NEW SENSORS FOR FOOD INDUSTRY

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Outline

• Extending sensing capabilities in CAFÉ project
• Approach to new sensors
  • Ultrasounds
  • Electric impedance
  • Gas sensors
    • Electronic nose
• Applications to case studies
• Conclusions
## Sensors available in case study plants

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<th>Temperature sensors, flowmeter for injected O\textsubscript{2}, flowmeter for produced CO\textsubscript{2}, on-line GC</th>
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CAFÉ approach to extend sensing capabilities

• During the processes a number of physical and chemical properties are altered.
• Considering the complexity of food composition and the changes occurring during the process the use of non-specific broadly selective sensors was considered
  • Physical properties
    • Ultrasound probes
    • Electric impedance
  • Chemical properties
    • Gas sensor arrays
Ultrasonic probes

- Ultrasonic sensors investigate the propagation of acoustic waves in a media.
- Waves are reflected, transmitted and absorbed.
- The acoustic properties of materials depend generally on the density (amount of material moved by the wave) and the mechanical resistances (resistance to movement).
- There are several examples of applications of ultrasounds to the characterization of foodstuff.

Sound velocity vs. concentrations of simple and complex food ingredients
Data from Saggin and Coupland, J. Food Sci. 2001
Emission-receiver and electronic unit

Piezocomposite transducer

Emission – reception – treatment unit

Measurement modes:
- transmission
- pulse/echo

Measurement features:
- delay time
- level

Delay: sound velocity
Attenuation: impedance loss
Freeze-drying process

Ultrasonic unit A in emission/reception mode.

Ultrasonic unit B in echoes mode.

Ultrasound frequency 1.25 MHz
Ultrasonic monitoring of Freeze-drying

Temperature (°C)

Propagation time (µs)

Mode E/R mode echo

Temperature

Transition zone at $T=-10.6°C$

Abrupt change in E/R mode.

Slow transition of echo mode signal due a progressive stratification down to $T=-14.8°C$. 
Electric impedance

- The dielectric properties of foods are studied because of their implications with microwave cooking and processing.
- However, the impedance even at lower frequency can provide interesting information about the content and the structure of the food.
- Dielectric properties depend on a wide range of physical and chemical properties of the material, including:
  - conductivity
  - viscosity
  - density
  - composition
  - temperature …
Impedance probe

- Simple probe design to allow impedance measurements in the presence of dielectrics under test
- Impedance measurements can be calibrated to give real and complex permittivities: $\varepsilon_r(f)$ and $\varepsilon''_r(f)$.
- Two dielectric standards are required for calibration (usually air and water)
- For CAFÉ monitoring actual dielectric values not required, just signals that change with target processing properties
Fingerprint method with the reflection coefficient

1) The frequency dependence of the reflection coefficient of the initial states is measured
   - The reflection coefficient is related to the change of dielectric constant with respect to the external medium.

2) The frequency dependence of the reflection coefficient of the ongoing state is measured

3) The frequency dependence of the difference between the two reflection coefficients is produced
Beers mixtures

Flat Hoegarden beer added to flat Leffe beer

Flat Hoegarden added to fizzy Leffe

Bubbly Hoegarden added to bubbly Leffe

Fizzy Hoegarden added to fizzy Leffe
Physical and chemical changes

- Heating
- Stirring
- Ethanol addition
- Water addition

Graphs showing changes in magnitude of reflection coefficient with frequency (Hz).
Test in real conditions
Pilot plant in Wageningen

Real permittivity at 100 MHz

Filtered and Unfiltered Beer: 100MHz

- A difference between filtered and unfiltered sample is observed
- Sensitivity to temperature disturbance
- Necessity of a better screening from environmental noise.
Headspace composition

- In principle gas sensors can be used to monitor the evolution of headspace during the processing of foods.
- But:
  - Headspace build-up may require a large time with respect to the typical time scale of the process.
  - Physical conditions of food during the process (e.g. temperature and pressure) do not allow for the formation of a readable headspace.
- Nonetheless, gas sensors can be used in selected processes and they are valuable to determine the quality of the final product.
- In CAFÉ the properties of sensors based on metalloporphyrins were considered.
Richness and versatility of porphyrins chemistry

Porphyrsins building blocks

Hydrogen Bond Acceptor
Hydrogen bond acceptor
Hydrogen bond donor
Hydrophobe
Aromatic
Hydrophobe
Coordination
Porphyrrins coated Quartz microbalances

- Mass to electric frequency converters
  \[ \Delta f \propto \Delta m_{abs} \propto \Delta n_{abs} \]
- TSMR sensors are simple to be prepared and the signal read-out can be done with great accuracy.
- Since any interaction results in a variation of the mass, the mass transducer is in principle non-specific.
- The resolution is of the order of 1 ng
- About $10^{12}$ - $10^{14}$ molecules have to be absorbed to have 1 Hz of frequency shift.

Brunink et al. Analytica Chimica Acta 1996
Porphydrins coated QMB based Electronic Nose
Some applications

**Food Quality and Control**
- Olafsdottir et al. Trends Food Sci Tech. 2004

**Medical Diagnosis**
- Santonico et al. Lung cancer, 2012
- Montuschi et al. Chest, 2010
- D’Amico et al. Skin Res. Techn. 2007

**Spacecraft air quality control**
Application to ice-cream volatile compounds vs. temperature

![SPME device](image)

![Graph showing abundance vs. temperature](image)

- Heneicosane, 3-methyl-
- 1,3,8-p-Menthatriene
- D-Limonene
- Crithmene
- Nerol acetate

Temperature [°C]

Abundance [a.u.]
Monitoring of ice-cream making

- Lemon sorbet
- 5 experimental conditions changing process parameters:
  - Flow ice-cream machine (35 Kg/h)
  - $T_{\text{evap}}$ refrigerant liquid (from -9°C to -16°C)
- aim: to predict from gas sensors signals the ice crystals size and the apparent viscosity
  - ice crystals size measured with Focused Beam Reflection
  - viscosity was model estimated
  - Ice fraction

Crystal size 6.53 μm

Crystal size 6.63 μm
Gas sensors measurements

- A measurement chamber is fixed at the output of the ice-cream machine.
- The chamber holds a fixed amount of ice-cream into a closed volume whose headspace is delivered into the sensors cell.
Crystal Size Prediction

- Feed Forward Neural Network.
  - Single hidden layer (with 3 neurons)
  - 2/3 of the dataset been used for training and 1/3 for test.

$\text{RMSE}_{\text{Train}} : 0.1133 \ \mu m$

$\text{RMSE}_{\text{TEST}} : 0.1980 \ \mu m$

about 8% of the range of variability of crystals size.
Estimation of viscosity and Ice fraction

**Apparent Viscosity**

- RMSE\text{Train} : 0.3920
- RMSE\text{TEST} : 0.9926

**Ice Fraction**

- RMSE\text{Train} : 0.0211
- RMSE\text{TEST} : 0.0326
Application to freeze-dried bacteria quality

- Concentrates of lactic acid bacteria are used as starters of fermentation processes for the production of cheeses, yogurts, …
- Freeze-drying is the method of choice to improve the shelf-life of concentrates.

Quality criteria
- water content (<3%)
- activity
- cells viability
Experimental

- six batches of *lactobacillus delbrueckii sbsp. bulgaricus*
  - samples were prepared with different salts to favour the drying
  - different freeze-drying conditions were applied to change the quality of the products.
    - Nucleation LyoGamma Telstar
- half of each batch was used to measure water activity, acidification activity, and cells viability
- half for headspace analysis: electronic nose and GC/MS
Measurement setup

- Tor Vergata Electronic nose equipped with eight porphyrins coated quartz microbalances
- room temperature measurements
Measured quality parameters

- PCA of parameters indicates two groups of samples separated by the acidification activity.
- As expected, acidification activity is anticorrelated to the cells viability.
Electronic nose data

- The PCA of electronic nose data is largely distorted with respect to the quality parameters.
- Nonetheless, the two groups of samples found in the PCA of quality parameters and GC abundances are visible also in electronic nose data.
PLS prediction of quality parameters

- PLS was used to estimate the three quality parameters
- leave-one-out cross-validation was used for latent variables choice
- 4 latent variables minimize the RMSECV
GC PCA

The diagram shows a principal component analysis (PCA) plot with two ellipses representing high and low Tmax. The data points are distributed across the plot, indicating the variation in Tmax among different samples or conditions.
compounds identification

- The chemical functional descriptors of VOCs more correlated with the acidification activity suggest a good detectability with porphyrins coated QMB.
Detection of filtration stages in beer production

• three formulations from a local brewery
  • Rajah: indian pale ale with large hop content
  • Kerala: indian pale ale spiced and flavored with orange, apple and cinnamon
  • Spiga: weiss beer (31% filtered in the final product)

• three samples for each formulation
  • unfiltered (as is from brewery)
  • paper filtered
  • siringe filtered

sample of unfiltered
Principal component analysis of ENose data

- Filtration affects the ENose signal
- The removal of particulate increases the differences between samples
- The discrimination among beers largely increases after filtration.
- Results show that the QMB electronic nose is sensitive to filtration
- On line application in filtration unit is hindered by low-temperatures and high pressure.
Conclusions

• Broadly-selective sensors for physical and chemical quantities can provide useful information to monitor the evolution of processes in food industry.

• Electric and acoustic impedance can be used to estimate composition, density and texture properties.

• The headspace composition can reveal changes in activity in the liquid material (e.g. due to crystalization) and to signal the presence of compounds affecting the quality.

• Eventually, these sensors can complement the sensors aimed at controlling the process parameters with feedback information about the quality of the processed product.