Production of protein isolates from pelagic fish and its by-products using the pH-shift technology

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Our vision: Use more of the catches of marine raw materials for food production.
Marine protein isolates in foods

- **Surimi**: Its gelation capacity very attractive in all gelled fish products (fish balls, fish cakes, crab sticks..)

- **Powder**: can replace milk-/soyproteins in soups, energy drinks, bakery products

- **Marinades**: injection into fillets for improved water holding/juiciness (replaces phosphates with a natural product)

- **Coating**: on fried products (nutrilean™)

- **Biodegradable films**: with antimicrobial and antioxidative properties

And to the last, new studies have shown positive effects from fish proteins on diabetes and high blood pressure
Which volumes of proteins are yielded by Nordic herring fisheries?

Total landing: 1 508 000 ton in SW/DK/IS/NO

Consumer use: ~1 184 000 ton

- Butterfly fillets: 46.8%
- Guts: 21.2%
- Frame: 18.2%
- Head: 13.8%

Industry use: ~324 000 ton

- Butterfly fillets: 46.8%
- Guts: 21.2%
- Frame: 18.2%
- Head: 13.8%

Muscle: 45-50%

- 173 440 ton muscle
- Protein: ~17%
- 29 485 ton proteins

- 64 075 ton proteins

- 203 472 ton muscle
- Protein: ~17%
- 34 590 ton proteins

Källor: RUBIN, Sintef
Which volumes of proteins are yielded by Nordic herring fisheries?

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Källor: RUBIN, Sintef
But, HOW to isolate the proteins without causing denaturation/proteolysis?

New techniques for protein isolation have been patented during the last 10 years that can be applied on complex muscle raw materials

”The pH-shift processes”


Homogenization
raw material + water (1:6)

↓

Protein solubilization
pH → ~3 eller 11

↓

Separation
(≤10 000g)

↓

Protein precipitation
pH → ~5.5

↓

Neutrala Lipider

Lösta proteiner

Skal, ben, pigment,
membran mm

↓

Protein isolation
(≤10 000g)

↓

E.g surimi production
(+cryoprotectants)

↓

Gelation (pH →7.1, 2%
salt, 20 min 90°C)
The whole raw material can be used as starting material. Bones, skin etc do not create problems.

Lipids, pigments and contaminants drastically reduced in many cases.

The protein functionality increased.

<table>
<thead>
<tr>
<th>Homogenization</th>
</tr>
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<tr>
<td>raw material + water (1:6)</td>
</tr>
<tr>
<td>↓</td>
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</table>

Uses significant amounts of water
Choice of acid/base important

Centrifugation a costly step
Oxidation of pigments, lipids, proteins
We have since 2000 worked with the acid and alkaline processes on herring of different complexity;

- herring light muscle
- herring fillets
- whole gutted herring
- whole herring

Funding from NICE, Formas, Fiskeriverket/EU structural funds

In the last year we have gone from lab to pilot scale
What parameters to determine success?

- Recovery (total and in the 2 separation steps)
- Purity
- Ash
- Functionality
- Emulsification
- Foaming ability
- (Salt solubility)
- Stability during processing and subsequent storage
- Lipid oxidation
- Protein oxidation
- Microbial growth

*The use of the protein isolates will determine which factor that is the most important*
Recovery of proteins with acid and alkaline processing of different herring raw materials

<table>
<thead>
<tr>
<th></th>
<th>Acid method</th>
<th>Alkaline method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Herring light muscle</td>
<td>74%</td>
<td>68%</td>
</tr>
<tr>
<td>Herring fillets</td>
<td>70% /65%*</td>
<td>57%*</td>
</tr>
<tr>
<td>Whole gutted herring</td>
<td>59%</td>
<td>57%</td>
</tr>
<tr>
<td>Whole herring</td>
<td>71%*</td>
<td>65%*</td>
</tr>
</tbody>
</table>

* Very few replicates

Marmon & Undeland, 2010; Undeland et al; 2002; 2005; Marmon & Undeland-unpublished
Composition of protein isolates produced with acid and alkaline processing of gutted Baltic herring

<table>
<thead>
<tr>
<th></th>
<th>Herring mince</th>
<th>Alkali-made isolate</th>
<th>Acid-made isolate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (%)</td>
<td>78.0</td>
<td>89.3</td>
<td>89.8</td>
</tr>
<tr>
<td>Lipids (%, dry weight)</td>
<td>35.9</td>
<td>17.7</td>
<td>22.2</td>
</tr>
<tr>
<td>Protein (%, dry weight)</td>
<td>56.5</td>
<td>81.0</td>
<td>81.3</td>
</tr>
<tr>
<td>Ash (%, dry weight)</td>
<td>8.8</td>
<td>1.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Significant increases in water and protein content. Significant reductions in lipids and ash.
Changes in dioxins/dioxin-like PCB’s during pH-shift processing of Baltic herring

<table>
<thead>
<tr>
<th></th>
<th>Herring mince</th>
<th>Protein isolate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat %</td>
<td>7.1</td>
<td>2.1</td>
</tr>
<tr>
<td>(On 80% water basis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dioxins TEQ</td>
<td>5.7</td>
<td>2.0</td>
</tr>
<tr>
<td>(pg/g, on 80% water basis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dioxin-like PCB’s TEQ</td>
<td>3.3</td>
<td>1.0</td>
</tr>
<tr>
<td>(pg/g, on 80% water basis)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Average value based on isolates from acid and alkaline processing

EU limits: 4/8 pg/g
This herring: 5.7/9 → 2/3 pg/g

Marmon et al. 2009
Changes in color during pH-shift processing of gutted Baltic herring

<table>
<thead>
<tr>
<th></th>
<th>Herring mince</th>
<th>Alkali-made isolate</th>
<th>Acid-made isolate</th>
</tr>
</thead>
<tbody>
<tr>
<td>L* (Lightness)</td>
<td>43.2</td>
<td>57.9</td>
<td>61.7</td>
</tr>
<tr>
<td>a* (Redness)</td>
<td>4.8</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>b* (Yellowness)</td>
<td>6.9</td>
<td>6.3</td>
<td>6.9</td>
</tr>
<tr>
<td>Whiteness</td>
<td>42.5</td>
<td>57.4</td>
<td>61.0</td>
</tr>
</tbody>
</table>

Significant increases in lightness and whiteness
Significant reductions in redness and yellowness

Marmon & Undeland, 2009
Lipid oxidation can develop during pH-shift processing of sensitive materials like herring.

- But, good effects of antioxidants

Undeland et al. 2005
Some antioxidants were also very effective during further storage of the isolate (erythorbate and EDTA).

Undeland et al. 2005
## Functionality of proteins produced by pH-shift processing of Baltic herring

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<th>Alkali-made isolate</th>
<th>Acid-made isolate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gel strength (g)</strong></td>
<td>810</td>
<td>827</td>
</tr>
<tr>
<td><strong>Elasticity (mm)</strong></td>
<td>9.8</td>
<td>10.7</td>
</tr>
<tr>
<td><strong>Folding</strong></td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

The herring protein isolatates produced have had decent functionality.
Additional possibilities with herring/herring by products

- Isolation of **marine oils** with "pH-shift" methodology (*Okada & Morrisey, 2007*)

- Isolation of **antioxidative liquids** (wash waters, brines, surimi waste water, press juice)

- **Combining** pH-shift protein isolation with oil and press juice isolation would be the ideal way of better utilizing herring for the food ingredients