

# IFTPS 31.10.2007

**PhD-programme:**

*Optimization of  
thermal processing  
of convenience  
Products from  
farmed cod*

KATHOLIEKE UNIVERSITEIT  
**LEUVEN**

**Research related to novel heating  
techniques:  
Heat induced changes in farmed  
Atlantic cod (*Gadus morhua*) muscle**

Skipnes, D.<sup>1</sup>, van der Plancken, I.<sup>3</sup>, Van Loey, A.<sup>3</sup>, Østby, M.L.<sup>2</sup>  
& Hendrickx, M. E.<sup>3</sup>

1. Norconserv AS, Seafood Processing Research, Niels Juelsgt. 50, N-4008 Stavanger, Norway
2. Norwegian College of Fishery Science, Institute of Marine Biotechnology, Breivika, 9037 Tromsø, Norway (formerly)
3. K.U.Leuven, Center for Food and Microbial Technology, Laboratory of Food Technology, Kasteelpark Arenberg 22, B3001 Leuven, Belgium



# Introduction

- Minimally processed convenience foods a growing segment in the European marketplace
  - Fish underrepresented among these foods due to:
    - Short shelf life
    - Sensitive to heat preservation
      - Flaking
      - Tenderness
      - Juiciness
    - Unstable delivery (seasonal variation, weather, over fishing etc.)
  - Farmed cod provide stable delivery and predetermined quality
  - Different from wild cod with respect to pH, fat content, texture etc.
- ⇒ Need for optimisation of thermal processing of farmed cod



# Novel heating techniques

- Examples of novel heating methods
  - Improved conventional heating (e.g. SHAKA)
  - Induction heating
  - Electromagnetic heating (MW/RF)
- Trends for novel heating systems:
  - Faster heating (and cooling)
  - Non-isothermal heating (ambient temperature not constant)
  - Short process times

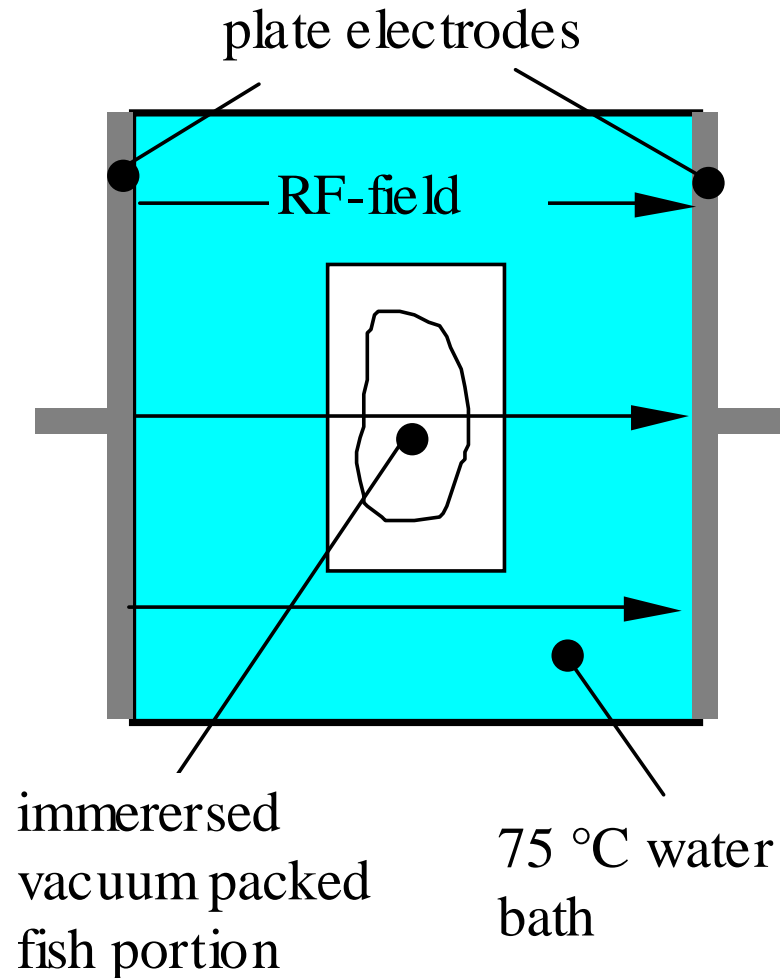


# Improving quality by rapid heating

## Hypothesis

- Rapid heating improves product quality
  - Reduces the difference in heat load between surface and core of the product
  - Reduced total cycle time
- Calculation example: Rapid vs. Conventional heating for portion of salmon fillet (140 g)
  - Same inactivation of bacteria
    - $P_{70}^{10} \approx 30$  for both heating methods (i.e. same inactivation as if 70°C for 30 minutes at core of the portion).
  - Better retention of quality by rapid heating
    - The heat load to all parts of the portion except the cold spot is significantly reduced.

## *Example: Scheme of RF-heater*



- Water bath with de-ionized water to couple electric field uniformly into food item
- Water bath placed in pressurized vessel
- Heat generation based on electric resistance heating due to electric (ionic) conductivity of food.
- Inactivation of bacteria by heat

# Experiments with RF-heating

- Species
  - Atlantic salmon (*Salmo salar*)
  - Cod (*Gadus morhua*)
- Raw material
  - Fresh fillets, 3 days post slaughter
- Samples
  - Small (10 g, Ø26 mm)
  - Portions (140 g ± 10g), vacuum packed
- Holding times calculated by CTemp (CCFRA, UK) to achieve equivalent thermal effects on bacteria



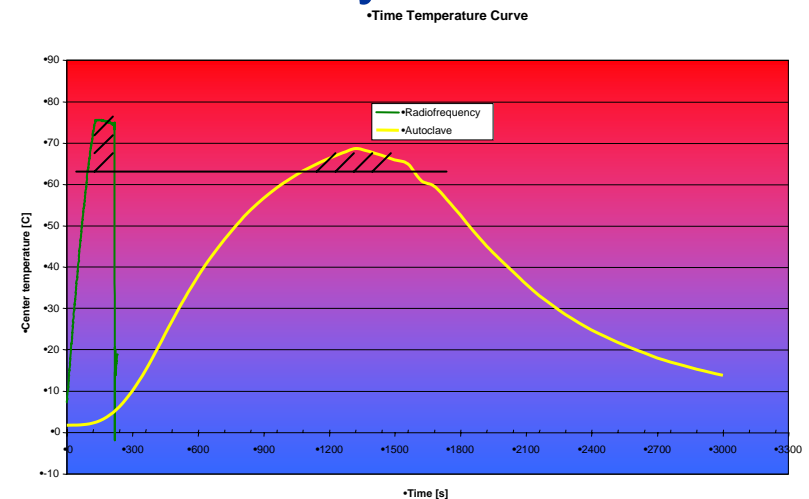
## Results on rapid heating (presented at TAFT 2003)

- Water holding capacity of cooked salmon was significantly improved when using rapid MW heating compared to conventional heating.
- RF-heated cod samples were significantly more juicy and tender than conventionally heated samples.
- Rapid heating reduced the thermal load on the edges of fish samples, thus giving a less dry product.
- Effects of rapid heating on texture and WHC were not conclusive and seem to depend on the tested fish species (cod, salmon).



# Safety considerations

- The rapid heating may be targeted to the same lethality as for a conventional heating at the cold spot of the product.
- The average *lethality over the whole portion* may be lower (possibly much lower)
- Cold spot pasteurization values can be used for determination of safety but cannot be compared to pasteurization values of conventionally heated products





# Pathogenic bacteria associated with fish products

From sea or sediments:

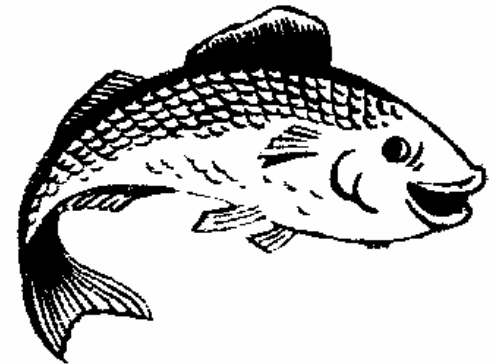
- *Clostridium botulinum*
- *Vibrio parahaemolyticus*

From the environments:

- *Listeria monocytogenes*
- *Salmonella*
- *Yersinia, Aeromonas*
- *Bacillus spp.*

From insufficient production hygiene:

- *Staphylococcus aureus*
- *Coliformes, Enterococci*



# Optimisation problem

- Microbial safety
  - Minimum heat load: 6 log reduction of *Listeria monocytogenes*, i.e.  $P_{70^{\circ}\text{C}}^{7.5^{\circ}\text{C}} = 2 \text{ min}$  in general, however in some environments some strains might have a lower heat resistance, e.g.  
 $P_{70^{\circ}\text{C}}^{5.7^{\circ}\text{C}} = 0.30 \text{ min}$  for cod (Ben Embarek, 1993)
- Quality
  - Inactivation of enzymes
  - Denaturation of proteins (must appear to be cooked)
  - Minimise cook loss and water holding capacity
  - Avoid flaking before the fish is on the plate



# Quality attributes of fish studied

- Thermally induced changes in cod
  - Kinetics of WHC and protein denaturation
  - Comparison of protein denaturation to cook loss and water holding capacity (WHC)
  - Discussion on possibilities for optimisation of thermal processing of vacuum packed cod portions



Still unaware they are going to give  
their lives to science...



The research fish farm outside Tromsø

# The challenge of WHC analysis

- How to obtain kinetics for WHC, texture and colour?
  - Uniform and rapid heating/cooling of sample to obtain isothermal heat treatment
  - Avoid loss/gain of water during heating /cooling
  - Centrifugation of sample on net
  - Measure cook loss, WHC, texture and colour without removing the sample from the sample holder
- The problem is discussed in:
  - Skipnes, D., Østby, M. L., & Hendrickx, M. E. 2007, "*A method for characterising cook loss and water holding capacity in heated cod (*Gadus morhua*) muscle*", *Journal of Food Engineering* vol. 80, pp. 1078-1085.



# The solution



Top lid



Sample cup



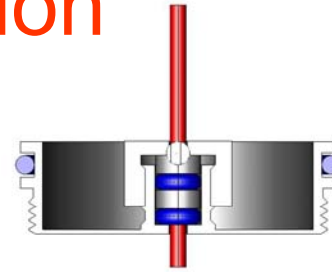
Filter



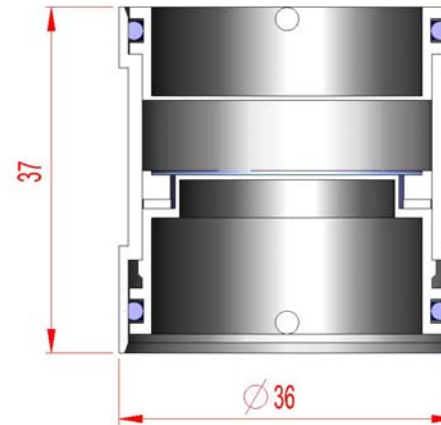
Bottom lid  
Heating



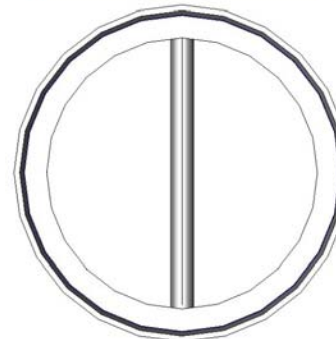
Bottom lid  
Centrifugation



Top lid  
Temperature probe



Assembled sample cup



Patented test cell produced under license by Hettich Zentrifugen (Tuttlingen, Germany)

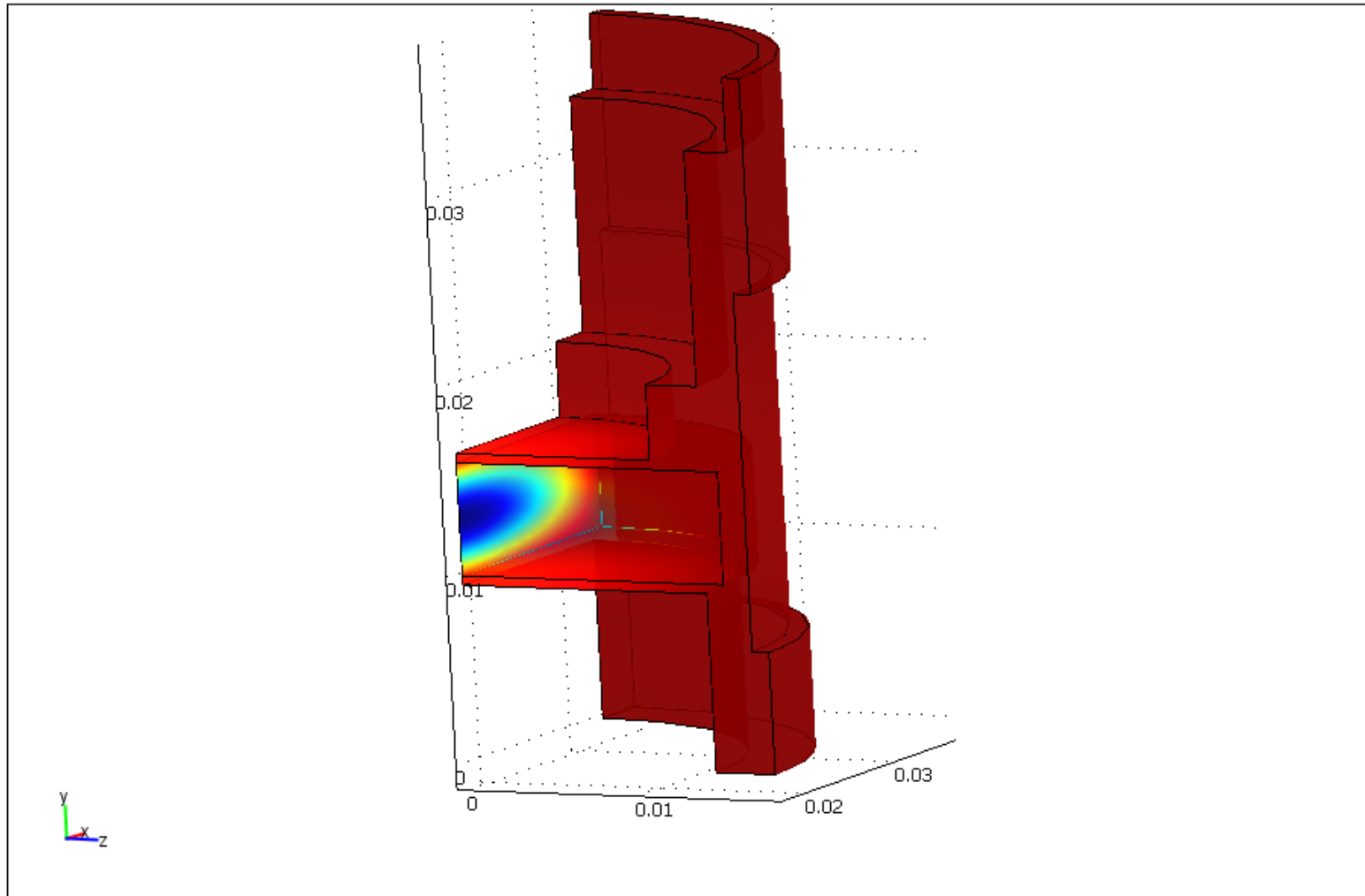
# Modelling of heating uniformity

Heating uniformity and distribution was determined by single point measurements and a 3D finite element method model programmed in Comsol Multiphysics 3.2 (Comsol AB, Lund, Sweden).

| <b>Sub domain</b>              | <b>Fish</b> | <b>Steel</b> | <b>Oil</b> |
|--------------------------------|-------------|--------------|------------|
| Thermal conductivity (W/(m K)) | 0.5146      | 44.5         | 0.14       |
| Density (kg/m <sup>3</sup> )   | 1060        | 7850         | 941        |
| Heat capacity (J/(kg K))       | 3650        | 475          | 1500       |
| Initial temperature (K)        | 275.15      | 293.15       | 363.15     |

# Temperature uniformity

Time=220 Boundary: Temperature [°C]



Max: 91.0

90.98

90.96

90.94

90.92

90.9

90.88

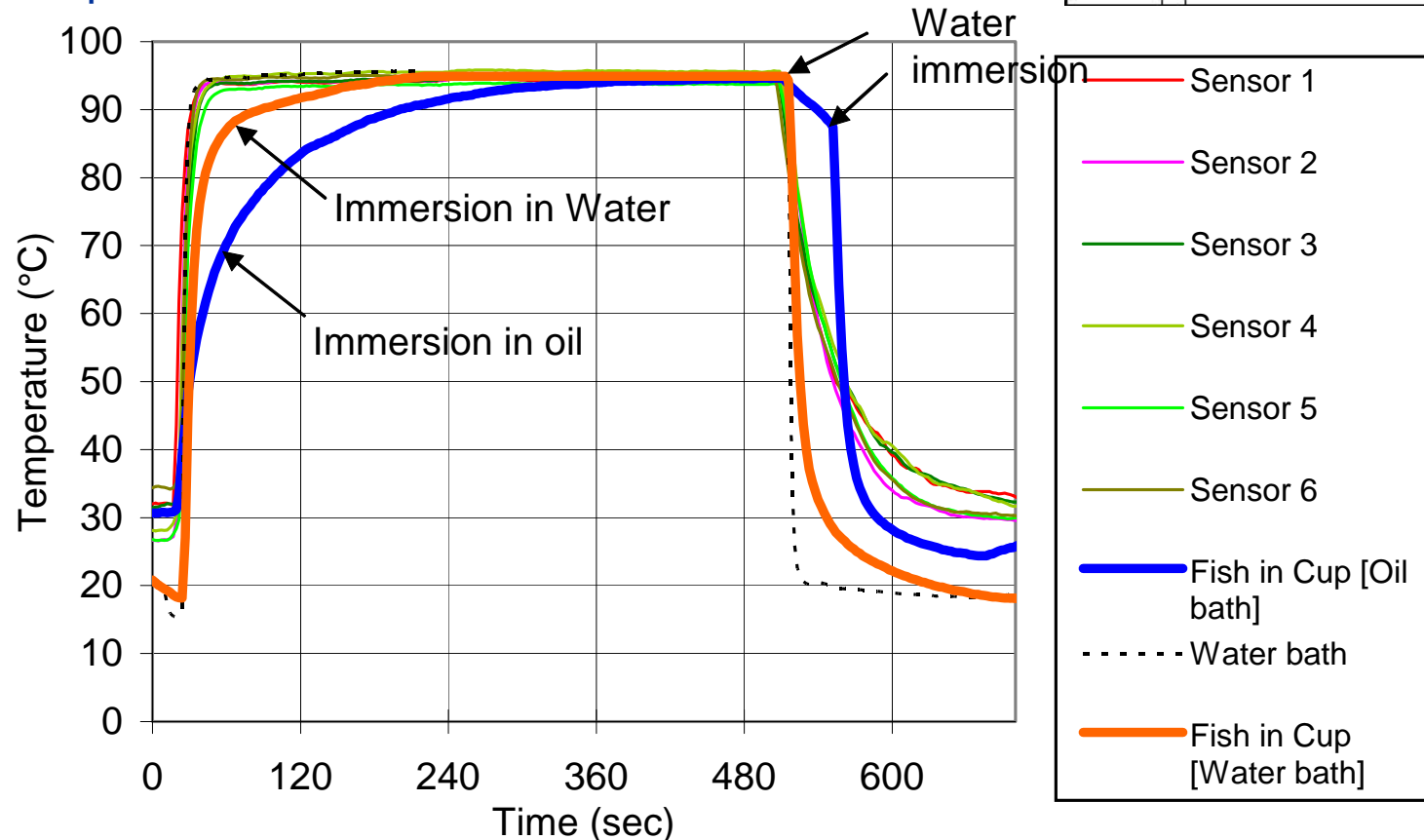
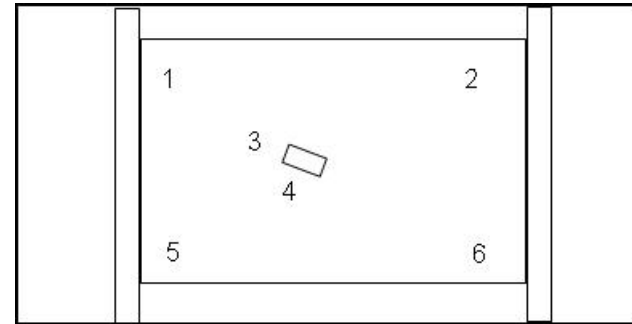
90.86

90.84

Min: 90.828

# Heating and cooling time

Sample cup placed in water bath (top view). The numbers indicate positions of each fibre optic temperature sensor.



Temperature measured in fish within sample cup during immersion in water and oil at equal conditions. The sensor numbers are corresponding to position numbers indicated in figure above



# Calculation of WHC

## Traditional method:

WHC of raw samples calculated as percentage remaining water of initial water in sample;

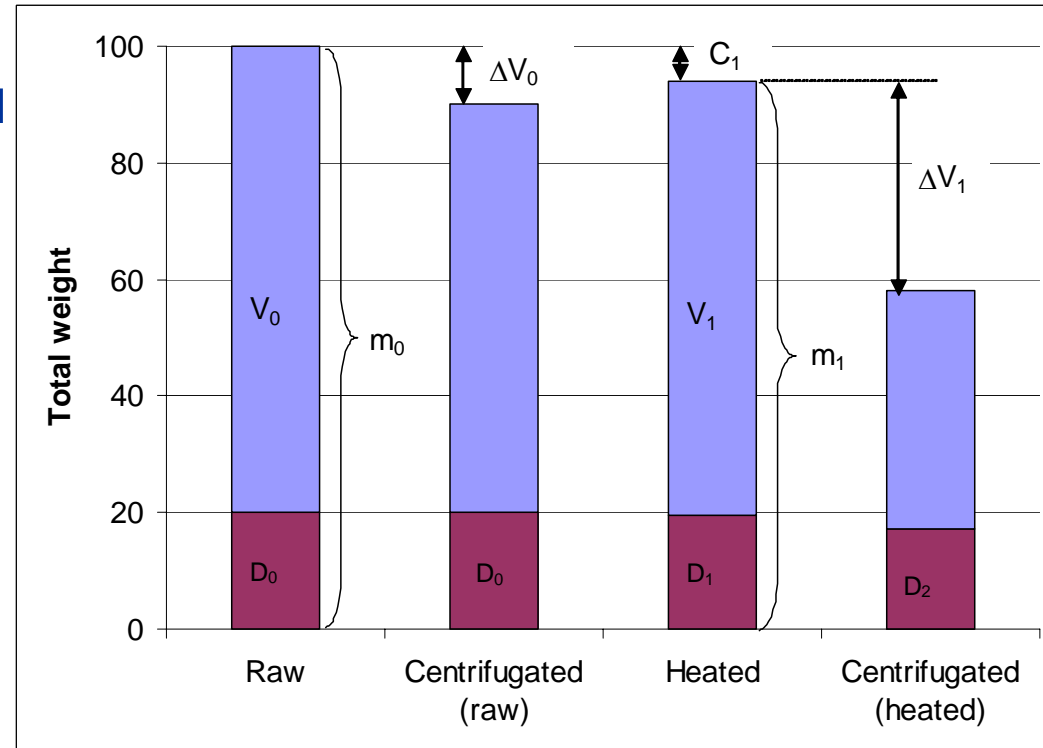
$$WHC = \frac{W_0 - \Delta W}{W_0} \cdot 100\%$$

where,

$$W_0 = \frac{V_0}{V_0 + D_0} \cdot 100$$

and

$$\Delta W = \frac{\Delta V_0}{V_0 + D_0} \cdot 100$$



Weight of sample before ( $m_0$ ) and after heating ( $m_1$ ) split in dry material ( $D$ ) and water content ( $V$ ). Cook loss is shown as  $C_1$  and centrifugation losses as  $\Delta V_0$  and  $\Delta V_1$  for raw and cooked material respectively

## Limitations of existing model

- The cook loss,  $C_1$ , is subtracted from the initial sample weight. Thus, an increase in cook loss result in higher WHC => cannot describe quality changes with only one parameter
- If cook loss is included, dry material in the exudates may be a problem.

$$WHC_1 = \frac{V_1 - \Delta V_1}{V_1} \cdot 100\%$$

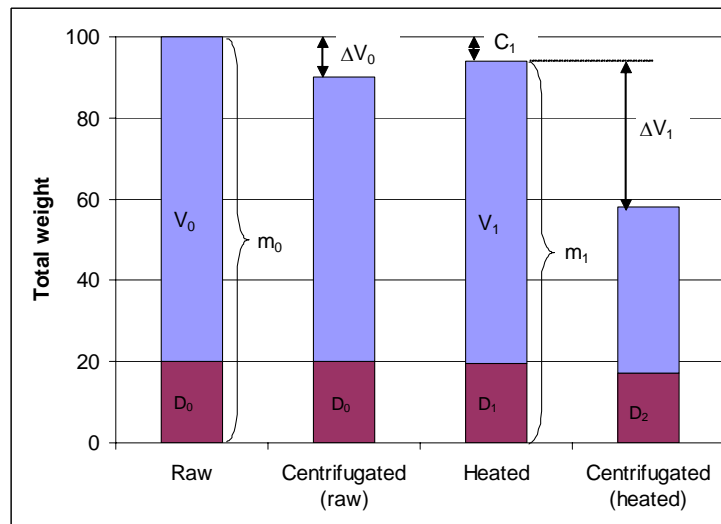


# Novel calculation method

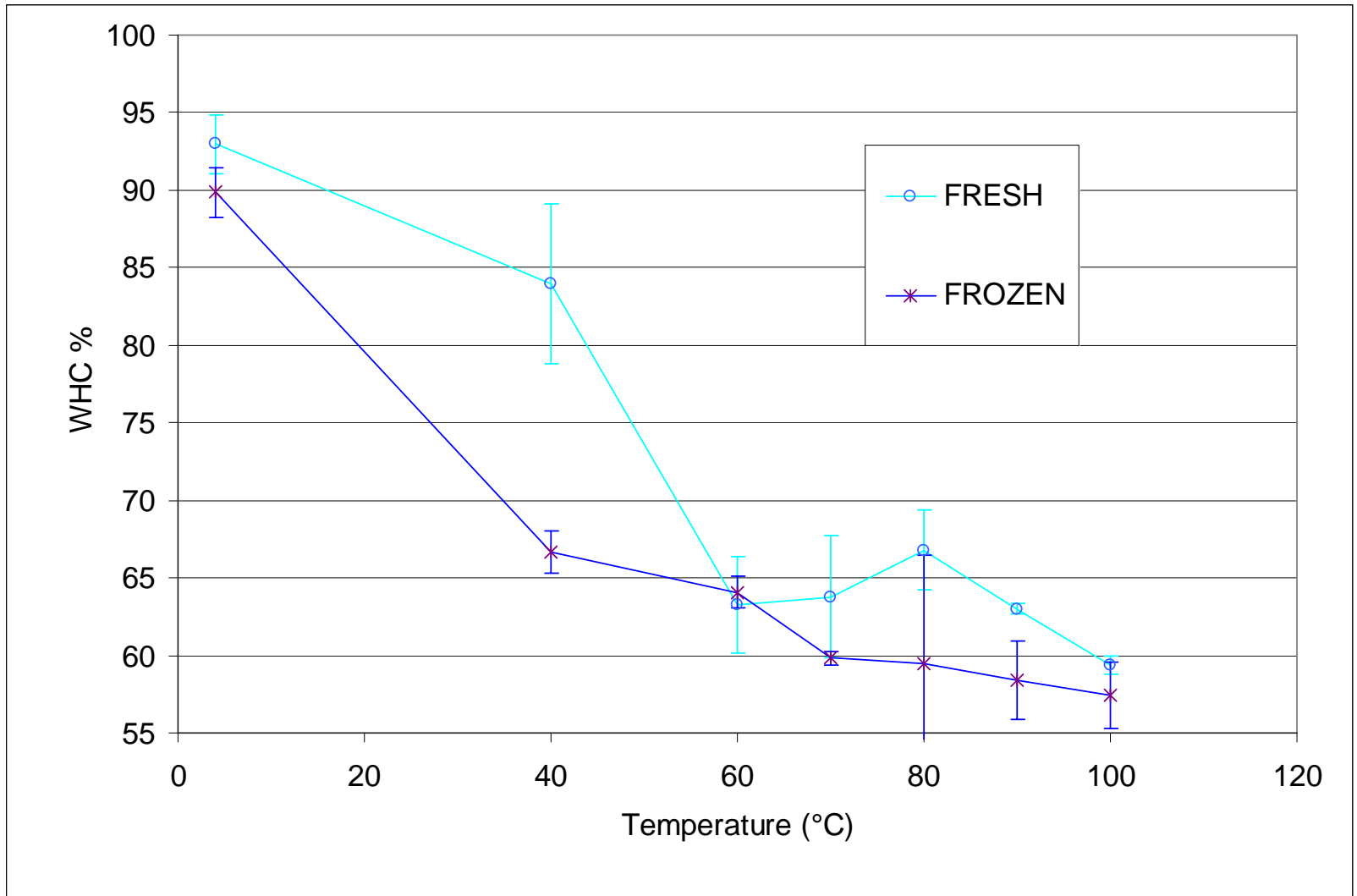
$$WHC_{TOT} = \frac{W_0 - \Delta W_{TOT}}{W_0} \cdot 100\% \quad \text{where} \quad \Delta W_{TOT} = \frac{\Delta V_1 + C_1}{V_0 + D_0} \cdot 100$$

Which leads to the new definition:

$$WHC_{TOT} = \frac{V_0 - (\Delta V_1 - C_1)}{V_0} \cdot 100$$



# Ability to measure WHC



## Ability to measure texture

| Treatment         | Hardness,<br>maximum<br>average force (g) | Standard<br>deviation | Standard<br>deviation<br>in % of hardness |
|-------------------|---|-----------------------|---|
| Raw               | 139                                       | 23                    | 16  |
| 10 min at<br>75°C | 468                                       | 67                    | 14  |
| 10 min at<br>90°C | 776                                       | 133                   | 17  |

# Characteristics of the novel method

- Easy and accurate determination of WHC
- Isothermal heating in the cup without any transfer of sample between heating and centrifugation
- Rapid heating by immersion in liquids (water) and immediate analysis of any of the following parameters:
  - Cook loss
  - WHC
  - Texture
  - Colour
- No liquid loss from the sample system
- No absorption of liquid in the sample tube
- Easy cleaning
- High mechanical strength makes high centrifugation speeds possible



# Protein denaturation during heating

## - Raw material and preparations

- 94 farmed atlantic cod (*Gadus morhua*) from Havbruksstasjonen AS, Skulgambukt, Tromsø, ground and frozen to  $-80^{\circ}\text{C}$
- The fish powder thawed on ice and kept at  $0^{\circ}\text{C}$  until filling of  $69 \pm 1$  mg in stainless steel DSC-pans  $\text{Ø}7.2$  mm and height 2.4 mm (Perkin-Elmer, Norwalk, USA)
- Heating in water bath
- Cooling in ice water and storage at  $0^{\circ}\text{C}$  overnight until recording of DSC-thermograms.

Described in detail in:

- Skipnes, D., van der Plancken, I., Van loey, A., & Hendrickx, M. 2008, "*Kinetics of heat denaturation of proteins from farmed Atlantic cod (*Gadus morhua*)*", *Journal of Food Engineering*, vol. 85, no. 1, pp. 51-58.



# DSC-analysis

- Analyzed by DSC7 (Perkin-Elmer, Norwalk, USA)  
Heating rate 10°C/min fra 0°C to 110°C (n=3)
- A global approach, non linear regression model based on literature (Van Loey, 1996). Reference D-value and a z-value estimated by the NLIN procedure SAS (1982) from the model below:

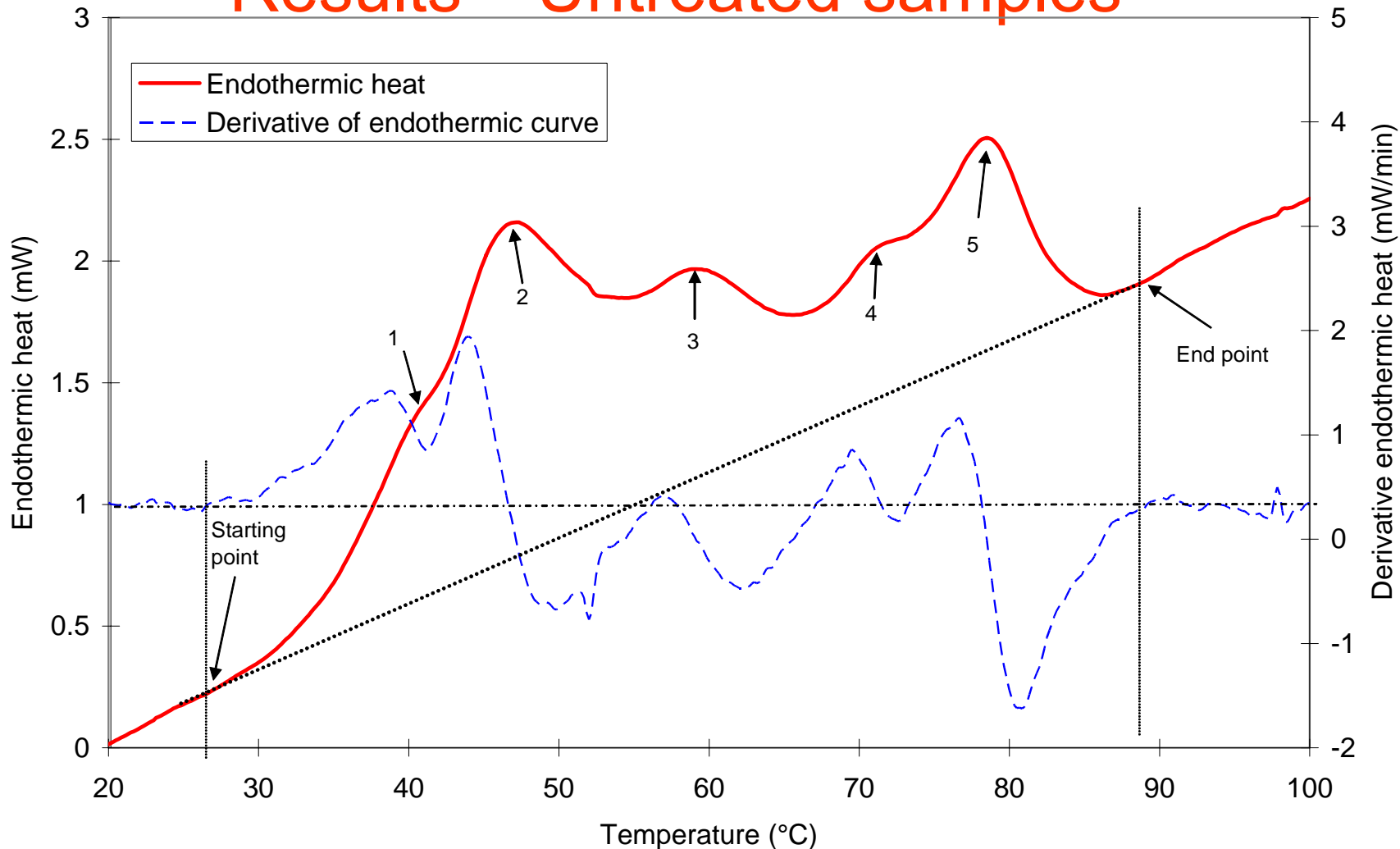
$$\Delta H = \Delta H_0 \cdot 10^{\left( -t \cdot \left( D_{ref} \cdot 10^{\frac{T_{ref}-T}{z}} \right)^{-1} \right)}$$



DSC-pans on top of the furnace



# Results – Untreated samples



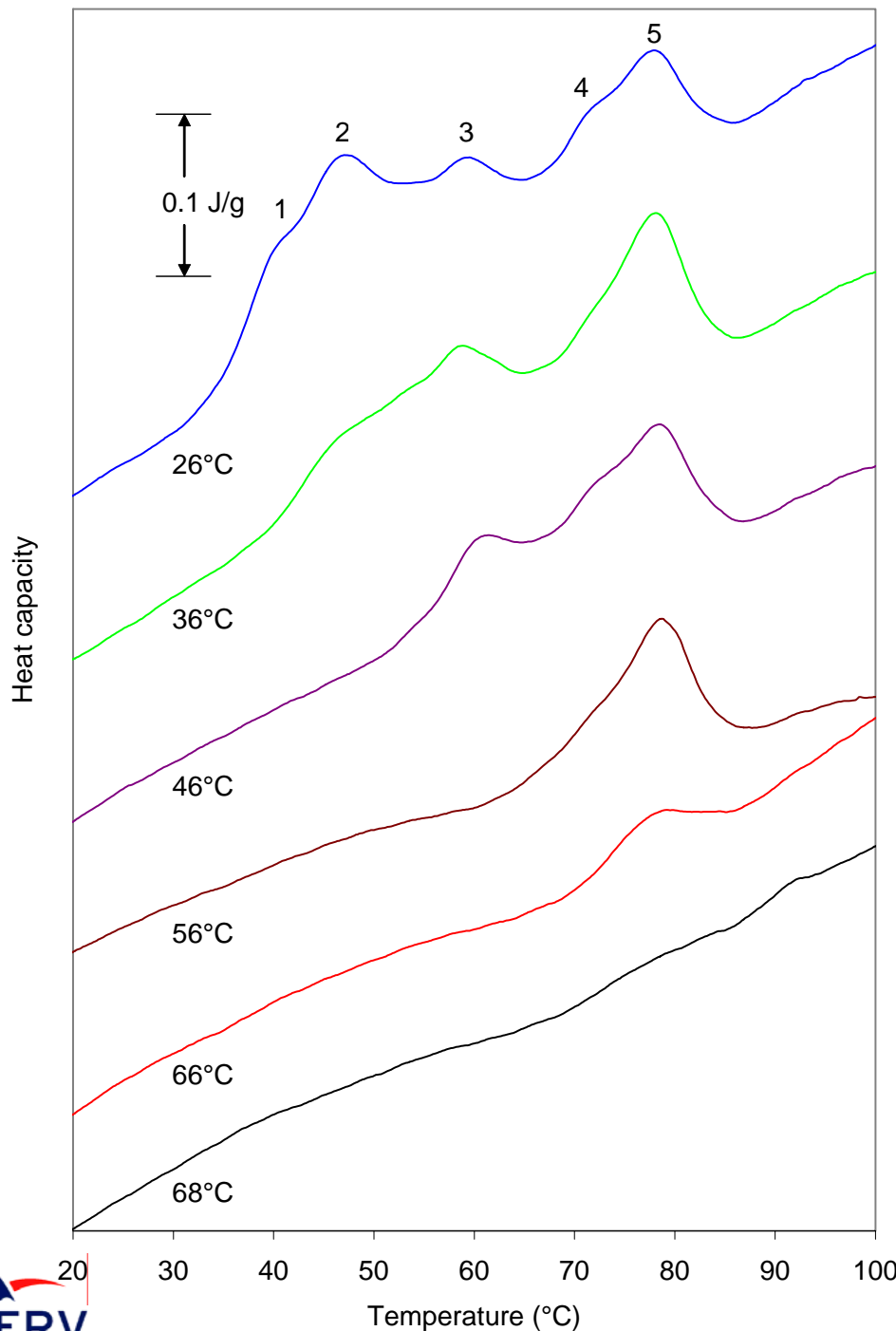
DSC-Thermogram a untreated samples with numbers indicating the position of the five peaks (red). Derivative (blue) of sample with position of the corresponding peaks marked. The positions of the peaks are determined by the position of the peaks on the derivative curve. The total peak area is defined as the area between the red curve and the base line

# Peak positions

Table 1. Average values and standard deviation for temperature at peak maximum for untreated cod based on the current work and literature data.

| Material                         | Peak 2<br>Myosin<br>(°C) | Peak 3,<br>Sarcoplasmic<br>proteins (°C) | Peak 5,<br>Actin<br>(°C) | References                          |
|----------------------------------|--------------------------|--|--------------------------|-------------------------------------|
| Farmed frozen<br>(-80°C)         | 44.1 ± 0.2               | 57.3 ± 0.1                               | 76.1 ± 0.7               | Present work<br>(n=13)              |
| Wild, natural,<br>frozen (-30°C) | ~45                      | ~54                                      | 70-80                    | (Jensen &<br>Jorgensen, 2003)       |
| Wild, natural,<br>frozen (-24°C) | 43.5 ±0.2                | 59.3 ±0.9                                | 73.6 ±0.7                | (Thorarinsdottir et<br>al., 2002)   |
| Wild and fed,<br>fresh           | ~42                      | ~ 56-57                                  | ~73-74                   | (Ofstad et al., 1996)               |
| Wild, fresh                      | ~44                      | ~58                                      | ~76                      | (Hastings et al.,<br>1985) (1 fish) |
| Wild, fresh                      | ~44                      | ~54                                      | ~74                      | (Poulter et al.,<br>1985)(n=2)      |
| Wild, frozen                     | ~42                      | ~52                                      | ~74                      | (Poulter et al.,<br>1985) (n=2)     |

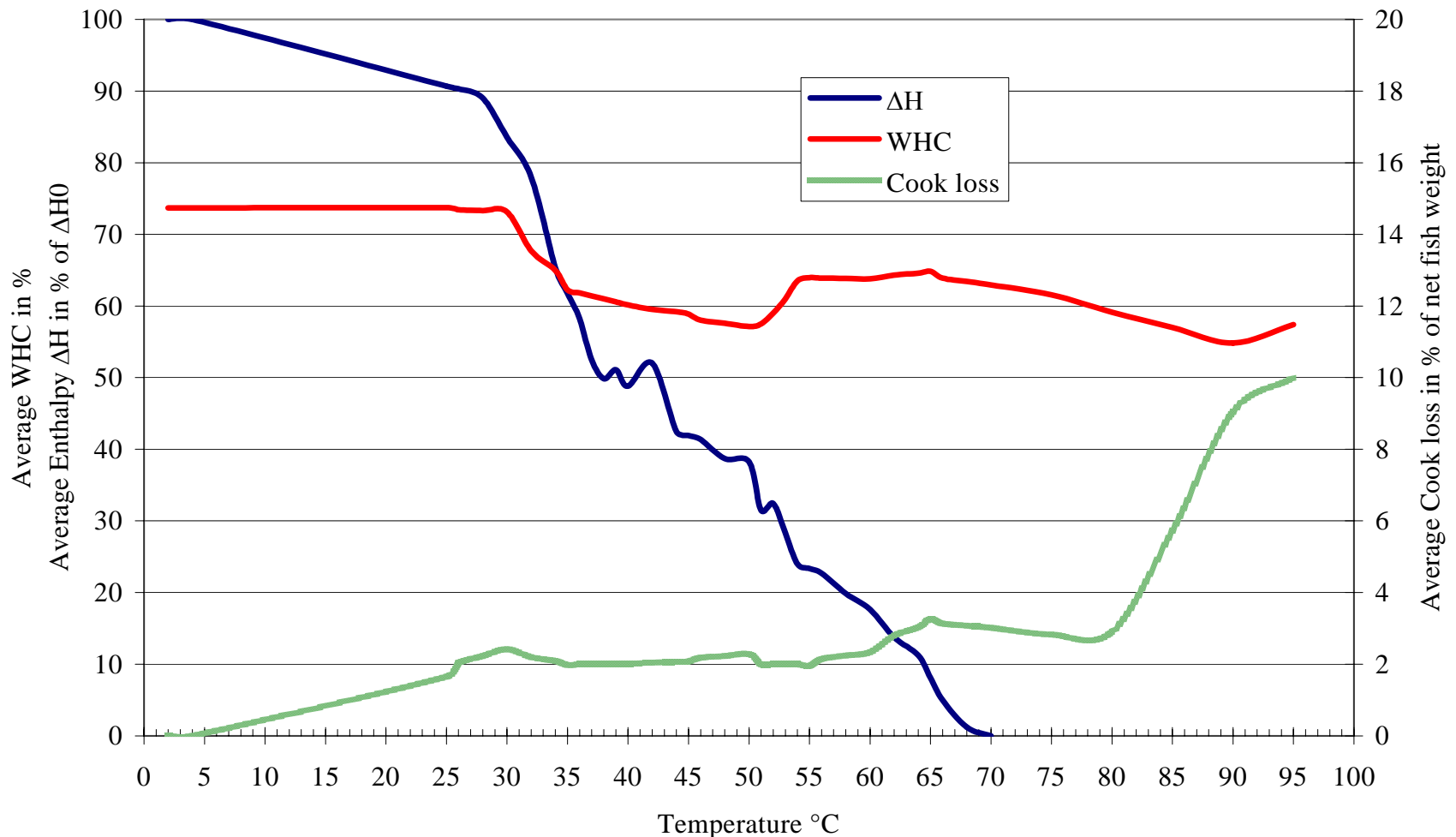
# Results – screening study



DSC-Thermograms (heating rate of 10°C/min) of cod muscle heated for 10 min at 26°C (equal to untreated), 36°C, 46°C, 56°C, 66°C and 68°C (from top to bottom).

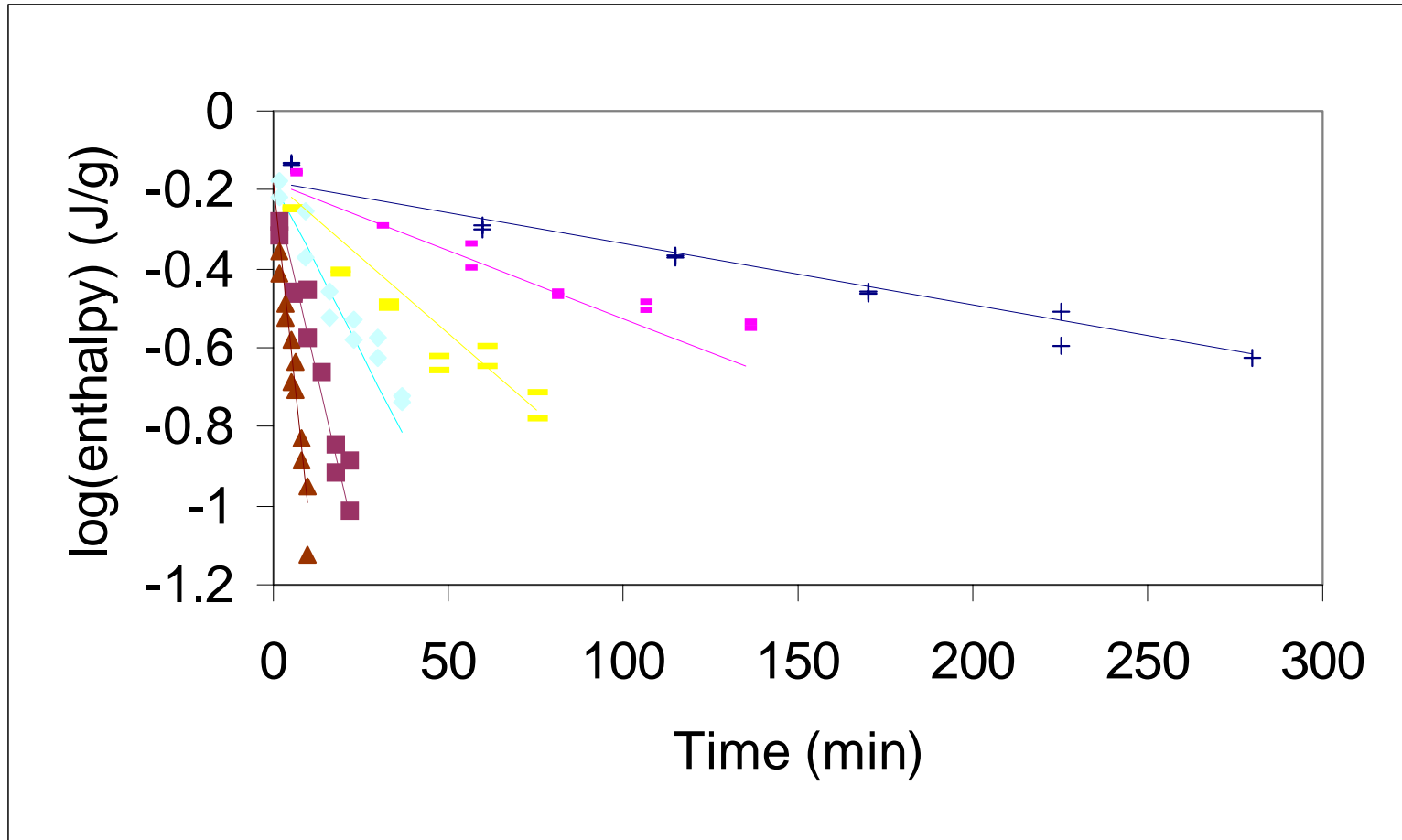
With increasing temperatures up to 68°C, the 5 peaks diminished gradually until no peak could be detected

# Water loss and protein denaturation



Denaturation enthalpy  $\Delta H$  for samples heated for 10 min in % of untreated samples, plotted together with WHC cook loss extracted from experiments with isothermal heating for 10 min as described by Skipnes, Østby, & Hendrickx

## Results – Kinetic study



Denaturation enthalpy for temperatures in the range 58°C to 68°C plotted against holding time in min together with regression lines from the global non-linear model

# Results - Kinetics

Table 3. Parameters calculated from the enthalpy data by global non-linear regression analysis for a first order model of the measured data except the only pre heated samples.

| Parameter               | Estimate | Standard Error | Approximate 95% Confidence Limits |        |
|-------------------------|----------|----------------|-----------------------------------|--------|
| $D_{ref}$ (at 62°C) min | 130.1    | 5.4            | 119.3                             | 140.8  |
| $z$ °C                  | 5.74     | 0.11           | 5.52                              | 5.97   |
| $H_0$ J/g               | 0.658    | 0.014          | 0.6313                            | 0.6855 |



# Conclusions

- To take advantage of novel, rapid heating processes, the inactivation of target organisms have to be studied carefully
- A pasteurisation value used for a conventional process may not necessarily be sufficient for a rapid heating process
- When heating cod, the proteins are denaturated before the major cook loss occurs and will appear to be cooked without a major cook loss.
- It is indicated that *Listeria monocytogenes* is inactivated by a heat load of the same order of magnitude as actin is denaturated, while the cook loss is still moderate. An optimal processing temperature may therefore be found around 68°C.





From raw material



Seafood Processing Research



- to meal



## Acknowledgement

This work was funded by The Research Council of Norway  
(NFR no: 158929/I10 )

Many thanks to

Professor Marc Hendrickx (my promotor) at  
K.U. Leuven - Laboratory of Food Technology,

the staff at Norconserv and Thomas Pfeiffer at Fraunhofer IVV

