Recent advances in the infrared analysis of milk

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Confidential to Fonterra Co-operative Group
Overview

• Infrared analysis of milk

• Mid infrared spectroscopy
  – Measurement of minor components
  – Targeted and non-targeted analyses
  – Instrument developments

• Near infrared - current applications

• A vision of future applications
Principle of IR-Spectroscopy

Transmission \( T = \frac{I}{I_0} \)

Absorption \( A = \log \frac{1}{T} = \varepsilon \cdot c \cdot d \)

\( I_0 = \) intensity of reference beam
\( I = \) intensity of sample beam
\( d = \) sample thickness
\( c = \) concentration
\( \varepsilon = \) molar absorption coefficient
What’s in liquid milk?

• Evolved as a complete food

• Complex mixture of fat, protein and carbohydrates

• Extensive microstructure 1-100µm

• Fat globules and casein micelles
Milkfat globules – scatter light

Typical Bovine milkfat size distribution
MIR and NIR

• Mid IR
  - Transmission through thin sample
  - Discrete peaks
  - More sensitive

• Near IR
  - Good for reflectance
  - Broad overlapping peaks
  - More potential light scattering
Near vs. mid infrared for milk

• **Mid IR**
  – Transmission through 37-50um cells using Fourier transform infrared (FTIR) wavelength range 1000-4000cm\(^{-1}\)
  – Widely used for liquid dairy products
  – Both in- and at-line
  – Traditionally measures fat, protein and lactose

• **NIR**
  – FTNIR, diode array and dispersive systems, wavelength range 700-2500nm
  – Reflectance or transmission at- or in-line
  – Widely used for solid and semi-solid products, also for liquids
  – Traditionally measures moisture, fat and protein
Where infrared spectroscopy fits in....
Mid IR spectroscopy

1. Measurement of “minor components” in milk

2. The use of targeted and untargeted calibration models to assess milk quality

3. The development of lower cost instrument platforms
Mid IR spectra of liquid milk
1. Measurement of “minor components” in milk

- 1980-90s: Traditional quantitative calibration are for gross composition
  - Fat, protein, lactose, total solids, solids not fat
- 2000: Major fractions of fat and protein
  - Casein, saturated and unsaturated fatty acids
- 2010: Individual fatty acids and proteins
- Adulterants at concentrations below 1000ppm
  - What is the correlation model (calibration) based on
  - Beware of covariance!
MIR new applications 2014-5 published


• Detection of whey in milk/whey quality (Food chemistry, 174/176, de Carvalho et al and Kucheryavkiy et al 2014)

• Within milking variation of milk composition and fatty acid profile (Journal of Dairy Science, 97/7, Rico et al 2014)

• Estimation of genetic and cross breeding parameters of fatty acid concentrations in milk fat (Journal of Dairy Science, 81/3, Holroyd et al, 2014)

• Screening methods for detection of five adulterants by FTIR (Food chemistry, 181, 31, Botelho et al 2015)
2. The use of targeted and untargeted calibration models

- Melamine crisis (2008) with contaminated milk powder
- Liquid milk deliberately adulterated for economic gain
- Collaborative project between Fonterra, Arla and Foss
- Resulted in development of targeted and untargeted models for detecting milk adulteration at economic levels
- In 2014 Foss has commercial release of FTIR models using abnormal spectrum module (ASM) as well as targeted models for specific adulterants
1. Quantitative (targeted analysis)

Reference test melamine (ppm)

FTIR predicted melamine (ppm)
Qualification (untargeted analysis)

- Defines a single “good” group
- Anything outside is by definition “abnormal”
- Advantage – you can find what you are not looking for
Untargeted evaluation of spectra

New sample
Abnormal
Long distance

New sample
Normal
Short distance
Results – untargeted analysis of liquid milk by FTIR
Fingerprint FTIR analysis of NZ milk

FT2 - ASM Score 07.01.13
Challenge with untargeted analyses

Limit of Detection (ppm) vs. % Acceptable false positives

- Melamine
- Ammonium sulphate
- Urea
Combining Untargeted and Targeted models

Does the untargeted (FTIR) model indicate a deviating sample?

Yes

Is there a targeted (FTIR) model indicating the nature of the deviation?

Yes

The sample is most likely adulterated

Confirmatory chemistry

No

The deviating sample must be investigated further with confirmatory chemistry

No

Is there a targeted (FTIR) model indicating adulteration with a specific adulterant?

Yes

The sample is most likely adulterated

Confirmatory chemistry

No

The sample is normal
3. FTIR instrument platforms

- Traditional FTIR based instruments
  - Foss FT1, FT2, FT+
  - Bentley DairySpec
  - Delta Lactoscope
- Highly accurate (0.02% for fat and protein)
- Automated flow/cleaning system with temperature control and precise homogenisation for consistent sample presentation
- In widespread use
Lower cost mid IR/FTIR

- Smaller, less automated = substantially cheaper

- Measure gross composition, but less accurate

- Use proprietary technology to reduce interference from lack of homogenisation

- IndiFoss MilkoScreen

- MIRIS - The Dairy Milk Analyser (filter instrument)

- Foss MilkoScan Mars

Images from Foss and MIRIS
Milkoscreen in use at Fonterra Sri Lanka
Prevention of economically motivated adulteration

- Use FTIR to manage risks associated with accessing larger part of global milk pool
- Business support systems for effective decision making
NIR for liquid milks

- More commonly used for solids and semi-solids
- Liquid milk applications can be challenging
- NIR used a number of applications
  - On farm analysis of composition
  - Differentiation of milk from cows with different diets
  - Organic/non-organic milk
  - Different calibration protocols for dealing with light scattering effects due to fat globule size
  - Scattering shown to contribute to 50% total absorbance in a liquid milk sample
  - Milk coagulation
  - Somatic cell detection

Source - The use of NIR on milk and milk products (Holroyd, Journal of NIR, 21/5 2013)
Liquid Sampling Module (LSM)

Attachment to existing NIR system

LSM features

- Homogenizer for raw milk
- Peristaltic pump for high viscousity dairy products, e.g. concentrates and premixes
- Flow cell with 1mm (1000\(\mu\)m) pathlength
- Automated sampling and repeated measurements
- Basic and advanced cleaning (0.5 and 2% detergent)
- Similar accuracy to FTIR systems

Info courtesy of Bruker Optics
Vision of the future

• Mid IR - wide range of FTIR systems with accuracy dependent upon value chain in specific location
  – Cost vs accuracy
  – Calibration models used for range of quality parameters
  – Targeted and non targeted models common

• Near IR systems fill niche roles
  – Single instrument for multiple uses, liquids and solids
  – On farm applications

• Used with guidance from international standard setting groups