Learning from other industries – Insights from coffee on advanced sensory-analytical correlations

Imre Blank et al.

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Sydney, July 16, 2013
Why to learn from coffee research?
There are so many differences ...

Raw materials:
Beans vs grapes

Technology:
Roasting vs fermentation

Consumption:
Hot vs cold/ambient
Why to learn from coffee research? There are quite a few similarities as well ...

Quality aspects

*Freshness, off-flavours*

Composition:

*Aroma, different structures*

*Taste, polyphenols*
Wine Flavour
Ageing aromas

Sotolon
Perception threshold: 2 µg/L:

2,4,6-Trichloroanisole
Cork taint
(Silva Ferreira 2003; Pons et al 2008; Tanner et al. 1981)

2-Furanmethanethiol
Perception threshold: 0.4 ng/L

Development of 2FM content during bottle aging in champagne wines
(Tominaga, 2003)
Wine Flavour – Sulphur compounds

- Ethyl-2-sulfanylpropionate
- 2-Methyl-3-furanthiol
- 2-Sulfanylethyl acetate
- Ethyl-3-sulfanyl propionate
- 2-Methyl-3-sulfanylpropan-1-ol
- Sulfanylpropyl acetate
- Benzenemethanethiol
- 2-Methyl-3-sulfanylpentan-1-ol
- 2-Methyl-3-sulfanylbutan-1-ol

(Dubourdieu & Tominaga, 2009)
Why to learn from coffee research? There are similar challenges

1. Analysis of trace compounds
   
   Chemical structure

   Low thresholds

   Formation of key flavour compounds

2. Sensory / analytical correlation
   
   Predictive model

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Detection threshold: 0.8 ng/L
Analytical challenge: Flavour formation upon coffee roasting

Coffee Flavour Precursors

- **SUGARS**: Sucrose, glucose, fructose (arabinogalactans)
- **AMINO ACIDS** (Strecker-active AA)
- **TRIGONELLINE**
- **CHLOROGENIC ACIDS**
- **ORGANIC ACIDS**
- **LIPIDS**
- **CAROTENOIDS**

**Pyrolysis**
- Nicotinic acid
- Pyridine and derivatives

**Caramelization**
- Furaneol

**Fragmentation**
- Maillard, Strecker
- CO₂
- HCO₂H
- CH₃CO₂H
- HO⁻CO₂H
- CH₃

**Hydrolysis**
- Quinic acid lactone

**Cyclisation**
- Chlorogenic acid lactones

**Oxidation**
- Carbonyls

**Oxidative cleavage**
- E-β-Damascenone

**Formation**
- Formic acid
- Acetic acid
- Glycolic acid
- Lactic acid

**2-Furfurylthiol**

**3-Mercapto-3-methylbutyl-formate**

**Caffeic + Ferulic acids**

**Vanillin**

**Guaiacols**
The Approach: New experimental set-up

Biomimetic in-bean study


- Green coffee beans (GC)
- Spiking with precursors
- Water extraction at 95°C for 2 h
- Exhausted beans (EB)
- Spiked green beans
- Roasting
- Biomimetic recombinant (BR)
- Spiking with precursors
- Roasted beans spiked with precursors
- Omission
  - EB + BR
  - EB + BR omitted in sugars/AA
  - EB + BR + labeled precursors
  - Labelling
# Composition of the biomimetic recombinant (BR)

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<th>Components</th>
<th>Amount (g)</th>
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<th>Amount (g)</th>
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<td>Copper(II) sulfate</td>
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<td>L-Arginine</td>
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<td>Zinc(II) sulfate, heptahydrate</td>
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</table>
Formation of 2-furfurylthiol (FFT): Model studies

**Model System**

- **Tressl et al. (1993):** FFT is formed from arabinose/cysteine *via* 3-deoxypentosone (3-DP) and furfural while maintaining the intact carbon chain

**Figure:** Hypothetical formation of FFT in coffee from arabinogalactans or arabinose (R=H) and cysteine (protein-bound)

- **Grosch (1999):** Arabinogalactans suggested as precursor of FFT by isolating the polysaccharide from green coffee and roasting it in the presence of cysteine
Formation of 2-Furfurylthiol (FFT): Omission and spiking experiments

**In-bean experiment**

- Omission of sugars favored the generation of FFT, whereas furfural content was highly suppressed

- Spiking with sucrose increased furfural amounts but considerably decreased concentrations of FFT
- Spiking experiment with cysteine resulted in enhanced FFT amounts, thus indicating cysteine as a suitable sulphur source

Formation of 2-furfurylthiol (FFT): Labelling experiments

**In-bean experiment**


**2-furfurylthiol (FFT) is most likely not generated via the furfural pathway**
Analytical challenge: Formation of wine favour

**Grape compound**
- Nutrients
- Flavour precursors
- Non-precursor flavour-active compounds

**Metabolism**
- Catabolic/anabolic pathways
- Biotransformation
- Metabolism

**Metabolites**
- Fermentation bouquet
- Varietal compounds
- Phenolic adducts and polymers

Esters, higher alcohols, acids, carbonyls, polysaccharides, volatile sulphur compounds

**Aging**
- Oxygen / T effect
- Chemical reactions
- Controlled conditions
- Final wine flavour

**Product storage**
- Temperature effect
- Uncontrolled conditions
- Modif. composition
- Off-flavour

→ Advanced analytics
→ Molecular understanding
→ Labelling experiments
→ Sensory dimension
→ Targeted vs. holistic
Sensory/Analytical challenge: Correlation & Predictive model

Can we predict sensory profiles by analytical data?

THE CHALLENGE
- SENSORY – ANALYTICAL CORRELATION
- DIFFERENT NATURE OF DATA

THE APPROACH
- ADVANCED ANALYTICS
- MONADIC SENSORY PROFILING
- ADVANCED STATISTICS

THE SOLUTION
- RELIABLE PREDICTIVE TOOL
The challenge: Understanding the coffee ‘melodie’

The flavour of coffee can be compared to a symphony played by an orchestra Fundamentally different nature of sensory & analytical data

SENSORY PROFILING

- Listen to the orchestra
- Describe specific instruments/tonalities
- Evaluate their intensities

AROMA ANALYTICS (targeted)

- Identification of the key players/instruments
- Evaluation of their concentrations & impact
- Reconstitute melodie
Relationship between “signal” intensity and aroma concentration

Major problem to overcome: The fundamentally different nature of analytical and sensory data

**Linear** relationship between peak intensity and aroma concentration

**Sigmoid** relationship between perceived aroma intensity and aroma concentration (Fechner, 1877)

Perception ~ \( k \log(\text{conc.}) \)
The Approach: Systematic study

- Develop a mathematical model based on quantitative analysis of flavour compounds to predict coffee sensory profiles
- Identify well correlated marker compounds for sensory descriptors

12 coffee blends (25 mL, 40 mL, 110 mL)

Quantitative analysis (42 odorants, 12 taste compounds)  
**Targeted approach**

Predictive analytical-sensory correlation model

Sensory analysis (12 panelists, 9 sensory descriptors)  
**Profiling**
Monadic sensory profiling with an expert panel (n=12)

THE BASIC ATTRIBUTES...
- roasty
- bitter
- acid

...describe the basic properties of an Espresso coffee

The 'subtle' aroma descriptors...
- fruity-floral
  red fruits, lemon, jasmine
- green-vegetal
  herbs, fresh vegetables
- dry-vegetal
  wood, malt, cereal
- vegetal-humus
  earthy, mushroom
- cocoa
  roasted, cacao, dark chocolate
- sweet
  vanilla, caramel, honey

...describe the signature aroma of an Espresso coffee
...are grouped based on olfactory similarity
Concentrations of 54 aroma and taste compounds were determined

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<th>substance</th>
<th>flavor quality</th>
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<th>flavor quality</th>
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<td>methanethiol</td>
<td>sulfur, garlic</td>
<td>2-acetylthiazole</td>
<td>roasty, popcorn</td>
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<td>dimethyl sulfide</td>
<td>cabbage, sulfur</td>
<td>furfural</td>
<td>grass, almond</td>
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<tr>
<td>dimethyl trisulfide</td>
<td>sulfur, cabbage</td>
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<td>2,3,5-trimethylpyrazine</td>
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<td>3-mercapto-3-methylbutylformate</td>
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<td>pyridine</td>
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<tr>
<td>2-acetylpyridine</td>
<td>popcorn</td>
<td>caffeine</td>
<td>bitter</td>
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</table>
Absolute quantification was carried out with different state-of-the-art methods

**Quantitative analysis of**

- 42 aroma compounds (quantification with isotope dilution assay)
  - a. SPME-GC-MS
  - b. SPME-GCxGC-TOF MS
  - c. SPE-GC-MS

- 12 taste compounds (external quantification)
  - a. HPLC-DAD
  - b. LC-MS/MS
Comprehensive GCxGC-TOF/MS for quantification of high impact trace coffee components

Analysis of methional

Methional peak hidden behind other peaks

Resolved by deconvolution and 2-dimensional techniques

RT: 1.35
AA: 10422

RT: 11.44
AA: 40188

RT: 13.08
AA: 41504

RT: 5.60
AA: 20990

RT: 1.35
AA: 10422

RT: 5.67
AA: 4261

RT: 8.61
AA: 4626

NL: 2.32E4
FID Analog ICIS 42GC6-
Pre-processing of analytical & sensory data is key to perform multivariate statistics

Fechner’s law:
perception ~ $k \log(\text{concentration})$

Sensory data

Normalize

Subtract (instrumental) intensity

Correlation of the two datasets
$X'' = Y'' + P$

Subtract intensity

Normalize

Take logarithm

Instrumental Data

Perceived aroma intensity vs. Aroma concentration

threshold
saturation

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Normalisation & transformation of analytical data

### Log 10 (conc.)

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<th>Value 2</th>
<th>Value 3</th>
<th>Value 4</th>
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### Pseudo-concentration

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### Pseudo-composition

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<td>Compound 3</td>
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</table>

**Standardize 'weight' of each compound across coffees**

Y1 = (X1 – mean) / SD

**Subtract pseudo-concentration as per coffee**

Y2 = Y1 – mean conc.
The solution: Predictive model

Coffees are widely distributed over sensory space

PCA from Sensory data
(subtracted 'intensity effect')
Combination of sensory & analytical spaces using PCA

- Correlated arrows are close to each other
- The longer an arrow, the better its representation in sensory space
Quality markers – 30 compounds exhibit strong correlation to the sensory descriptors

- 2,3,5-trimethylpyrazine
- 2-furfurylthiol
- sweet
- furfuryl acetate
- phenylacetaldehyde
- 2-acetylpyridine
- pyridine
- fruity-flowery
- acetaldehyde
- methanethiol
- 2,3-butanedione
- 2,3-pentanedione
- dimethyl sulfide
- methional furfural
- fruity-flowery
- sotolon furaneol
- acid
- 2-methylbutanal
- green-vegetal
- vanilline
- 2-acetylthiazole
- hexanal
- vegetal-humus
- 2-isobutyl-3-methoxypyrazine
- 2-methylpropanal
- p-cresol
- vegetal-humus
- 2-methyl-3-furanthiol
- 3-methyl-2-butene-thiol
- N-methylpyrrole
- bitter
- 2-isopropyl-3-methoxy-pyrazine
- 4-ethylguaiacol
- guaiacol
- 4-vinylguaiacol
- dimethyl trisulfide
- 2,3-diethyl-5-methylpyrazine
- cocoa
- dry vegetal
The robust statistical model allows a reliable prediction of the sensory profile.

Principle components regression: 101 out of 106 data are below LSD.
Holistic analytical approach – Also suitable to build predictive sensory models from head-space data

Lindinger et al. (2008)

Analytical data

Sensory profile: by expert

Predicted sensory profile
Major source of data: Key literature

**When Machine Tastes Coffee: Instrumental Approach To Predict the Sensory Profile of Espresso Coffee**

Christian Lindinger,*,† David Labbe,† Philippe Pollien,† Andreas Rytz,† Marcel A. Juillerat,† Chahan Yeretzian,†‡ and Imre Blank†,§

Nestlé Research Center, Vers-Chez-les-Blanc, 1000 Lausanne 26, Switzerland

**Advanced analytical-sensory correlation – Towards a better understanding of coffee flavor perception**

(Proceedings of the ASIC Symposium, 2010)

BAGGENSTOSS, Juerg†; POISSON, Luigi†; GLABASNIA, Arne†; MOSER, Mireille†, RYTZ, Andreas†, THOMAS, Edouard*, BLANK, Imre†, KERLER, Josef†

† Nestlé PTC Orbe, Switzerland, ‡ Nestlé Research Center, Vers-chez-les-Blanc, Switzerland, * Nestlé Nespresso S.A., Lausanne, Switzerland
Conclusions & Enjoy your coffee!

A mathematical model has been developed which allows predicting the sensory profiles of coffee.

Deeper understanding of link between sensory descriptors and aroma markers.

Useful tool to support product development of coffee blends with new taste experiences.

My thanks go to ... ... and to you for your attention!

J. Baggenstoss, T. Davidek, A. Glabasnia, J. Kerler, Ch. Lindinger, F. Mestdagh, L. Poisson, Ph. Pollien, A. Rytz, E. Thomas, Ch. Yeretzian

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