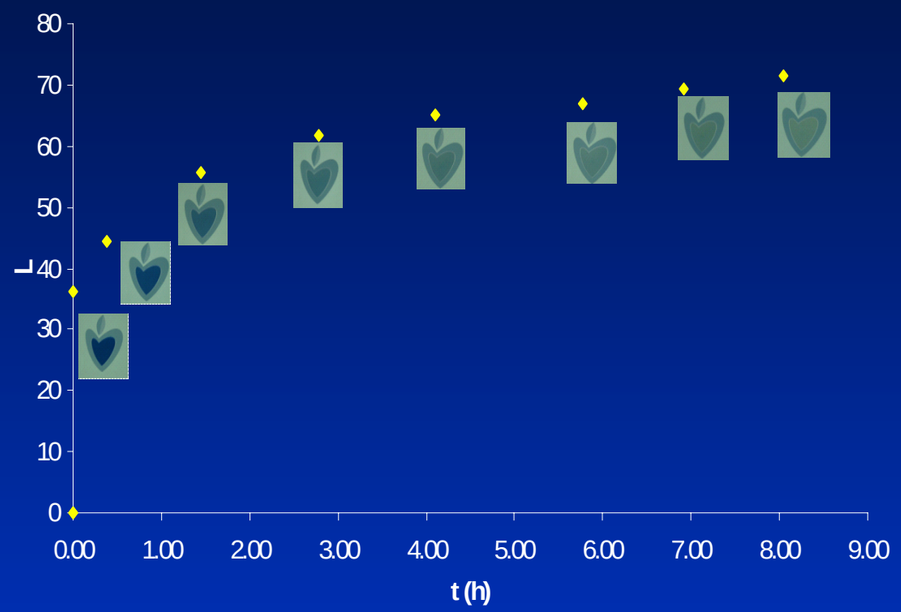


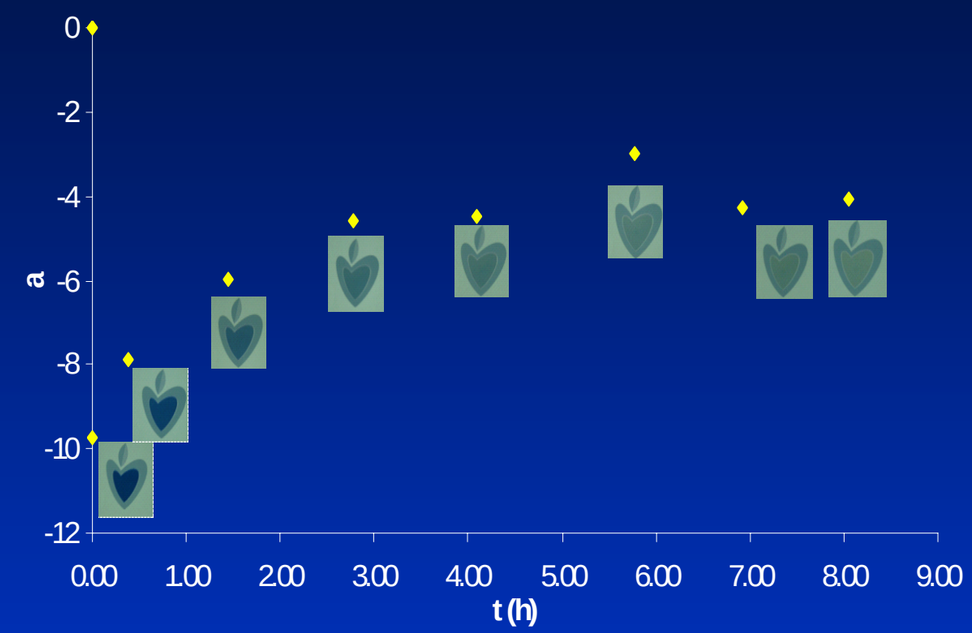
Measurement of visual response with CIE *Lab*

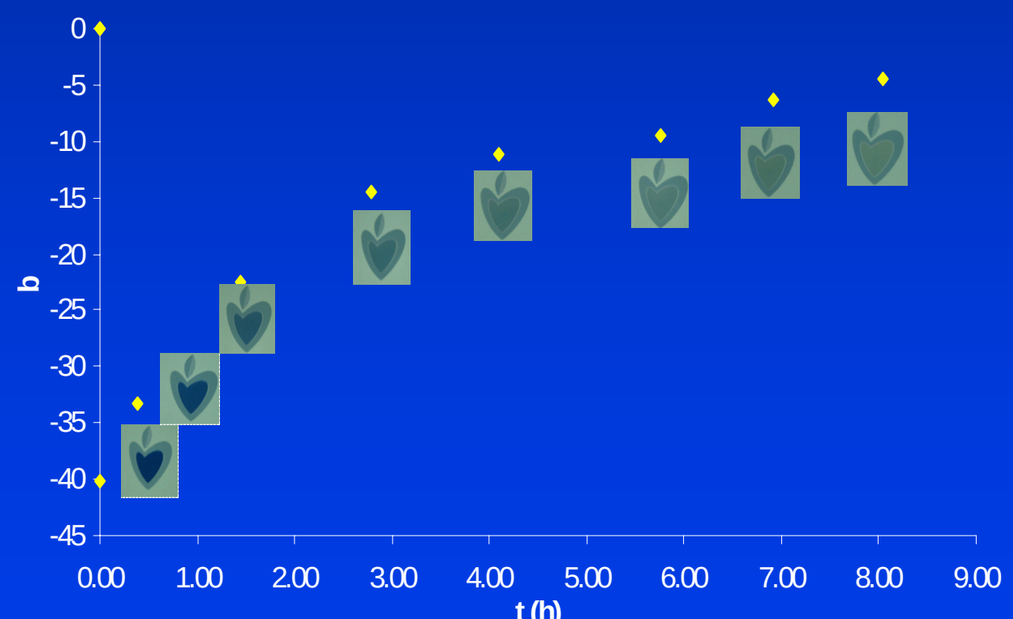
X-rite Eye1pro Colorimeter

Illumination D50

Instrumental measurement of Photochemical TTI colour





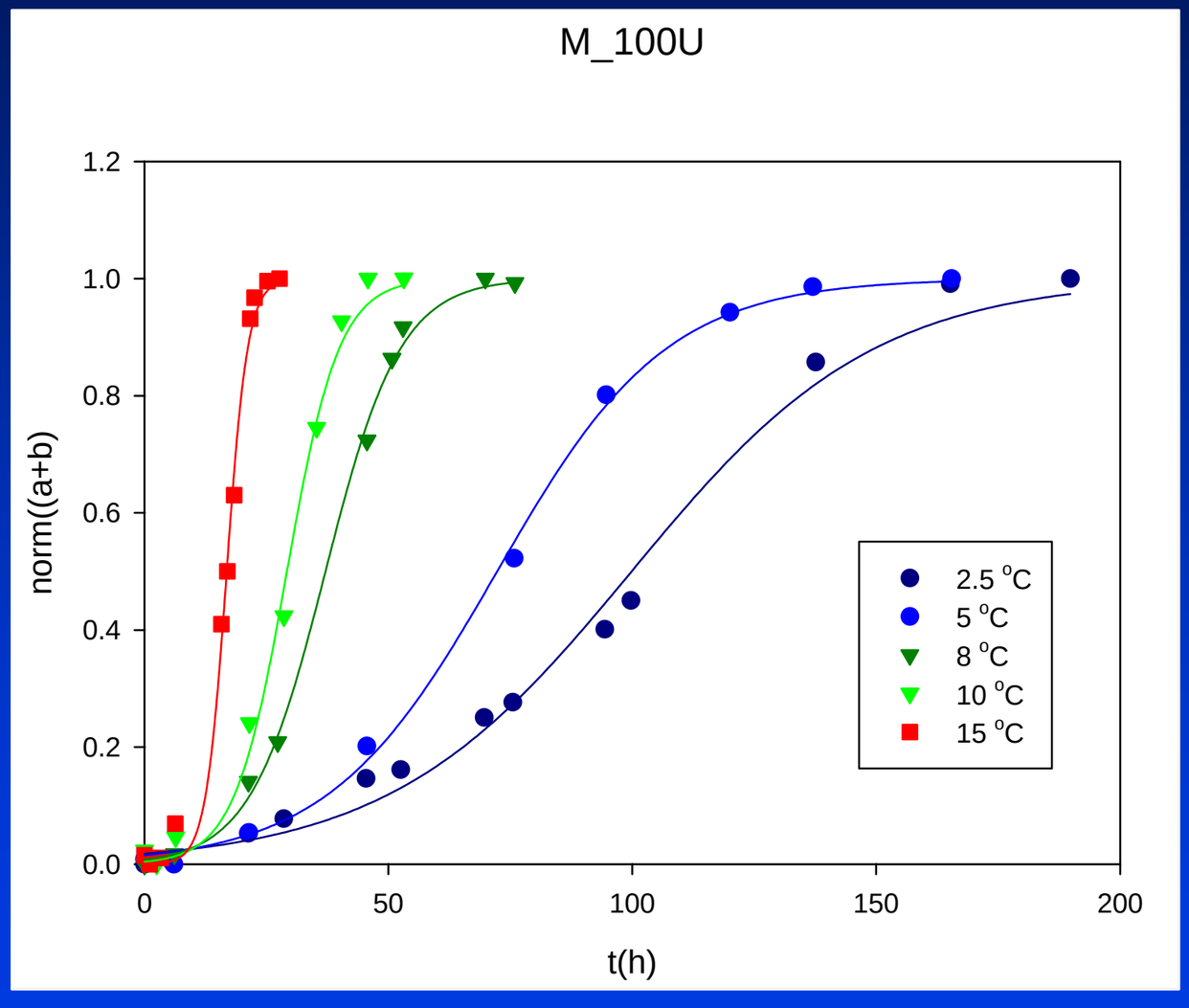


Response function

$$\frac{\Delta E}{\Delta E_0} = \exp^{-kt}$$

$$\Delta E = \sqrt{(L - L_{max})^2 + (a - a_{min})^2 + (b - b_{max})^2}$$

Instrumental measurement of Enzymatic TTI colour



Response function

$$X = \frac{(a+b)-(a+b)_{\min}}{(a+b)_{\max}-(a+b)_{\min}}$$

$$F(X) = \frac{1}{1+e^{\frac{k_1-t}{k_2}}}$$

Kinetics of Food Quality Deterioration

- Degradation of quality index A: $f(A) = kt$

Apparent reaction order	Quality function Q(A)t
0	$A_o - A_t$
1	$\ln(A_o - A_t)$
2	$1/A_o - 1/A_t$
m(m≠1)	$\frac{1}{m-1}\left(A_t^{1-m} - A_o^{1-m}\right)$

- Temperature dependence of **quality function:**

$$f(A) = k_{A_{ref}} \exp\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$$

Kinetics of Food Quality Deterioration

- Quality deteriorartion for **variable** temperature distribution

$$f(A)_t = \int_0^t k[T(t)]dt = k_{A_{ref}} \int_0^t exp\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)dt$$

T_{eff} : constant temperature that results in the same quality change as the variable temperature distribution over the same time period

$$f(A)_t = k_{A_{ref}}\ exp\left(\frac{-E_a}{R}\left(\frac{1}{T_{eff}} - \frac{1}{T_{ref}}\right)\right)t$$

TTI response kinetics

X: measurable change of TTI

Response function:

$$F(X) = kt = k_{I_{ref}} \exp\left(\frac{-E_{a_I}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) t$$

- *For variable temperature distribution:*

$$F(X)_t = \int_0^t k[T(t)]dt = k_{I_{ref}} \int_0^t \exp\left(\frac{-E_{a_I}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) dt$$

- *Using effective temperature:*

$$F(X)_t = k_{I_{ref}} \exp\left(\frac{-E_{a_I}}{R}\left(\frac{1}{T_{eff}} - \frac{1}{T_{ref}}\right)\right) t$$

TTI Application scheme

Measurement of the TTI response

Response function:

$k_{I_{ref}}, E_{a_I}$

F(X)

$$T_{eff}^{-1} = T_{ref}^{-1} - \frac{R\,ln\left(\frac{F(X)_t}{k_{I_{ref}}}\right)}{E_{a_I}}$$

T_{eff}

$E_{a\ (TTI)} = E_{a\ (food)}$

T_{eff}

$$f(A)_t = k_{A_{ref}}\, exp\left(\frac{-E_a}{R}\left(\frac{1}{T_{eff}} - \frac{1}{T_{ref}}\right)\right)t$$

$k_{A_{ref}}, E_a$

f (A)

Quality function

A_t

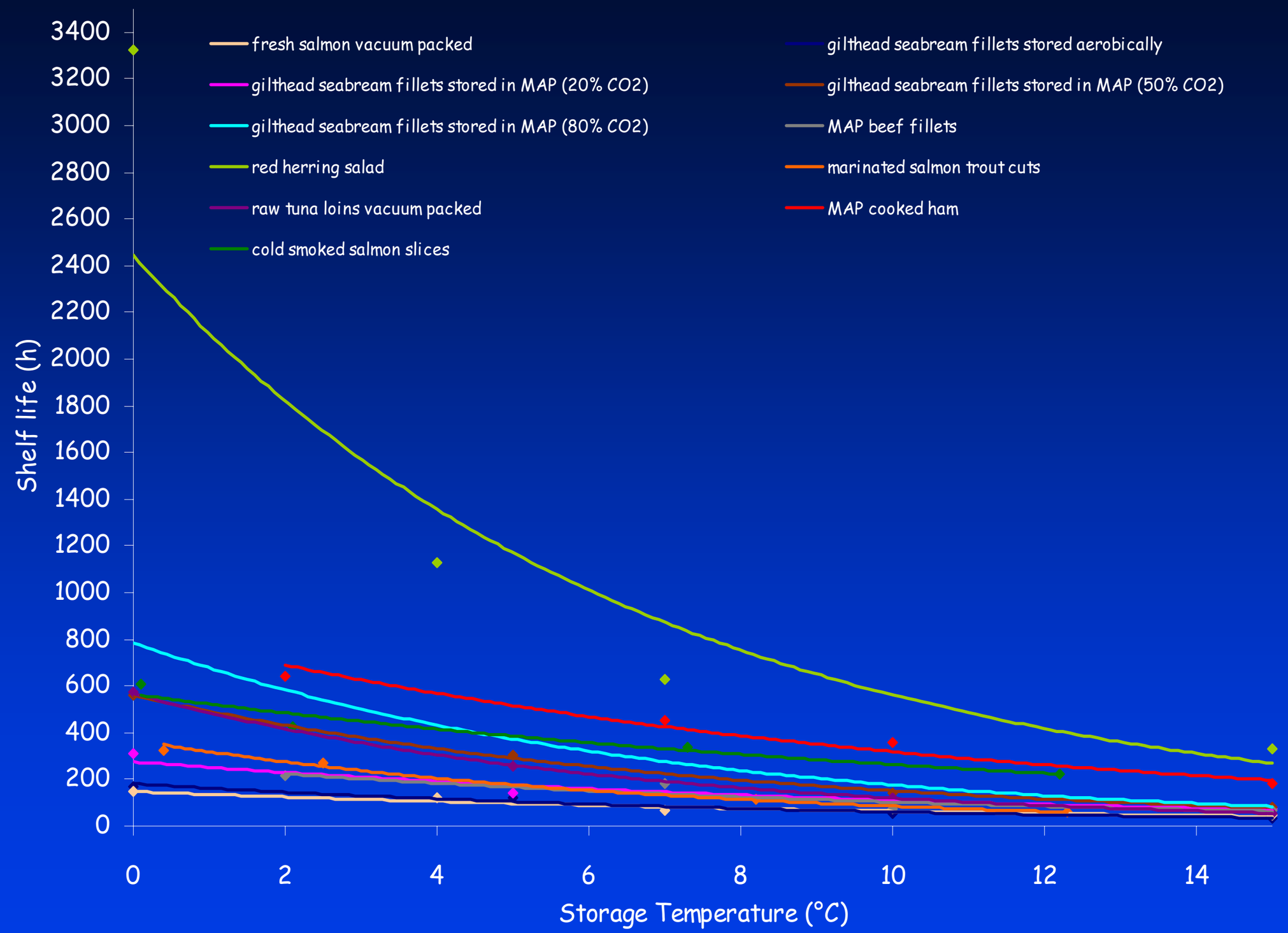
Quality at time t

Studies of different types of TTIs for monitoring chilled food shelf life

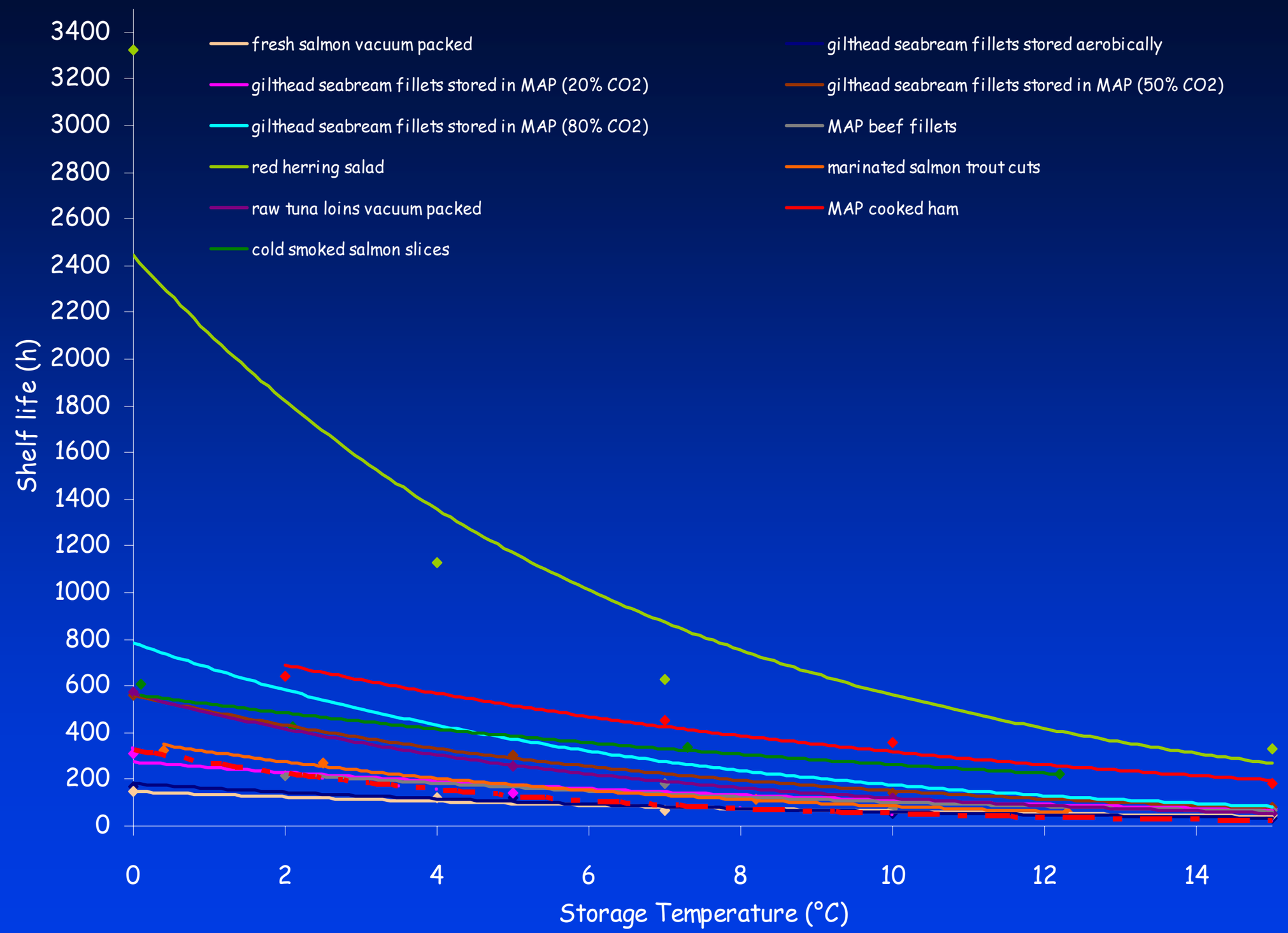
FRESHLABEL

Integrated Approach to enable Traceability of the Cold chain of Fresh Chilled Meat and Fish Products by means of tailor-made Time/Temperature Indicators

http://www.freshlabel/net

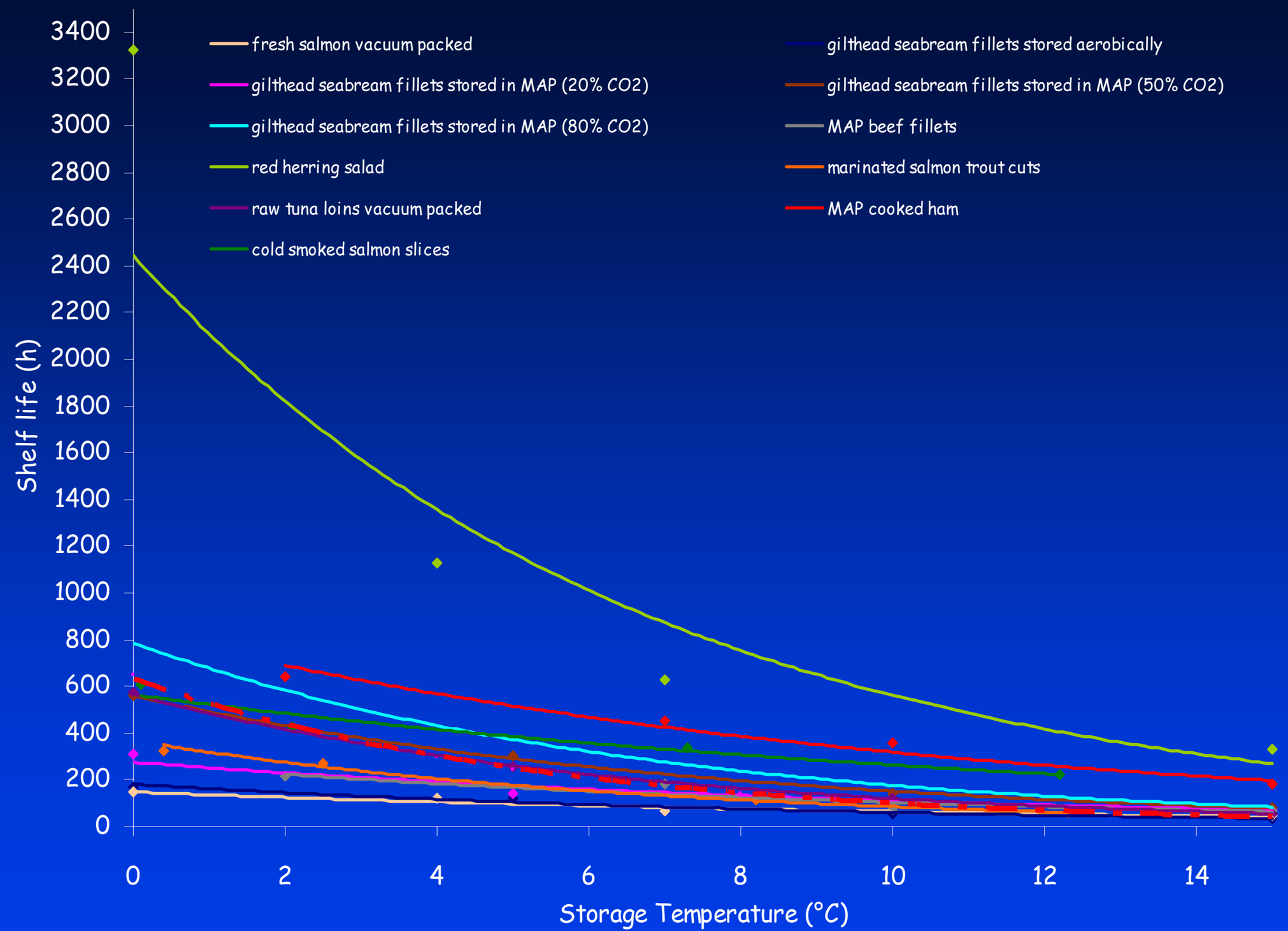


Ciba OnVu Handcharger



1s

Ciba OnVu Handcharger



2s

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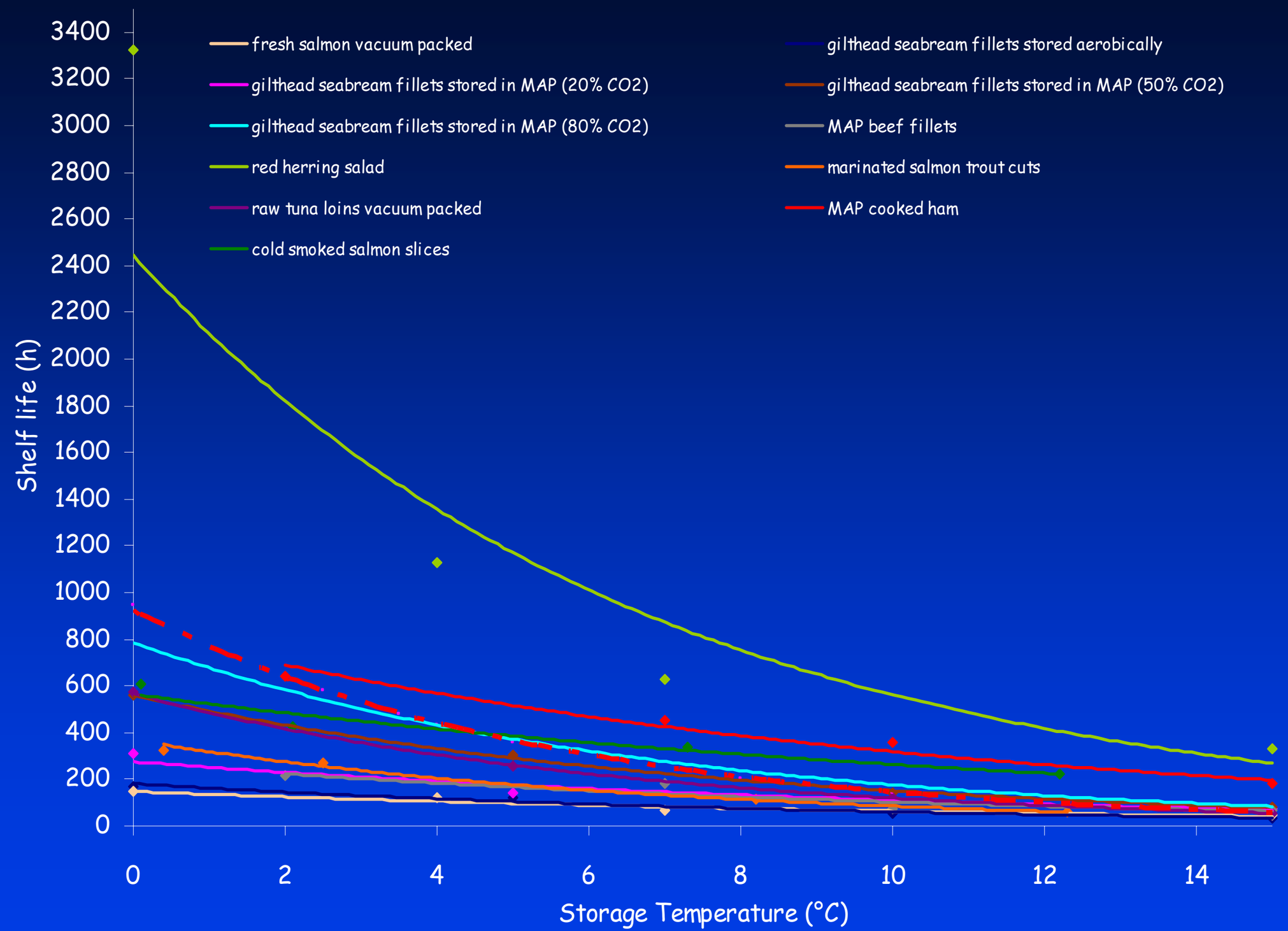

3s

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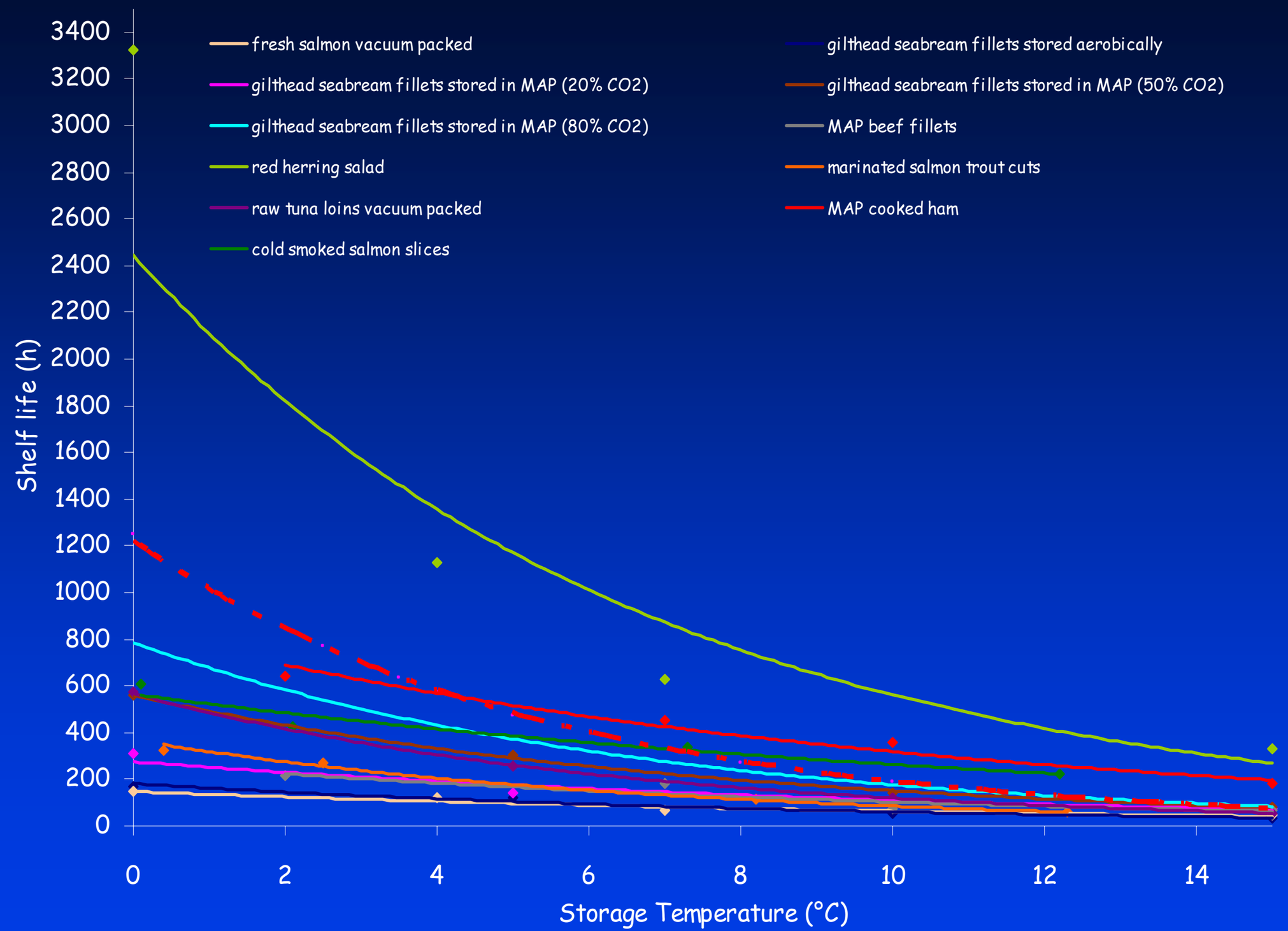

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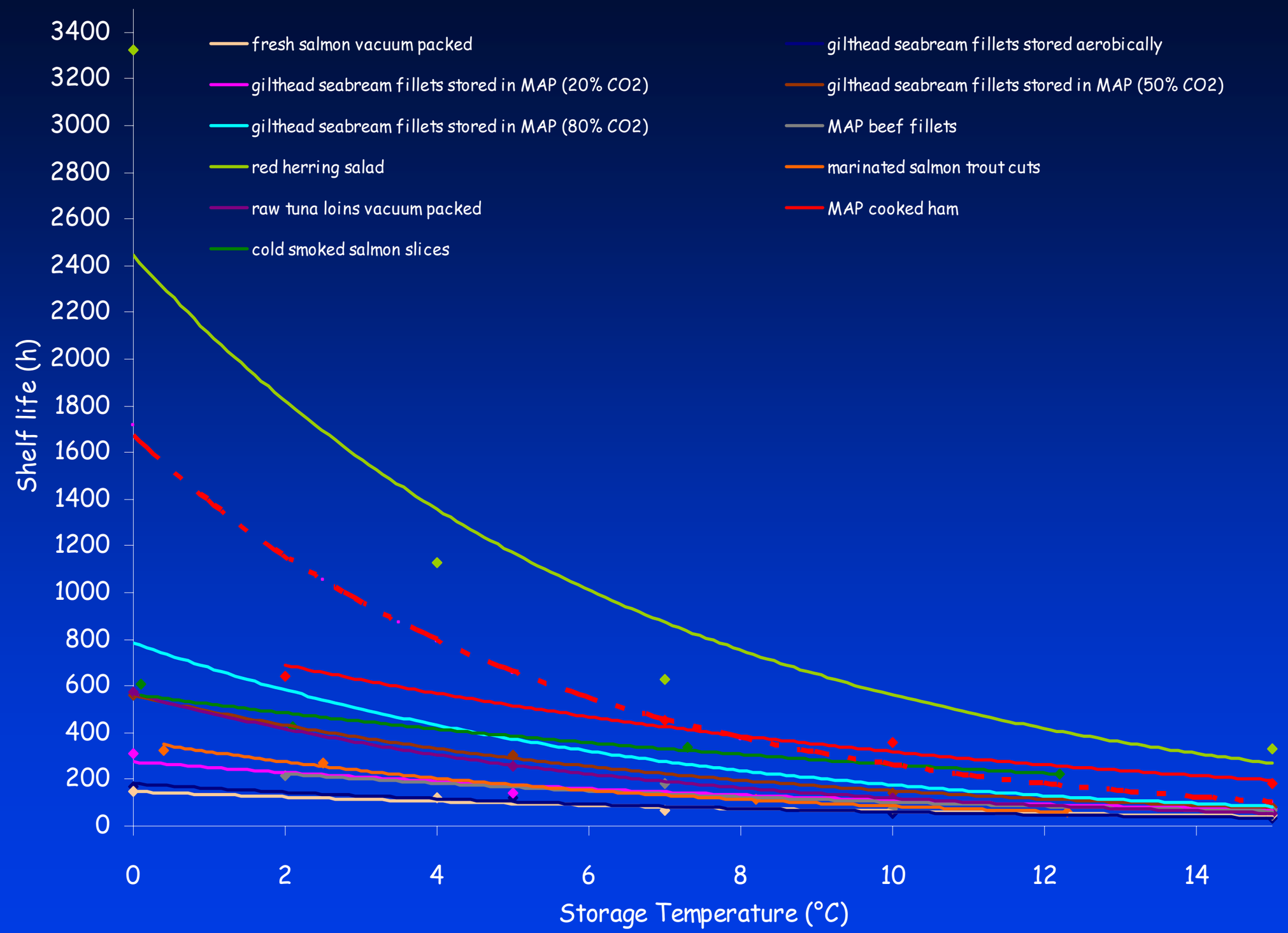

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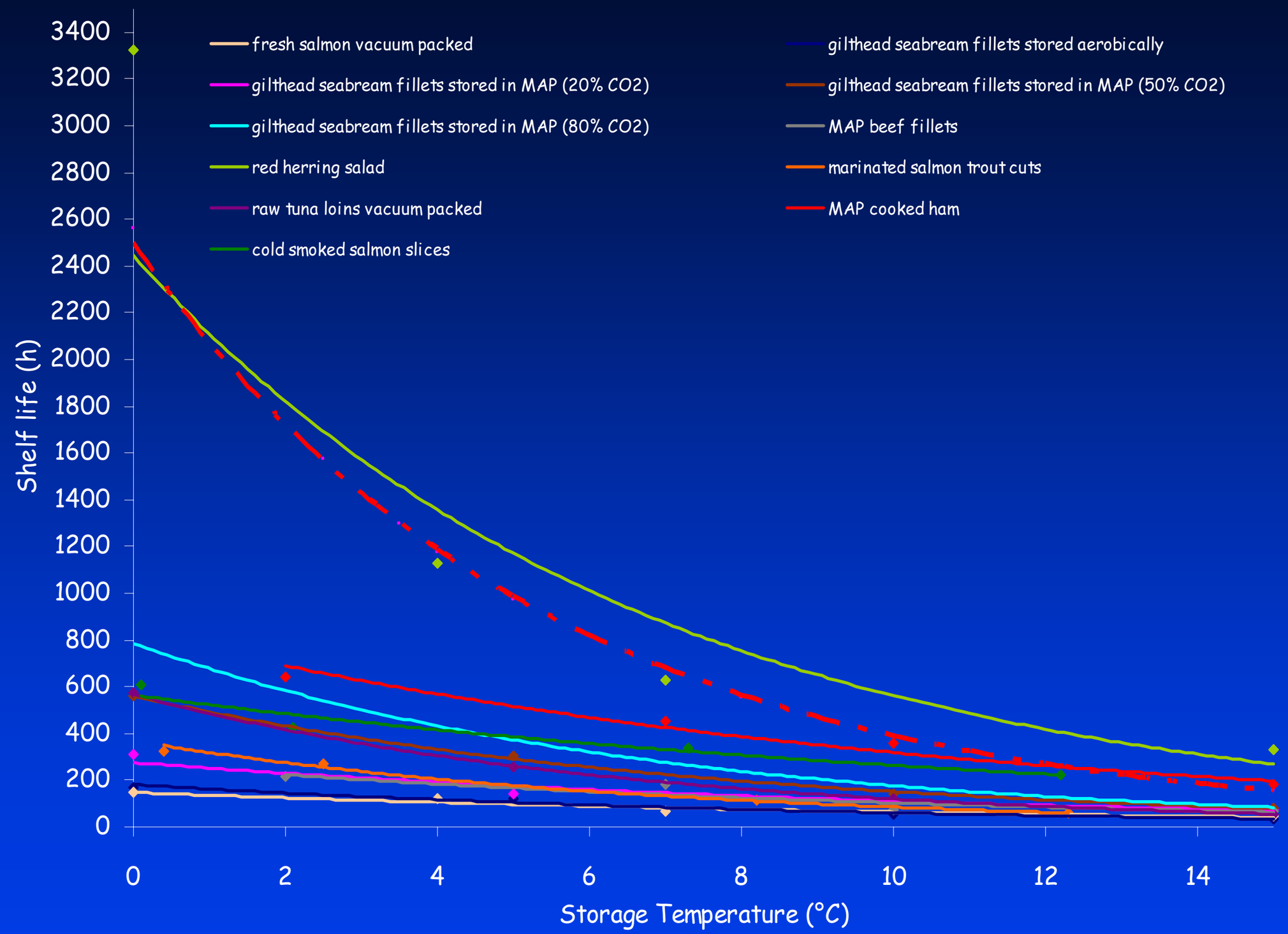
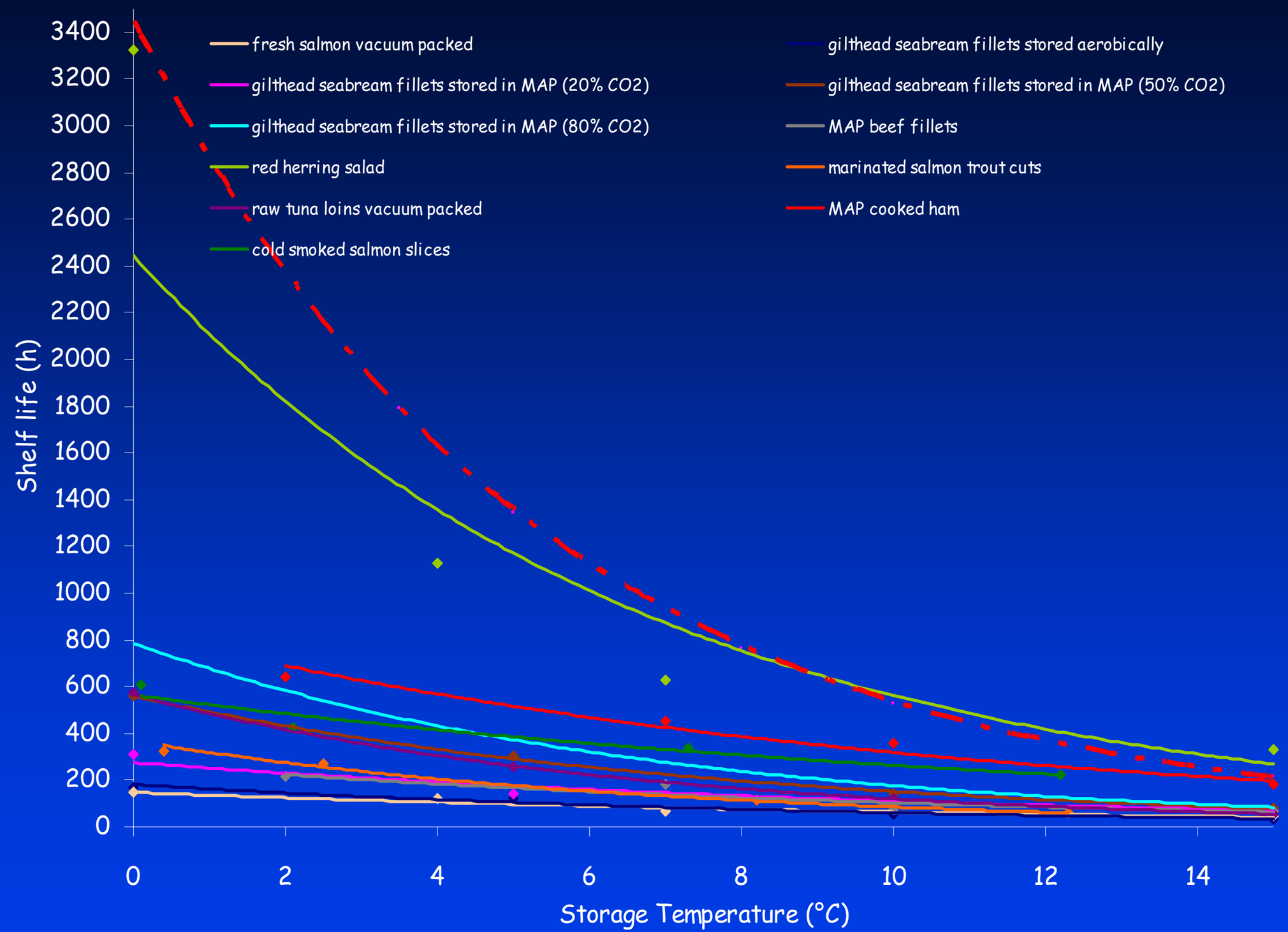


10
s

Ciba OnVu Handcharger



15
s

Ciba OnVu Handcharger

Shelf life study of gilthead seabream fillets packed under modified atmosphere

Gilthead seabream fillets (*Sparus aurata*)

- The limited and variable shelf life of chilled fish products is a major problem for their quality assurance and commercial viability.
- Products like chilled fillets from marine cultured Mediterranean fish such as gilthead seabream have high commercial potential if their shelf life can be extended through packaging or minimal processing.

Gilthead seabream fillets (*Sparus aurata*)

- Marine cultured gilthead seabream fillets were MA packed and stored at controlled isothermal conditions 0, 5, 10 and 15°C.

- 20% CO_2 - 80% air
- 50% CO_2 - 50% air
- 80% CO_2 - 20% air

Microbiological analysis

- Total viable count
- *Pseudomonas* spp.
- Lactic acid bacteria

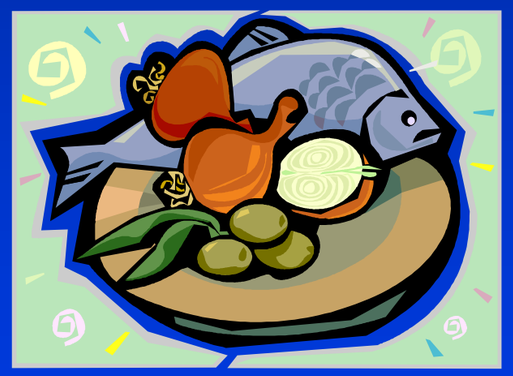
The microbial growth was modeled using the Baranyi Growth Model

pH measurement

Sensory evaluation

- Sensory panel of 8
- Rating on a 1-9 descriptive hedonic scale

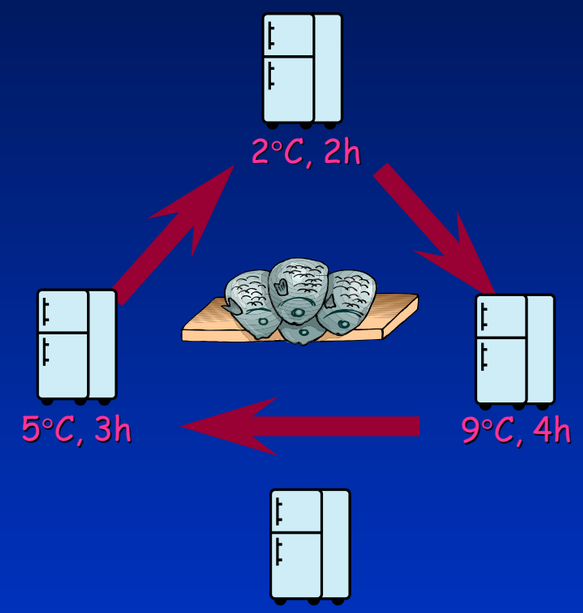
Appearance
Odour
Freshness
Texture
Taste

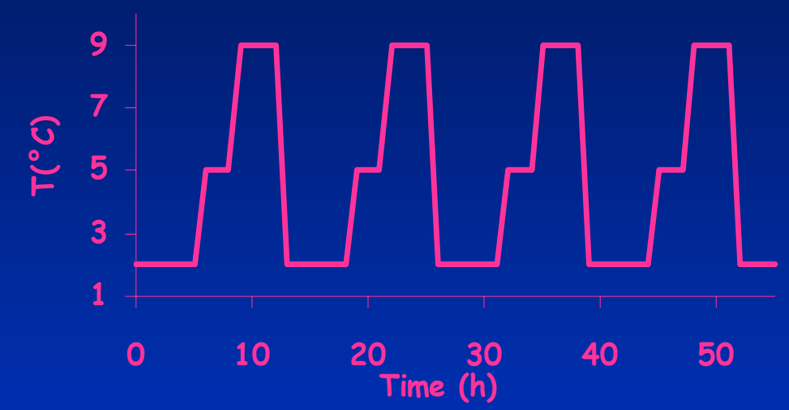


Validation of the developed kinetic models under dynamic temperature conditions

- Samples were stored under non isothermal conditions

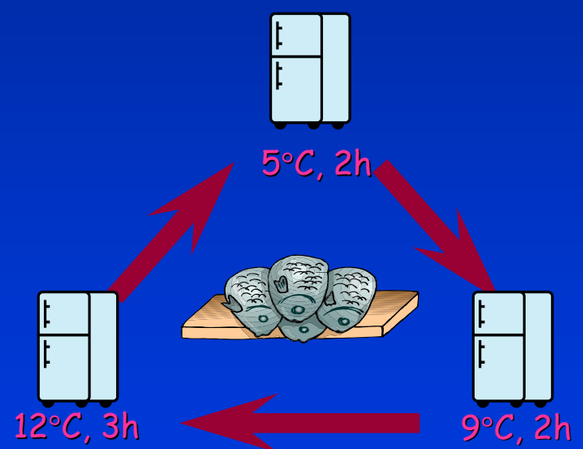
- Scenario 1:

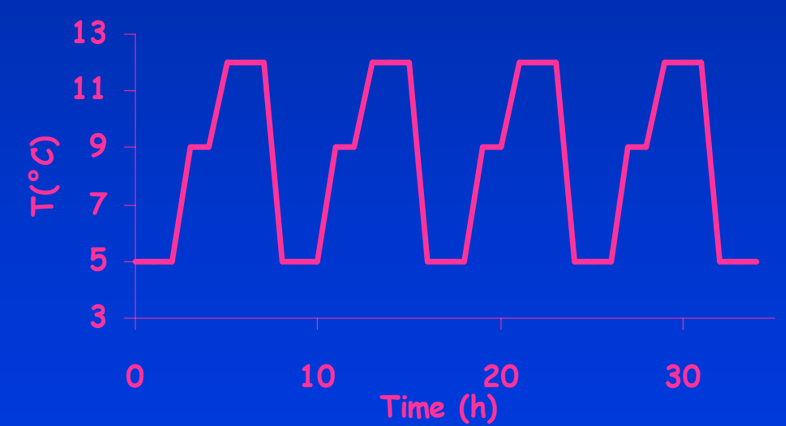




T_{eff} =5.4°C

- Scenario 2:



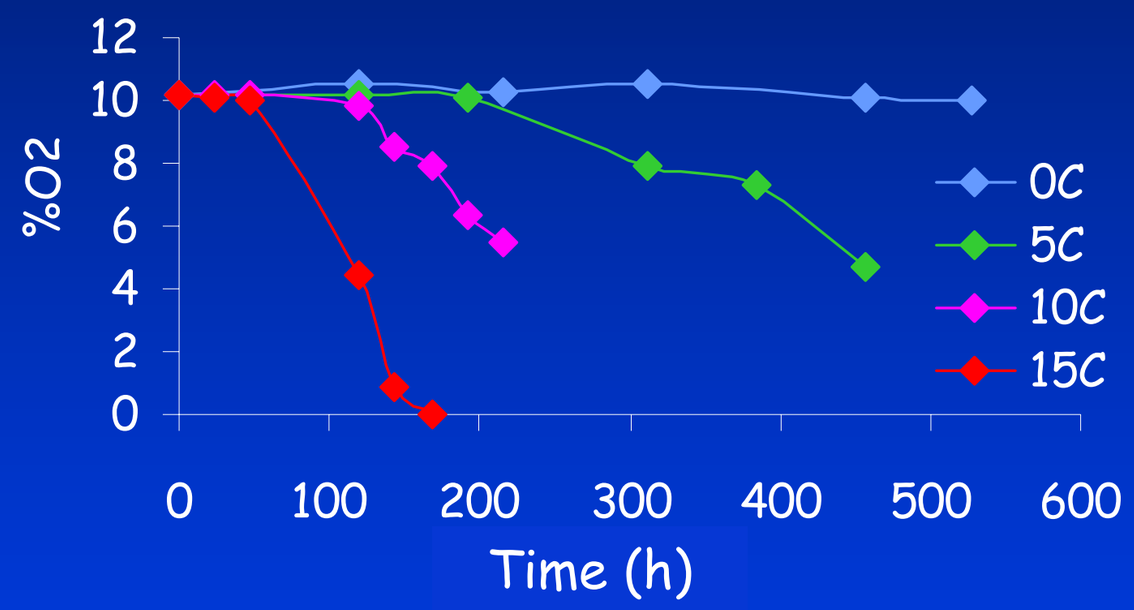


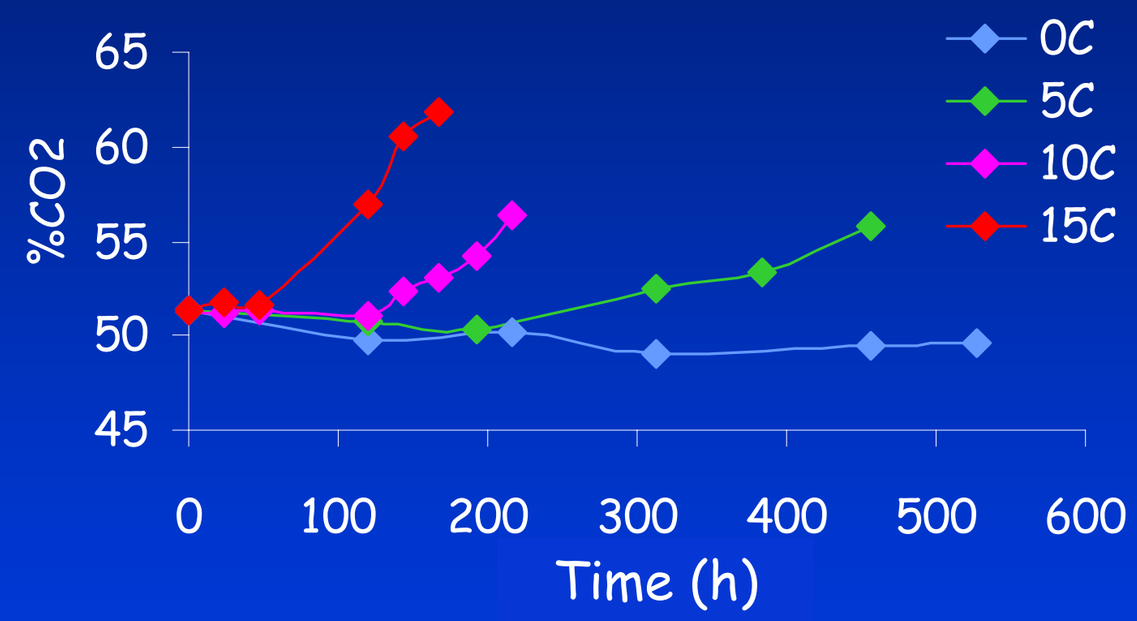
T_{eff} =9.4°C

Temperature profiles were obtained from electronic data loggers (COX TRACER™, Belmont, NC)

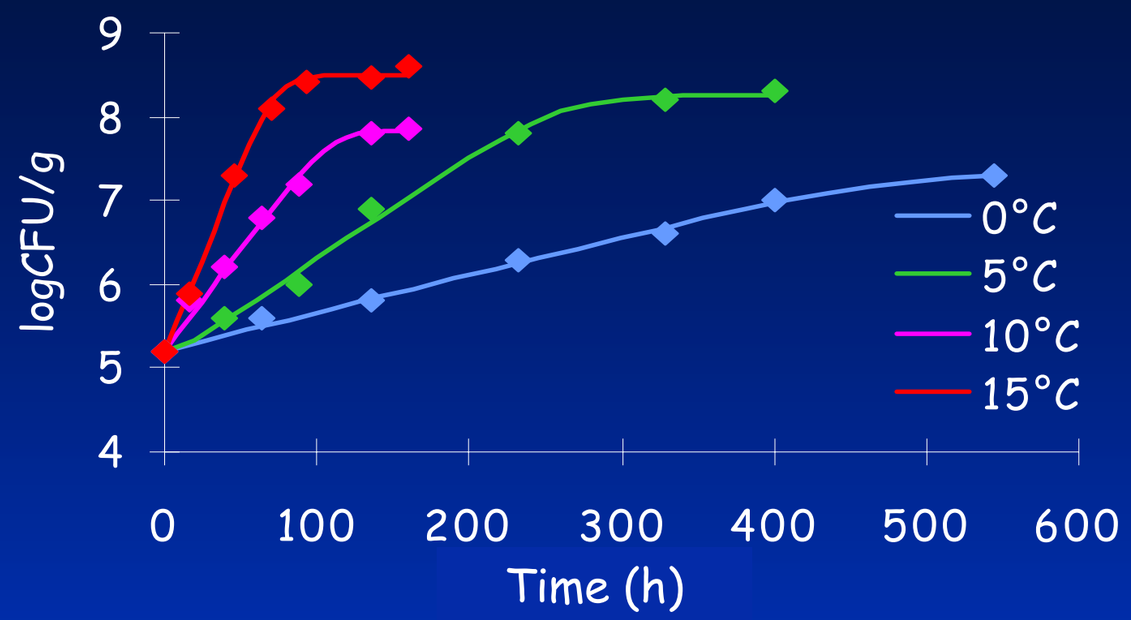
Gas headspace changes (CO_2 and O_2) in fish fillet packages

50% CO_2-50% air

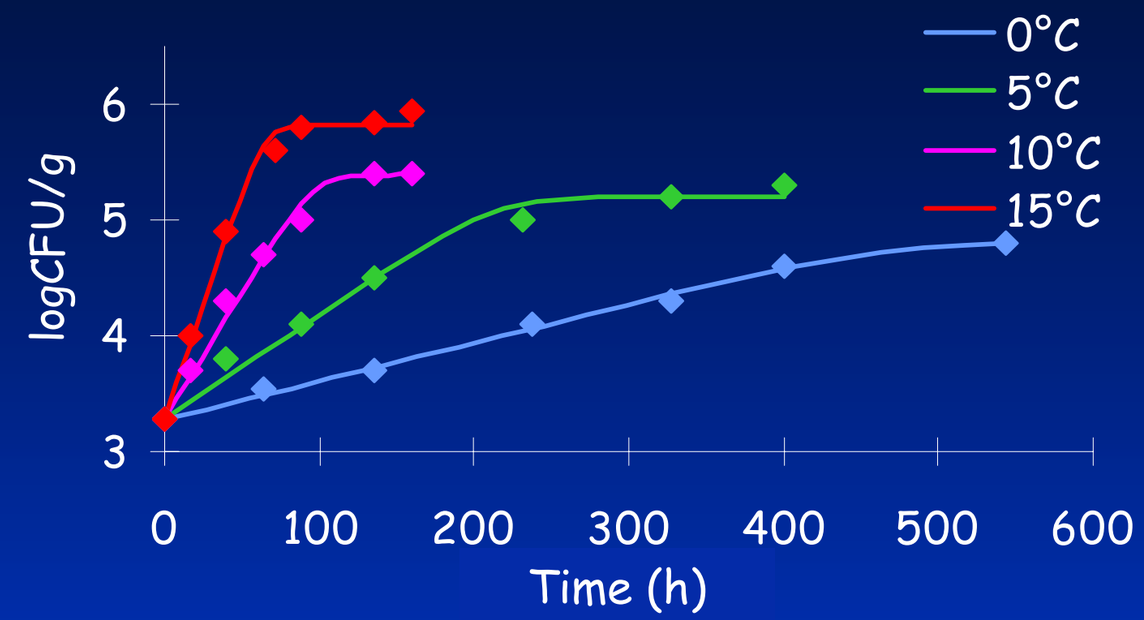




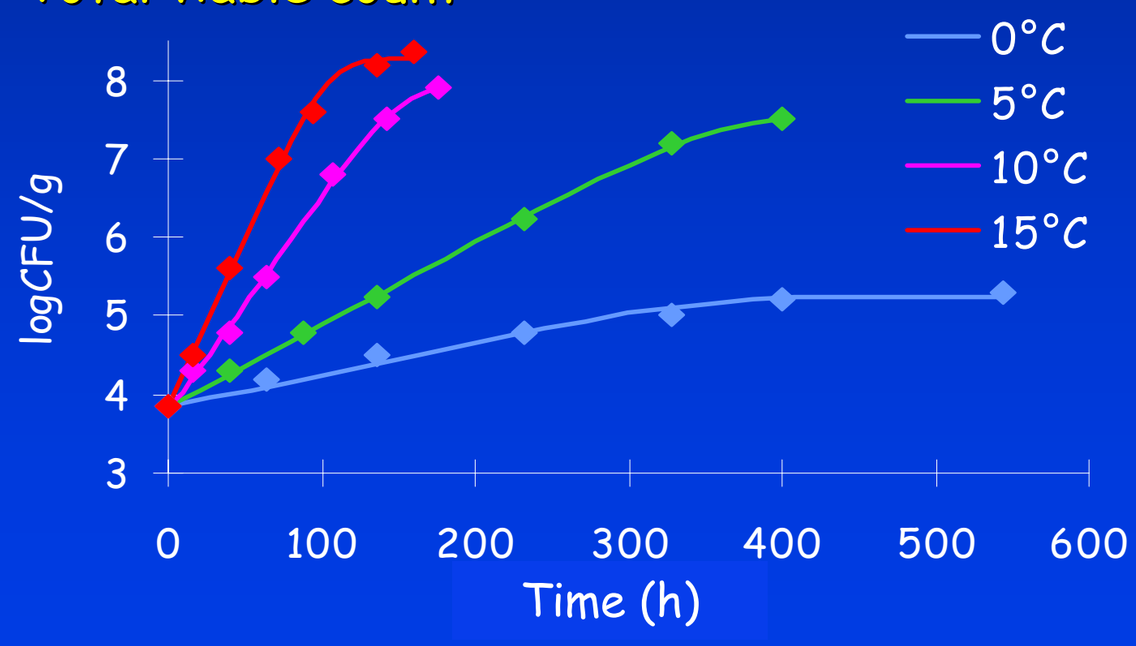
Microbial growth on chilled gilthead seabream fillets packed under MA 50% CO_2 at 0, 5, 10 and 15°C



Total viable count



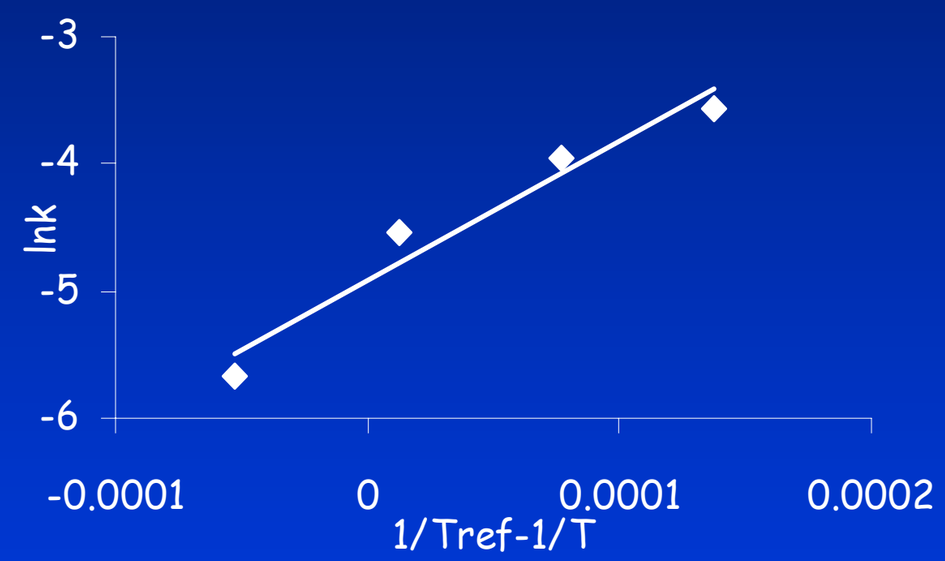
Pseudomonas sp.



Lactic acid bacteria

Specific growth rates k (h^{-1}) and kinetic parameters of lactic acid bacteria in MAP (50% CO_2 – 50% air)

T	k (h^{-1})
0°C	0.00342
5°C	0.01078
10°C	0.01925
15°C	0.02829



Arrhenius equation

$$\ln k = \ln k_{ref} + \frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)$$

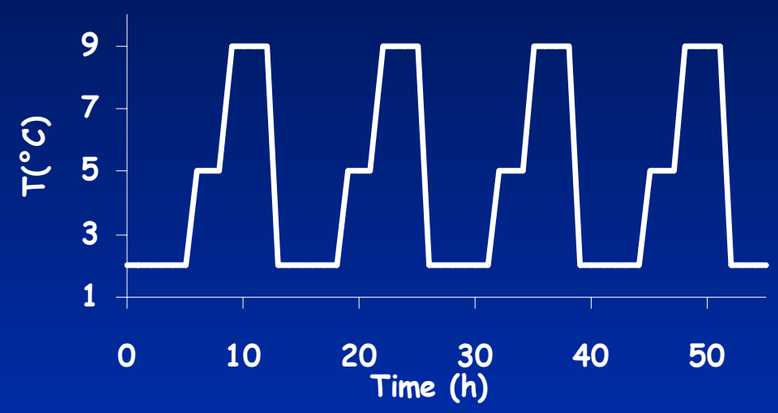
E_a= 91 kJ/mol

$k_{ref(4°C)}$=0.00739 h^{-1}

R^2=0.947

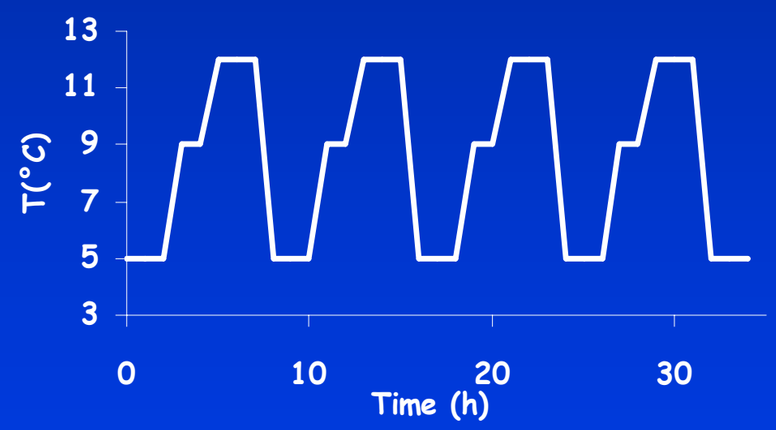
Predicted (SL_{pred}) and experimental shelf life (SP_{exp}) of MAP gilthead seabream fillets under nonisothermal conditions

	50% CO_2
SL_{pred} (h)	235
SL_{exp} (h)	233
% error	-1.0



Scenario 1

	50% CO_2
SL_{pred} (h)	127
SL_{exp} (h)	112
% error	-12.8



Scenario 2

Shelf life evaluation of gilthead sea bream stored in MAP (50% CO_2)

Storage temperature	Shelf life (h) evaluated by microbiological growth (lactic acid bacteria <6 logCFU/g)	Shelf life (h) evaluated by sensory analysis (total impression>5)
0°C	612 (25 d)	563 (23 d)
5°C	268 (11 d)	301 (12 d)
10°C	129 (5 d)	140 (6 d)
15°C	76 (3 d)	82 (3 d)
	E_a= 90.8 kJ/mol	E_a= 85.5 kJ/mol

Application of the Arrhenius-type model for shelf life prediction of chilled gilthead seabream fillets under MAP

$$k = \left(k_{ref} \frac{CO_{2max} - CO_2}{CO_{2max}} \right) \exp\left(\frac{E_a}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right)$$

% CO_2 concentration
Temperature T

→

Shelf life

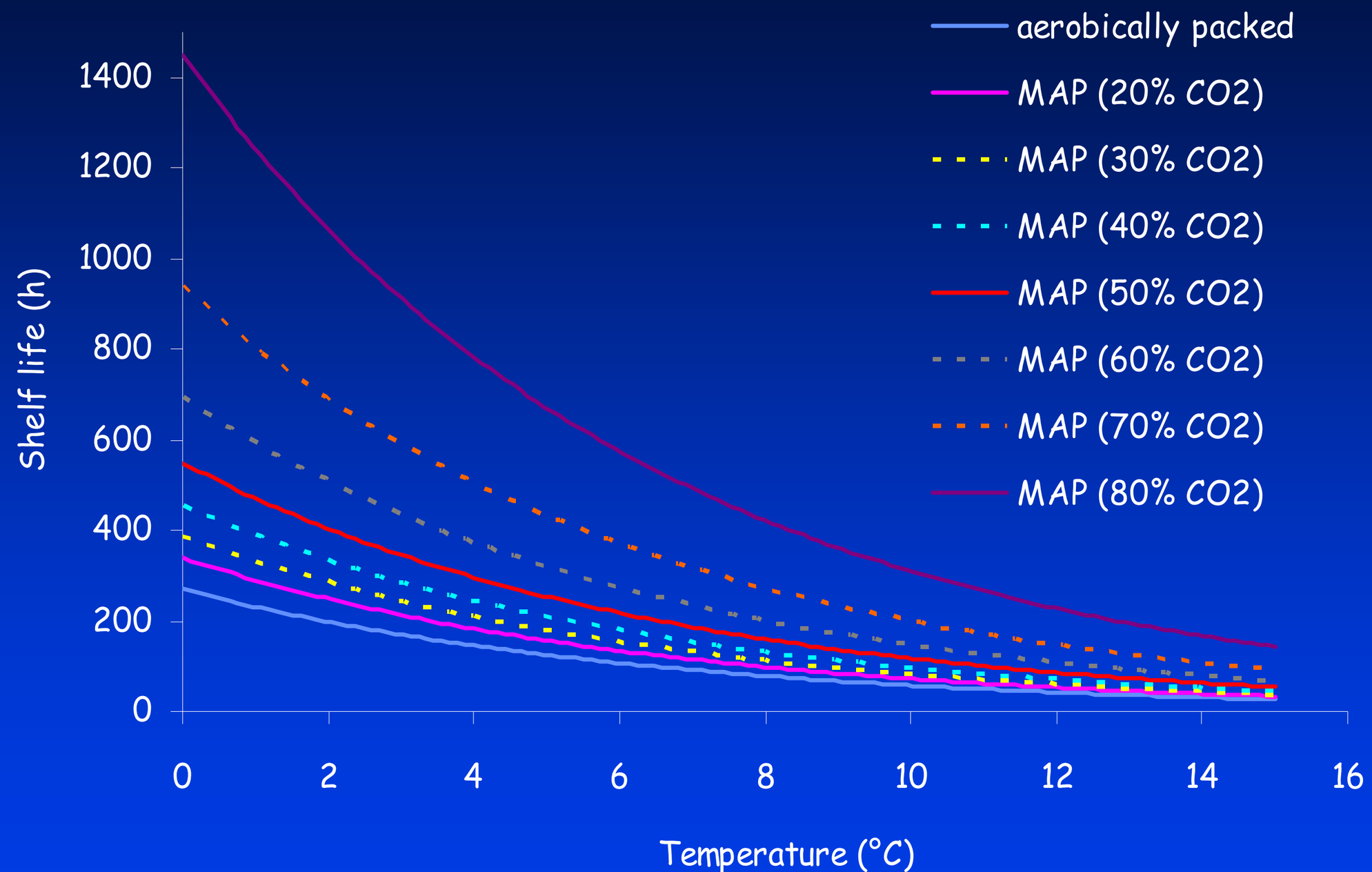
Limit: 10^6 for LAB*

CO_2 concentration

T	20%	30%	40%	50%	60%	70%	80%
0°C	14 d	16 d	19 d	23 d	29 d	40 d	61 d
5°C	6 d	7 d	9 d	10 d	13 d	18 d	28 d

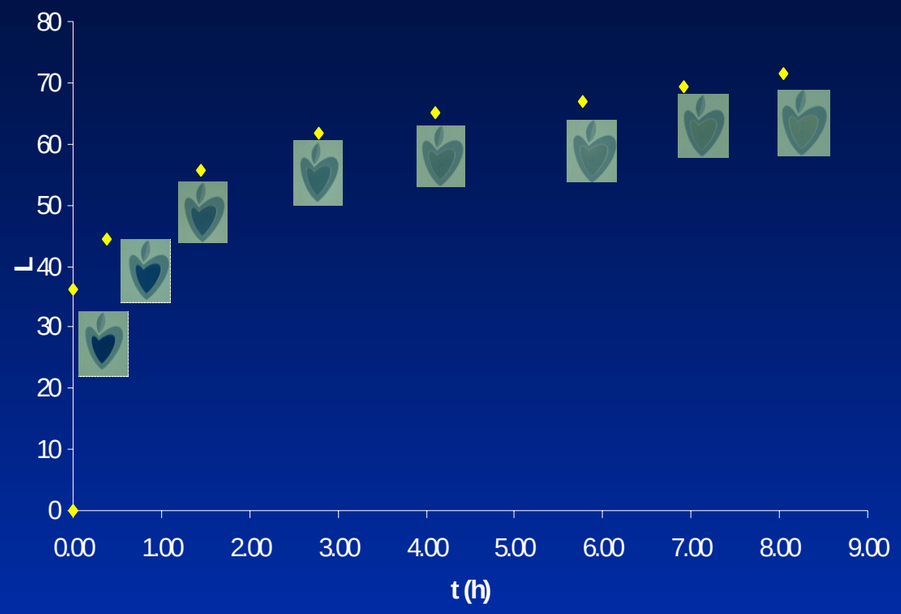
* Based on organoleptic acceptability the end of shelf life coincided with 10^6 LAB for MAP stored samples.

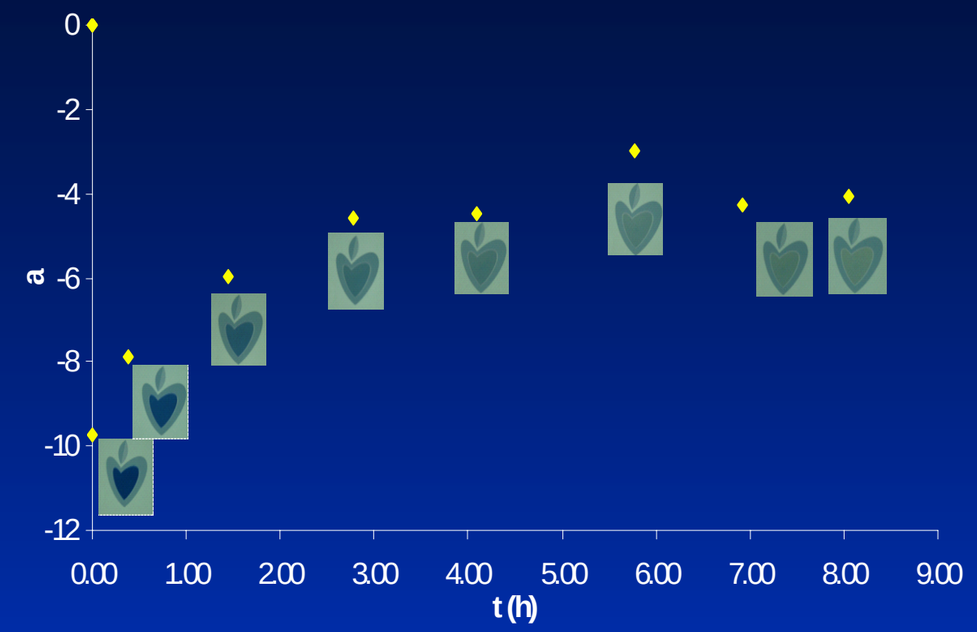
Application of the Arrhenius-type model for shelf life prediction of chilled gilthead seabream fillets under MAP

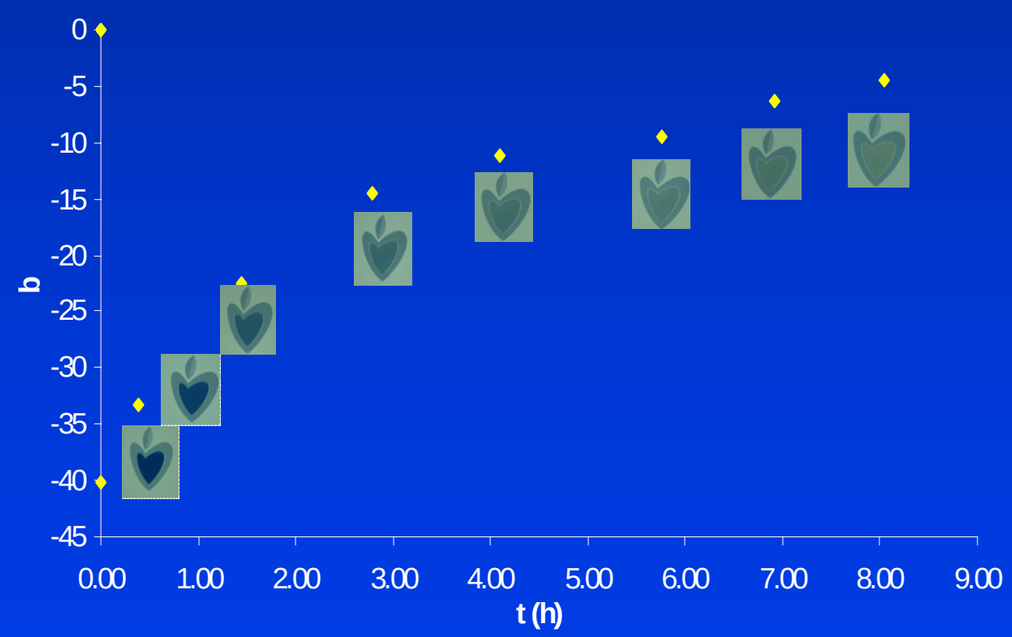


Kinetic Study of the TTIs

Instrumental measurement of TTI colour





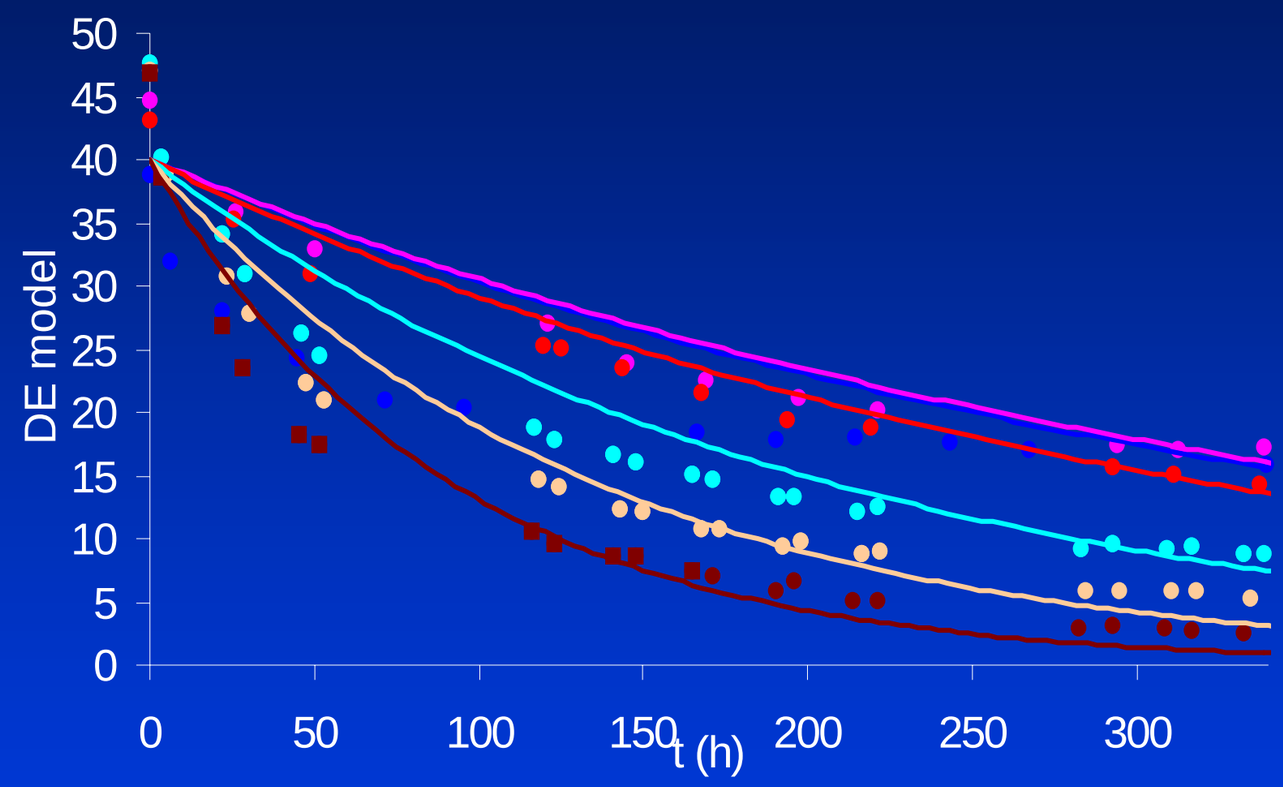


Response function

$$\frac{\Delta E}{\Delta E_0} = \exp^{-kt}$$

$$\Delta E = \sqrt{(L - L_{\max})^2 + (\mathrm{a} - \mathrm{a}_{\min})^2 + (b - b_{\max})^2}$$

B1 TTI response modelling

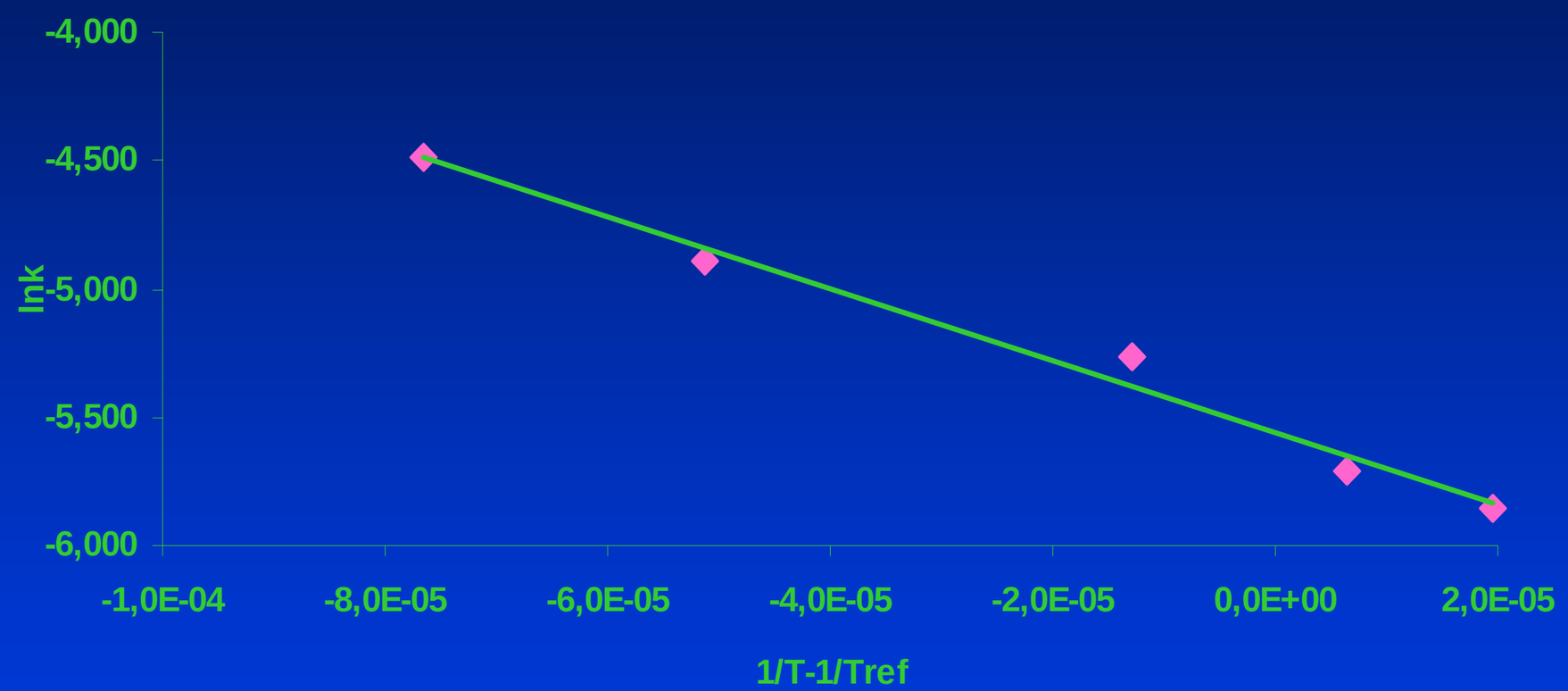


Storage temperature (°C)	Rate k (h^{-1})	Shelf life (hours)
0	0,0019	645,98
2.5	0,0031	396,75
3.5	0,0037	327,27
5	0,0049	245,82
8	0,0087	139,96
10	0,0125	96,79
15	0,0308	39,36

TTI Activation: UV lamp exposure for 2 seconds

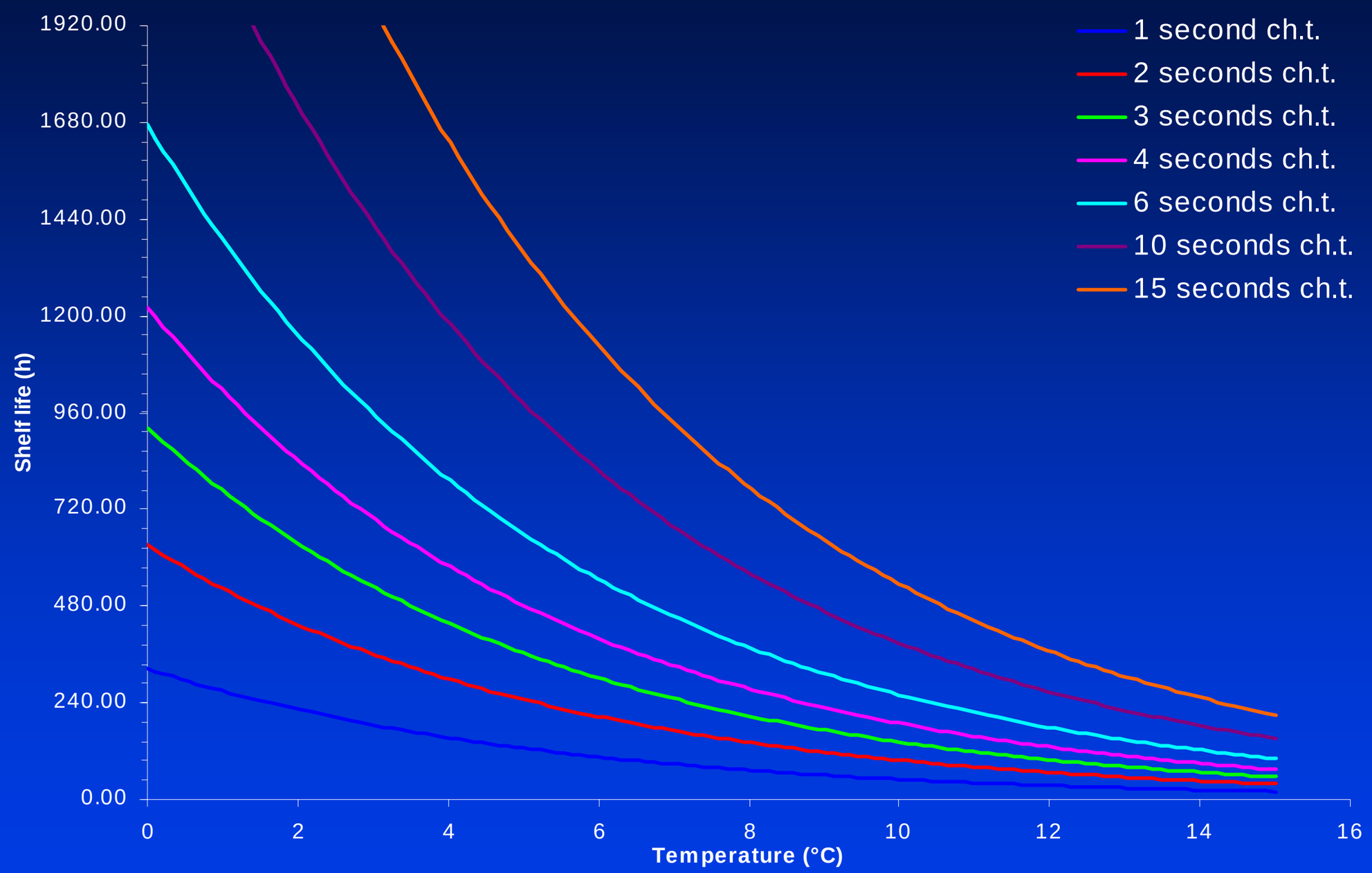
B1 TTI response modelling

E_a=116KJ/mol



TTI Activation: UV lamp exposure for 2s

B1 TTI response modelling



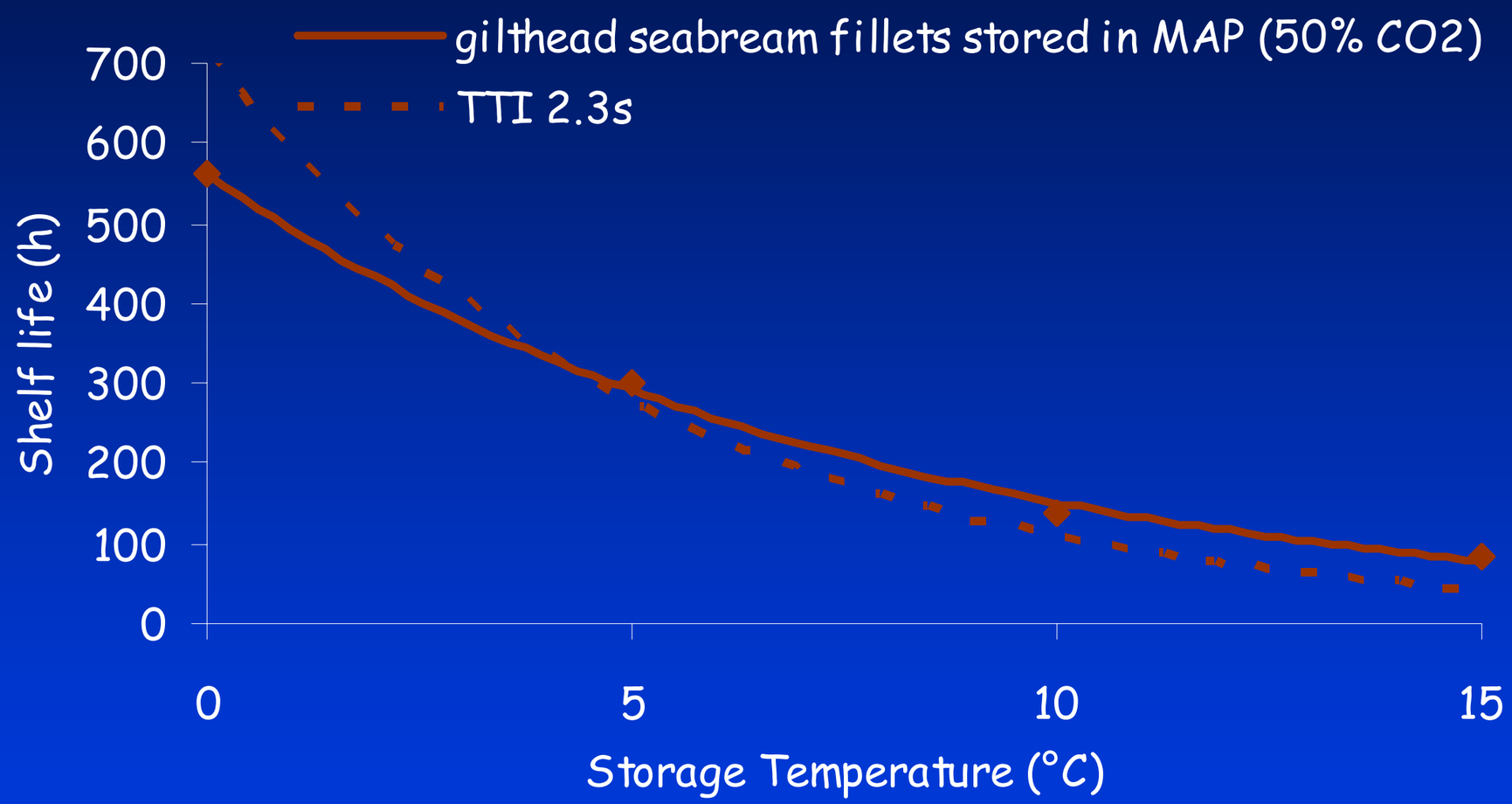
B1 TTI response modeling based on charging energy

$$k = k_{ref\,(4C,1sec)} \cdot t_c^{-a} \cdot \exp\left(\frac{-E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$$

$$k = 0{,}00667 \cdot t_c^{-0{,}71031} \cdot \exp\left(\frac{-122071}{8{,}314} \cdot \left(\frac{1}{T} - \frac{1}{277{,}16}\right)\right)$$

$$E_{UV}(mJ/cm^2) = 50 \cdot t_c(s)$$

$$k = 0.1074 \cdot E_{UV}^{-0{,}71031} \cdot \exp\left(\frac{-122071}{8{,}314} \cdot \left(\frac{1}{T} - \frac{1}{277{,}16}\right)\right)$$



Ciba OnVu Handcharger

Studies of different types of TTIs for monitoring chilled food shelf life

Study of different types of TTIs for monitoring chilled chopped MAP (80% O_2, 12% CO_2, 8% N_2) beef shelf life

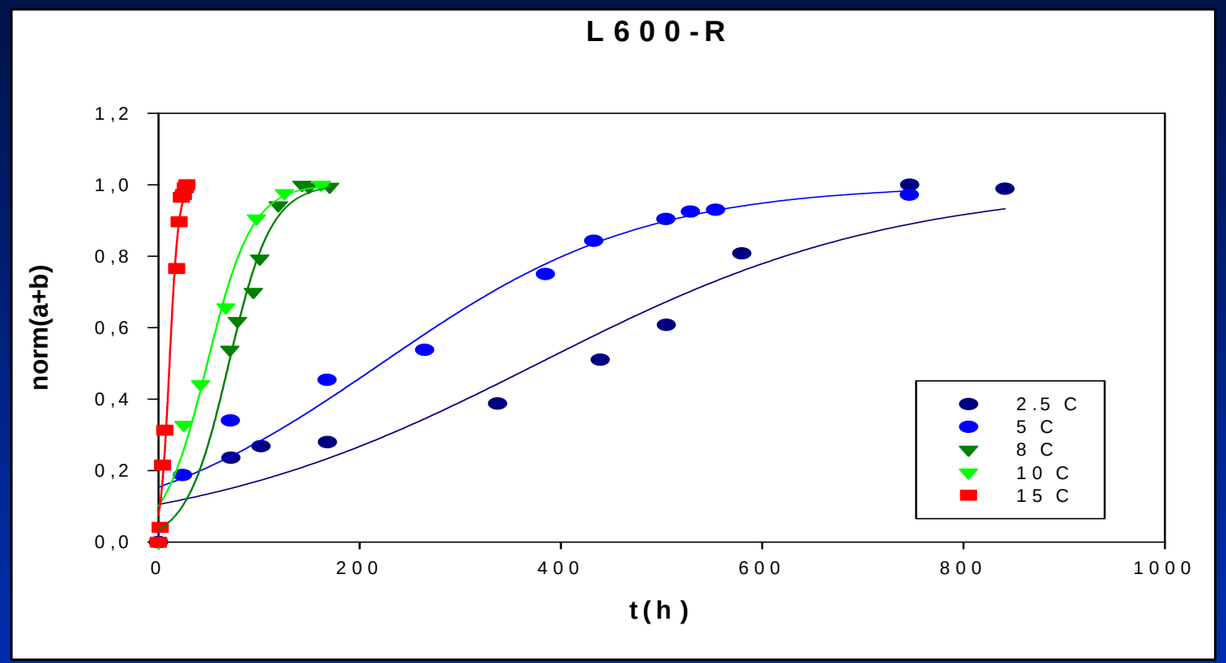
- Kinetic study of three different types of enzymatic TTIs. From each type three TTIs with different concentrations of the enzyme were studied during storage at 2.5, 5, 8, 10 και 15°C.

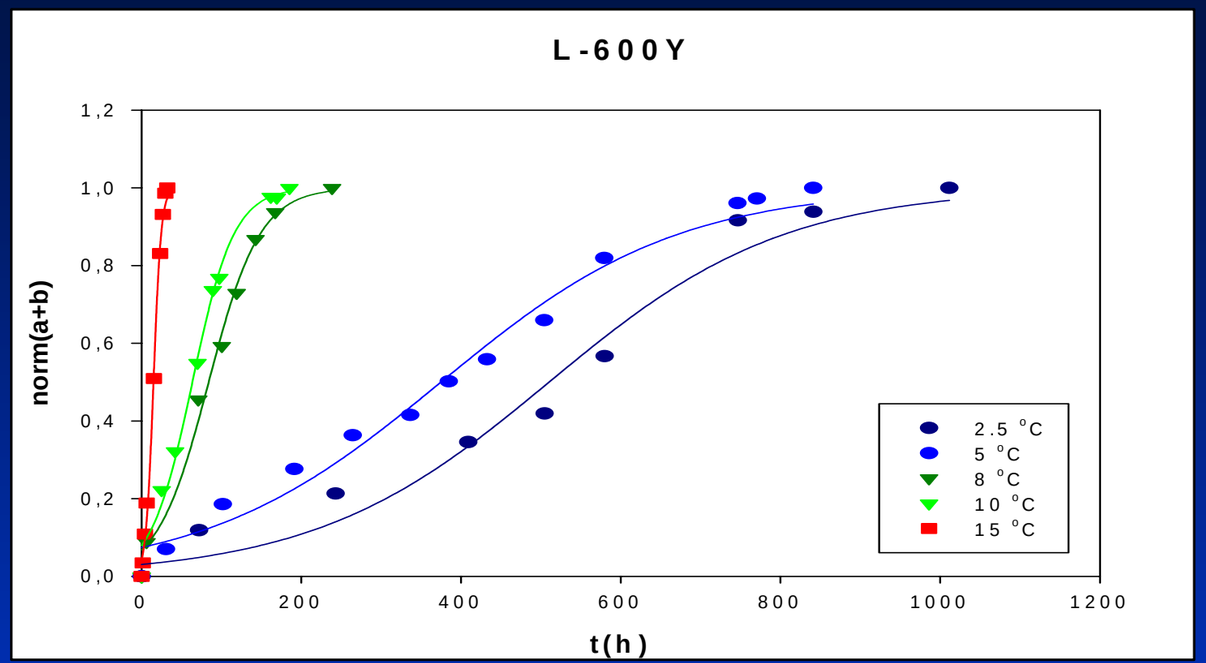
  LP: LP-600U, LP-800U, LP-1000U

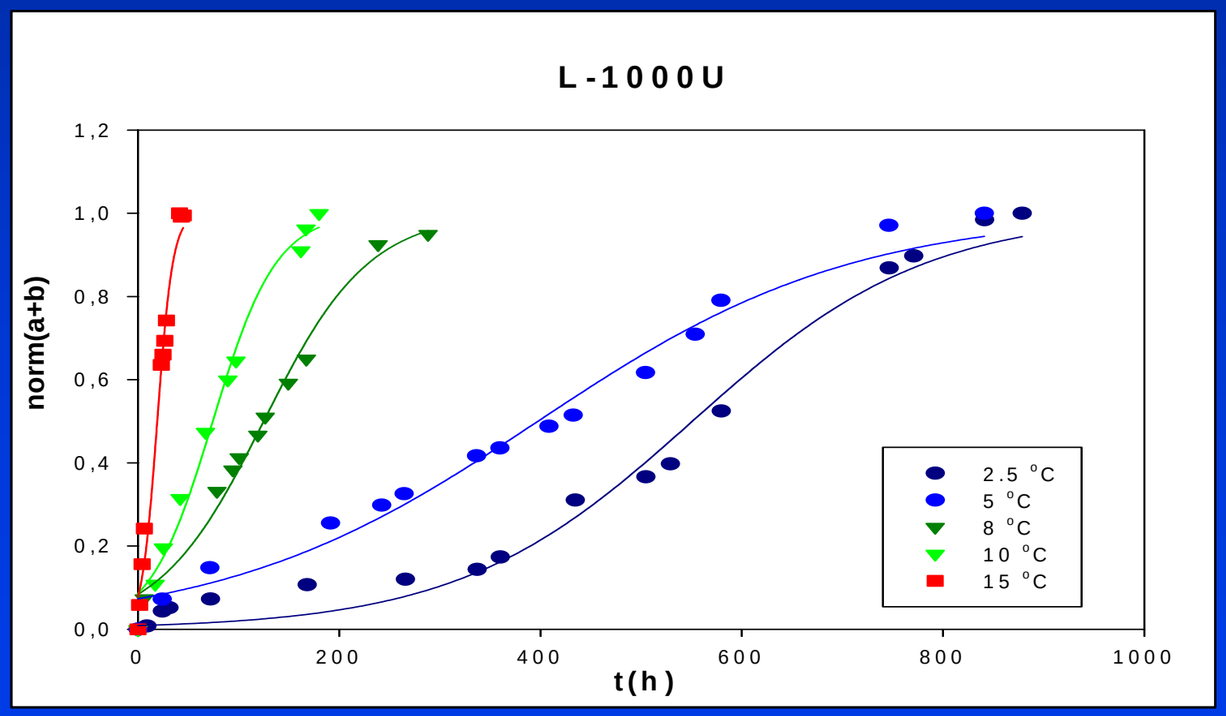
  L: L-600Y, L-600R, L-1000U

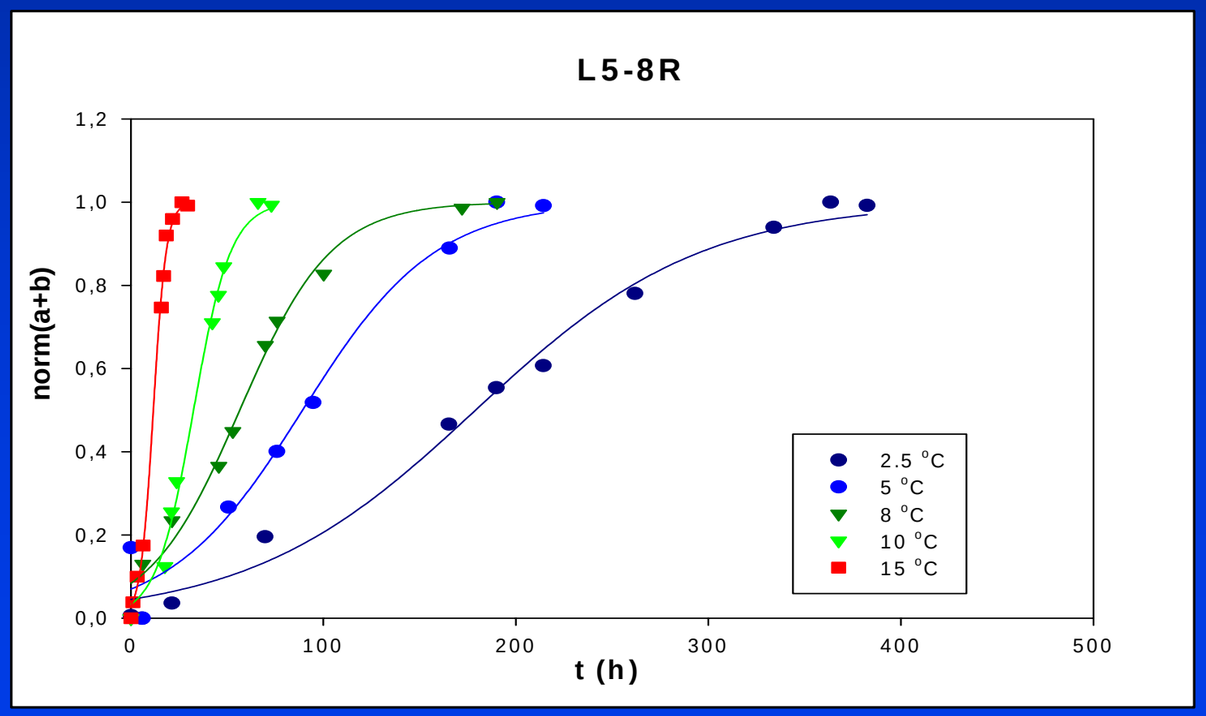
  M: M-50U, M-100U, M-200U
- Kinetic study of photochemical TTI exposed at the UV radiation for 0.2, 0.4, 0.6, 0.8 and 1 sec during storage at 2.5, 5, 8, 10 και 15°C.
- OnVu B1
- Kinetic study of the TTIs at a variable time-temperature profile (5°C -> 4 h, 9°C -> 4 h, 12°C -> 4h)
- Kinetic study of the microbial growth of the chopped meat
- Correlation of the kinetic characteristics of the main microbial growth of the chopped meat with the kinetic characteristics of the TTIs and selection of the appropriate one

Enzymatic TTI response







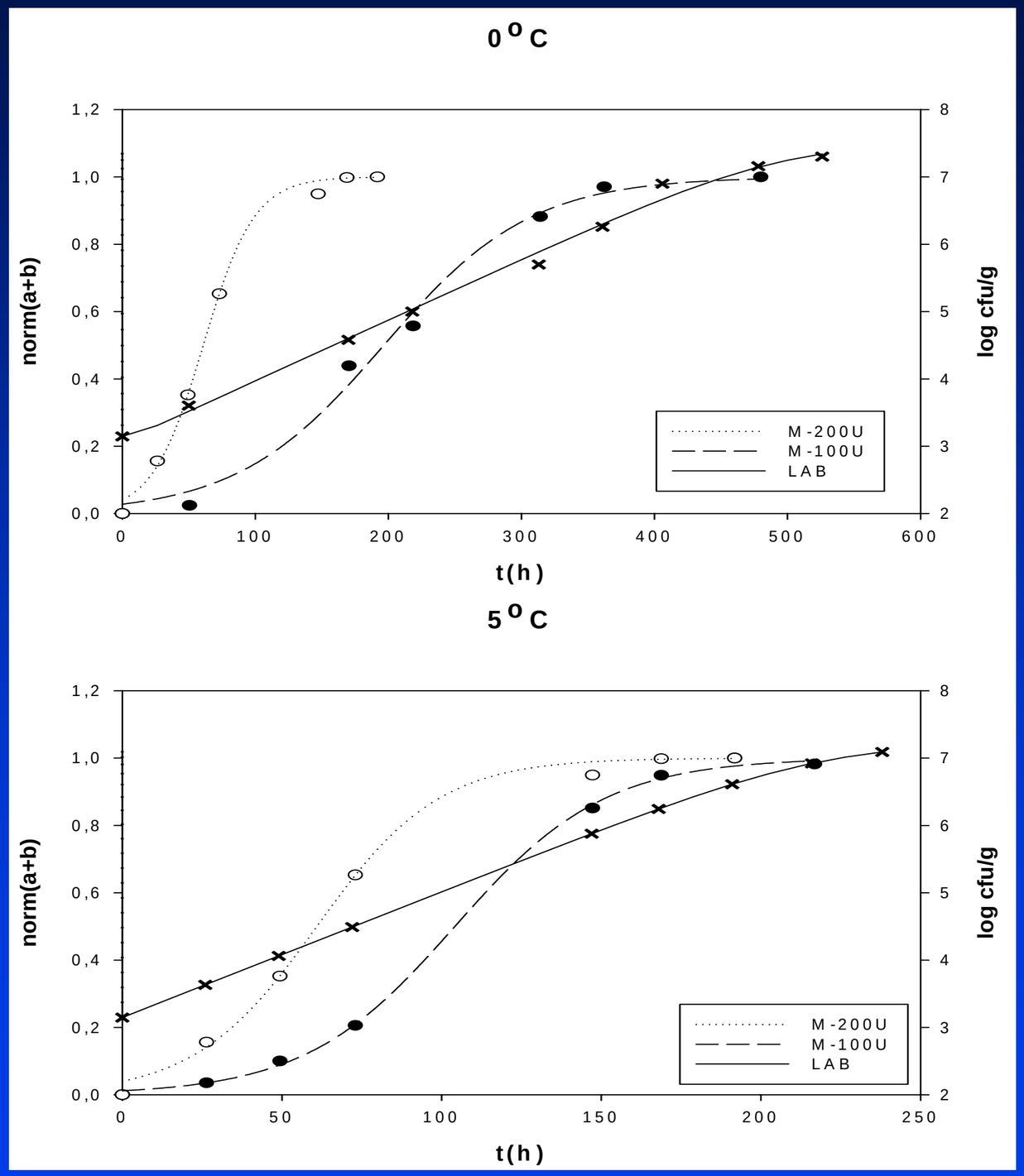


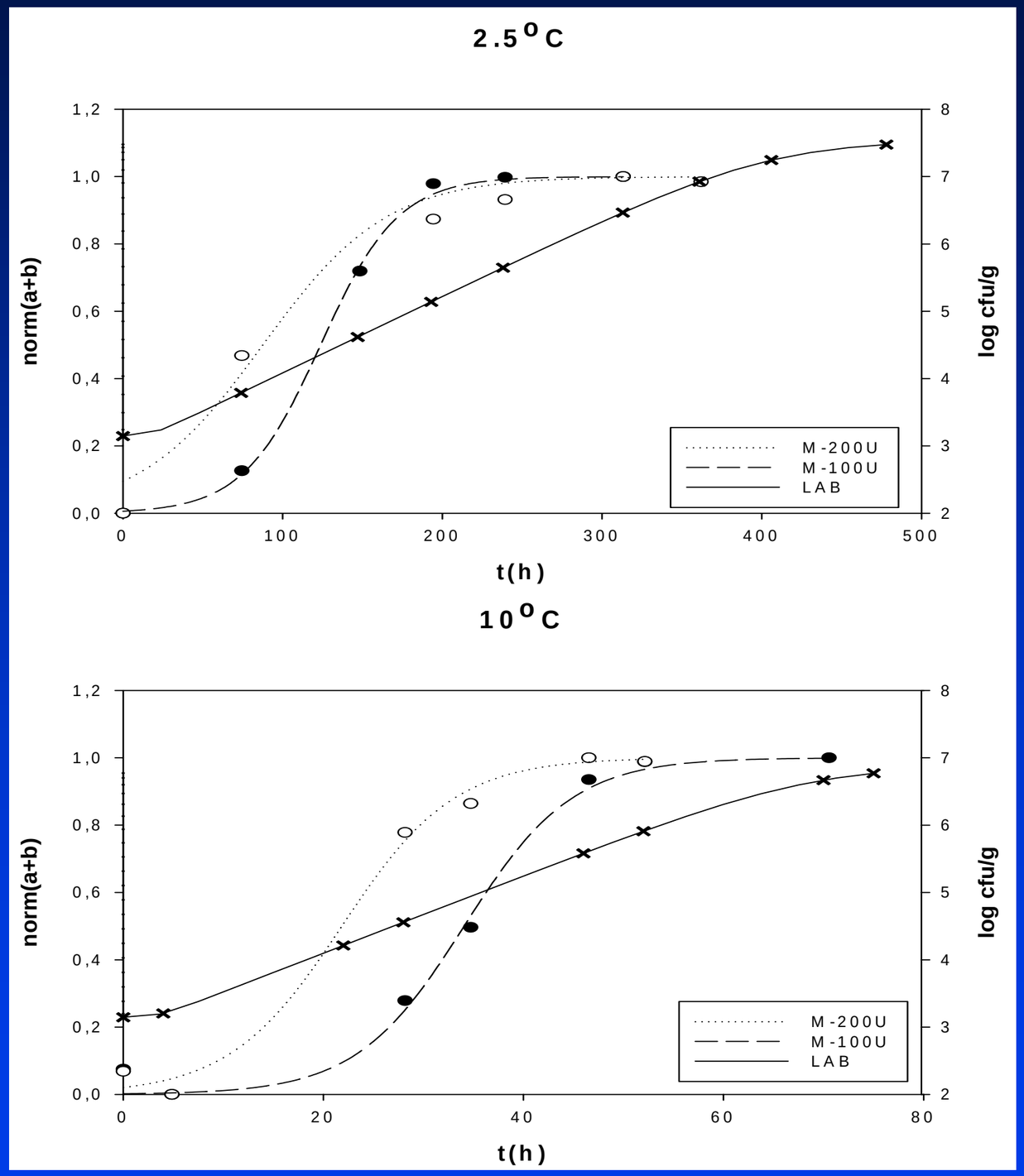
chilled chopped MAP beef shelf life

Kinetic characteristics of the Enzymatic TTIs

Enzymatic TTI	E_A (kJ/mol)	k_{1ref} (h^{-1})	k_{2ref} (h^{-1})	R^2
LP-600U	185.7	39.68	11.24	0.956
LP-800U	181.8	27.80	9.24	0.974
LP-1000U	149.0	16.65	6.05	0.967
L-600R	192.8	74.43	33.68	0.943
L-600Y	194.6	107.88	42.98	0.909
L-1000U	179.4	132.47	49.98	0.915
L5-8R	145.3	55.3	17.44	0.981
M-50U	95.8	81.79	19.09	0.980
M-100U	97.3	41.64	8.94	0.974
M-200U	107.2	24.61	5.32	0.992

Correlation of the response of the Enzymatic TTIs with *lactic acid bacteria* growth





chilled chopped MAP beef shelf life

Determination of a total mathematic model of the Enzymatic TTIs

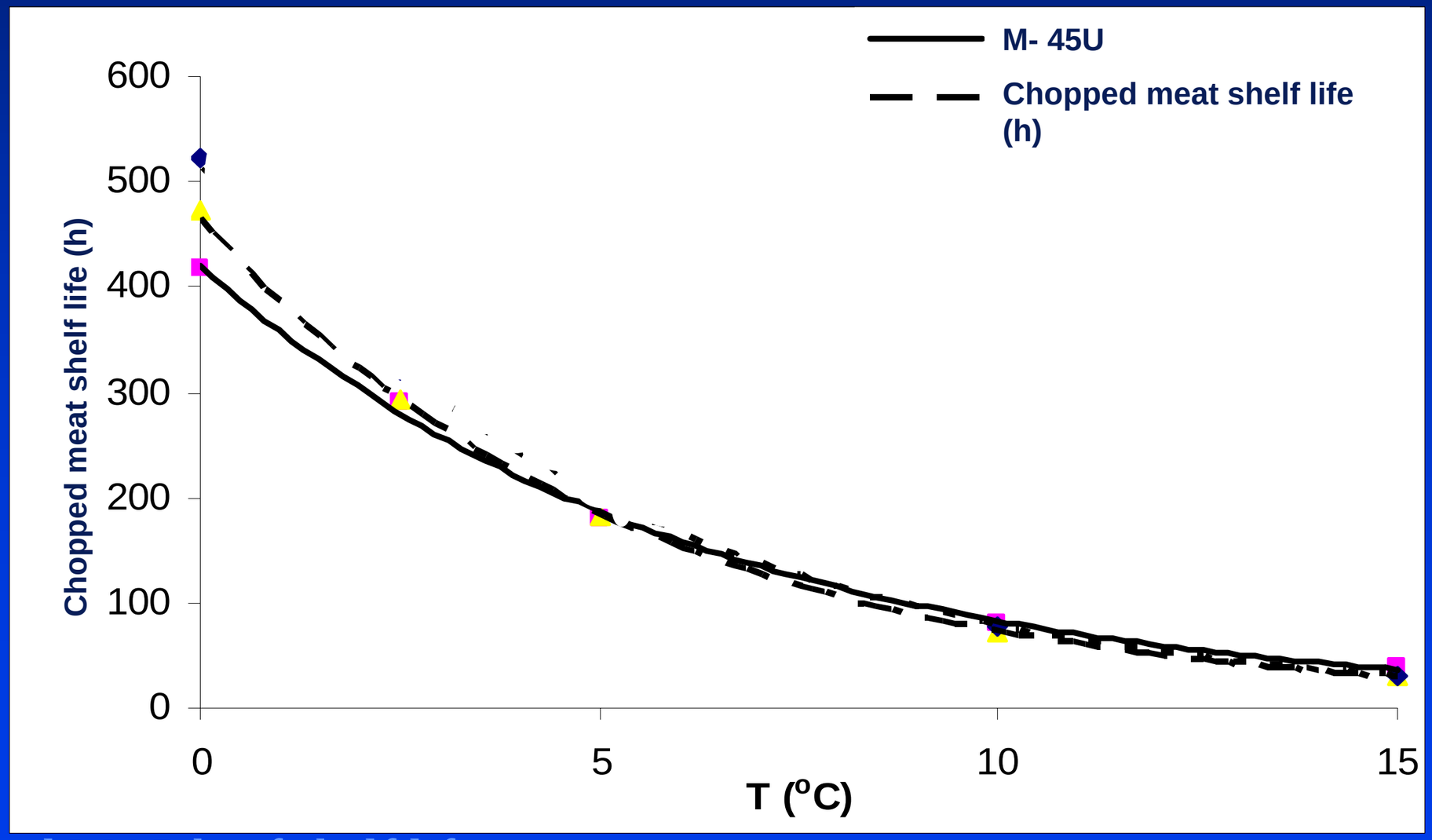
The following mathematic model describes the effect of the time, temperature and the concentration of the enzyme of the TTI on the response of the TTI:

$$X = F(X_C) = \frac{1}{1+\exp\left(\frac{2363.9 * C^{-0.8663} \exp\left[\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right] - t}{675.27 * C^{-0.9217} \exp\left[\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right]}\right)}$$

Parameter	Estimated value
T_{ref} (°C)	4
Eα (KJ/mol)	105.5
R^2	0.987

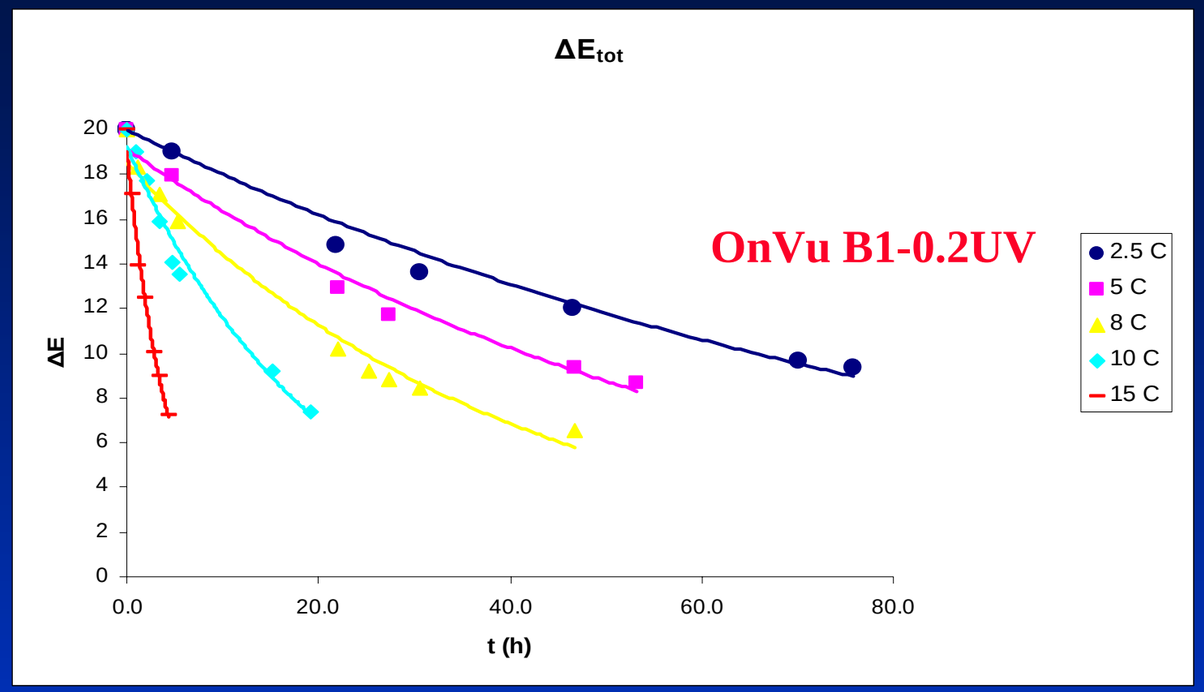
Correlation of the response of the Enzymatic TTI M-45U with the chopped beef shelf life

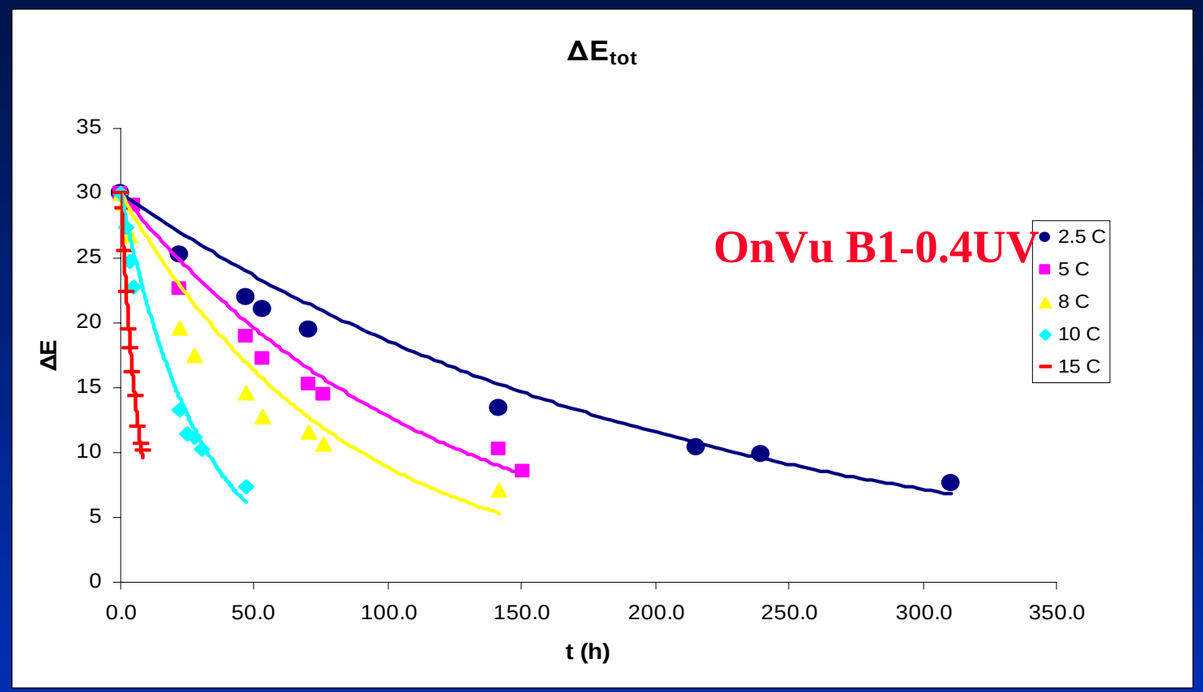
- For the selection of the appropriate enzymatic TTI for monitoring chopped meat shelf life the total mathematic model was used…

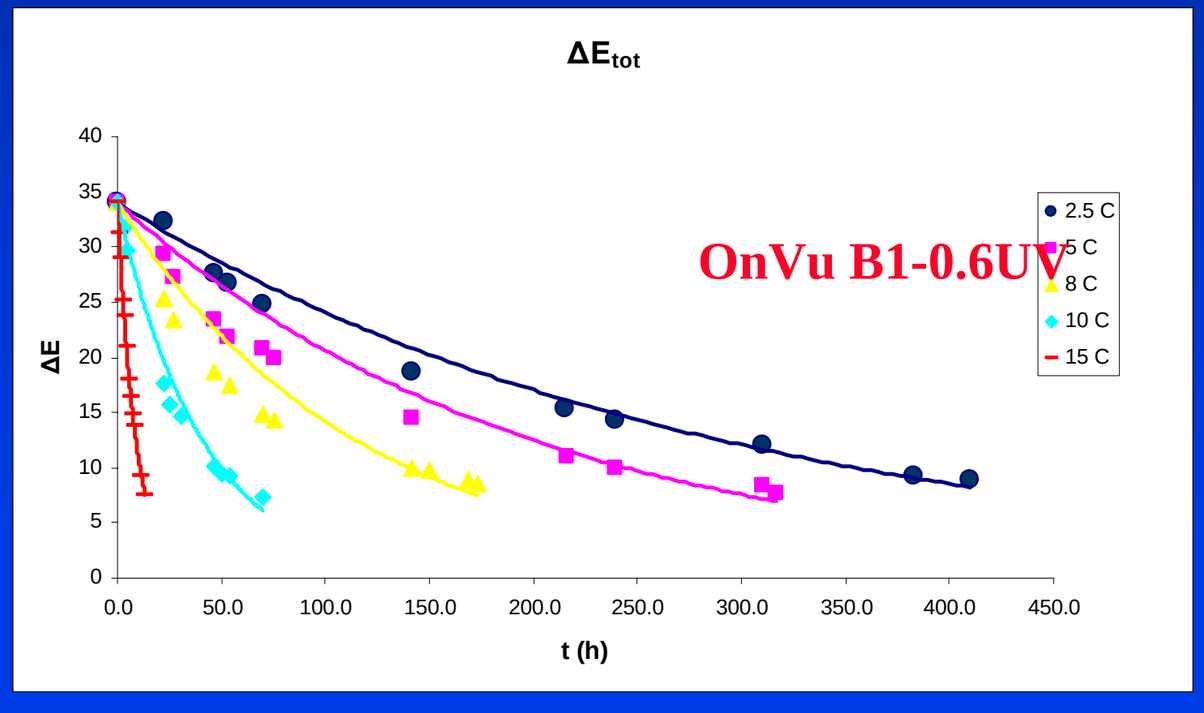


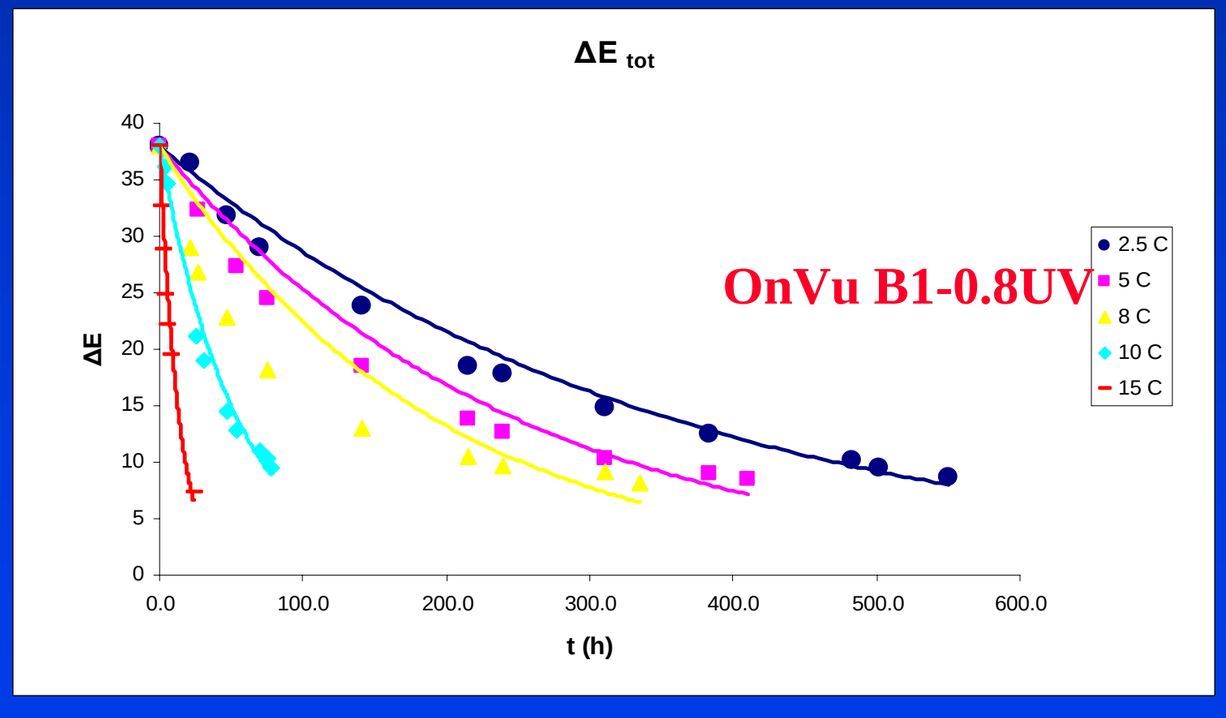
chilled chopped MAP beef shelf life

Photochemical TTI response



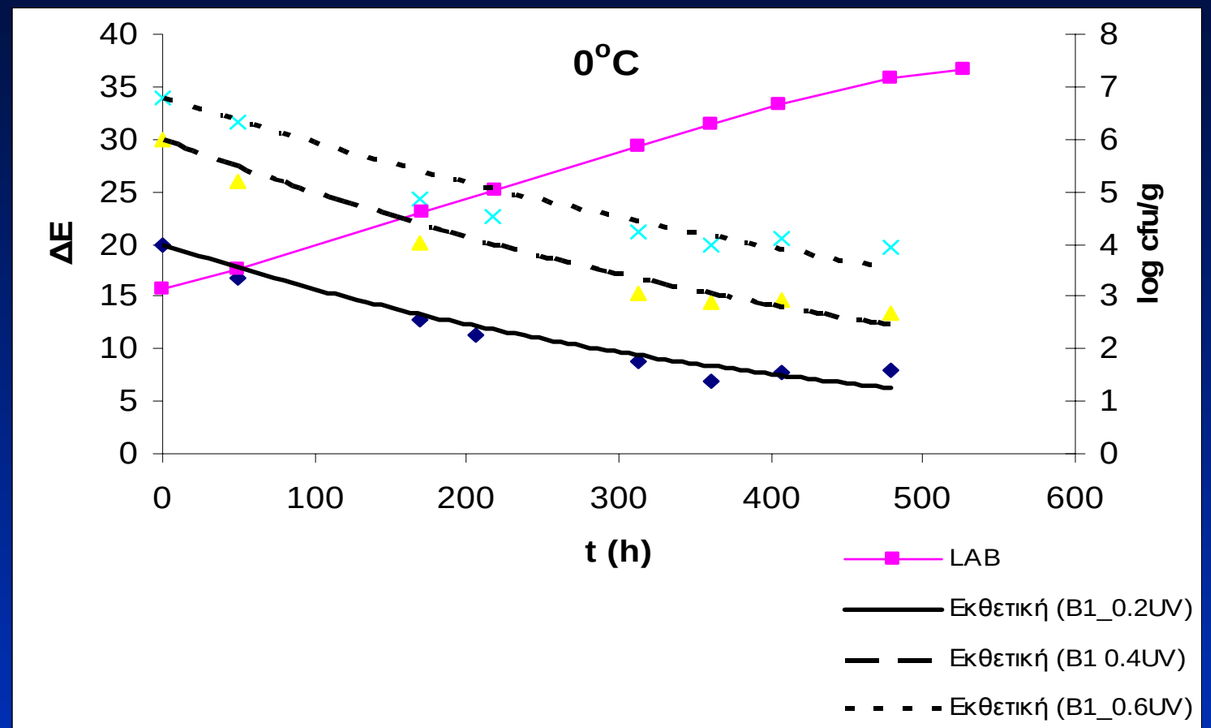


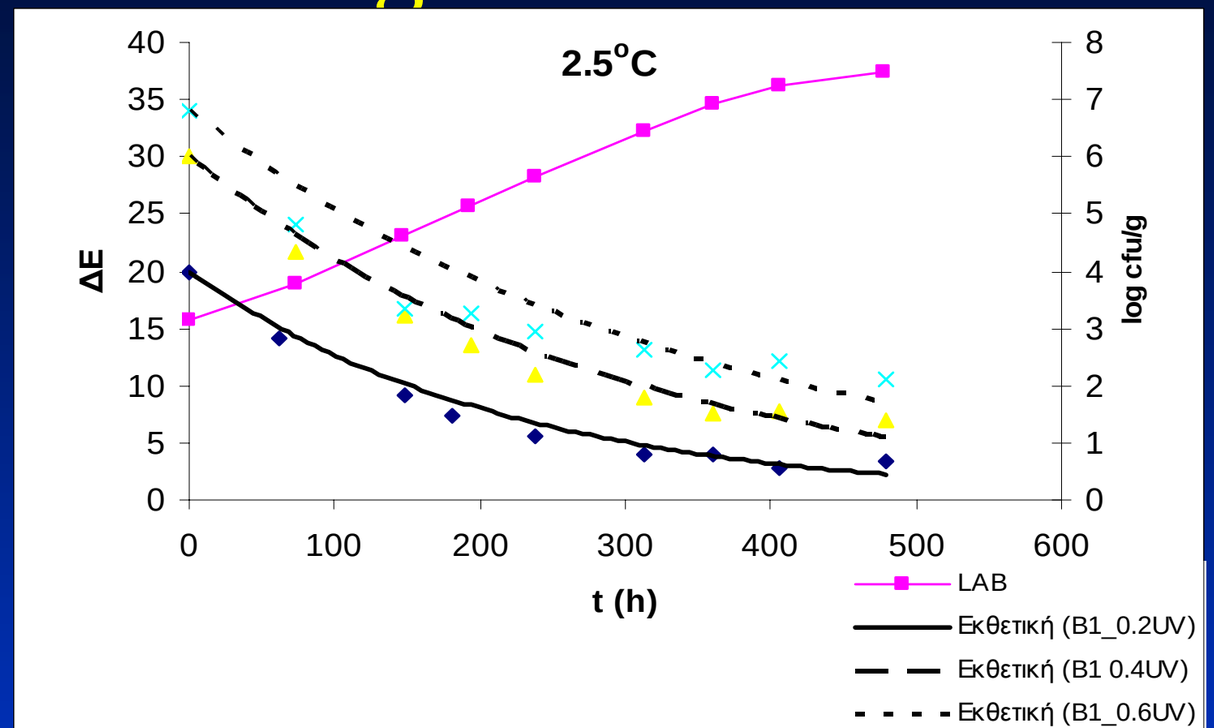


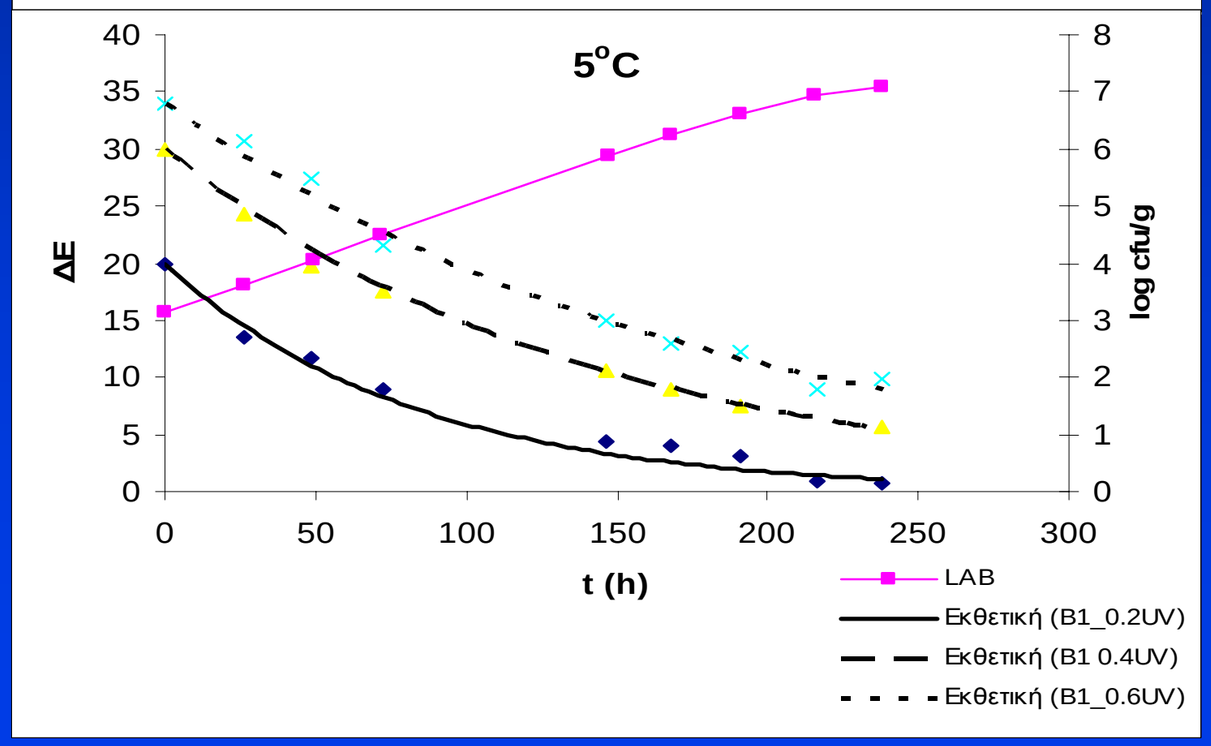


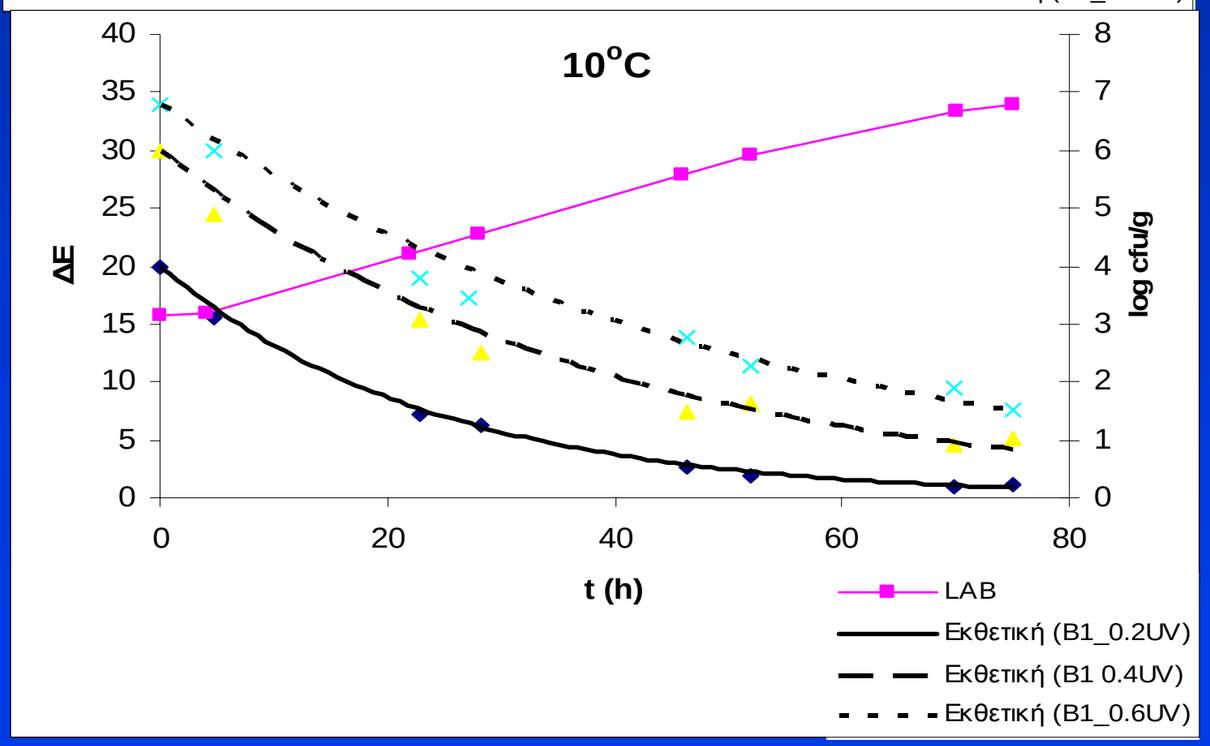
chilled chopped MAP beef shelf life

Correlation of the response of the Photochemical TTI with *lactic acid bacteria* growth









chilled chopped MAP beef shelf life

Kinetic characteristics of the Photochemical TTI

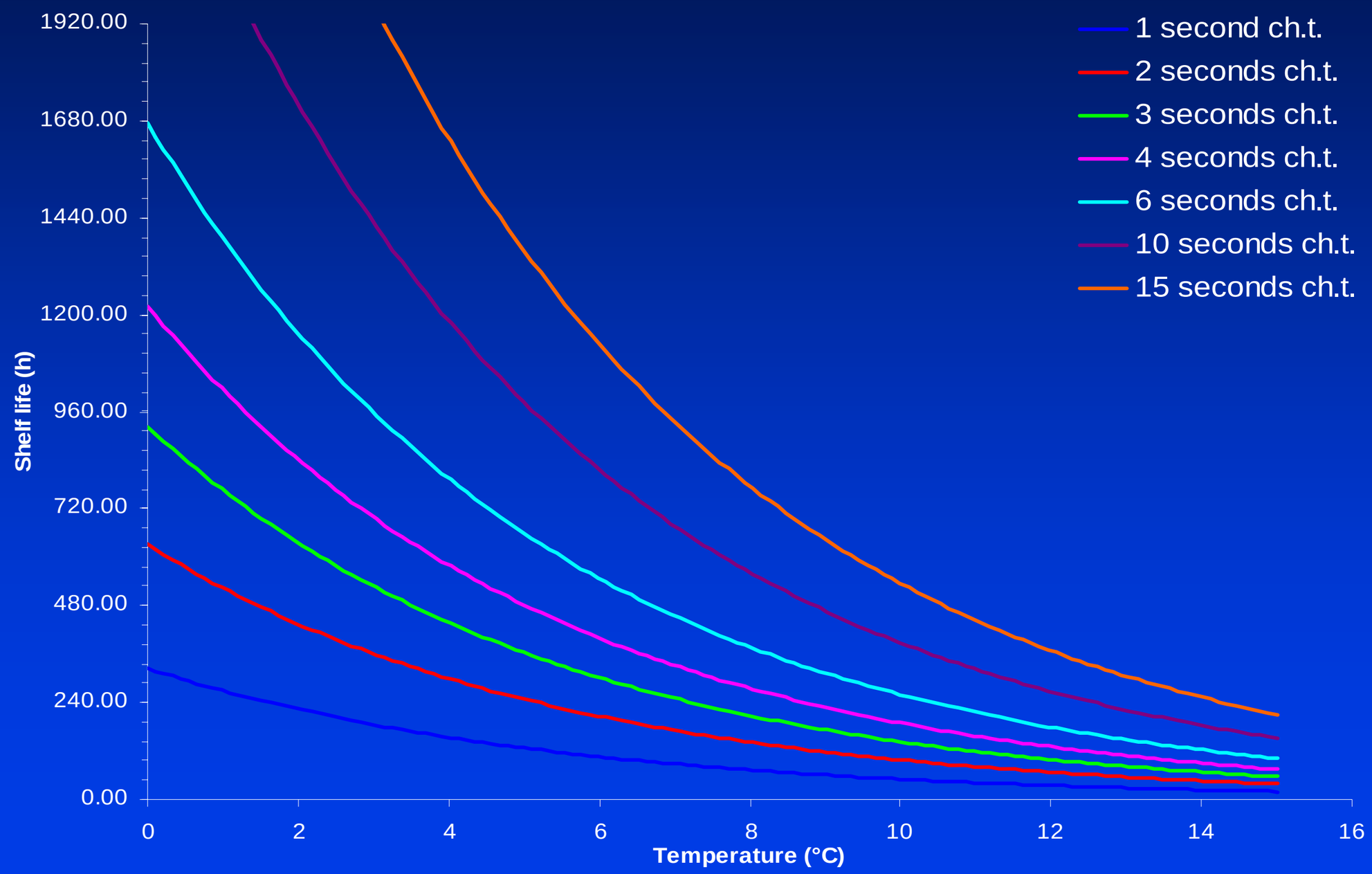
Photochemical TTI	E_A (kJ/mol)	k_A(h^{-1})	R^2
OnVu B1-0.2UV	165.6	0.1296	0.974
OnVu B1-0.4UV	179.4	0.0061	0.967
OnVu B1-0.6UV	188.9	0.0041	0.965
OnVu B1-0.8UV	178.0	0.0037	0.992
OnVu B1-1UV	166.2	0.0035	0.994

Determination of a total mathematic model of the Photochemical TTI OnVu B1

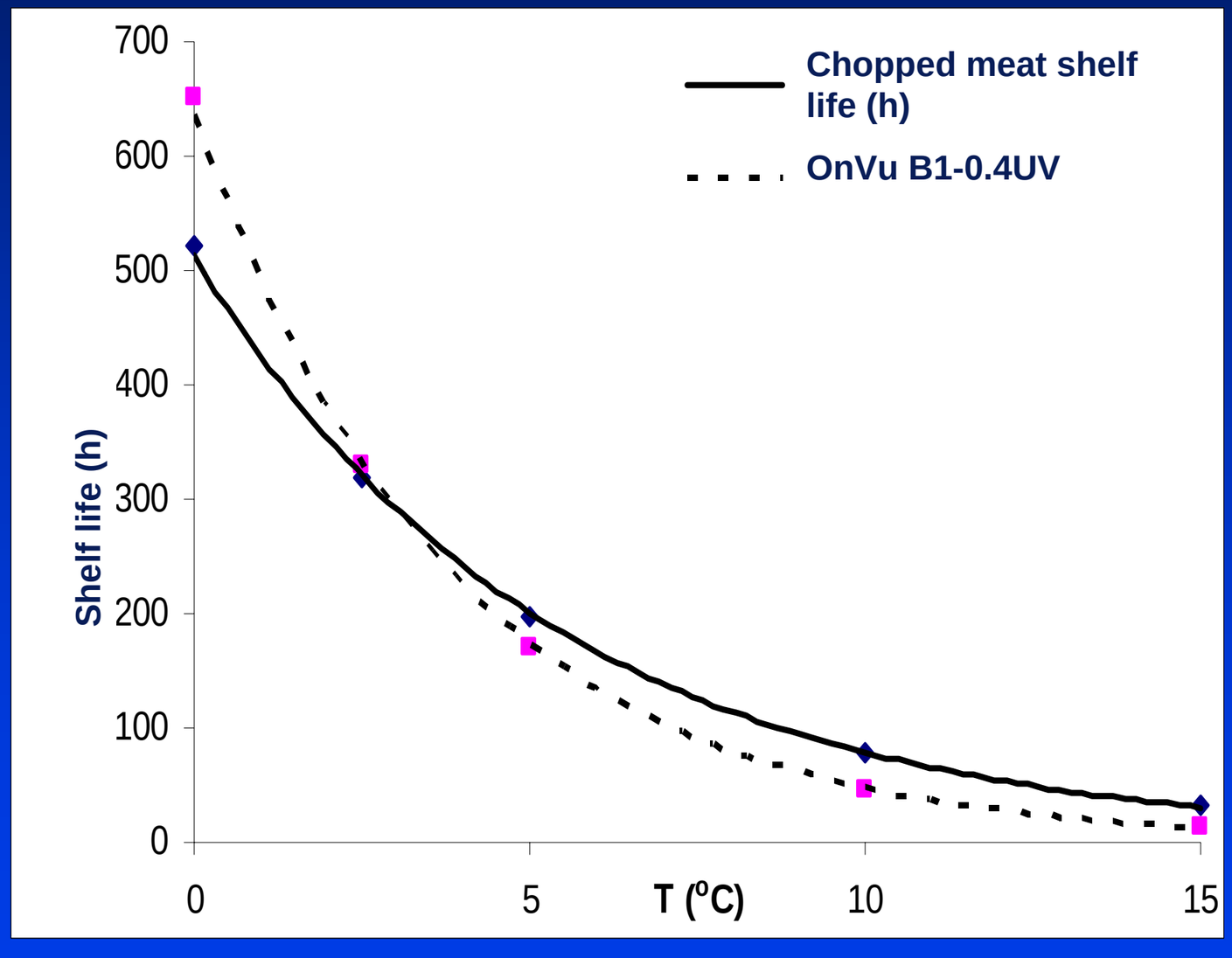
The following mathematic model describes the effect of the temperature and the charging time on the TTI rate constant (k):

$$k = k_{ref\,(Tref, t_c = 0.6s)}\, t_C^{-a} \exp\left(\frac{-Ea}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$$

Parameter	Estimated value
$k_{ref}(h^{-1})$	0.002
α	0.815
Ea (KJ/mol)	199.9


1920.00
1680.00
1440.00
1200.00
960.00
720.00
480.00
240.00
0.00
Shelf life (h)
0
2
4
6
8
10
12
14
16
Temperature (°C)
1 second ch.t.
2 seconds ch.t.
3 seconds ch.t.
4 seconds ch.t.
6 seconds ch.t.
10 seconds ch.t.
15 seconds ch.t.

Correlation of the response of the Photochemical TTI B1-0.4 s UV with the chopped meat shelf life



chilled chopped MAP beef shelf life

S M A S

Development and application of a TTI based Safety Monitoring and Assurance System for Chilled Meat Products

A European Commission Research and Technology Development Project

Quality of life and management of living resources

http://smas.chemeng.ntua.gr

Current practice: First In- First Out (FIFO)

Disadvantages:

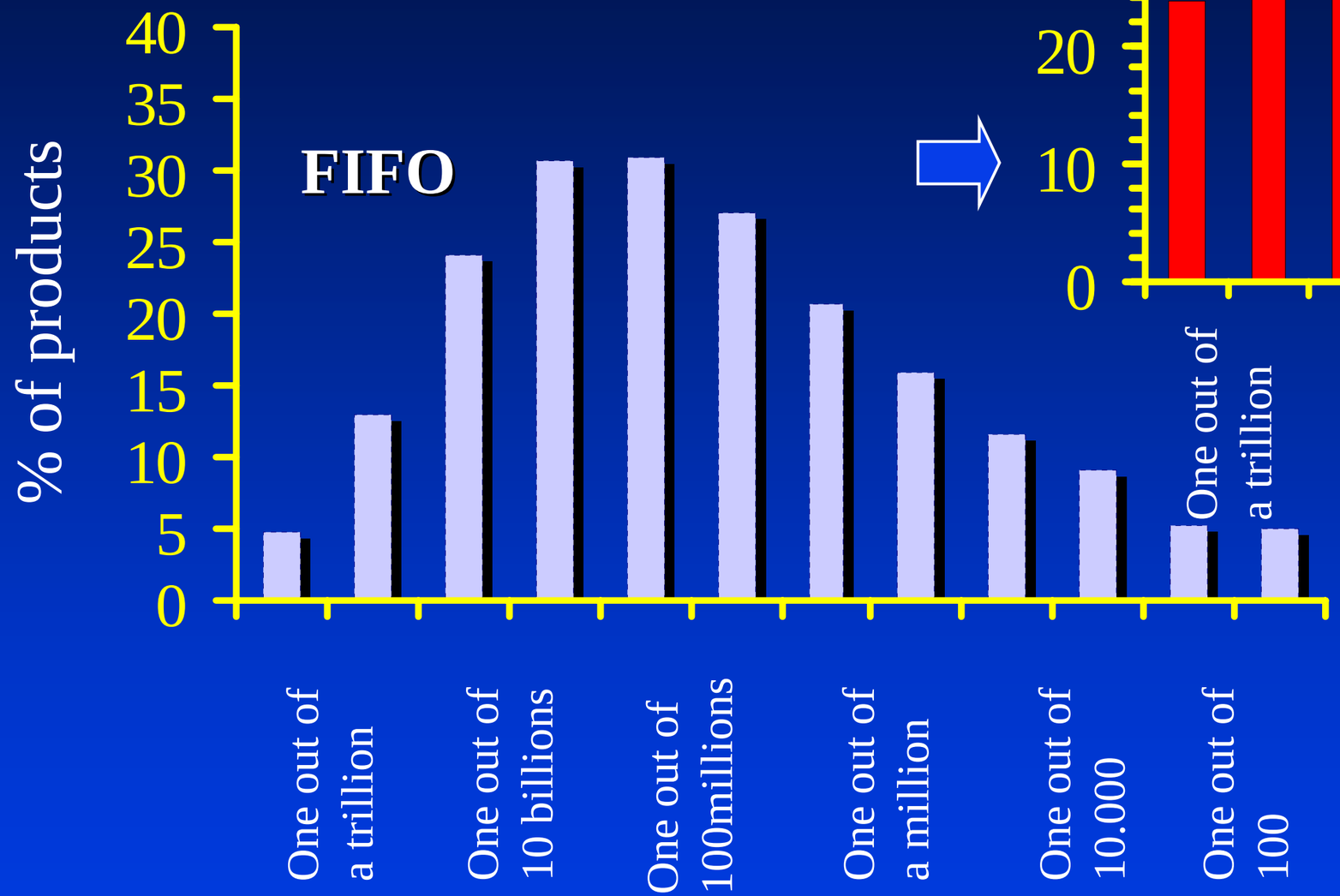
✓ ignores variations of product characteristics
✓ ignores the REAL time-temperature history of the product

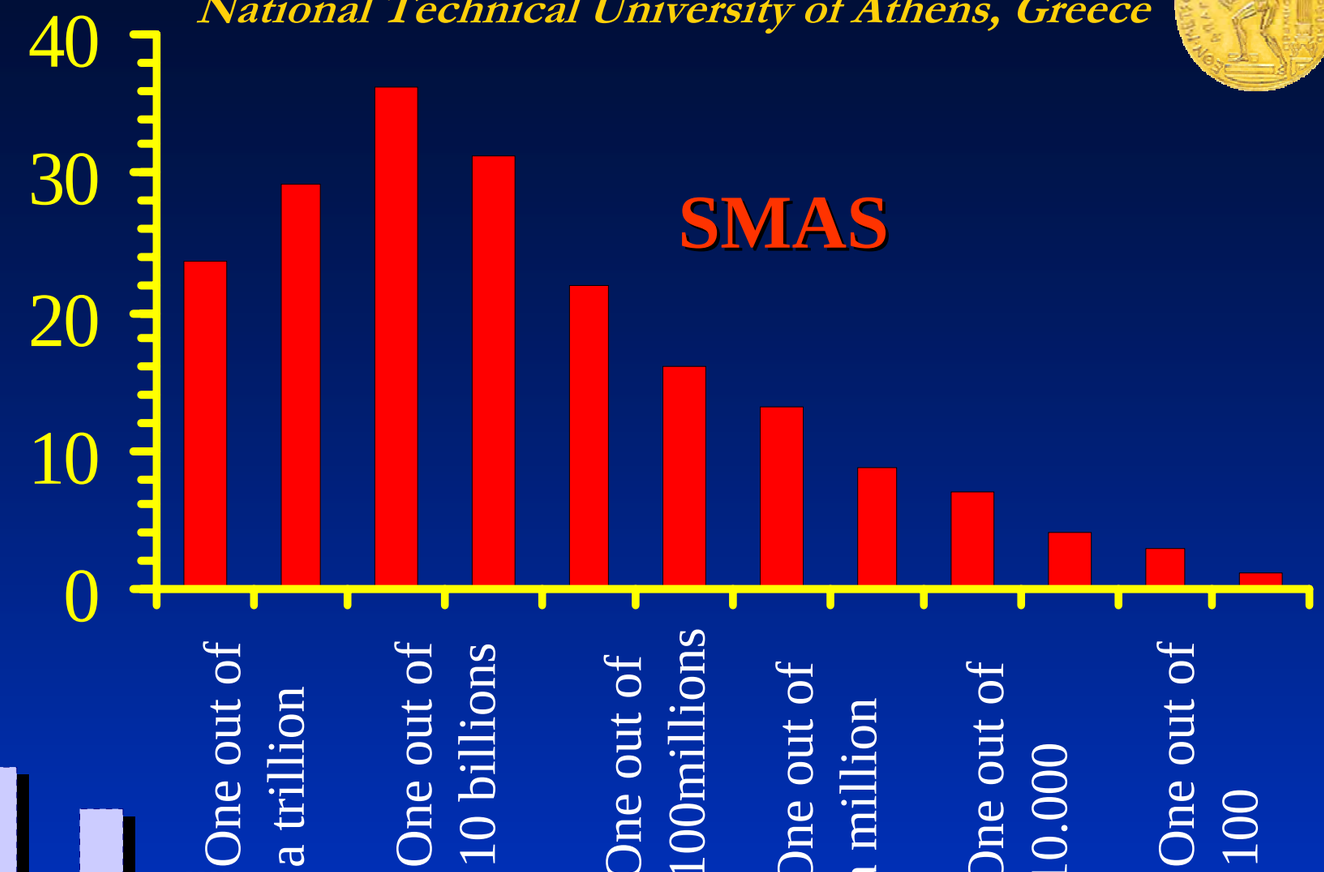
Proposed practice: SMAS

Main Advantages:

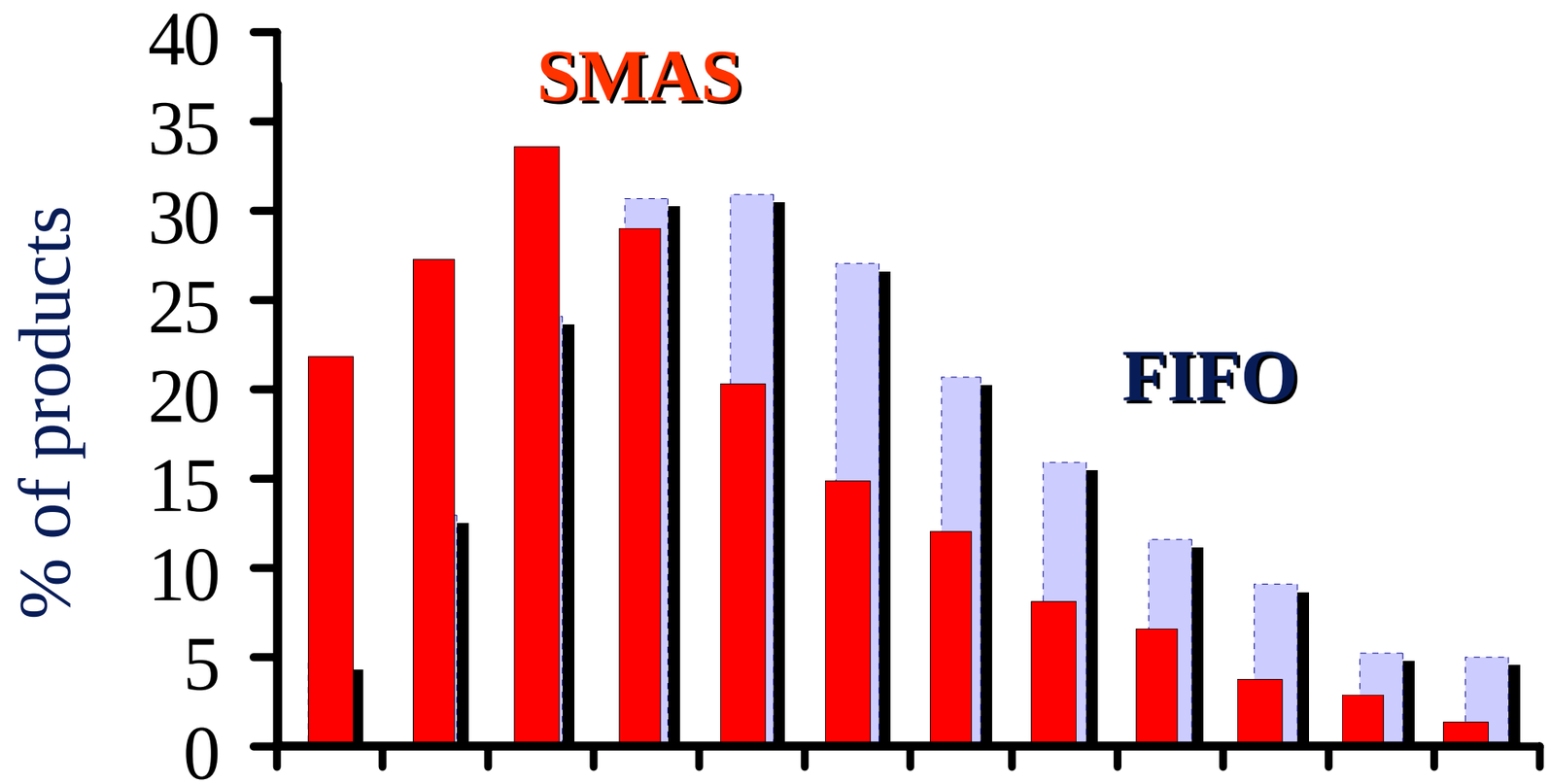
✓variations of product characteristics are considered
✓the REAL time-temperature history of the product is taken into account based on TTI response

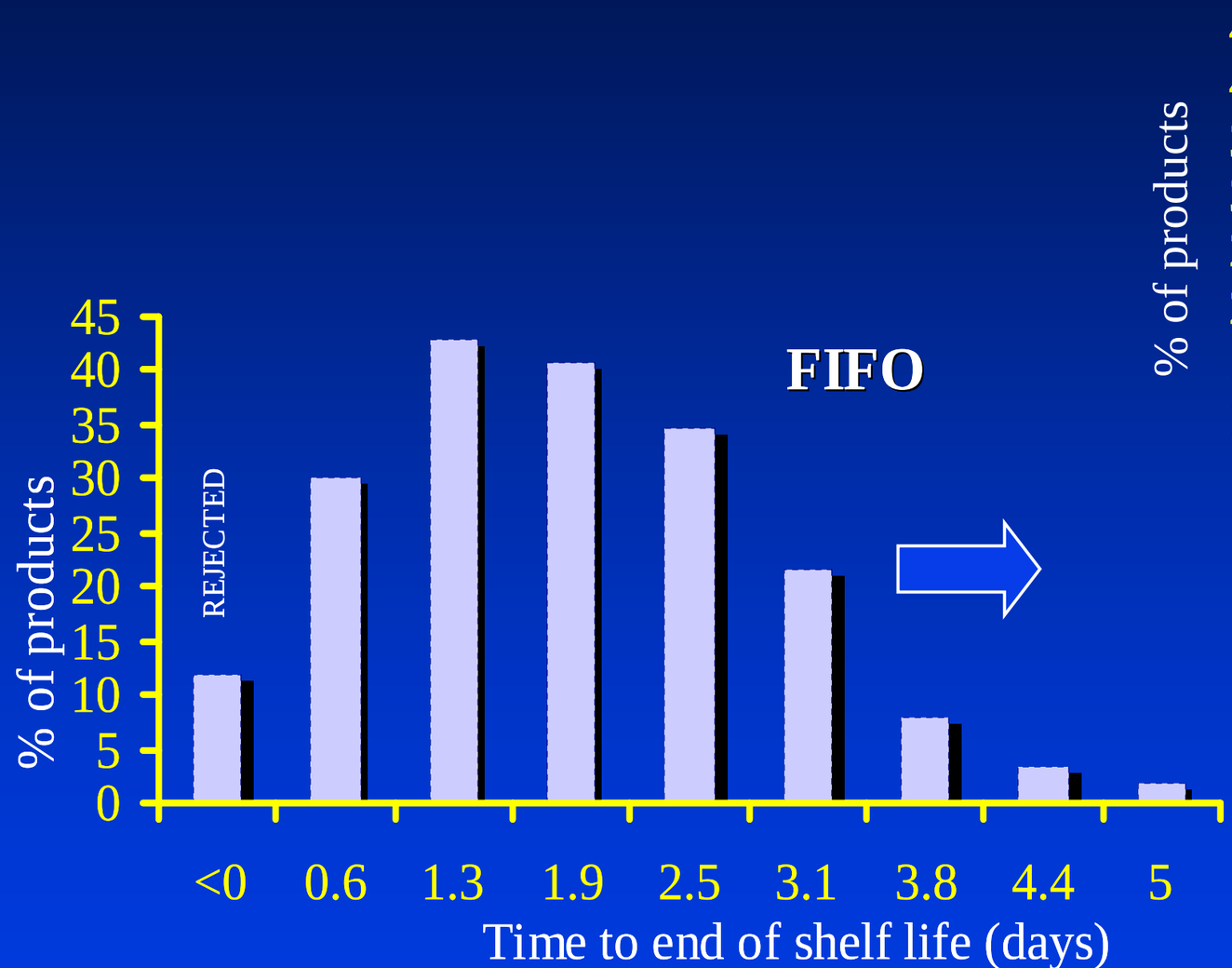
The contribution of SMAS in the chill chain management can be visualized as a minimization of risk for illness and optimisation of the product quality at the time of consumption

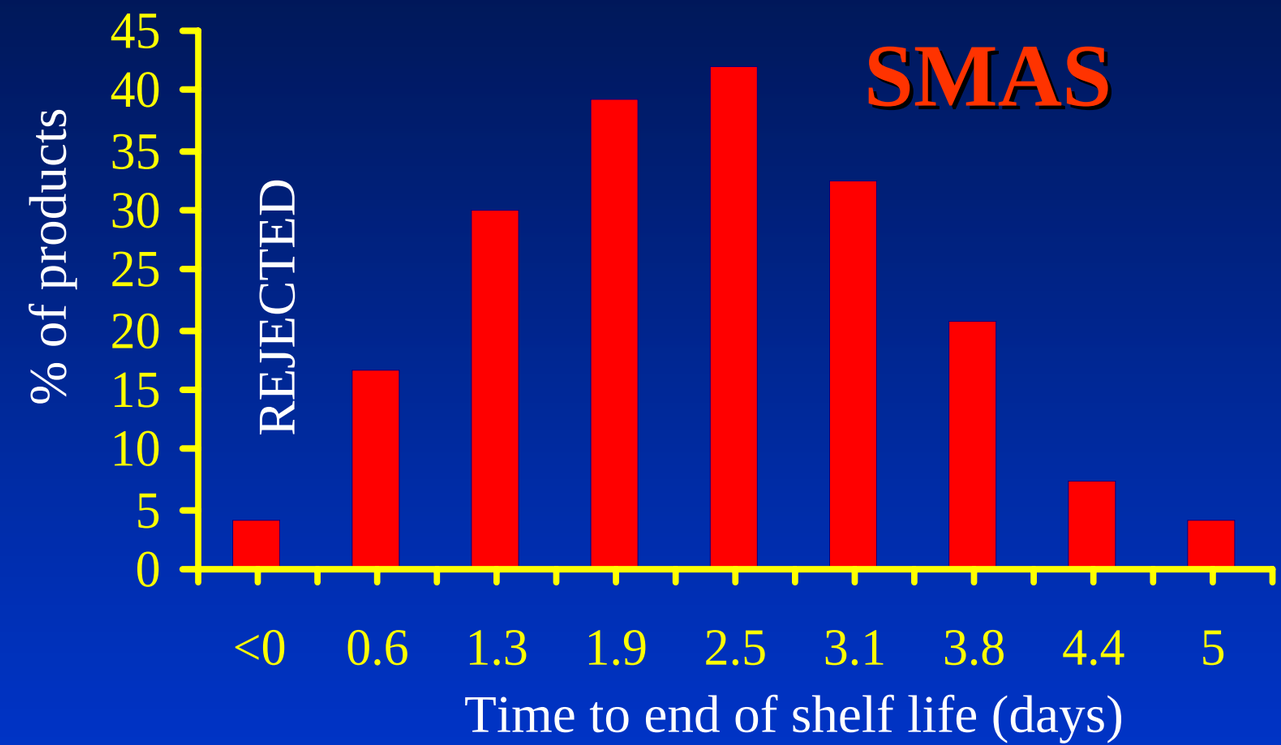

FIFO
% of products
40
35
30
25
20
15
10
5
0
One out of a trillion
One out of 10 billions
One out of 100millions
One out of a million
One out of 10.000
One out of 100

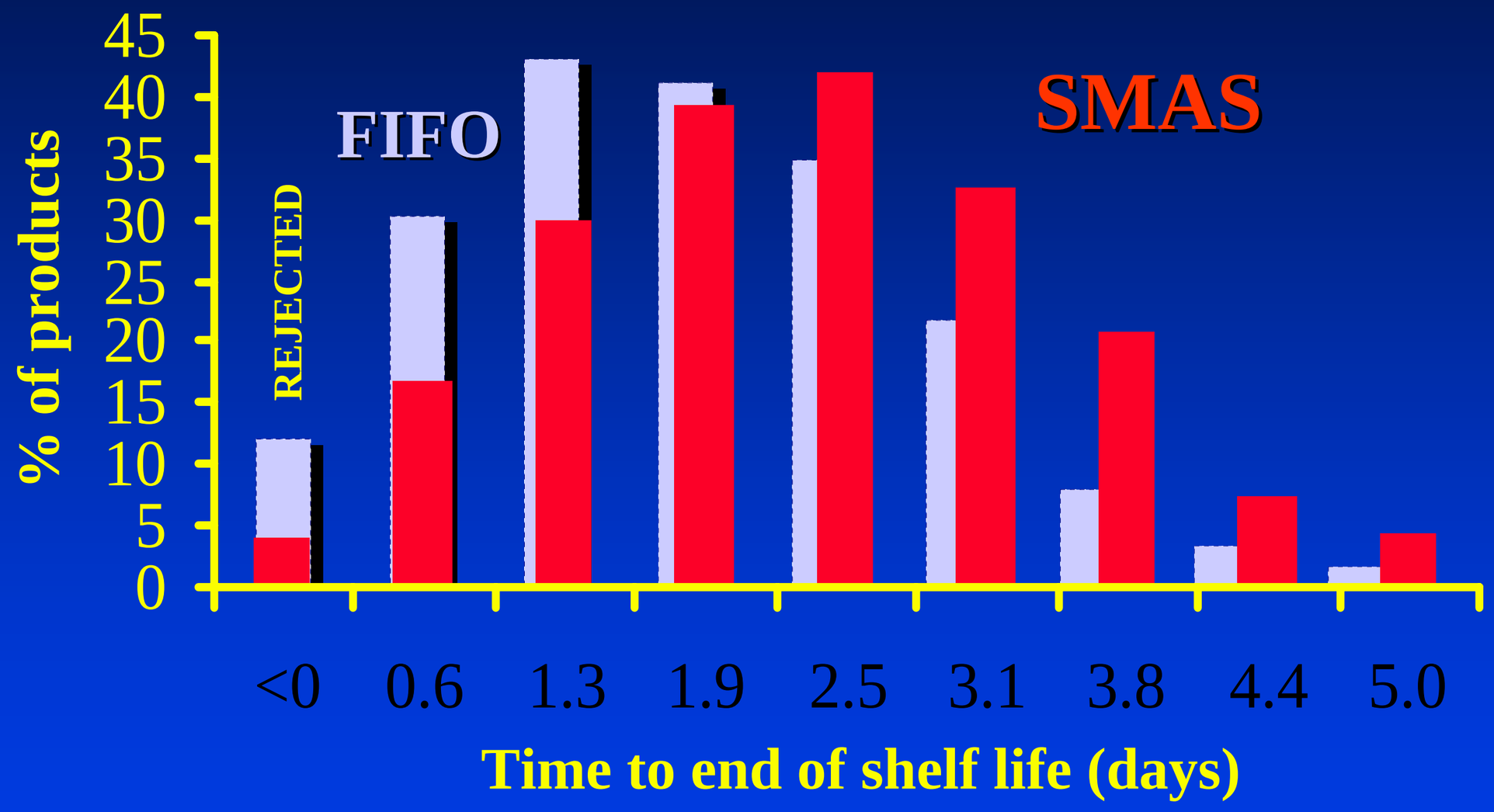

SMAS
40
30
20
10
0
One out of a trillion
One out of 10 billions
One out of 100millions
One out of a million
One out of 10.000
One out of 100

Probability of illness

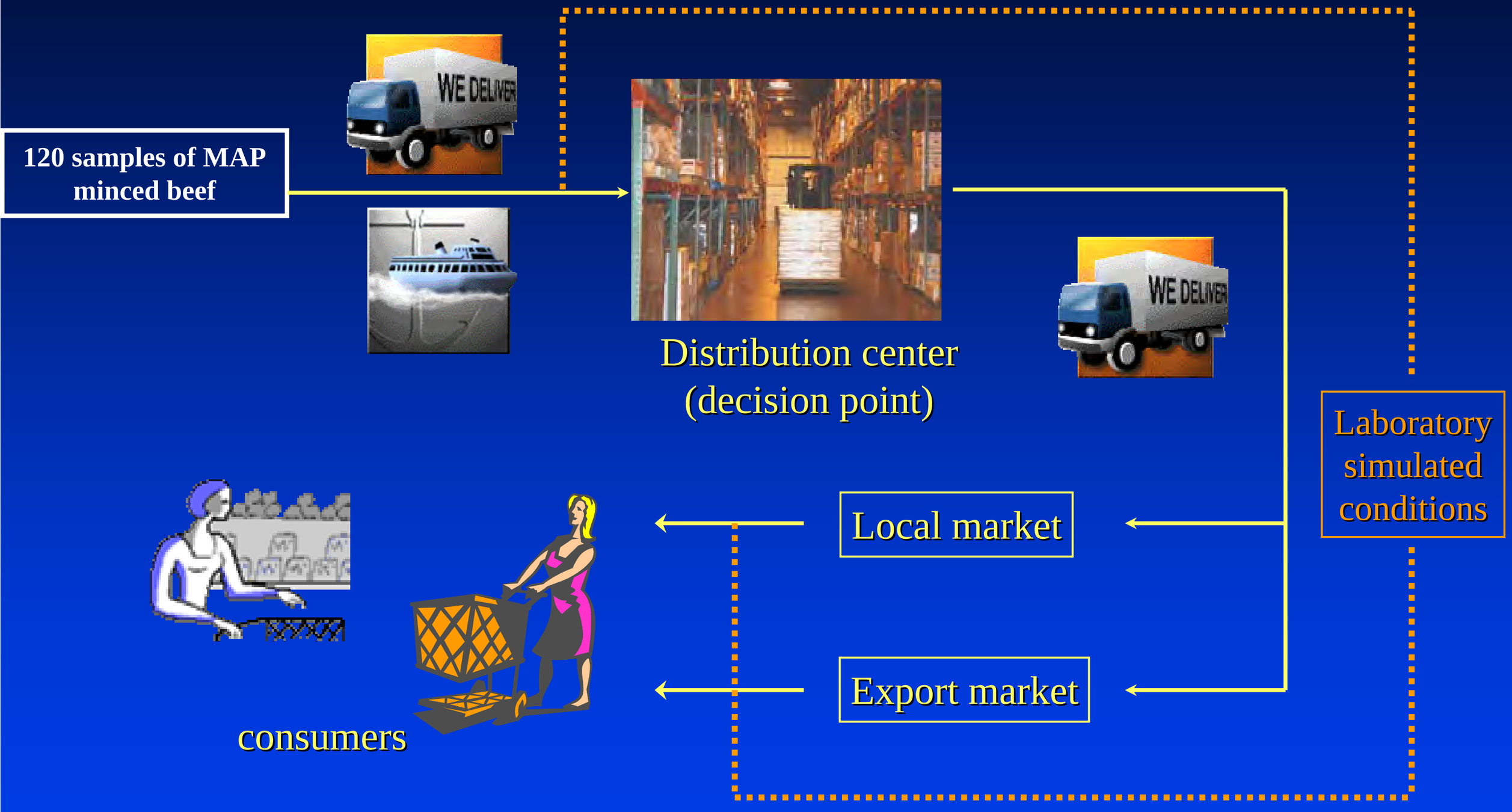



FIFO
% of products
REJECTED
45
40
35
30
25
20
15
10
5
0
<0
0.6
1.3
1.9
2.5
3.1
3.8
4.4
5
Time to end of shelf life (days)


SMAS
% of products
REJECTED
45
40
35
30
25
20
15
10
5
0
<0
0.6
1.3
1.9
2.5
3.1
3.8
4.4
5
Time to end of shelf life (days)


FIFO
SMAS
REJECTED
% of products
45
40
35
30
25
20
15
10
5
0
<0
0.6
1.3
1.9
2.5
3.1
3.8
4.4
5.0
Time to end of shelf life (days)

Field Test Design



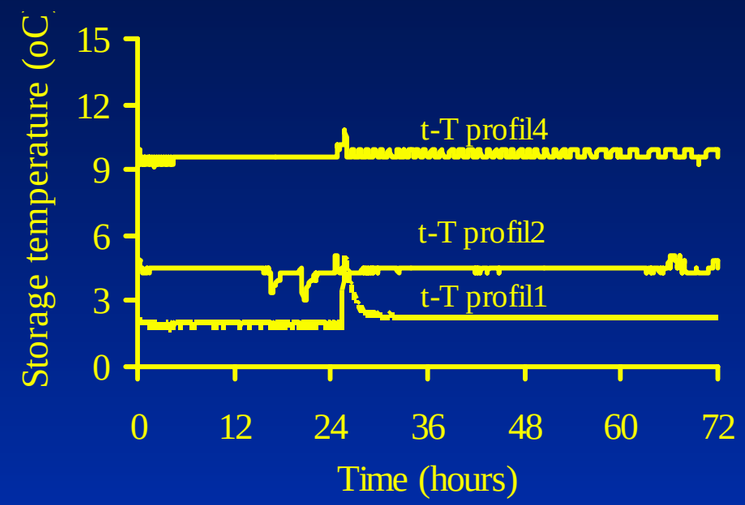
Field test Design

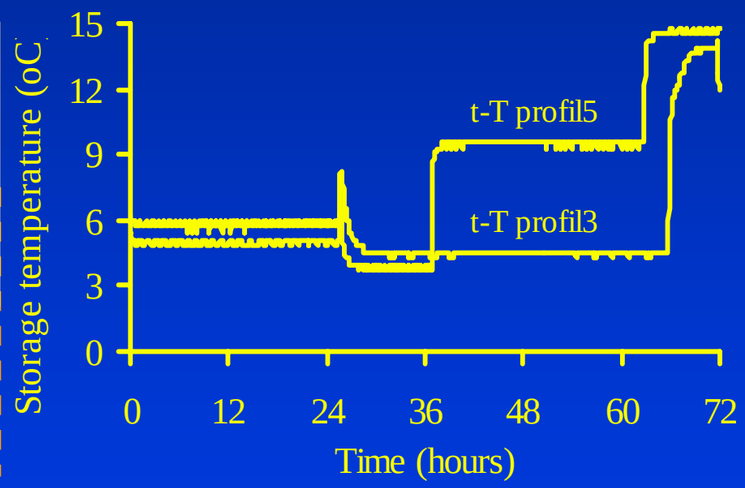
60 packages without TTIs

120 packages

60 Packages
TTI tag attached on each package

1st step





2nd step
24 h at various T conditions

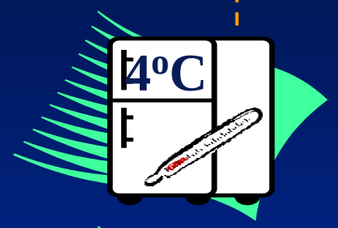
TTI based split

Decision point

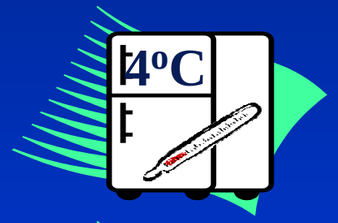
TTIs reading

3rd step

Local market
12, 24, 36 hours



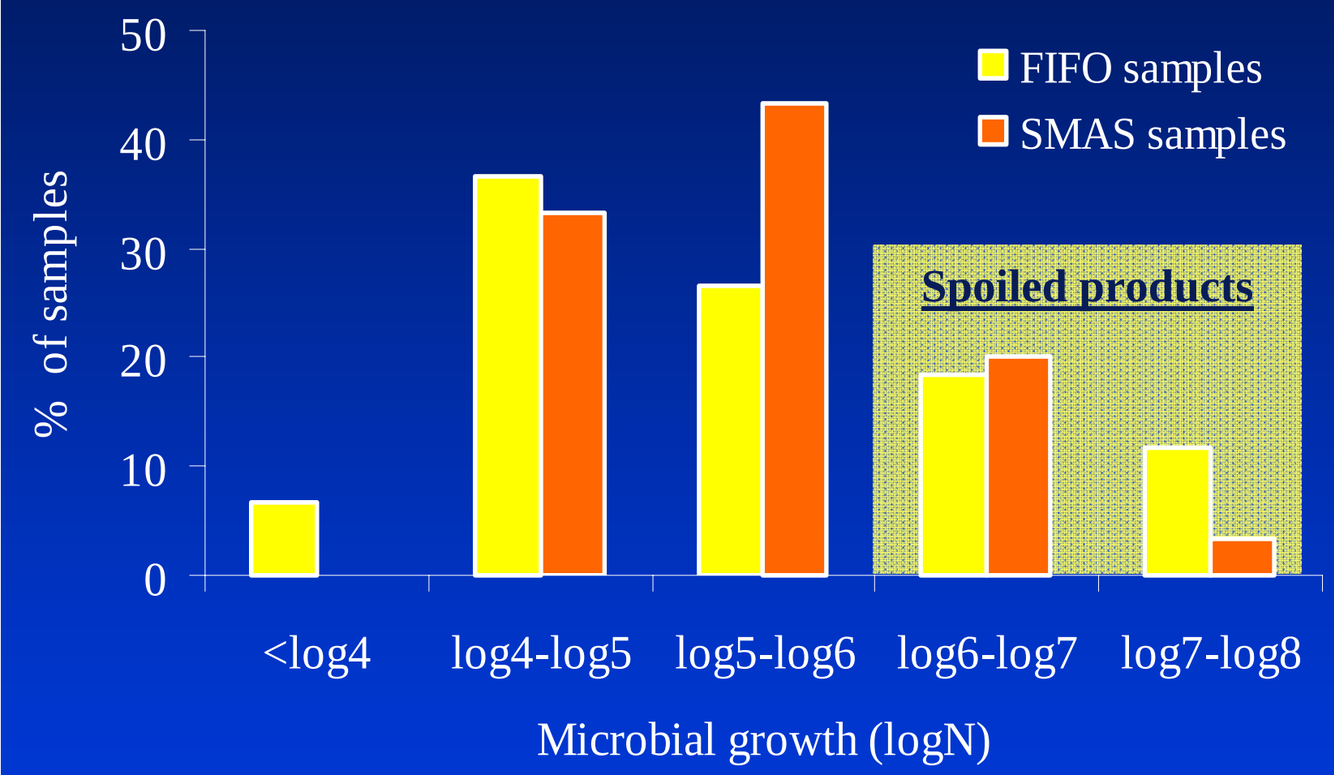
Export market
48, 72, 96 hours

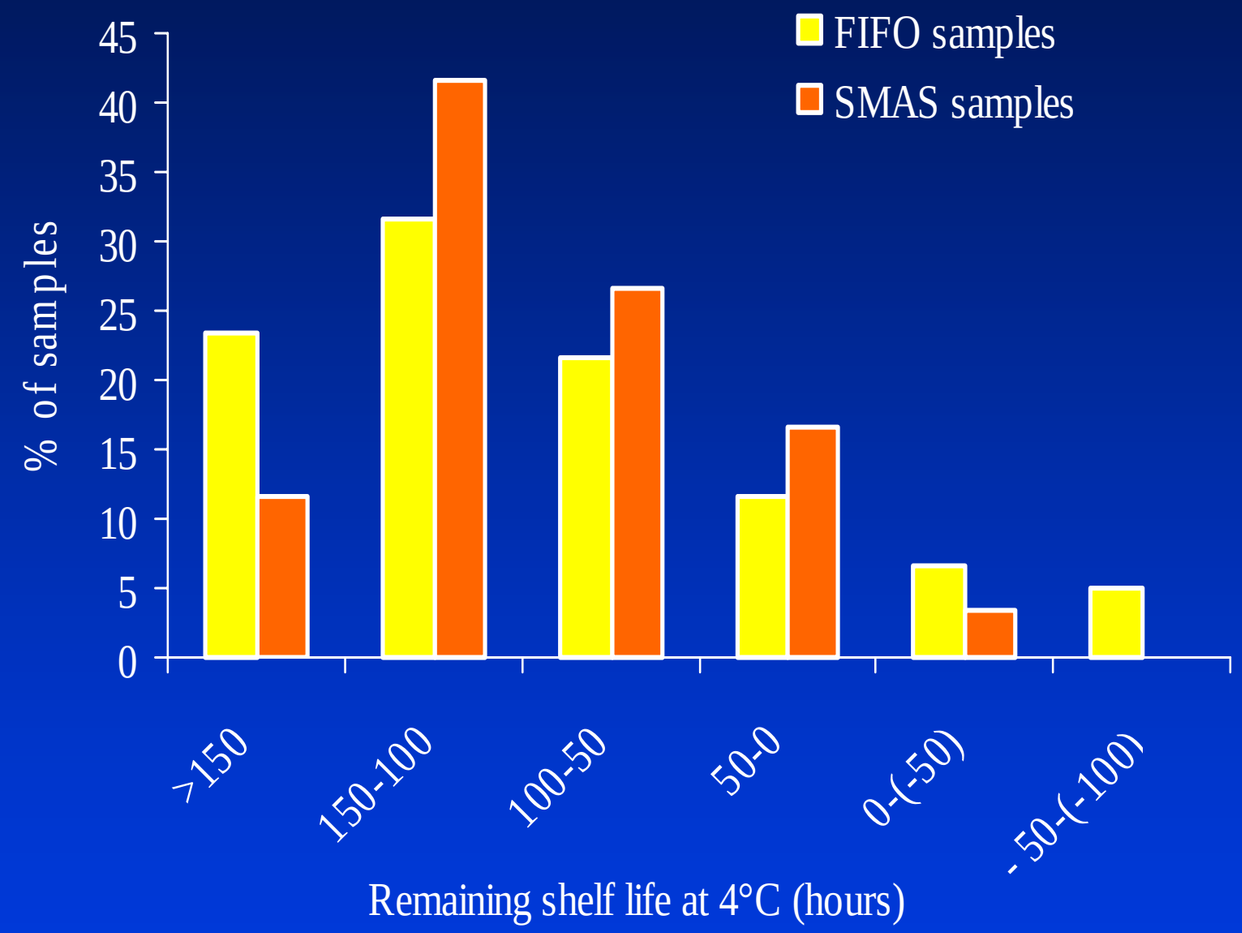


Microbiological analysis
4th step

FIELD TEST RESULTS

Distribution of Lactic acid bacteria growth for all samples at time of microbiological analysis - time of 'consumption'.





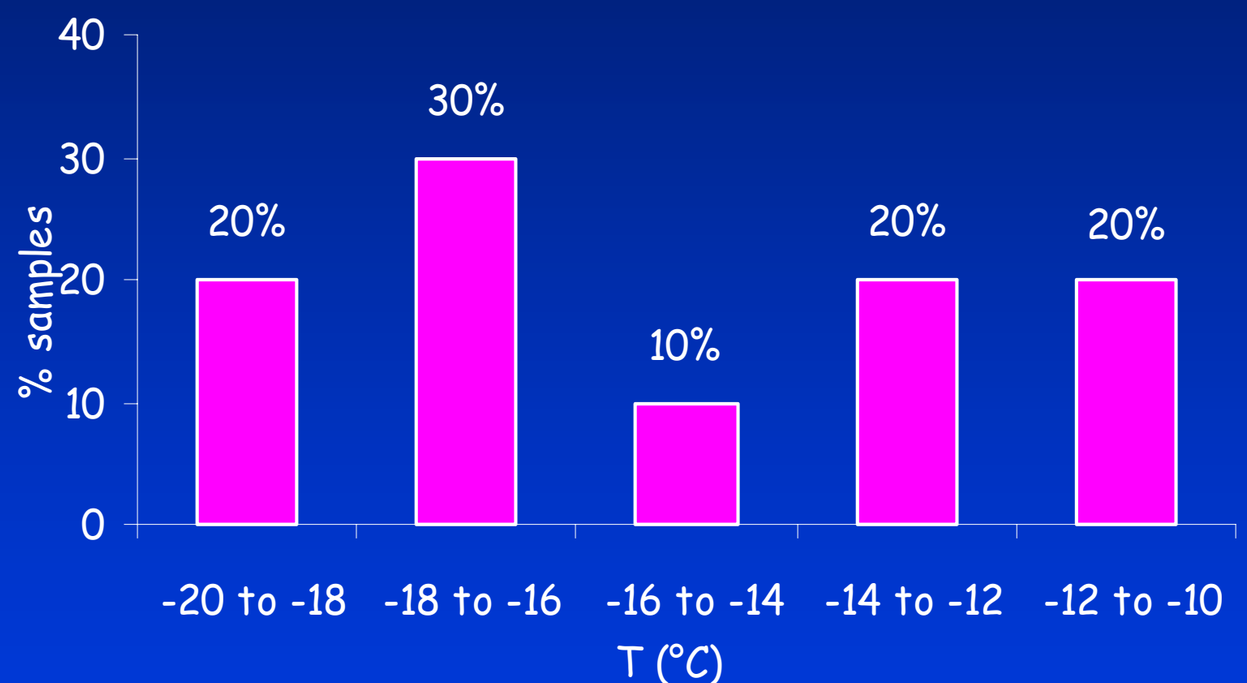
The distribution of microbiological growth moves to the left, to lower values, for the TTI bearing products

FROZEN FOODS

FROZEN FOOD QUALITY ASSURANCE

- Quality of optimally processed frozen food products depends on the temperature conditions of storage, handling and distribution. Monitoring and control of these conditions would allow chill chain optimization and reliable product shelf life prediction.

It has been reported that a substantial portion of frozen products are exposed, throughout the distribution, including retail and domestic storage, to effective temperatures that deviated significantly from the recommended range.



Average storage temperatures measured in different types of retail freezers in several stores of a large supermarket chain.

(Temperature data from recent surveys conducted by NTUA in collaboration with a leading supermarket chain).

Optimization of shelf life distribution of frozen products based on modelling and TTI monitoring

IQ-Freshlabel

Project IQ-Freshlabel

Developing novel intelligent labels for chilled and frozen food products and promoting the influence of smart labels application on waste reduction, food quality and safety in the European supply chains

Thank you for your attention!

National Technical University of Athens, School of Chemical Engineering,
Laboratory of Food Chemistry & Technology

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Abstract Submission Deadline

15 October 2010