MULTIVARIATE QUALITY PREDICTION OF COD (*GADUS MORHUA*) AND HADDOCK FILLETS (*MELANOGRAMMUS AEGLEFINUS*) STORED UNDER SUPERCHILLING AND TEMPERATURE ABUSIVE CONDITIONS

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OBJECTIVES

- to achieve **better understanding** of the **effect of temperature** on the **complex spoilage** changes of fish
  - volatile compounds as **quality indicators**
    - **GC** (gas chromatography) analysis
    - characterize the spoilage potential of **specific spoilage organisms (SSO)**
- to apply an **electronic nose** as a **rapid** technique to monitor classes of volatile compounds as indicators of **quality changes** during storage of chilled fish
  - storage studies of chilled cod and haddock fillets – natural products
    - explore the correlation of **microbial, chemical, sensory and e-nose** data by using multivariate models **(PLSR / PCA - SIMCA)**
    - predict the quality or classify products according to **sensory criteria**.

Various factors influence the spoilage of fish

- Species
  - cod and haddock
- Seasonal condition
  - autumn
- Fishing grounds
  - Northeast and Southwest Iceland
- Catching methods
  - longline / bottom trawl
- Handling
  - Flake ice / slurry ice
  - Superchilling CBC (contact blast and cooling)
- Processing
  - skinless fillets
- Storage techniques
  - styrofoam boxes
- Time / temperature
  - -1,5 to 15°C

Complex spoilage changes in fish

Identify quality indicators

Fresh odor

Spoilage odor

Endogenous enzymes
lipoxygenase, cathepsin, calpain →

Oxidation
pro- and antioxidants →

Microbial growth
SSO
Specific Spoilage Organisms →

Glycolysis **pH↓, Lactic acid↑**

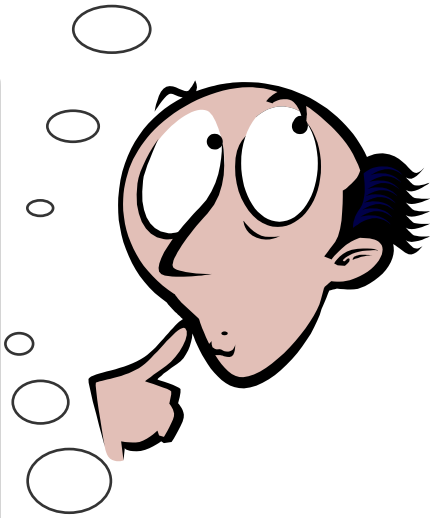
Rigor mortis **ATP→ Inosine →Hx →Urea**

Autolysis

Protein / i.e. sarcoplasmic proteins
→ peptides→ amino acids

Lipids / i.e. phospholipids → PUFA

Soluble substances in the muscle
Nucelotides
NPN non protein nitrogenous components
TMAO → TMA/DMA, FA, pH ↑



Texture firm – soft

Color changes

QUALITY INDICATORS in chilled fish

- Spoilage odors
- Volatile microbial metabolites
- Specific Spoilage Organisms (SSO)

Ammonia odor, dried fish, old fish odor

Amines: TMA/DMA

NH_3

Sweet - sour, malty and fruity odors

Alcohols, aldehydes, ketones, esters

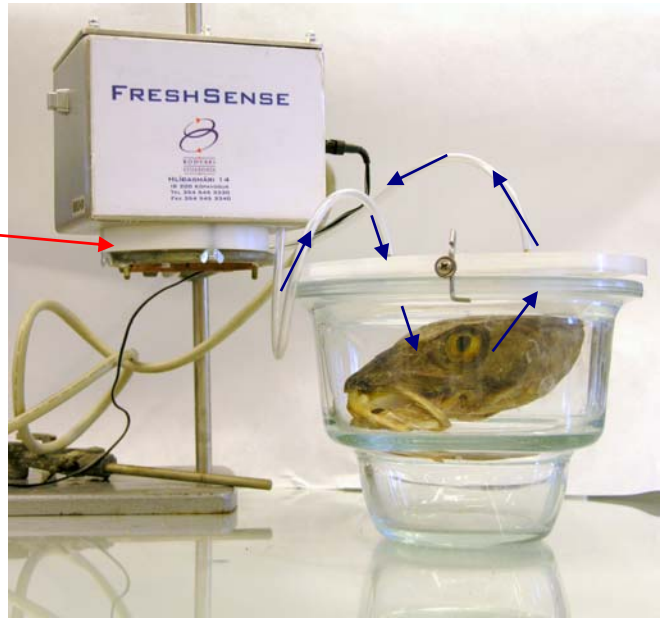
Putrid odor, onion like, old cabbage, rotten egg

Sulfur compounds

SSOs ***Pseuodomonas* spp.** ***P. phosphoreum*** **H_2S producers**

METHODS – analysis of volatile compounds

- **Electronic nose FreshSense**
  - Maritech, Iceland (prototype)
  - Electrochemical sensors
    - CO, NH_3, H_2S, SO_2
  - 2.6L sampling vessel
  - Pump
  - Continuous sampling for 5 minutes
  - Approx. 500 g fillets
  - Temperature monitoring /control

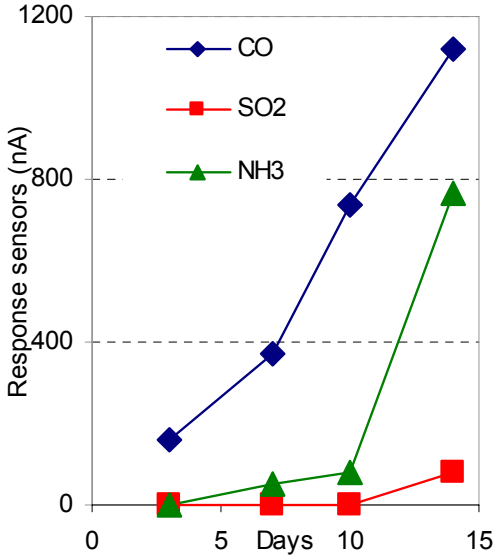


- **Rapid technique**
  - A few sensors sensitive to the main classes of compounds produced in chilled fish

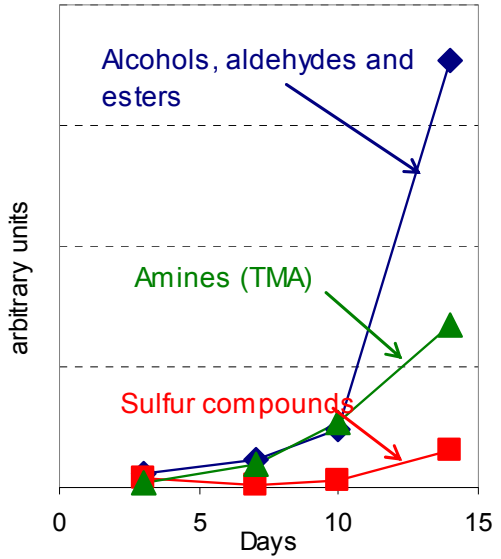
- **Comparison with gas chromatography**
  - Identify the main classes of compounds produced during storage to select appropriate sensors
  - GC-MS / GC-O

Storage study of haddock fillets
Comparison of the e-nose sensors and GC analysis of the main classes of volatile compounds produced during chilled storage

Electronic nose sensors



Gas chromatography



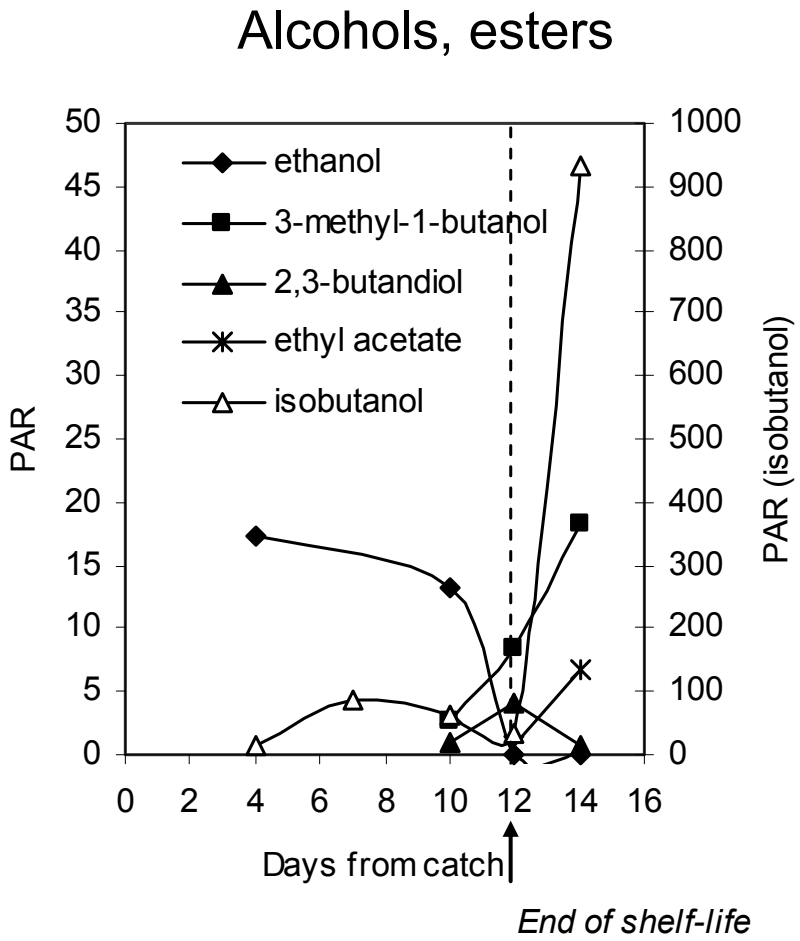
CO sensor ⇨ alcohols, aldehydes and esters

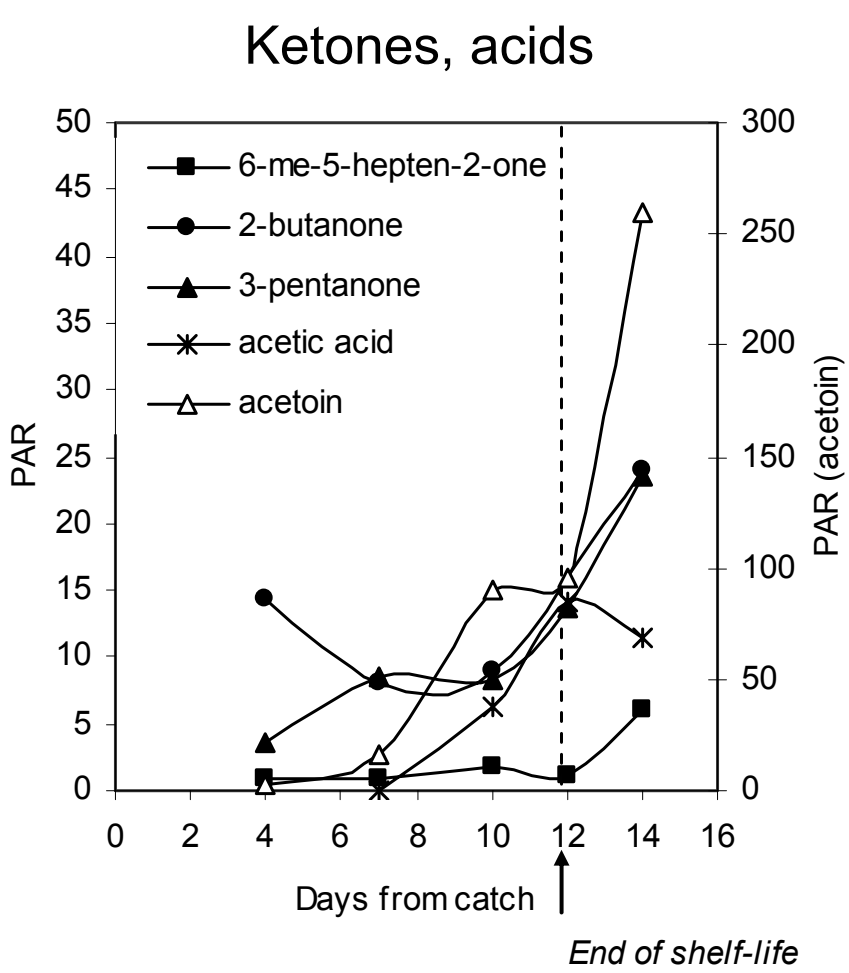
SO_2 sensor ⇨ sulfur compounds

NH_3 sensor ⇨ amines

In: Olafsdottir G. 2003. Developing rapid olfaction arrays for determining fish quality. In Ibtisam E Tothill (Ed) RAPID AND ON-LINE INSTRUMENTATION FOR FOOD QUALITY ASSURANCE. Woodhead Publishing Ltd, Cambridge, England, pp. 339-360

Examples of the dynamic evolution of volatile compounds in spoilage of fish (cod fillets 0°C)





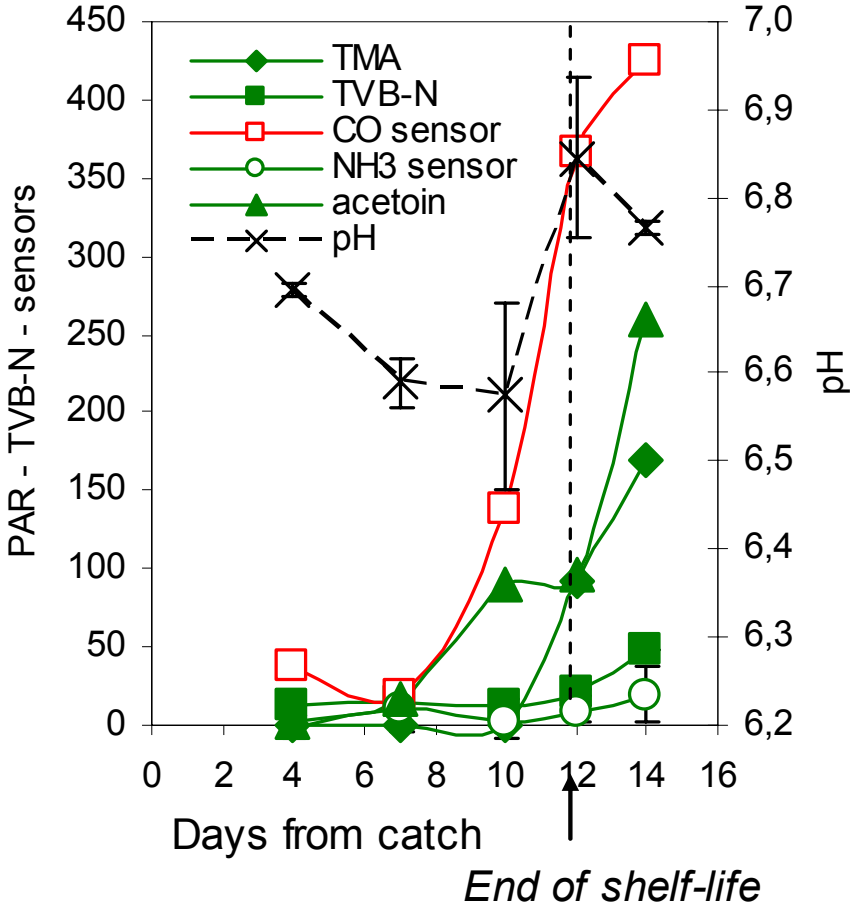
From: Olafsdottir, G., Jonsdottir, R., Lauzon, H.L., Luten, J., Kristbergsson, K. 2005. Characterization of volatile compounds in chilled cod (*Gadus morhua*) fillets by gas chromatography and detection of quality indicators by an electronic nose. JAFC, 53 (26), 10140 -10147.

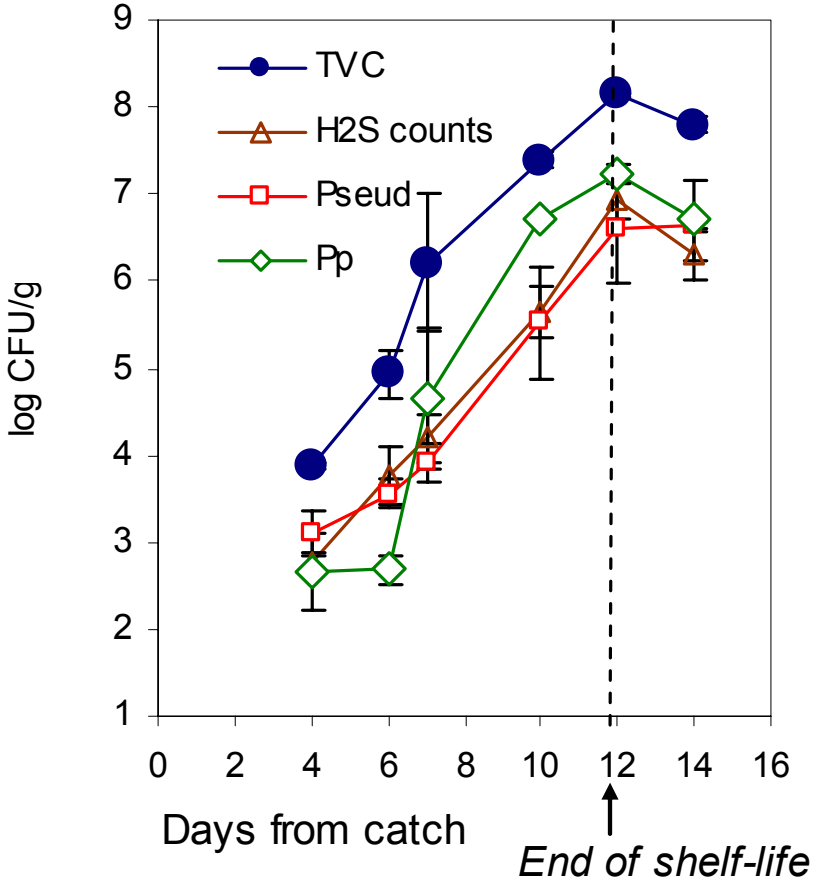
Potential quality indicators in cod fillets (0°C)

Volatiles: TMA (trimethylamine), TVB-N
acetoin (3-hydroxy-2-butanone)

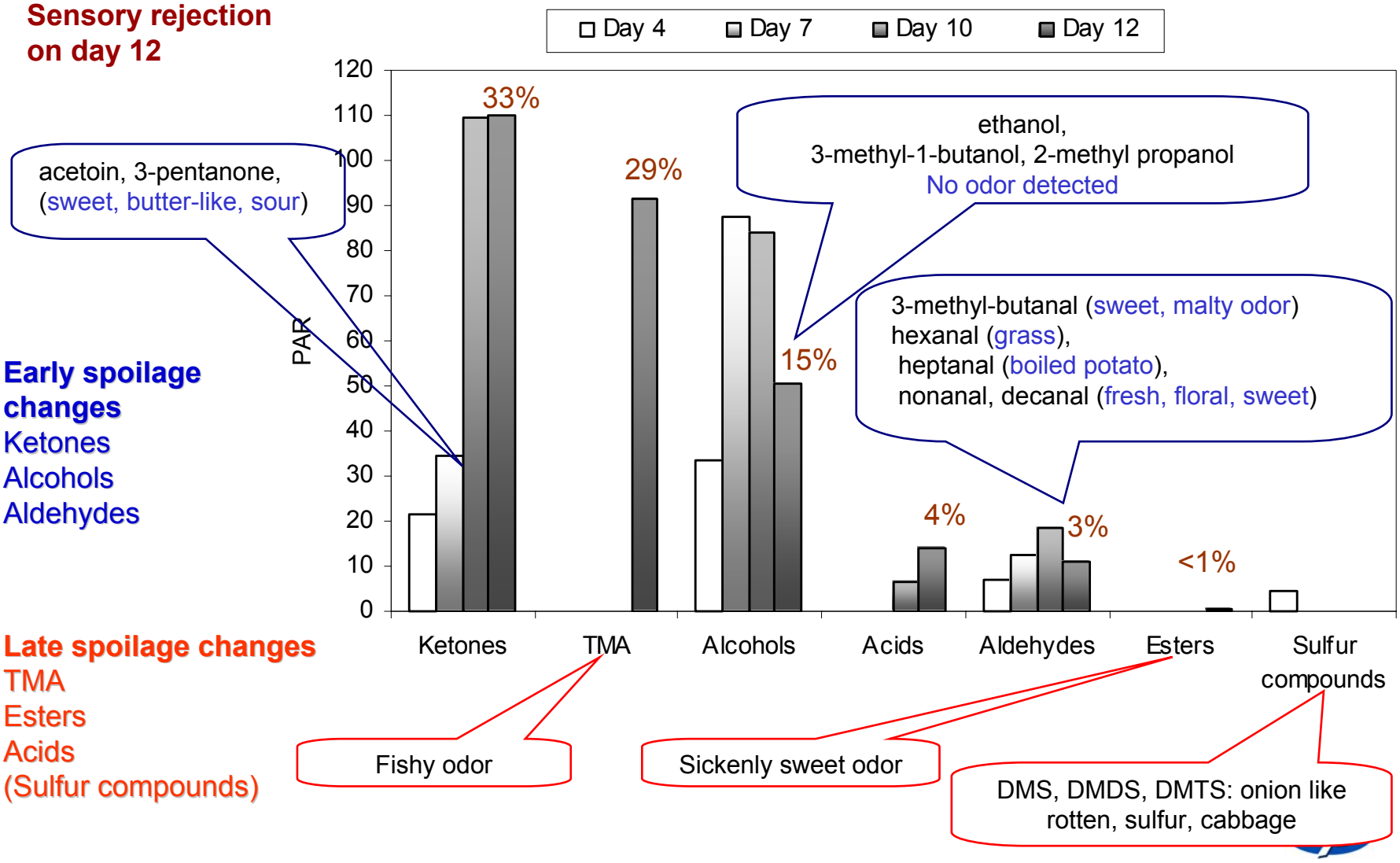
E-nose: CO and NH_3 sensor

Microbial counts:
TVC (total viable counts)
H_2S producers
Pseudomonas spp.
P. phosphoreum (predominating)





Quantification and identification of the main classes of compounds in cod fillets during storage (0°C) by GC-MS and GC-O



Storage studies - METHODS

- Five storage studies on cod and haddock fillets packed in styrofoam boxes
  - from two factories in Iceland
  - different temperatures (-1,5 to 15°C)

- Traditional reference methods
  - Sensory analysis
    - Torry score
  - Microbial counts
    - TVC (total viable counts) (15°C)
    - *SSO (specific spoilage organisms)*
      - *Pseudomonas spp*
      - H_2S-producers
      - *Photobacterium phosphoreum*
  - Chemical analysis
    - TVB-N (total volatile basic nitrogen)
- Electronic nose

Data analysis

Multivariate models
- PLSR / PCA /SIMCA
  - Unscrambler Camo

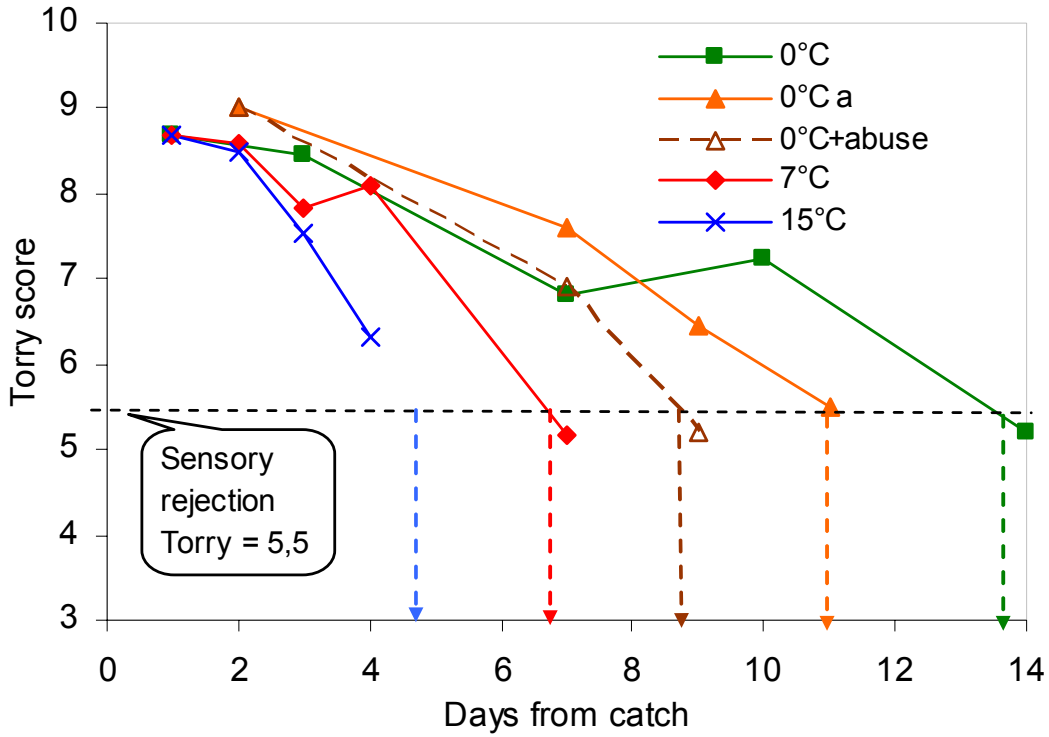
Influence of different storage temperature on the shelf-life of haddock fillets

Storage conditions:

Study 1: 0°C, 7°C, 15°C

Study 2: 0°C, 0°C + abuse

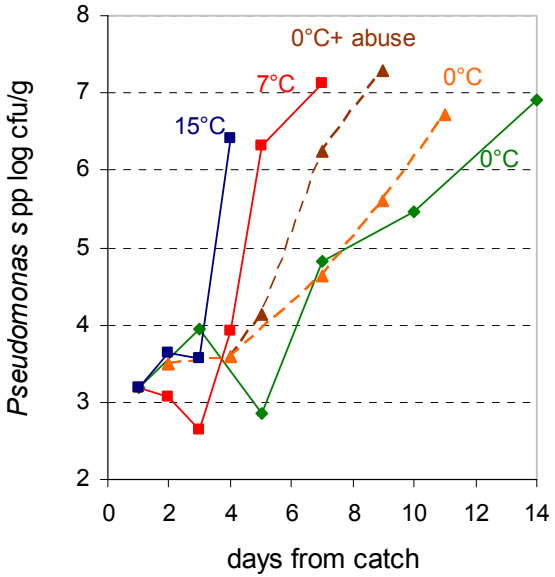
Shelf-life determined by sensory analysis



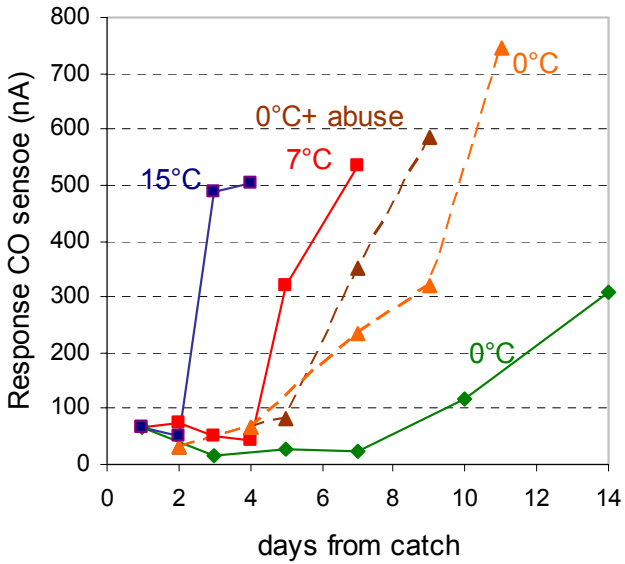
From: Olafsdottir G, Lauzon HL, Martinsdottir E, Kristbergsson K. 2005. Influence of storage temperature on microbial spoilage characteristics of haddock fillets (*Melanogrammus aeglefinus*) evaluated by multivariate quality prediction. *In press*.

Influence of different storage temperature (0°C, 7°C, 15°C and 0°C, 0°C + abuse) on the rate of spoilage changes haddock fillets

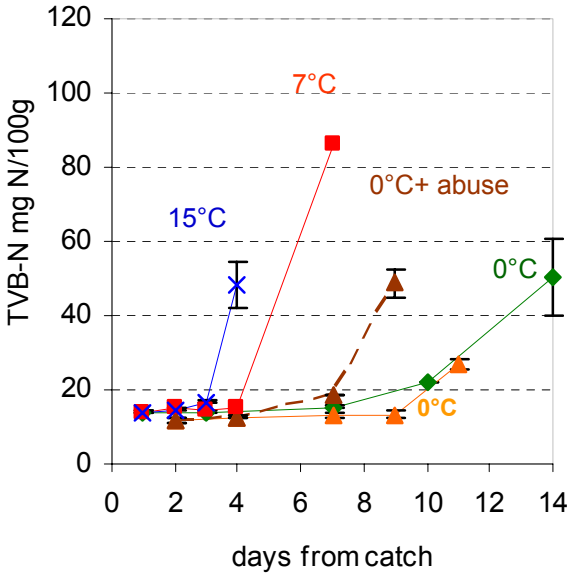
Microbial counts *Pseudomonas* spp.



E- nose: CO sensor



TVB-N



Quality indictors do not always agree on the spoilage rate of sample groups

From: Olafsdottir G, Lauzon HL, Martinsdottir E, Kristbergsson K. 2005. Influence of storage temperature on microbial spoilage characteristics of haddock fillets (*Melanogrammus aeglefinus*) evaluated by multivariate quality prediction. In press.

Partial Least Squares Regression (PLSR) model to explore the correlation of the variables

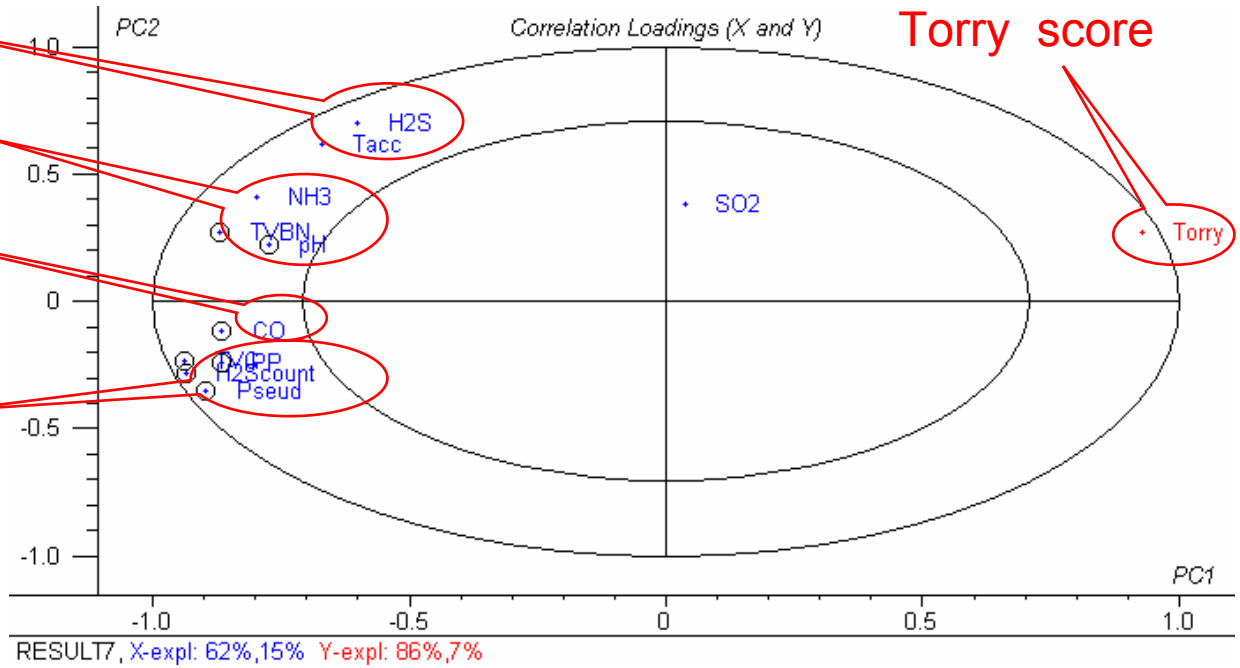
- Selection of quality indicators [X] to predict sensory quality [Y] of haddock fillets (stored at different temperatures 0°C, 7°C, 15°C - 0°C, 0°C + abuse)

Quality indicators [X]

- H_2S sensor - T_{acc}
- NH_3sensor – TVB-N - pH
- CO sensor
- *Pseudomonas spp.*
- H_2S producers
- *P. phosphoreum*
- TVC

(Total viable microbial counts)

Sensory Quality [Y]
Torry score

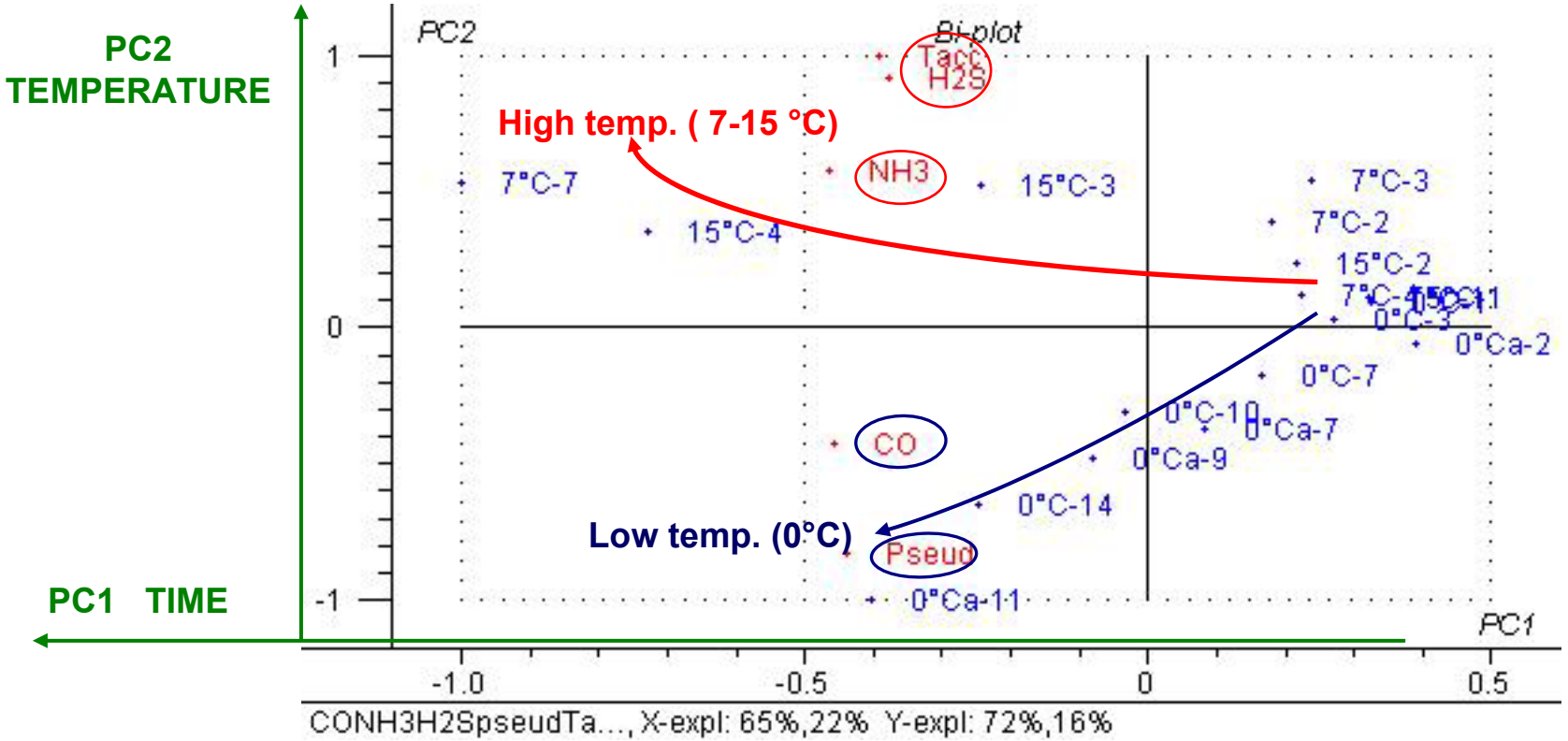


- Different models were explored to select the best quality indicators
- Best models when all significant variables were used
- Of interest to use rapid techniques like the e-nose sensors (CO, H_2S and NH_3)

Partial Least Squares Regression (PLSR) model for haddock samples (0°C, 7°C, 15°C - 0°C, 0°C + abuse)

Models based on pseudomonads counts and the CO, NH_3 H_2S sensors, and T_{acc} (time / temp) gave best results to predict sensory scores

(r^2=0.94; RMSEP: 0,49)



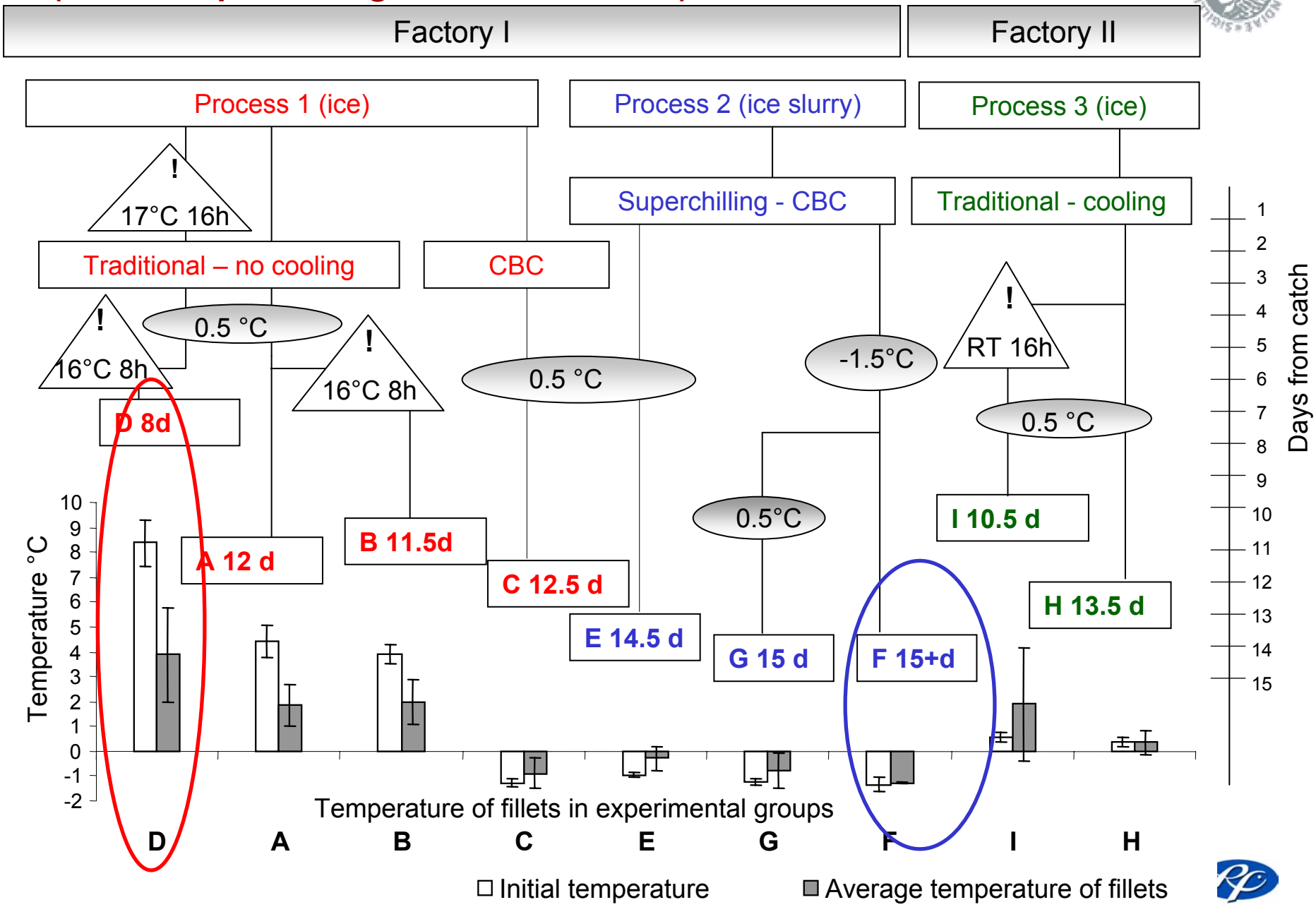
5% error between predicted sensory scores and experimental values when using a subset of the data

Storage studies on cod fillets at low temperature
-1.5 (superchilling) to 0.5°C and temperature abuse

- **Factory 1:**
  - Process 1 Traditional (no cooling of fillets) + abuse
  - Process 2 Superchilling (CBC)
- **Factory 2:**
  - Process 3 Traditional (cooling of fillets)

  - Important to study natural products
  - Catching, handling and storage conditions were not the same
  - The aim was to select the best quality indicators (microbial, chemical, e-nose) to predict the sensory quality

Influence of different processes and temperature conditions (-1.5 °C superchilling, 0.5 °C and abuse) on the shelf-life of cod fillets



Partial Least Squares Regression (PLSR) model to explore the potential of the quality indicators (X) to predict sensory quality (Y)

Cod fillets stored at -1.5 (superchilling) to 0.5°C + abuse

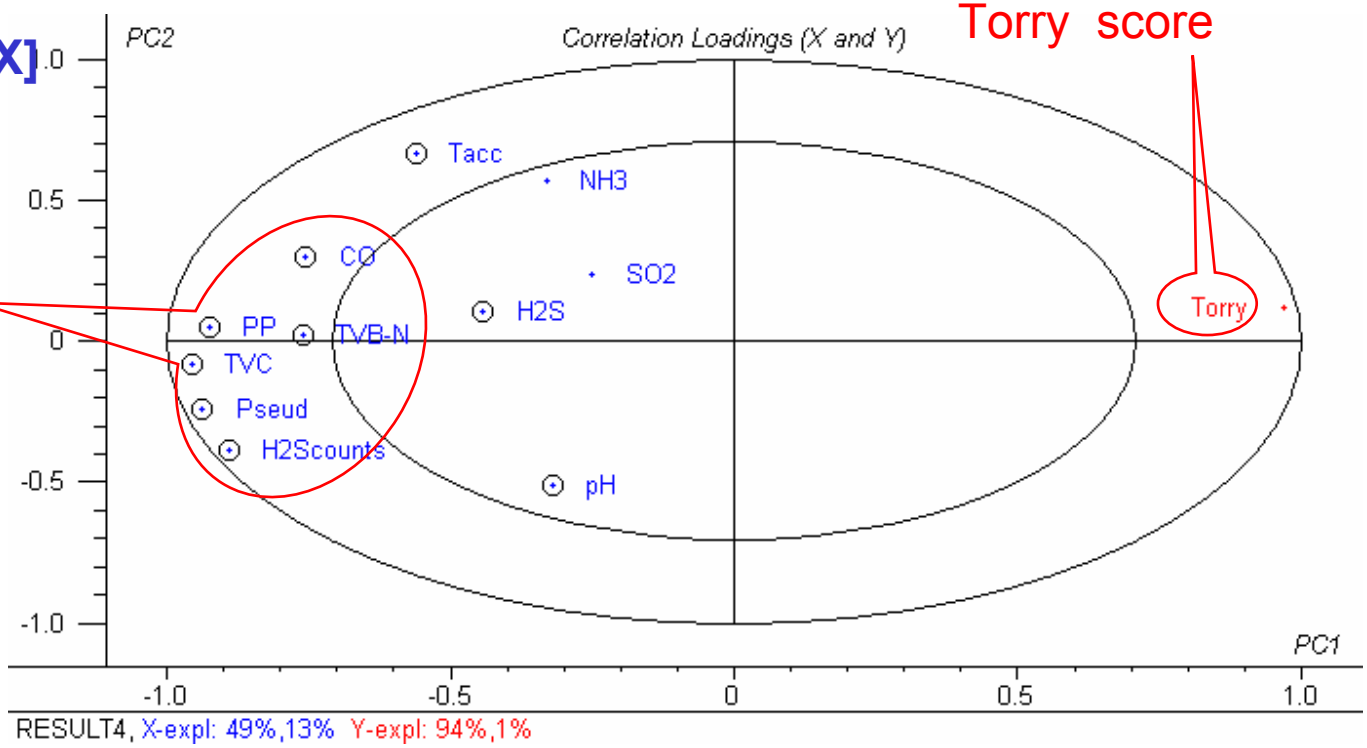
– different factories and processes

Sensory Quality [Y]

Torry score

Quality indicators [X]

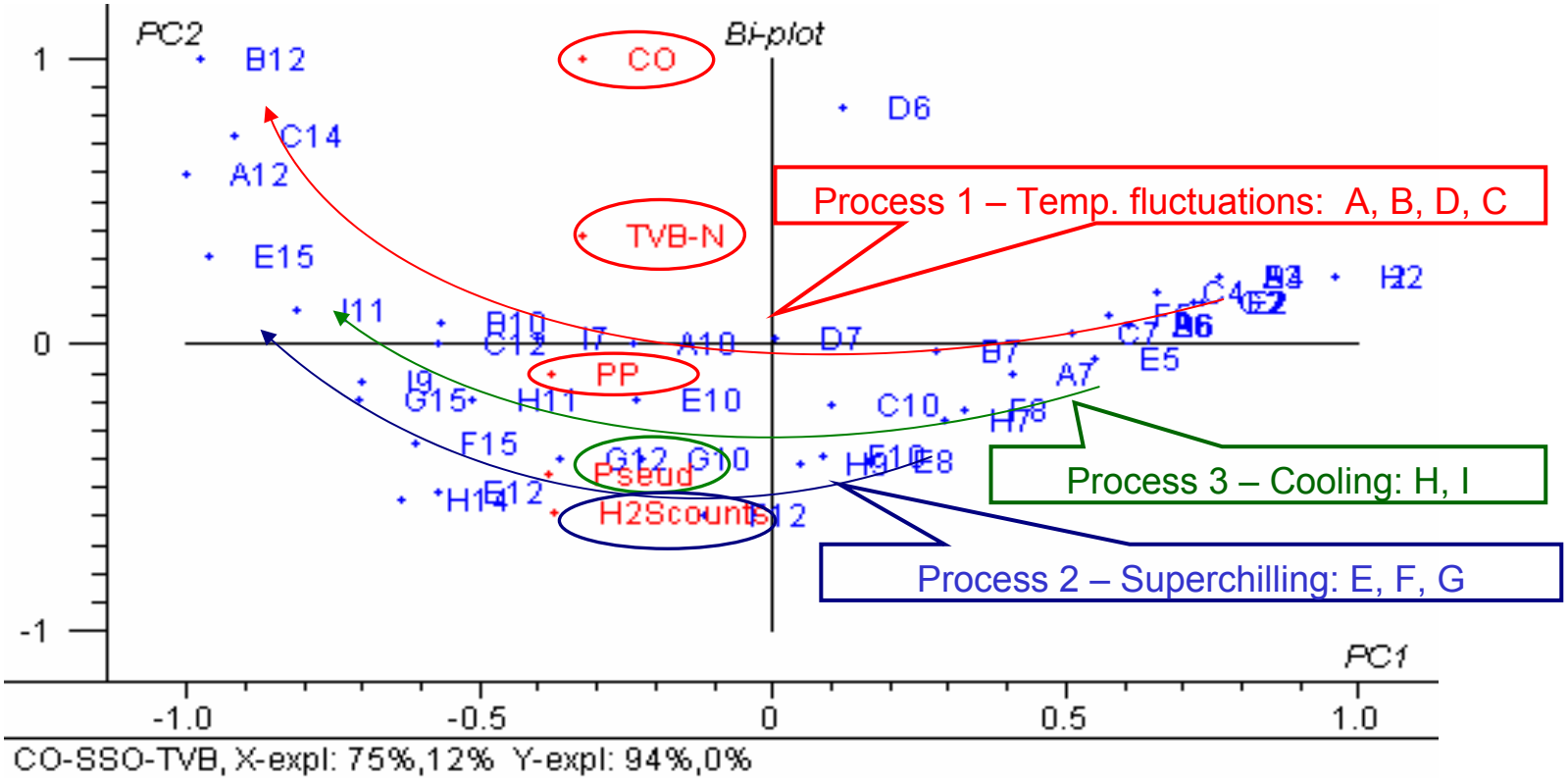
- CO sensor
- TVB-N
- *P.phosphoreum*
- TVC
- pseudomonads
- H_2S-producers



From: Olafsdottir G, Lauzon HL, Martinsdottir E, Oehlenschläger J, Kristbergsson K. 2006. Evaluation of shelf-life of superchilled cod (*Gadus morhua*) fillets and influence of temperature fluctuations on microbial and chemical quality indicators. J. Food Sci 71 (2): 97-109.

PLSR model for chilled and superchilled cod fillets

Multiple quality criteria based on 5 variables, the SSOs (*P. phosporeum*, H_2S-producers, pseudomonads), CO sensor and TVB-N was needed when using a global model to classify samples from different factories stored at different temperatures



- 85% correct classification based on sensory criteria (Torry score 7)

CONCLUSIONS

- Volatile compounds contributed by different SSOs give information about the spoilage processes in fish

- Electronic nose is a multi-indicator device
  - selective sensors for ketones, amines, alcohols, aldehydes, acids, esters and sulfur compounds
  - e-nose can give more information than a single reference measurement for example TVB-N.

- Establishment of quality critera or fixed values to determine the end of shelf-life or the quality of fish based on electronic nose responses, microbial counts and TVB-N reference methods will have to be developed for each product and the respective storage conditions.

FUTURE PERSPECTIVES

Implementation of the electronic nose technique for quality monitoring of fish products?

- The fast development of sensor technologies and data processing techniques will improve the possibility of quality monitoring in the food industry.

- On-line monitoring ? Handheld devices ? “Smart” sensors in packaging?
  - sampling
  - temperature control
  - exclusion of background odors and contaminants
  - sensitive / selective sensors for quality indicating compounds
  - rapid detection of SSOs
  - specific applications - establishment of quality criteria for different products and temperature conditions

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