NOVEL NMR-TECHNOLOGY TO ASSESS FOOD QUALITY AND SAFETY

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Overview

• What can Nuclear Magnetic Resonance (NMR) accomplish in food analysis

• NMR-based screening features

• The JuiceScreener Concept as template
  • Targeted analysis (quantification)
  • Non-targeted analysis (statistics)

• The WineScreener solution

• NMR in analysis of other food (e.g. edible oil, honey, …)
What can NMR accomplish in Food Analysis?

Non-Targeted Screening / Targeted Screening in a single measurement

- Conventional food tests are Targeted!

- What is not tested for, will likely be over-looked!

The Non Targeted Screening (NTS) enables the discovery and analysis of unexpected and unknown (!!) parameters, which can not detected with conventional analytical methods!

Over and above that concentration differences of known substances could be detected.
NMR-based Screening Features

**Minimal sample preparation**
- 10% buffer addition
- Might need centrifugation

**Inherently quantitative linearity and huge dynamic range**
- Intact mixtures
- High throughput

**Highest Reproducibility and Transferability**
- Targeted analysis
  - Quantification of compounds
- Non-targeted /statistical analysis
  - Metabolic Fingerprinting (Classification/Verification)
Highest reproducibility / transferability

Full automated models need to be applicable to data generated:
- By someone else
- At an other spectrometer
- In another lab
- Anywhere in the world
- At any time

**Need of common standard and protocols** in order to secure models and their applicability

30 replicate samples prepared & measured **under full automation** at **3 400MHz spectrometers** by 6 different **operator**!!
Juice Quality Control by JuiceScreener / SGF-Profiling™

Fruit Juice Analysis

- **Full automated** push-button system
- Only one measurement (~ 15 minutes)
- Minimal sample preparation
- Targeted analysis
  - Quantification of more than 30 compounds
- Non-Targeted analysis (up to 10 results)
  - Authenticity
  - Frauds
  - Fruit content
  - Quality
- Database of more than 16,000 juice spectra
- PDF report of all results

German Industry Award 2008
Category: Automation

Greentech Asia Shanghai 2010: Award for most innovative Food Analysis System!
Conclusions made by Quantification

- **Sugar Profile** (Sucrose, Glucose, Fructose) => Addition of sugar
- **Acids Profile** => Addition of acid (e.g.: Citric acid in apple juice)
- **Ratio Malic Acid/Quinic Acid** => Ripeness of the apple
- **Ratio Citric acid/Iso-citric Acid in Lemon Juice** => Addition of citric acid
- **Concentration of Galacturonic Acid** => Enzymatic treatment in apple juice
- **Concentration of Phlorin in Citrus Fruit** => Usage of peels
- **Concentration of spoilage parameters** => Lactic Acid, Fumaric Acid, HMF, Formic Acid, Gluconic Acid
- **Detection of Other Fruits** => For example, pear in apple juice, citrus fruit in apple juice, grapefruit in orange juice
\(^1\)H-NMR Profile of Fruit Juices

Ausschnitt zeigt ca. 15% des NMR Profils

Probe passt nicht zum Modell
Example: Fruit content

**Fruit content of Red-Fruits Purees**

- **Red fruits**: High value products
  - High number of adulterated products (2008/2009)

- **Adulteration**: Dilution by *addition of sugar*
  - Compensation by: *Addition of minerals* and
    - of 1 or several *amino acids*
    - to *adjust* the *sugar/formol ratio*
Fruit Content of Red-Fruits Purees

NMR Results

The fruit content is lower in the tested sample
The results of the conventional analyses have estimated the fruit content of the sample as 'normal' but...
Fruit Content of Red-Fruits Purees

Results of Isotopical Analyses

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<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Status</th>
<th>Difference</th>
<th>Share of added sugar:</th>
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<td>Glucose/Fructose ratio</td>
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</table>

Fruit Content Estimation: 105 % ✓
Summary of all Results → PDF Report

Classification

Quantification

Verification

Fruit Content

Mixing Models

Bruker BioSpin

Bruker SFG Profiling

NMR Sample Profile

M-SD-OS-11096-22-10-2007

Sample provided by: unknown
Inspection/Lot Number: unknown
Inspection/Lot Date: unknown
SGF Order Number: unknown

Results Summary

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<thead>
<tr>
<th>Type of Analysis</th>
<th>Analysis ID</th>
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Display of additional value of NMR-quantification:

Automatic Report Fruit Juice Screener

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<th>Compound</th>
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<td>-</td>
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<tr>
<td>acetone</td>
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<td>mg/l</td>
<td>○</td>
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<td>-</td>
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<td>○</td>
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<td>mg/l</td>
<td>○</td>
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<td>●</td>
<td>5.0</td>
<td>30.0</td>
<td>6.5 39.6</td>
</tr>
</tbody>
</table>

Report of a non-conforming apple juice
• Automated generation of a PDF-document after the acquisition
• First Page: conclusions, details follow on other pages
The next step in NMR based Food Quality Control has arrived
From JuiceScreener to WineScreener

Analysis Report

Sample ID: Bruker_3Oberkircher_2011
Measuring Date: 20-Mar-2012 16:42:27
Reporting Date: 21-Mar-2012 09:32:04, Version: 1.0.0

Additional Information
Variety: Riesling

Results Summary

<table>
<thead>
<tr>
<th>Type of Analysis</th>
<th>Analysis ID</th>
<th>Result</th>
<th>Status</th>
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</thead>
<tbody>
<tr>
<td>Targeted Analysis</td>
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<tr>
<td>Quantification</td>
<td>Q</td>
<td>~</td>
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<td>Untargeted Verification Analysis</td>
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<tr>
<td>Multivariate Verification</td>
<td>1000/75</td>
<td>In-Model</td>
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</tbody>
</table>

Please note, that Wine-Profiling™ is a screening method with extensive inhouse validation, but it is not an method. Quantitation is regularly validated taking part in official ring tests.
Wine Analysis by WineScreener™

Wine by NMR:

- Determination of grape variety
- Geographical origin for selected countries/areas
- Company product profile / identity comparison
- Detection of irregularities of any kind
- Vinification / Aging
Very simple sample preparation - can be done manually or by robotic system

- pH controlled by automated pH titration system
Very simple sample preparation - can be done manually or by robotic system

- Addition of 10 % Buffer (KH$_2$PO$_4$, D$_2$O, NaN$_3$, TSP ((trimethyl-silyl)propionic acid))

Total sample volume typically 600 µl
$^1$H-NMR spectrum of wine (without suppression)

Quantification of ethanol directly from spectrum
experiment time < 1 min

H$_2$O + EtOH (-OH)

EtOH (CH$_3$)

EtOH (CH$_2$)
$^1$H-NMR spectrum of wine (with suppression)

- Malic acid
- Succinic acid
- Acetic acid
- Glucose
- Alanine
- Sorbic acid
- Lactic acid
- Glucose
- Tartaric acid
- Glycerol
- Methanol
- Acetoine
- 2,3-Butandiol
- 13C-satellites EtOH

Additional compounds: HMF, trigonelline, sucrose, fructose, citric acid, fumaric acid, proline, …
Targeted Analysis

In the following tables the results of the quantitative analysis are given. Parameters labelled with * are calculated parameters.

### Standard Parameters:

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<thead>
<tr>
<th>Compound</th>
<th>Degradation Path</th>
<th>Amino Acids:</th>
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<td>sucrose</td>
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<td>Cadaverine</td>
<td>proline</td>
<td>&lt;25 mg/L</td>
<td>222</td>
<td>○</td>
</tr>
<tr>
<td>Higher Alcohols</td>
<td></td>
<td>HMF</td>
<td>(Poly-)phenols:</td>
<td>20 mg/L</td>
<td>15</td>
<td>○</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Furfural</td>
<td>Caftaric acid</td>
<td>&lt;20 mg/L</td>
<td>20</td>
<td>○</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Epicatechin</td>
<td>&lt;5 mg/L</td>
<td>30</td>
<td>○</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gallic acid</td>
<td>&lt;25 mg/L</td>
<td>30</td>
<td>○</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Shikimic acid</td>
<td>&lt;25 mg/L</td>
<td>20</td>
<td>○</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Trigonolene</td>
<td>&lt;25 mg/L</td>
<td>13</td>
<td>○</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Benzoic acid</td>
<td>&lt;5 mg/L</td>
<td>10</td>
<td>●</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sorbic acid</td>
<td>&lt;5 mg/L</td>
<td>10</td>
<td>●</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Salicylic acid</td>
<td>&lt;5 mg/L</td>
<td>30</td>
<td>○</td>
</tr>
</tbody>
</table>

**Sources for Reference Values**

a) EU-Verordnung
b) Resolution CEN 19/2004
c) Weinverordnung (Germany, 21. April 2009)
Reproducibility

1 wine, 11 times prepared and measured
Statistical Modelling with authentic wine

- In cooperation with several wine laboratories about 6000 wine samples have been collected and measured at 400 MHz.
- NMR, once trained, can predict parameters, that are not related to a special molecule.
- NMR can deliver statistical results beyond quantification.

In statistical modelling, we have to deal with orthogonal parameters that influence the spectra considerably.
# Differentiation of grape varieties

## Classification & verification models

<table>
<thead>
<tr>
<th>Model</th>
<th>Group by</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>German/Austria white wine</td>
<td>Varieties</td>
<td>Riesling Weiss, Müller Thurgau, Pinot Blanc/Gris, Welschriesling, Grüner Silvaner, Sauvignon Blanc, Chardonnay Blanc, Grüner Veltliner</td>
</tr>
<tr>
<td>German/Austria red wine</td>
<td>Varieties</td>
<td>Dornfelder, Pinot Noir, Blauer Portugieser, Blaue Zweigeltrebe</td>
</tr>
</tbody>
</table>
Differences caused by grape variety

Riesling, Weißburgunder

Shikimic acid

In cooperation with CVUA Karlsruhe
Wine: Differentiation of grape varieties

Based on 100 Wines from Baden (Rhine Valley)

Problems Within the Group of 100

Cleaning Agent left

White wine Added to Red wine

R.Godelmann
CVUA Karlsruhe
**Differentiation of grape varieties**
**Classification & verification models**

<table>
<thead>
<tr>
<th>Model</th>
<th>Group by</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>World Wide Red Wine</td>
<td>Varieties</td>
<td>Cabernet Sauvignon, Merlot Noir, Syrah,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tempranillo</td>
</tr>
<tr>
<td>World Wide White Wine</td>
<td>Varieties</td>
<td>Chardonnay Blanc, Riesling Weiss,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sauvignon Blanc</td>
</tr>
</tbody>
</table>
Red wine world wide: Determination of Tempranillo Quantification and concentration profiles

Classification Analysis
Model: Red Wine Variety
Result: Most probable class is Tempranillo

Targeted Analysis
In the following tables the results of the quantitative analysis are given.
Parameters labelled with * are calculated parameters.

Standard Parameters:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Value</th>
<th>Unit</th>
<th>LOQ</th>
<th>Official Reference</th>
<th>NMR Reference Database</th>
</tr>
</thead>
<tbody>
<tr>
<td>total alcohol</td>
<td>116.5</td>
<td>g/L</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>total alcohol-v</td>
<td>14.8</td>
<td>%vol</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ethanol</td>
<td>116.1</td>
<td>g/L</td>
<td>5.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ethanol-v</td>
<td>14.7</td>
<td>%vol</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>glycerol</td>
<td>9.7</td>
<td>g/L</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>glucose</td>
<td>&lt;0.5</td>
<td>g/L</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>fructose</td>
<td>&lt;0.5</td>
<td>g/L</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>glucose/fructose*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>sucrose</td>
<td>&lt;0.2</td>
<td>g/L</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>arabinose</td>
<td>448</td>
<td>mg/L</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>total sugar (bef. inv.)</td>
<td>&lt;1.0</td>
<td>g/L</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>total fermentable sugar*</td>
<td>&lt;1.0</td>
<td>g/L</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>tartaric acid</td>
<td>2.1</td>
<td>g/L</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>malic acid</td>
<td>&lt;0.2</td>
<td>g/L</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>lactic acid</td>
<td>1.5</td>
<td>g/L</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>citric acid</td>
<td>&lt;200</td>
<td>mg/L</td>
<td>200</td>
<td>-</td>
<td>1000 *)</td>
</tr>
<tr>
<td>energy value*</td>
<td>3650</td>
<td>kJ/L</td>
<td>-</td>
<td>-</td>
<td>2070</td>
</tr>
<tr>
<td>bread units*</td>
<td>&lt;0.2</td>
<td>1/L</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>carbohydrate units*</td>
<td>&lt;0.2</td>
<td>1/L</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Differentiation of geographical origin
Classification & verification models

<table>
<thead>
<tr>
<th>Model</th>
<th>Group by</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>German/Austria Area for Riesling</td>
<td>Area</td>
<td>Germany, Austria</td>
</tr>
<tr>
<td>German Area for Riesling</td>
<td>Region</td>
<td>Rheinhessen, Württemberg, Pfalz, Mosel, Baden, Rheingau</td>
</tr>
</tbody>
</table>
## Differentiation of vintage
### Classification & verification models

<table>
<thead>
<tr>
<th>Model</th>
<th>Group by</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>German Riesling vintage</td>
<td>Year</td>
<td>2011, 2012</td>
</tr>
</tbody>
</table>
Wine by NMR:

- Determination of grape variety
- Mixture of grape varieties
- Geographical origin for selected countries/areas
- Company product profile / identity comparison
- Detection of irregularities of any kind
- Vinification / Aging
The $^1$H-NMR wine consortium strategy

All partners task is to **collect authentic wine materials to build our database for statistical analysis.** The statistical model will be generated by Bruker.

Typically we need about 50 samples per class, meaning e.g. per geographical origin or per wine variety. Goal will be to generate models regarding geographical origin, varieties, mixtures (blends), adulteration, ...... **Preferred solution is, the partners buy an instrument and run the measurement. They will be compensated later by license fees.** The share depends on their financial input. We try to establish a world wide coverage of important wine regions having different partners in the different regions.

Whenever in this consortium a wine from e.g. Argentina is measured, a license fee is asked for, that our Argentinean partners will benefit from. The Argentinean partners will not pay a license fee for Argentinean wines. However if the Argentinean partners are measuring a wine from outside Argentina, they can get the evaluation against a license fee.
The $^1$H-NMR wine consortium strategy

1) **Help in the validation of the NMR method for wine analysis**

2) **Help in establishing the NMR analysis method of wine as an official method**

3) **Help in the establishment of the country-specific wine database (Associate member status)**
   - Important remarks:
     Only possible if the partner can provide samples that Bruker can use for commercial purposes (Written declaration required)

4) **Consortium (Full member status)**
   - This is a long-term commitment (several years)
   - Once the method commercialized, Bruker and the consortium members perceive a license fee, each time that a wine sample of their country, is analyzed worldwide.
The $^1$H-NMR wine consortium strategy

Co-operation partners were defined in:
France  => Authentic sample measurements are still in progress
Germany => ~3000 authentic samples were still measured
Portugal => Authentic sample measurements are still in progress

Co-operation partners under discussion:
Austria
South Africa
Hungary
Australia

To find co-operation partners in:
Argentina
Chile
Uruguay
Brazil
China
Italy
Spain
USA
Proof-of-Principle

Same methodology for other areas of mixture analysis

- **Food**
  - Edible oil
  - Honey
  - Milk powder
  - Soft-Drinks and Energy-Drinks
  - Cheese
Edible Oil (Under development)

Olive / Palm / Rape seed / Soya bean / ...

- Preparation in CDCl$_3$
Food adulteration
Need for reliable analytics

All the worse - like in other crimes - adulterators always have some lead!

On the other hand, most analytical methods
• may be limited in range, sensitivity or reproducibility
• can be levered out by "elaborated" frauds
• are targeted
• are too expensive to be practiced on a grand scale

Thus, adulteration of foodstuff is going on and on ...

Food fraud hints can find expression in single compounds within the complex mixture, or can be entangled in subtle matrices effects.

(Cost-)Effective analytical methods have to deal with both tasks simultaneously, and NMR screening can do the job

W W Norton & Co (2011)
Olive Oil: Comparison in Aromatic and Olefinic Region

Non-suppressed against 10-fold suppression

Red = non suppressed
Blue = with 10-fold suppression

Fat dissolved in Chloroform
The NMR lipid profile of edible oils

$^1$H signal assignments

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\delta$ (ppm)</th>
<th>Proton</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.95</td>
<td>-CH=CH-CH$_2$CH$_3$</td>
<td>Linolenic acid</td>
</tr>
<tr>
<td>B</td>
<td>0.85</td>
<td>-CH$_2$-CH$_2$-CH$_2$-CH$_3$</td>
<td>All acyl chains, except for linolenic</td>
</tr>
<tr>
<td>C</td>
<td>1.2</td>
<td>-(CH$_2$)$_n^-$</td>
<td>All acyl chains</td>
</tr>
<tr>
<td>D</td>
<td>1.6</td>
<td>-CH$_2$-CH$_2$-COOH</td>
<td>All acyl chains</td>
</tr>
<tr>
<td>E</td>
<td>2.02</td>
<td>-CH$_2$=CH=CH-</td>
<td>Allylic protons (all unsaturated fatty acids)</td>
</tr>
<tr>
<td>F</td>
<td>2.2</td>
<td>-CH$_2$-COOH</td>
<td>All acyl chains</td>
</tr>
<tr>
<td>G</td>
<td>2.76</td>
<td>-CH=CH-CH$_2$-CH=CH-</td>
<td>$\beta$-allylic protons (linolenic and linoleic acid)</td>
</tr>
<tr>
<td>H</td>
<td>4.19</td>
<td>-CH$_2$-O-COR</td>
<td>Glycerol ($\alpha$ position)</td>
</tr>
<tr>
<td>I</td>
<td>5.15</td>
<td>-CH-O-COR</td>
<td>Glycerol ($\beta$ position)</td>
</tr>
<tr>
<td>J</td>
<td>5.29</td>
<td>-CH=CH-</td>
<td>All unsaturated fatty acids</td>
</tr>
</tbody>
</table>

source: N. Chira, C. Todașcă, A. Nicolescu, G. Păunescu, Sorin Roșca,
Geographical origin of olive oils
Italy versus Greek Islands

- Dauno
- Terra di Bari
- Terra Terantina & Ortranto
- Korfu
- Lefkada
- Cefalonia
- Zacinto

~ 70 km
NMR screening of Greek olive oils
Classification by harvesting year

based on $^1$H-NMR spectra of 278 Greek olive oils
The global vegetable oil market
Production palm oil vs. other major vegetable oils

Major Vegetable Oils World Production
March 2012/13
in Million Metric Tons

Global palm oil production 2012
in Million Metric Tons

source: adapted from http://www.fas.usda.gov/oilseeds/Current/

source: adapted from US Department of Agriculture
Palm oil
A universal food and non-food component

Palm oil is a widespread ingredient of a multitude of products: chocolate bars, nougat creams, cookies, margarine, frying oil, cosmetics, candles, soaps, ink, polish, bio-fuel, ...

Some occurrences

- 2003 - banned Sudan Red I-IV found in palm oil
- 2009 – milk fat in ice-cream replaced by palm oil without labeling
- 2011 - Hongkong & Taiwan: Bis(2-ethylhexyl)phthalate (DEHP) softener used as palm oil replacement in various foods
- 2012 - Moldavia: palm oil instead of milk fat used for butter production
- refined palm oil used for "artificial" cheese production
- increased aldehyde concentrations in biofuels
Palm oil Certification of sustainable production

2004 Foundation of the Roundtable for Sustainable Palm Oil (RSPO), representing ~50% of global palm oil production, and members of major traders and processing industries

RSPO certifications (sustainable production, supply chains)

- Palm oil producers/suppliers have fundamental interest in methods confirming oil quality and certification compliance.

- NMR screening methodology may have the power to narrow palm oil production sites down to single plantations, proving that respective palm oil charges originate only from existing - and not from newly deforested - areas.
$^1$H-NMR screening of Malaysian palm oil
Crude versus refined palm oil

under development
first results
$^1$H-NMR spectra comparison of edible oils
Palm oils, pumpkin seed oils, and olive oil

Greek olive oil
non-Styrian Bio pumpkin seed oil
Styrian pumpkin seed oil
Malaysian refined palm oil
Malaysian native palm oil
Differentiation of edible oil types
Early state overview

First feasibility study with yet too few samples, nevertheless marked differentiation of oil types.
Gutter oil

• discarded cooking oil collected from restaurant fryers and cookshops, or even from slaughterhouses, grease traps, and rotten animal parts

• reprocessed by distillation, cooking, quite often by filtering only

• used for biodiesel, but also widely - and illegally - sold as new oil for consumption

China.org.cn

Xinhua, January 13, 2012

China's food safety authorities are carrying out studies in the hope of finding ways to detect "gutter oil," Vice Health Minister Chen Xiaohong said Friday at the national food safety and health inspection meeting.

Though a nationwide campaign has been launched to stamp out gutter oil, some scholars have warned that it is difficult to test for, because profiteers are already sophisticated enough to fool inspection devices with their illegal wares.
Gutter oil identification by NMR
Feasibility study: differentiation gutter oil / palm oil

under development
first results
Honey

• Preparation:
  24 % w/w in H$_2$O
  10 % buffer added

• Measurement:
  @ 400 MHz NMR
  @ 300 K
Some assignments in Honey $^1$H-NMR spectra aliphatic region

- Succinic acid
- proline
- Lactic acid
- citric acid
- alanine
- Quinic acid
- valine
- ethanol
Assignments in Honey, supported by rapid 2D NOESYGPS1D, JRESPS @ 400MHz

Whitethorn, FR
Blossom, FR
Forest, FR
Lime, FR

Citric acid
Aspartic acid
Malic acid
Succinic acid

NOESYGPS1D, JRESPS @ 400MHz
Identified Compounds in Honey by $^1$H-NMR

<table>
<thead>
<tr>
<th>Identified Compounds</th>
<th>Identified Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMF</td>
<td>Sucrose</td>
</tr>
<tr>
<td>Trigonelline</td>
<td>D-Maltose</td>
</tr>
<tr>
<td>Histamine / Histidine</td>
<td>Quinic Acid</td>
</tr>
<tr>
<td>Adenine</td>
<td>Citric Acid</td>
</tr>
<tr>
<td>Formic acid</td>
<td>Malic acid</td>
</tr>
<tr>
<td>Pyridoxic acid</td>
<td>Aspartic acid</td>
</tr>
<tr>
<td>Uridine</td>
<td>Succinic Acid</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>Acetate</td>
</tr>
<tr>
<td>Tropic acid</td>
<td>Proline</td>
</tr>
<tr>
<td>2-phenylacetamide</td>
<td>Alanine</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>Lactic Acid</td>
</tr>
<tr>
<td>Maleimide</td>
<td>Threonine</td>
</tr>
<tr>
<td>Shikimic acid</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>Valine</td>
</tr>
<tr>
<td>cis-Aconitic acid</td>
<td>Leucine</td>
</tr>
<tr>
<td>Glucose</td>
<td>Iso-Leucine</td>
</tr>
<tr>
<td>D-Fructose</td>
<td></td>
</tr>
</tbody>
</table>
Honey Varieties based on $^1$H-NMR

- PCA made on complete spectral range
- Scaled to total sugar
- 200 Buckets

- Shikimic acid
  (only in forest and pine tree honey)
Milk Powder

Non-targeted screening applied to the study of baby milk powder and the melamine scandal

Co-operation Bruker BioSpin, CVUA Karlsruhe, Dr. Lachenmeier
Study of the milk powder in semi-solid state

San-Lu milk powder: Melamine (460 mg/kg)

Melamine can be quantified directly
(Integral corresponds to 6 Protons, $M = 126\ \text{g/mol}$)

Solvent: DMSO; CPMG experiment
Study of milk powder in solution

H2O / NOESY 1D

San-Lu milk powder: Too high concentration of sucrose

Sucrose spectrum (from spectral base)
Conclusions

**FoodScreener systems ➔ a perfect analytical tool**

- Minimal sample preparation
- $^1$H-NMR deliver highest reproducibility and transferibility (country, lab, user and instrument independent)
- $^1$H-NMR combines targeted and non-targeted analysis within one single measurement (Detection of even unknown deviations !)
- Positive identification and quantification of a multitude of compounds

**NMR is the method of choice**
Conclusions

FoodScreener systems ➔ a perfect analytical tool

• $^1$H-NMR is fully quantitative (one calibration suffice for all compounds)

• Rapid and full automated push-button solution to analyze fruit juice and wine, inclusive automated PDF report of all results

NMR is the method of choice
Acknowledgements

University of Athens (Greece)
Emmanuel Mikros
Alexios-Leandros Skaltsounis

University of Ioannina (Greece)
Michael G. Kontominas

University of Bari (Italy)
Francesco Longobardi
Antonio Sacco
Andrea Ventrella

Malaysian Palm Oil Board

Bruker BioSpin GmbH (Rheinstetten, Germany)
Andrea Steck, Claire Cannet, David Krinks, Fang Fang, Léa Heintz, Eberhard Humpfer, Monika Mörtter, Hartmut Schäfer, Birk Schütz, Manfred Spraul

Bruker BioSpin S.l.r. (Milano, Italy)
Claudia Napoli

DLR Neustadt Rheinland Pfalz:
- Arbeitsgruppe Herr Prof. Dr. Fischer

Universität Koblenz-Landau
- Frau Bansbach

CVUA Karlsruhe:
- Arbeitsgruppe Herr Dr. Godelmann

SGF Niederolm:
- Herr Dr. Rinke, Frau Dr. Koswig

LGL Würzburg:
- Arbeitsgruppe Herr Dr. Wachter, Herr Dr. Christoph

Winespin-Analytics:
- Herr Kost, Herr Langenwalter, Herr Witowski
Your contact regarding FoodScreener™ questions (juice, wine, edible oil, honey, etc.):

Dr. Markus Link +49 172 639 69 40;
markus.link@bruker-biospin.de

You can also get in contact with us using the internet:

• www.bruker.com/sgf
Thank you for your attention