4th International Workshop on

# Water in Food

# Application of Freezing Point Determinations in Milk


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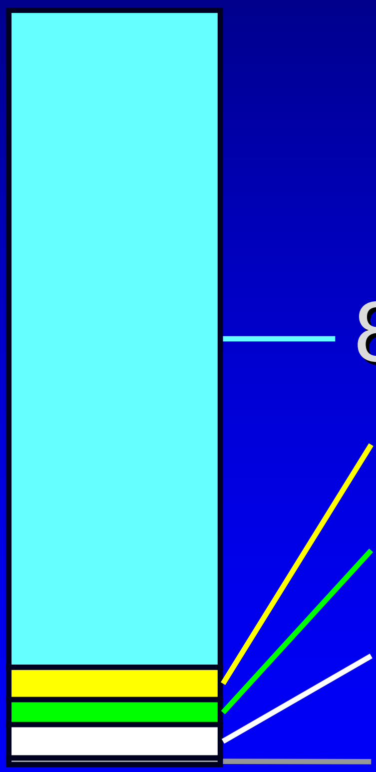
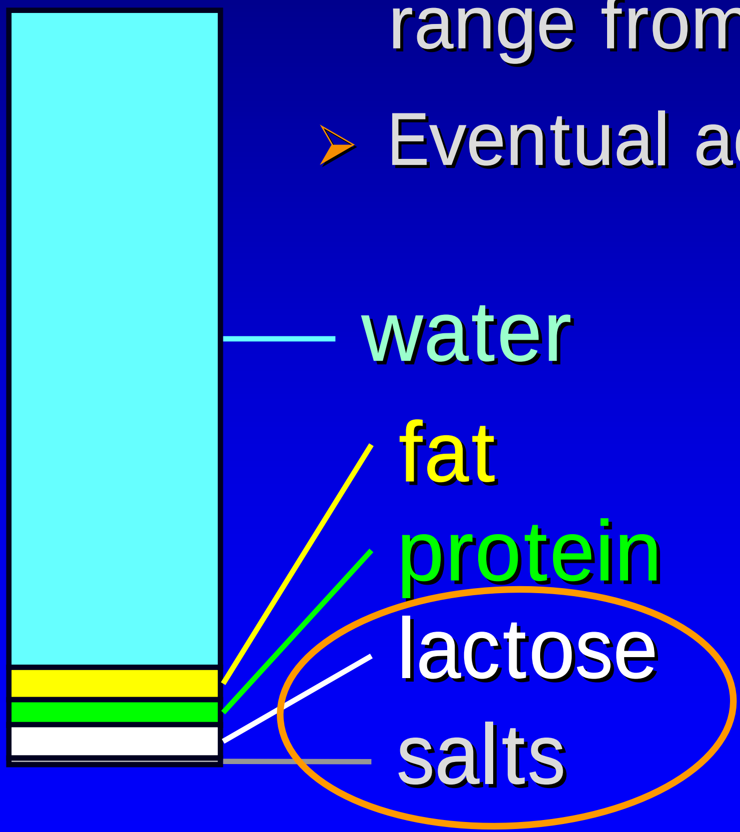
# Milk composition

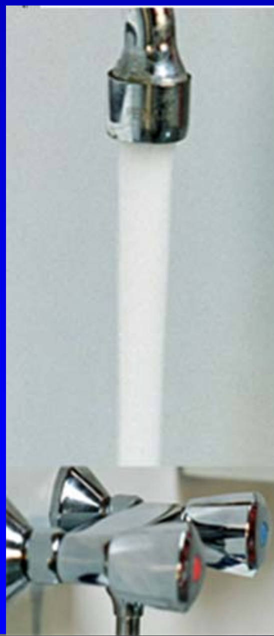


| Raw cow's milk | | Drinking milk (no additions) |
|---|---|---|
| 87 % | water | 87-91 % |
| 4,3 % | fat | 0,1-3,5 % |
| 3,4 % | protein | $3,4^{+}$ % |
| 4,4 % | lactose | $4,4^{+}$ % |
| 0,9 % | other, mainly salts | $0,9^{+}$ % |

# Freezing point of liquid milk (1)

- Values for authentic bulk cow's milk range from -0,515 to -0,530 °C
- Eventual adulteration can be estimated

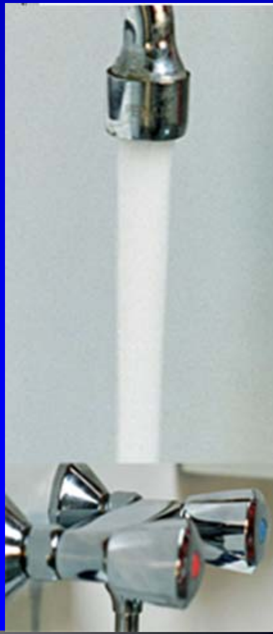


# Freezing point of liquid milk (2)

## Why controlling water content in liquid milk?

- Combat adulteration with extraneous water
- Avoiding residues and contaminants
  - detergents
  - disinfectants
  - microbiological contamination
- In a chain-oriented quality assurance approach to promote:
  - good farming practice
  - good dairy manufacturing practice



# Freezing point of liquid milk (3)

## Other influencing factors with raw milk:

- Species (average value NL goat milk: -0,540 °C)
- Breed
- Climate
- Feed and water

# EU demands

## EU 92/46 – Milk Hygiene Directive, art 5.9:

- Heat-treated cow's milk must have a freezing point not higher than -0,520 °C

## EU Council Regulation 2597/97, art. 4 (a):

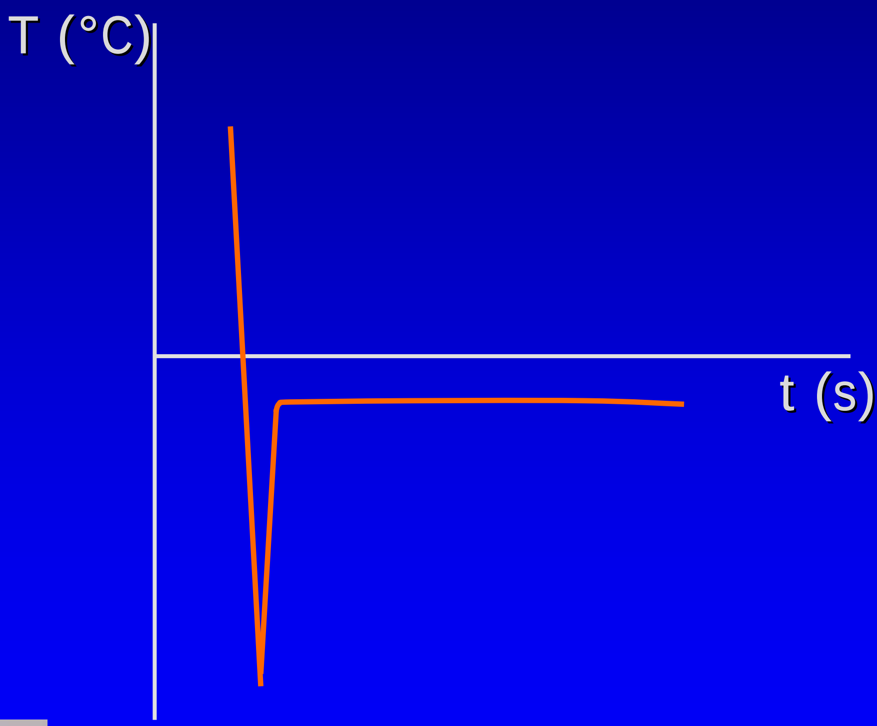
- Drinking milk must have a freezing point close to the average freezing point for raw milk recorded in the area of origin of the drinking milk collected

## EU Regulations 852/2004, 853/2004, 854/2004:

- Supersede EU 92/46
- No demands to freezing point of milk

# Analytical methodology (1)

- Thermistor cryoscopy (since 1956!)





- Supercooling (-3 °C)
- Inducement of crystallization
- Attaining equilibrium

Calibration with salt solutions

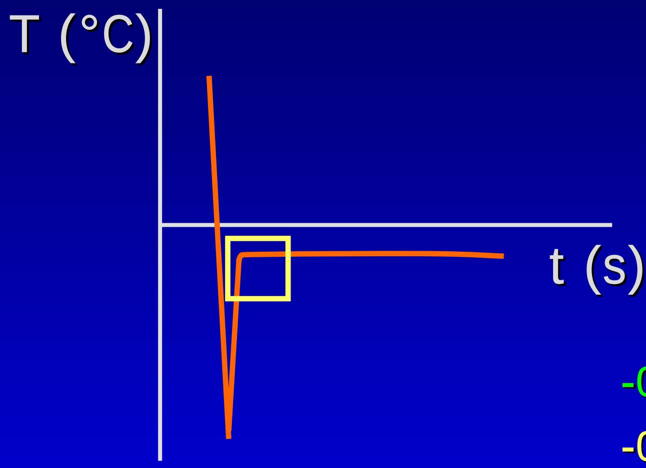
# Analytical methodology (2)
# Revision of ISO 5764|IDF 108

Period: 1995-2002

Main shortcomings:

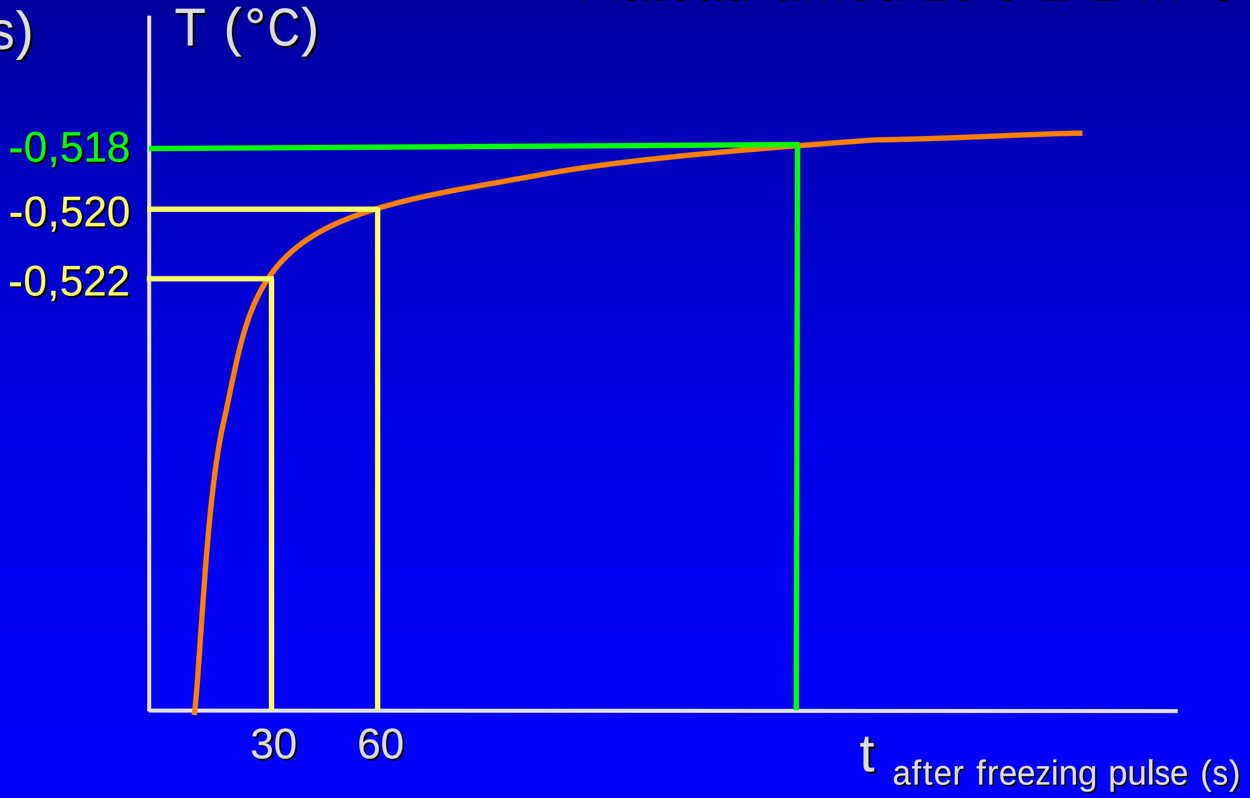
- Insufficient instrument specification
  - apparent from comparison of complete freezing curves with different instruments
- `Cut-off` point not strictly enough defined

# Analytical methodology (3)
# Revision of ISO 5764|IDF 108




Fixed-time, 30/60 s

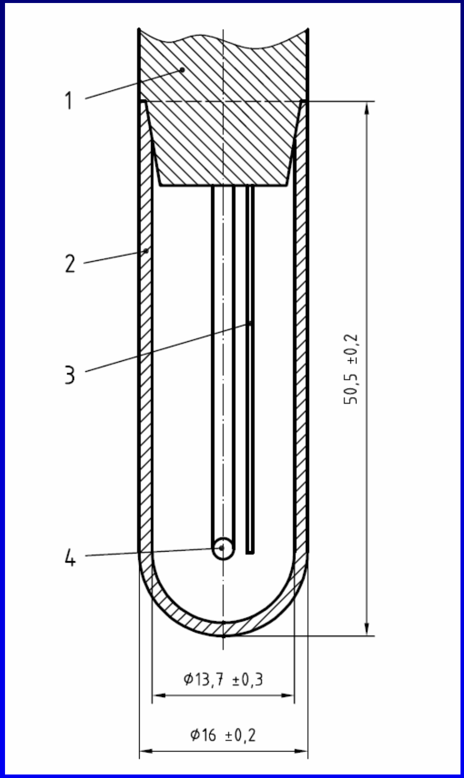
Plateau-timed 20 s ± 1 m°C



# Analytical methodology (4)
# Revision of ISO 5764|IDF 108

Main adaptations:

- Test tubes specified in more detail
- Test sample volume: 2,5 ml
- Temperature control cooling medium
- Standardization of thermistor probe:
  - position (centred)
  - electrical resistance
  - heat conductance of shank
- \`Cut-off\` point reached when rise in temperature during last 20 s $\leq$0,5 m°C




1 = mandrel
2 = sample tube
3 = stirring wire
4 = thermistor bead

# Analytical methodology (5)
# Revision of ISO 5764|IDF 108

## Precision characteristics from collaborative study:

| 18 labs | r (m°C) | R (m°C) |
|---|---|---|
| Raw milk (n=6) | 3,6 | 6,5 |
| UHT whole milk (n=6) | 4,1 | 6,1 |
| UHT skimmilk (n=6) | 3,1 | 4,2 |


# Analytical methodology (6)
# Revision of ISO 5764|IDF 108

Coming from:

- Different instrument specifications
- Operating with different 'cut-off' points
- Different temperature scales (°C, °H)

Annexes with guidance on:

- Keeping linkage between revised reference method and in-house applied methodology, i.e. establishing correction factors for equipment/method/product combinations (with demands to n and max $s_{diff}$)
- Adjusting earlier established values for genuine milk

# Analytical methodology (7)
# Revision of ISO 5764|IDF 108

INTERNATIONAL STANDARD

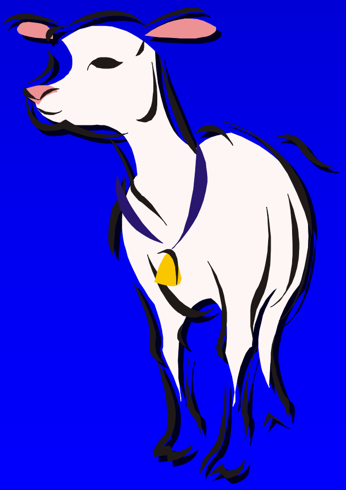
**ISO 5764**

**IDF 108**

**Milk — Determination of freezing point — Thermistor cryoscope method (Reference method)**

*Lait — Détermination du point de congélation — Méthode au cryoscope à thermistance (Méthode de référence)*

- Published in 2002
- Next revision underway: addition of precision characteristics for goat and sheep milk (ISO/DIS stage)



# Milk-based reference materials (1)

Calibration with salt solutions:

- Simple
- Easy to standardize
- Functions well in practice
- ‘Shorter’ freezing curves

# Milk-based reference materials (2)

Use of milk-based reference materials:

- Potential strengths
  - supporting harmonized measurement levels
  - cryoscopic behaviour more similar to test samples
- Potential weaknesses
  - stability (detoriation, salt equilibriums, gas)
  - variation due to shipment/storage conditions
  - possible influence of water quality with reconstitution
- Preferably also applicable with alternative methods

# Application of IR spectrometry (1)

- Principle first described by:

  Koops, J. Kerkhof Mogot, M.H. & van Hemert, H. 1989. Neth. Milk Dairy J. 43:3-16

- Using mid IR-signal (lactose!) in combination with measurement of conductivity (salts!),

  producing “freezing point equivalents”

- In practice combined with high-capacity compositional analysis

# Application of IR spectrometry (2)

Performance characteristics:

- Repeatability r: 2-3 m°C (r$_{cryosopy}$: 4 m°C)
- In case of a parallel measurement with the reference method in singular, the difference will in 95% of the cases be smaller than 5-6 m°C

(R$_{cryoscopy}$: 6 m°C)

(van Crombrugge, J. 2003. IDF Bull. 383:16-22)

# Application of IR spectrometry (3)

Strong points in application with raw milk:

- Attractive performance characteristics
- Cheap and easy in routine testing
- Allows continuous monitoring + trend analysis-> signalling irregularities!
- Fits perfectly in integrated chain quality control concepts!

Microsoft Office Excel-werkblad

# Application of IR spectrometry (4)

Considerations with application for checking compliance with official limits:

- Attractive performance characteristics
- Eventual selective confirmation with reference method
- Exceptional differences:
  - unlikely at the (herd) bulk milk level
  - likely related to other compositional abnormalities......

# Conclusions

- There is sound based and up to date analytical methodology available for the detection of extraneous water in liquid milk
- For the checks on the different control points in the production chain, choices from the analytical toolbox are to be based on:
  - performance characteristics
  - (legislative) demands
  - capacity, convenience, cost
  - potential to provide additional information for quality management purposes

# Thanks for your attention!