New knowledge about the mechanisms of seafood lipid oxidation

(LIPIDTEXT)

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Outline

- Oxidation in fish products
- Aims and partners of LIPIDTEXT
- Oxidation mechanisms in liposomes
- Oxidation mechanisms in emulsions
- Oxidation mechanisms in washed fish mince
- Conclusions

Background

- Fish and foods rich in n-3 lipids have a number of health beneficial effects
- BUT: Lipid and protein oxidation negatively affect color, odor, texture, taste and nutritional value of fish based products.
- To be able to prevent oxidation understanding of oxidation mechanisms is necessary
- Whole fish muscle is too complex to study the influence of individual factors on lipid and protein oxidation

Aims of LIPIDTEXT

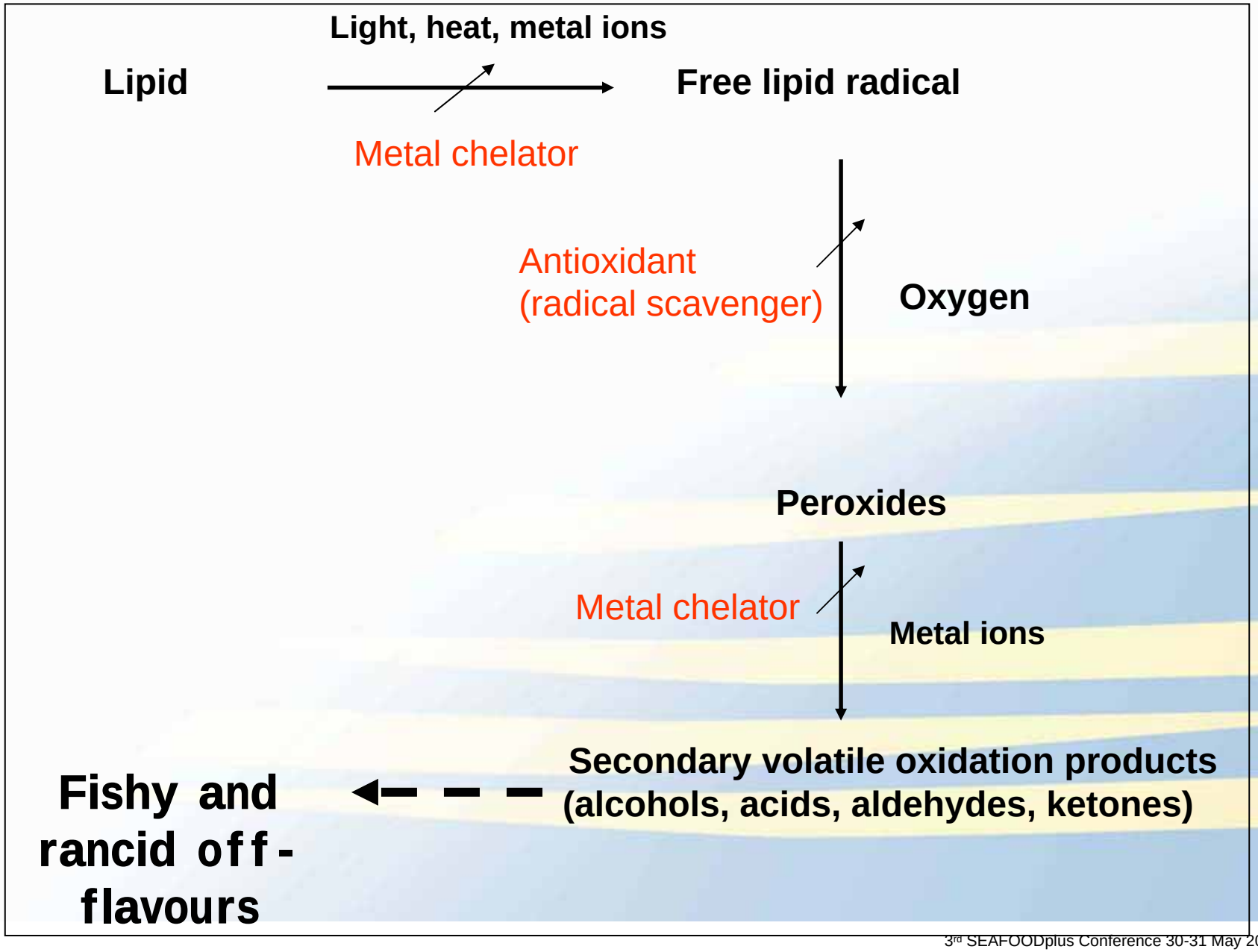
To secure and maintain:

- **high sensory quality**
  - **colour**
  - **flavour**
  - **texture parameters**
- **nutritional value**
  - **high level of anti-oxidants**
  - **n-3 lipids**
  - **low levels of oxidation products**

Partners in LIPIDTEXT

- Danish Institute for Fisheries Research (DIFRES), Denmark
- Chalmers University of Technology (CTH), Sweden
- Institut National de la Recherche Agronomique (INRA), France
- Instituto de Investigaciones Marinas (IIM), Spain
- Norwegian University of Science and Technology, Norway
- Icelandic Fisheries Laboratories (IFL), Iceland
- Unilever, United Kingdom
- Matforsk, Norway
- SINTEF, Norway

Oxidation in brief:



Results from liposomes studies

Oxidation of phospholipids (membrane lipids)

Effect of Fe, salt, temperature, pH and zeta potential

Measuring lipid oxidation

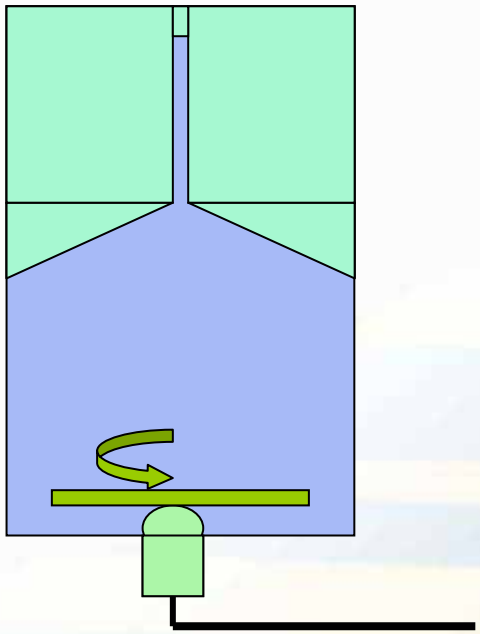
- Water contains oxygen dissolved in the water, like saltwater contains salt.
  - The dissolved oxygen makes fish survive in water.
- The dissolved oxygen can react with unsaturated fat and the fat oxidizes, (turn rancid).
- Oxidation of unsaturated fat consumes oxygen in the water
- This consumption of dissolved oxygen is a good measure for the oxidation of lipids.

Experimental setup

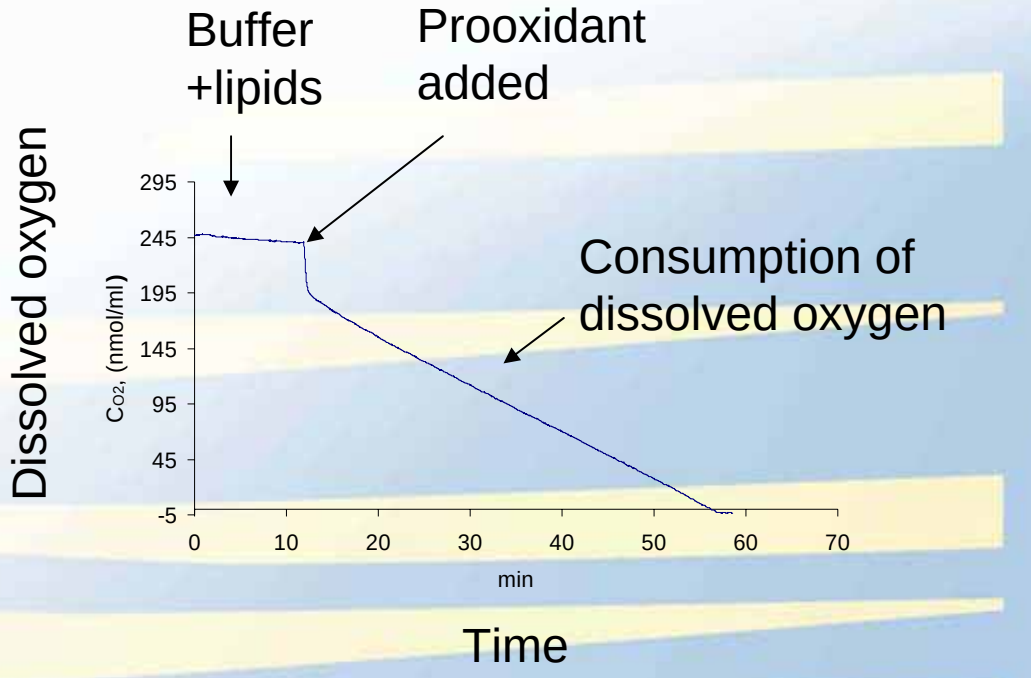
Liposome preparation by sonication

Consumption of dissolved oxygen measured by polarographic oxygen electrode

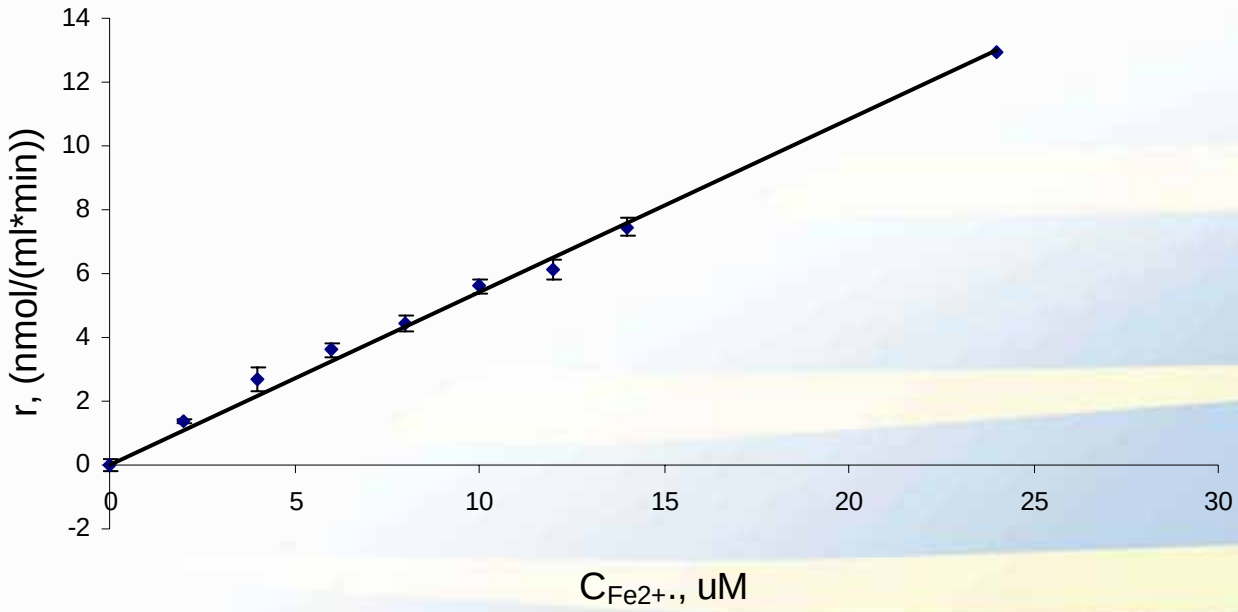
Measuring consumption of dissolved oxygen



Electrode for measuring dissolved oxygen

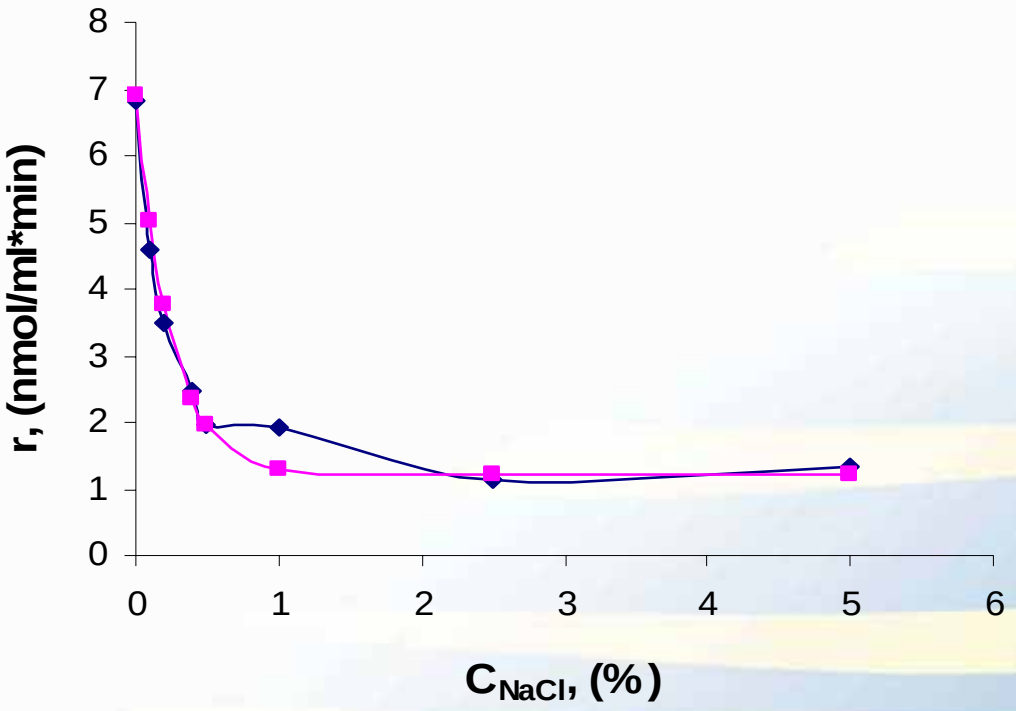


The influence of Fe^{2+} concentration on oxygen uptake rate (r)



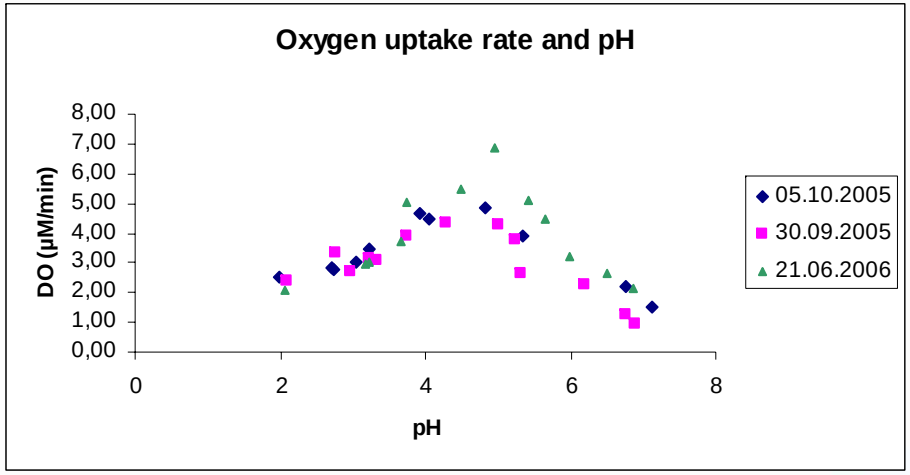
$$r = 0{,}54 * C_{Fe^{2+}}$$

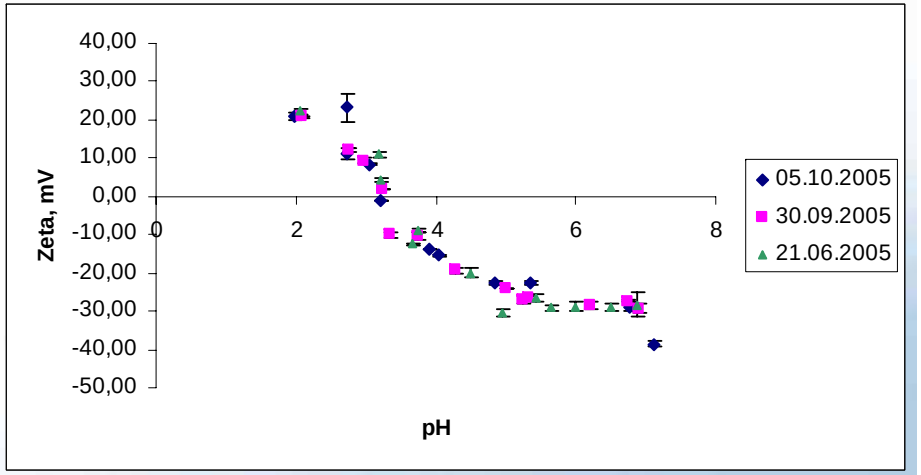
The influence of salt concentration on oxygen uptake rate (r)

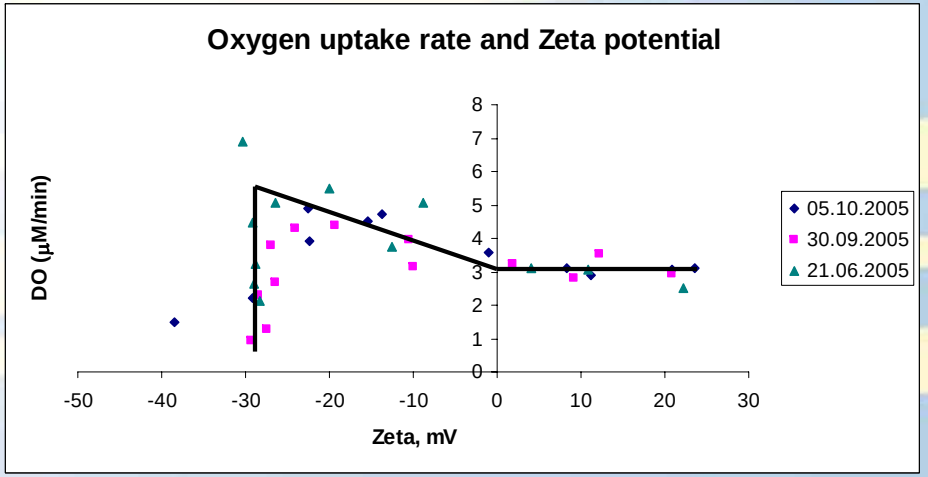


$$r = r_o + ae^{bC_{NaCl}}$$

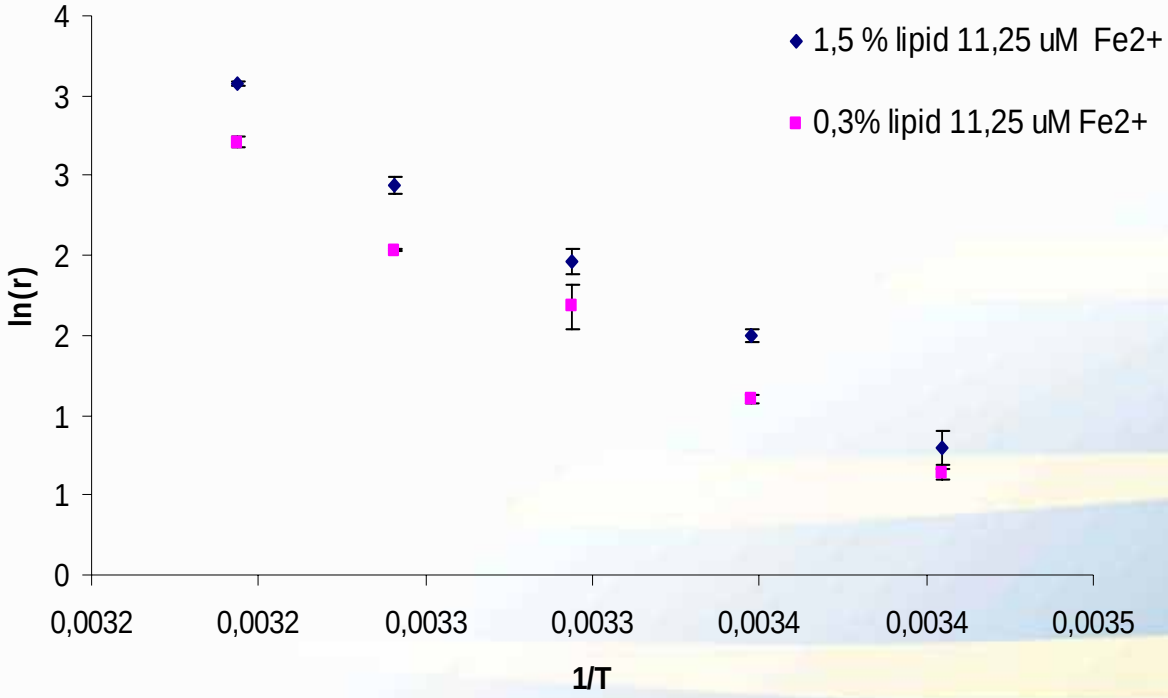
Zeta potential and pH







The influence of temperature on oxygen uptake rate (r)



$$r = r_o e^{-\frac{E_a}{RT}}$$

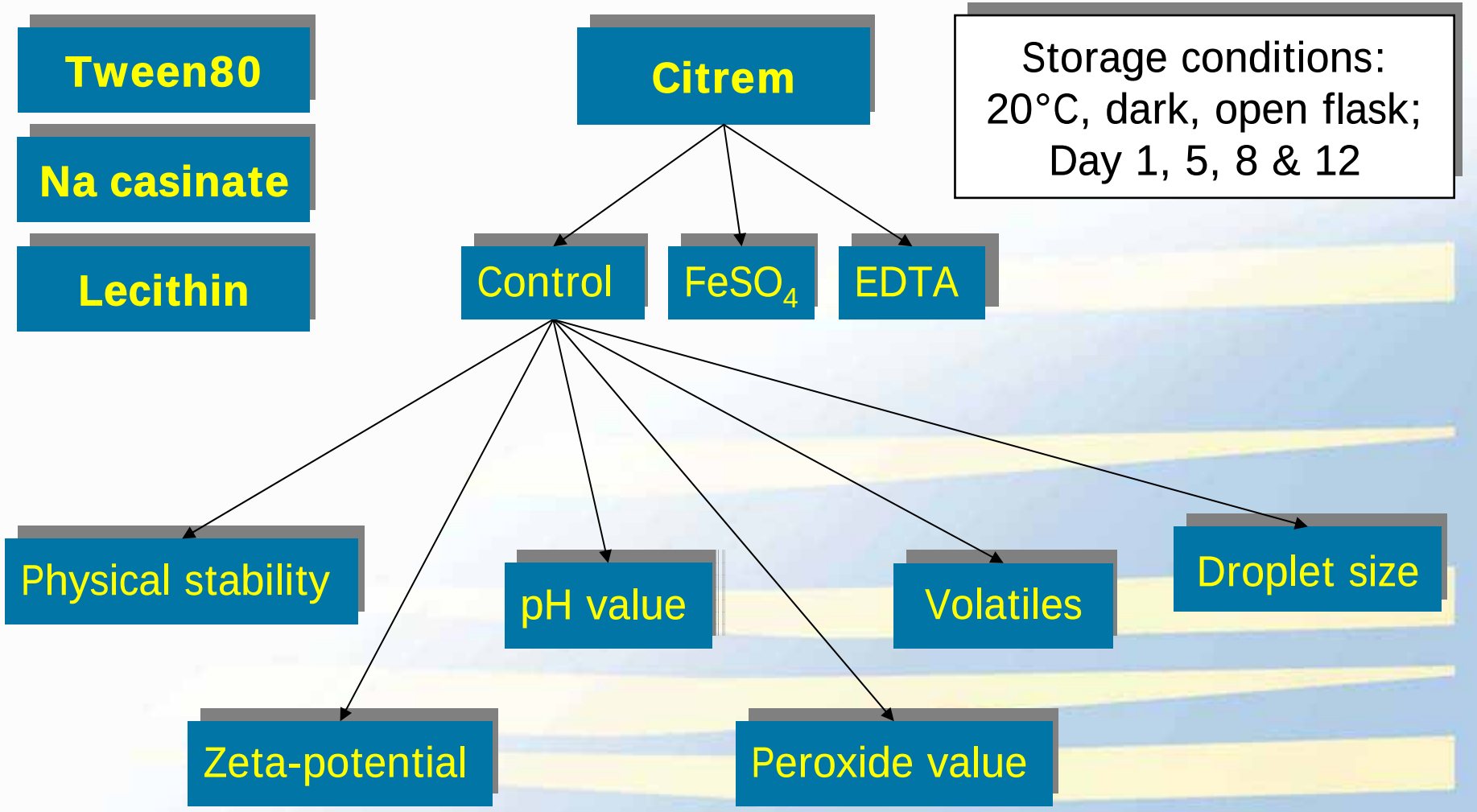
T- temperature, (K); r-uptake rate, (nmol/(min*ml))

E_a ~80kJmol^{-1}K^{-1}

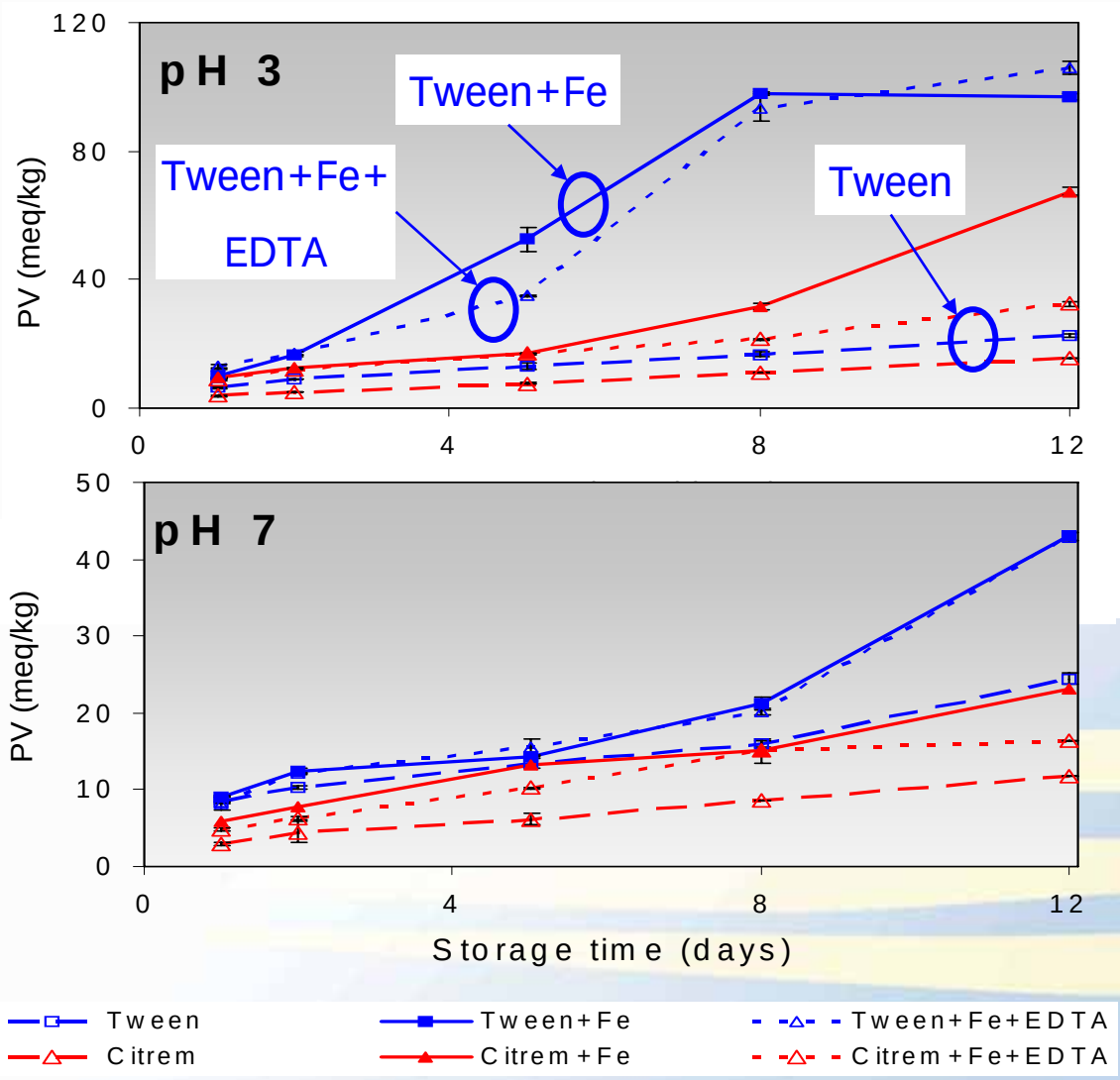
Results from emulsion studies

Effect of emulsifier type, pH, Fe and EDTA

Storage experiment



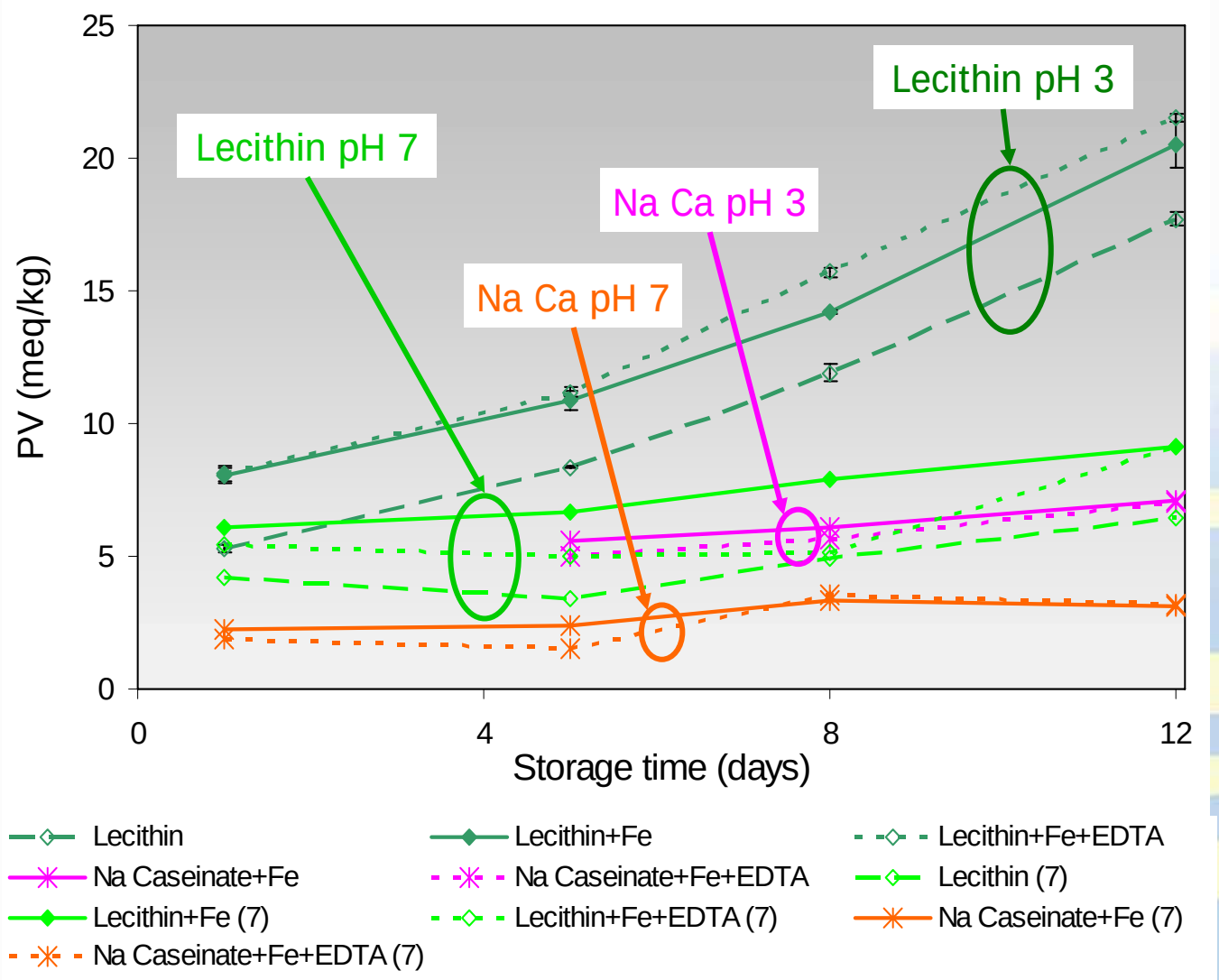
Development of peroxide values



Tween:
Fe^{2+} efficient pro-oxidant at pH 3. The chelating effect of EDTA was only found at pH 3

Citrem:
Fe2+ acted as pro-oxidant. The chelating effect of EDTA was more pronounced at pH 7 than at pH 3

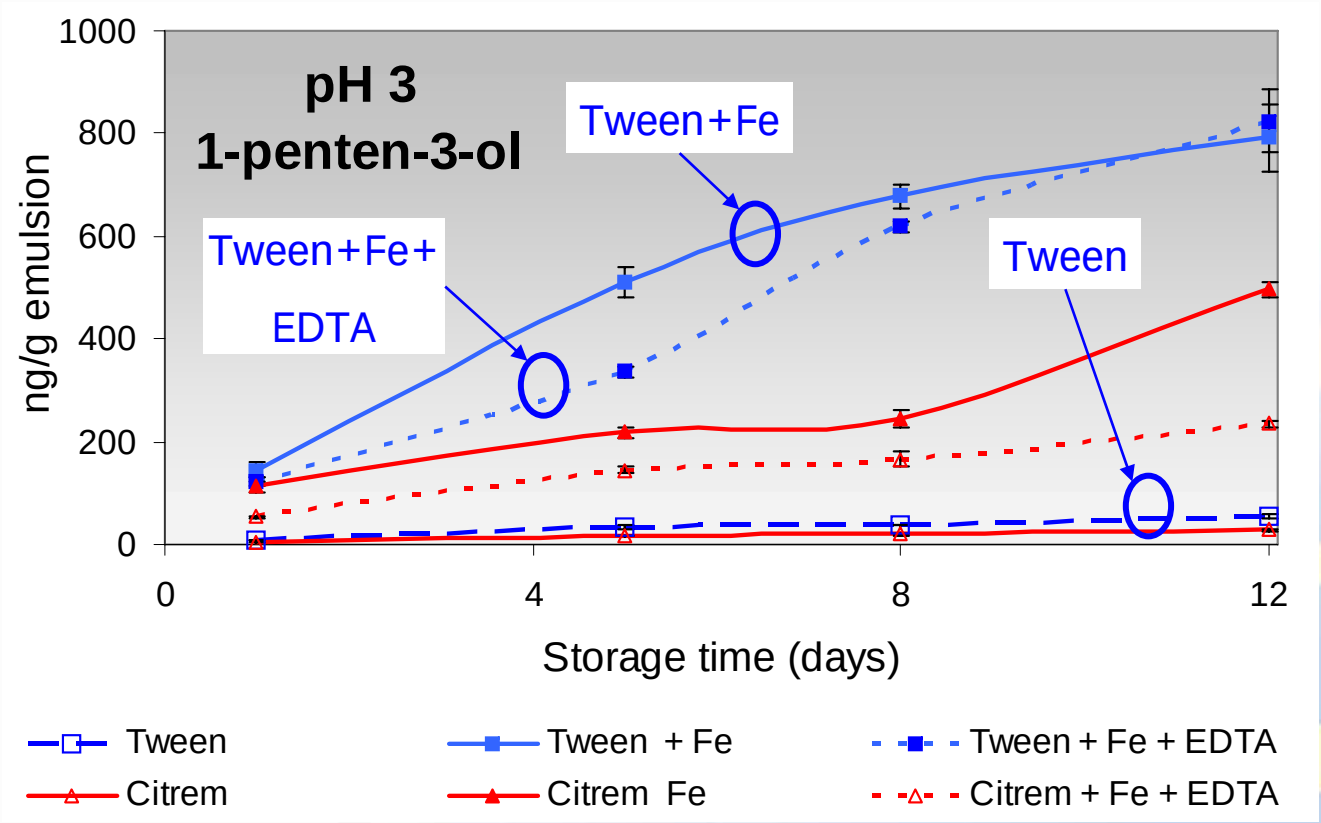
Development of peroxide values



Sodium caseinate:
No significant increase in PV. No effect of EDTA

Lecithin:
PV increases with time, particularly at pH 3. EDTA antioxidative effect at pH 7, but not at pH 3.

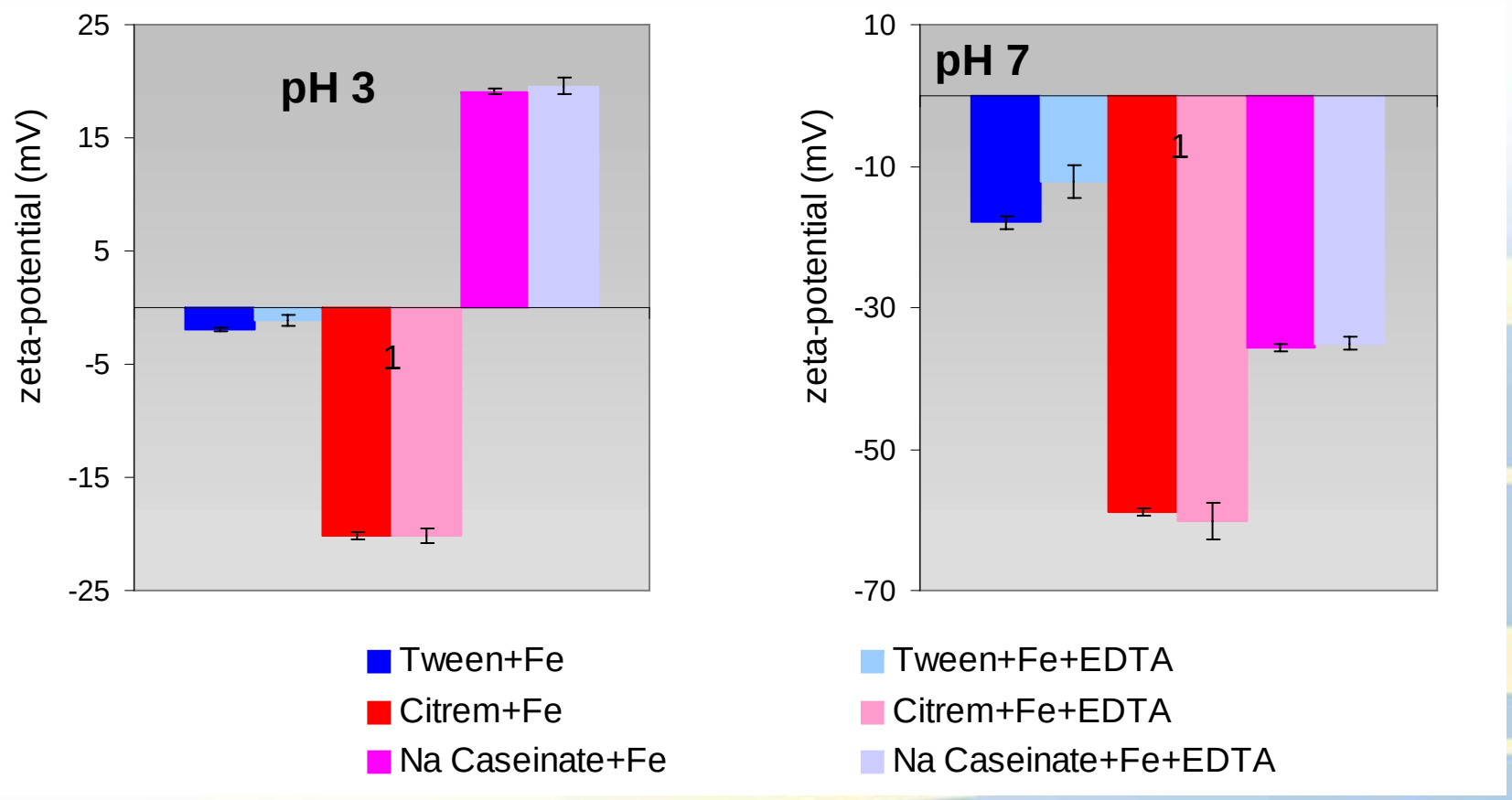
Development of volatiles



2,3-Butandione
2-Butenal
1-Penten-3-one
Pentanal
1-Penten-3-ol
2-Pentenal
Hexanal
2-Hexenal
Heptanal
2-Heptenal
1-Octen-3-ol
Octanal
2,4-Heptadienal
2-Octenal
Nonanal
2-Nonenal
2-Decenal

Volatiles increased during storage when Fe2+ was added The chelating effect of EDTA was found for both emulsifiers.

Zeta potential – Day 12



The measured zeta potential depended on the type of emulsifier and on the pH.

Results from washed fish mince studies

Effect of fish species, heme iron, Cu, ADP and ascorbic acid

Oxidation trial

Washed minces from cod, herring and salmon

pH 6.3

Streptomycin 200 ppm

Trout Hb 20 µM (or buffer)

Moisture adjustment 86 %

Chemical analysis of lipid oxidation

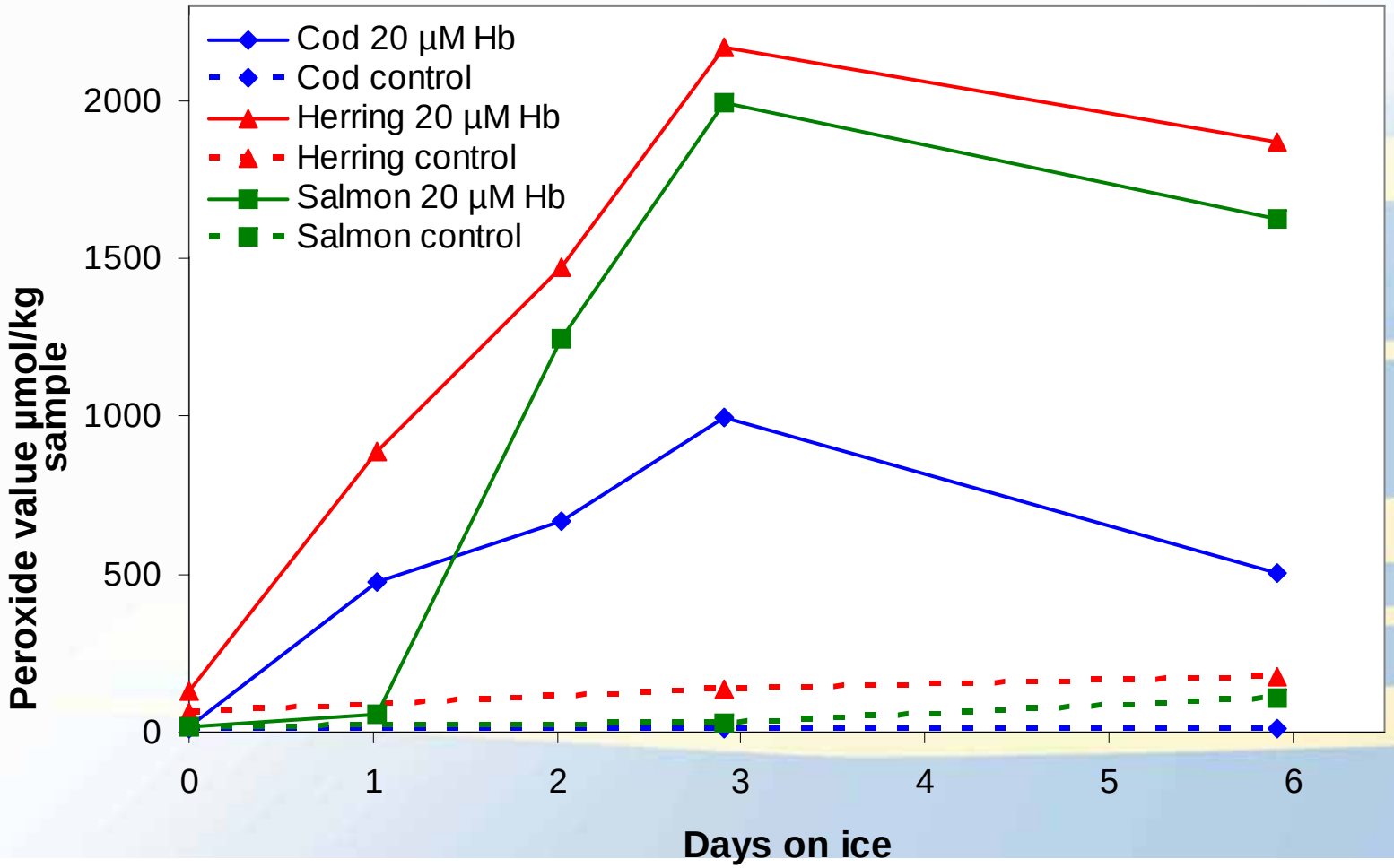
Chemical analysis of protein solubility

Colorimetric analysis of redness and yellowness

Sensory analysis of rancid odor

Fish species and oxidation

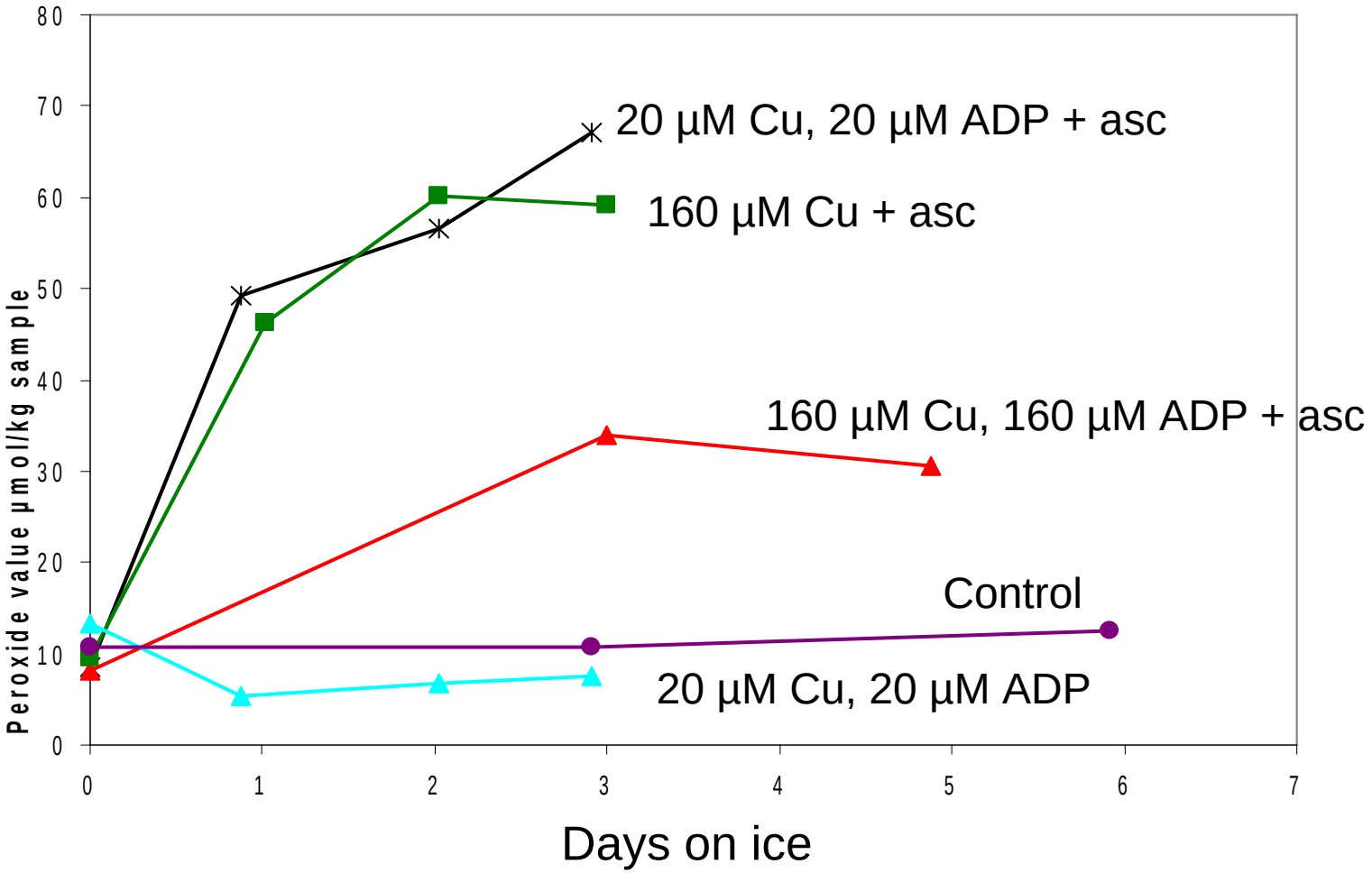
Hb fall models



Compositional table

Analysis	Cod model	Herring model	Salmon model
Moisture %	85,9	85,9	85,9
Lipid %	0,56	2,96	3,41
Tot PUFA %	0,19	0,72	0,86
Protein %	15,0	12,0	13,2
Pro- and antioxidants			
Cu µg/g sample	0,11	0,39	0,20
Zn µg/g sample	2,02	2,45	1,79
Fe µg/g sample	0,32	1,07	0,69
Vitamin E ppm	2,15	0,86	2,24

Effect of low molecular weight Cu, ADP and ascorbic acid



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Conclusions

Oxidation is governed by many different factors:

- In liposomes oxidation is dependent on temperature, salt, pH, Fe and zeta potential. Mathematical modeling possible
- In emulsions oxidation is highly dependent on pH and the emulsifier type. Surface charge can partly explain these findings
- In washed fish mince: Herring is more susceptible to oxidation maybe due to relatively low vit E level. Hb is the most important initiator of oxidation. ADP may have some antioxidative potential

Acknowledgements

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