MRFood2018

14TH EDITION OF THE INTERNATIONAL CONFERENCE ON THE APPLICATIONS OF MAGNETIC RESONANCE IN FOOD SCIENCE

September 17 - 21, 2018 - Rennes - France
CONFERENCE PROGRAM

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Organized by
Irstea – Rennes, France
National Research Institute of Science and Technology for Environment and Agriculture
Welcome to the MRFood2018

Following the successful tradition of earlier meetings, the International Conference on the Applications of Magnetic Resonance in Food Science (MRFood) comes back to France for its 14th edition (the tenth one was at Clermont-Ferrand in 2010). This year, it takes place in Brittany at Rennes in the new congress center “Le Couvent des Jacobins” founded in 1369 by the Order of Preachers (Dominicans) and the property of Rennes Métropole since 2002.

The conference will cover multiple aspects of the application of magnetic resonance to food (including plants as food resources) and food products by presenting the latest innovations to understand the functionality of foods, their processing, their stability and their impact on health and sensorial perception. Oral and poster presentations will deal with new techniques in low and high field NMR, quantitative NMR (qNMR), signal processing, food physics, postharvest and food technologies, foodomics, food authenticity, quality and safety as well as imaging and diffusometry. This conference is sponsored by NMR suppliers (Bruker, JEOL, Niugm, Oxford, Magritek), agro-food industries (Roullier, DianaPetFood), the Rennes metropolis, the Brittany region and the University of Bretagne-Loire (UBL). The organizing committee would like to thank each company/organization for their support to MRFood2018.

MRFood2018 will start with tutorials organized on Monday 17th in the afternoon with three subjects: 1- MRI hardware, bridging the gap between theories and images, 2- Measurement uncertainties in quantitative MRI and 3- Fat quantification with MRI.

From Tuesday to Friday, daily plenary presentations will be introduced by 7 renowned invited speakers from all over the world (Brazil, The Netherlands, Japan, Italy, New-Zealand, France), each for one session on 7 topics: NMR/MRI development, Signal processing, Food Physics, Postharvest Technologies, Food Technologies, Foodomics and Food Chemistry. Several of the invited speakers have been selected to foster AMPERE cross-division interactions. This year, submitted abstracts for oral presentations are eligible for publication into a special issue of the prestigious Magnetic Resonance in Chemistry journal (Wiley) after the standard peer-reviewing process.

On Thursday afternoon, participants will have the opportunity to visit the UNESCO-classed site of the Mont Saint-Michel before the Gala dinner in the course of which the price of the best poster will be attributed.

We wish you a pleasant and fruitful stay, good discussions, and new insights into the fascinating topic of Magnetic Resonance in Foods.

Corinne Rondeau-Mouro
on behalf of the Scientific and Organizing Committee
INVITED SPEAKERS

Petrik Galvosas  
School of Chemical and Physical Sciences, New Zealand

Luiz Alberto Colnago,  
Embrapa, Brazil

Roberto Consonni,  
CNR, Italy

Patrick Giraudet  
University of Nantes, France

Shingo Matsukawa  
Tokyo University, Japan

Hank Van As  
WUR, Netherlands

Said Moussaoui  
Ecole Centrale Nantes, France
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<tr>
<th>Scientific Advisory Board</th>
<th>Organizing Committee</th>
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<tr>
<td><strong>John van Duynhoven (Chair)</strong>&lt;br&gt;Wageningen University – NL</td>
<td><strong>Corinne Rondeau-Mouro (Chair)</strong>&lt;br&gt;Irstea Rennes – FR</td>
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<tr>
<td><strong>Jean-Marie Bonny</strong>&lt;br&gt;INRA Theix – FR</td>
<td><strong>Asma Allée</strong>&lt;br&gt;Irstea Rennes – FR</td>
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<tr>
<td><strong>Francesco Capozzi</strong>&lt;br&gt;University of Bologna – IT</td>
<td><strong>Sylvain Challois</strong>&lt;br&gt;Irstea Rennes – FR</td>
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<tr>
<td><strong>Søren Balling Engelsen</strong>&lt;br&gt;University of Copenhagen – DK</td>
<td><strong>Guylaine Collewet</strong>&lt;br&gt;Irstea Rennes – FR</td>
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<tr>
<td><strong>Antonio Ferreira</strong>&lt;br&gt;Federal University of São Carlos – BR</td>
<td><strong>Brigitte Marchix</strong>&lt;br&gt;Irstea Rennes – FR</td>
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<tr>
<td><strong>Gisela Guthausen</strong>&lt;br&gt;Karlsruhe Institute of Technology – DE</td>
<td><strong>Maja Musse</strong>&lt;br&gt;Irstea Rennes – FR</td>
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<tr>
<td><strong>Corinne Rondeau-Mouro</strong>&lt;br&gt;IRSTEA Rennes – FR</td>
<td><strong>Manfred Spraul</strong>&lt;br&gt;Bruker BioSpin GmbH – DE</td>
</tr>
</tbody>
</table>

**Honorary members**

**Peter Belton**<br>University of East Anglia – UK  
**Graham Webb**<br>Royal Society of Chemistry – UK

**Organizer**

National Research Institute of Science and Technology for Environment and Agriculture  
Irstea – Rennes, France
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<th>Day</th>
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<th>Event</th>
<th>Chair</th>
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<tr>
<td>Monday, Sept. 17</td>
<td>12:00-18:30</td>
<td>Welcome Mixer</td>
<td>Masse</td>
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<tr>
<td>Monday, Sept. 17</td>
<td>14:00</td>
<td>Welcome Tutorials</td>
<td>Masse</td>
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<tr>
<td>Monday, Sept. 17</td>
<td>15:40</td>
<td>Coffee, Posters</td>
<td>Masse</td>
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<tr>
<td>Tuesday, Sept. 18</td>
<td>8:20</td>
<td>Conference opening</td>
<td>MNRI/MRI development</td>
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<tr>
<td>Tuesday, Sept. 18</td>
<td>8:40</td>
<td>NMR/MRI development</td>
<td>M. Mariette</td>
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<tr>
<td>Tuesday, Sept. 18</td>
<td>9:00</td>
<td>9:00 Coffee, Posters</td>
<td>Masse</td>
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<tr>
<td>Tuesday, Sept. 18</td>
<td>10:00</td>
<td>Signal processing</td>
<td>G. Collewet</td>
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<td>Tuesday, Sept. 18</td>
<td>10:50</td>
<td>Food Physics</td>
<td>G. Collewet</td>
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<td>Tuesday, Sept. 18</td>
<td>12:30</td>
<td>Lunch, Posters</td>
<td>G. Guthausen</td>
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<td>Tuesday, Sept. 18</td>
<td>14:00</td>
<td>Food Technologies</td>
<td>G. Guthausen</td>
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<td>Coffee, Posters</td>
<td>G. Guthausen</td>
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<td>Tuesday, Sept. 18</td>
<td>16:10</td>
<td>Food Technologies</td>
<td>J. M. Banny</td>
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<td>Tuesday, Sept. 18</td>
<td>16:10</td>
<td>Coffee, Posters</td>
<td>J. M. Banny</td>
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<tr>
<td>Tuesday, Sept. 18</td>
<td>17:30</td>
<td>Meeting of the scientific committee</td>
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<tr>
<td>Thursday, Sept. 20</td>
<td>8:30</td>
<td>8:30 Ecostat Biochemistry</td>
<td>F. Capozzi</td>
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<td>Thursday, Sept. 20</td>
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<td>F. Capozzi</td>
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<td>Thursday, Sept. 20</td>
<td>10:30</td>
<td>Coffee, Posters</td>
<td>A. Ferreira</td>
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<td>Thursday, Sept. 20</td>
<td>11:00</td>
<td>Ecostat Biochemistry</td>
<td>A. Ferreira</td>
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<td>Thursday, Sept. 20</td>
<td>11:30</td>
<td>Coffee</td>
<td>A. Ferreira</td>
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<td>Thursday, Sept. 20</td>
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<td>Friday, Sept. 21</td>
<td>9:00</td>
<td>Ecostat Biochemistry</td>
<td>F. Capozzi</td>
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<td>Friday, Sept. 21</td>
<td>11:00</td>
<td>Closing remarks</td>
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<td>Friday, Sept. 21</td>
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<td>Coffee</td>
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<td><strong>Monday, Sept. 17</strong></td>
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<td><strong>PROGRAMME OVERVIEW</strong></td>
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### Monday Afternoon, Sept. 17

**12h00 – 18h30**  
Registration

**14:00**  
**Welcome**

**14:15**  
**Tutorials**  
*Chair: M. Musse*

- **14:20** MRI hardware: bridging the gap between theory and images  
  *H. Saint-Jalmes (LTSI, University of Rennes 1, France)*

- **15:20** Measurement uncertainties in quantitative MRI  
  *G. Collewet (IRMFood, IRSTEA, France)*

- **16:20**  
  Fat quantification with MRI  
  *F. Franconi (University of Angers, France)*

**17:30**  
**Welcome Mixer – the Halle**

**18:30**  
**Meeting of the scientific committee**
<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>8:20</td>
<td>Conference opening</td>
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<tr>
<td>8:40</td>
<td><strong>NMR/MRI development and signal processing</strong></td>
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<td>Chair: François Mariette</td>
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<tr>
<td></td>
<td><strong>Invited speaker</strong></td>
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<tr>
<td></td>
<td>Developments in Rheo-NMR</td>
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<td></td>
<td>P. Galvosas (University of Wellington, NZ)</td>
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<td>9:40</td>
<td>High field micro MRI velocimetry to obtain quantitative local flow curves of food dispersions with transient yield stress behaviour</td>
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<td></td>
<td>T. Nikolaeva, F. Vergeldt, H. Van As, J. van Duynhoven</td>
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<tr>
<td>10:00</td>
<td><strong>Detection of robust group-level fMRI brain responses to food tastes</strong></td>
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<td></td>
<td>M. Angeletti, S. Clerjon, J. Koko, J.-M. Bonny</td>
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<tr>
<td>10:20</td>
<td>Coffee break, Posters</td>
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<tr>
<td>10:50</td>
<td><strong>Signal processing</strong></td>
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<td></td>
<td>Chair: G. Collewet</td>
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<tr>
<td></td>
<td><strong>Invited speaker</strong></td>
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<tr>
<td></td>
<td>Optimized signal processing methods for NMR/MRI signal modeling and parametric estimation of relaxation time distributions</td>
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<td>S. Moussaoui (ENC, France)</td>
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<td>11:50</td>
<td>A robust and prior knowledge independent method to interpret non-negative least squares (NNLS) $T_2$ relaxation results</td>
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<td></td>
<td>G. Pagès, A. Traoré, J.-M. Bonny</td>
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<tr>
<td>12:10</td>
<td><strong>Fruit tissues classification from MRI multi-exponential $T_2$ maps</strong></td>
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<td></td>
<td>Ch. El Hajj, G. Collewet, M. Musse, S. Moussaoui</td>
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<tr>
<td>12:30</td>
<td>Lunch, Posters</td>
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<td>Time</td>
<td>Session</td>
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<tr>
<td>14:00</td>
<td><strong>Food physics</strong></td>
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<td></td>
<td><strong>Invited speaker</strong></td>
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<td>S. Matsukawa <em>(Japan)</em></td>
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<tr>
<td>15:00</td>
<td><strong>Self-diffusion studies on cocoa butter using PG-NMR and FFC-NMR</strong></td>
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<td>15:20</td>
<td><strong>Increasing water solubility with decreasing droplet size limits the use of water NMR</strong></td>
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<tr>
<td>15:40</td>
<td>Coffee break, Posters</td>
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<tr>
<td>16:10</td>
<td><strong>Low field NMR for quality monitoring of 3D printed surimi from cod byproducts:</strong></td>
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<td><strong>Effects of the pH-shift method compared to conventional washing</strong></td>
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<tr>
<td>16:30</td>
<td><strong>What can NMR learn us about how to make a healthy hotdog sausage?</strong></td>
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<td><strong>H. Christine Bertram, L. Hjelm Christiansen</strong></td>
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<td>17:00</td>
<td>Posters</td>
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<td>Time</td>
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<tr>
<td>9:00</td>
<td><strong>Food Physics</strong></td>
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<td>9:00</td>
<td>Relating crystal properties to water exchange kinetics in W/O/W double emulsions by low resolution $^1$H-NMR-diffusometry</td>
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<td>9:20</td>
<td>Utilization of FFC Relaxometry to Differentiate Frankfurters Made of Different Meat Sources</td>
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<tr>
<td>10:00</td>
<td>Coffee break, Posters</td>
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<tr>
<td>10:30</td>
<td><strong>Postharvest Technologies</strong></td>
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<td></td>
<td>Invited speaker</td>
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<tr>
<td>11:30</td>
<td>NMR study of fresh cut escarole: influence of temperature and storage time on leaf structure and water repartition</td>
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<tr>
<td>12:10</td>
<td>Multiscale NMR analysis of apple thermal denaturation</td>
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<tr>
<td>12:30</td>
<td>Lunch, Posters</td>
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<td>Time</td>
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<tr>
<td>14:00</td>
<td><strong>Food Technologies</strong>&lt;br&gt;<em>Chair: J.-M. Bonny</em>&lt;br&gt;&lt;br&gt;<strong>Invited speaker</strong>&lt;br&gt;New and improved pulse sequences for measuring food quality in low field NMR&lt;br&gt;<em>L. A. Colnago</em> (Embrapa Brazil)</td>
</tr>
<tr>
<td>15:00</td>
<td>In situ measurement of deposit layer formation during skim milk filtration by MRI&lt;br&gt;<em>N. Schork, S. Schuhmann, G. Guthausen, H. Nirschl</em></td>
</tr>
<tr>
<td>15:20</td>
<td>Methods to Probe Baking with Unilateral Low-Field NMR&lt;br&gt;<em>O. Sucre, N. Binti, T. Lucas, C. Rondeau-Mouro</em></td>
</tr>
<tr>
<td>15:40</td>
<td>Coffee break, Posters</td>
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<tr>
<td>16:10</td>
<td>NMR to understand complex food properties&lt;br&gt;<em>E. R. Alonso, F. J. Vergeldt, A. Jan van der Goot</em></td>
</tr>
<tr>
<td>16:30</td>
<td>Using NMR and MRI to characterize dry cat food physical properties&lt;br&gt;<em>M. Crémont, A. de Ratul, L. Bramouillé, P. A. Eliat, M. Cambert, F. Mariette</em></td>
</tr>
<tr>
<td>16:50</td>
<td>The Application of Low Field NMR in food quality analysis and monitoring&lt;br&gt;<em>Y. Zhang, G. Yangwen, Y. Peiqiang</em></td>
</tr>
<tr>
<td>17:15</td>
<td>General meeting of the division</td>
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<tr>
<td>Time</td>
<td>Session</td>
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| 8:30  | **Foodomics and Food Chemistry**  
   *Chair:* S. Balling Engelsen  
   **Invited speaker:** The potentiality of NMR based metabolomics in food science and food authentication assessment.  
   **R. Consonni** (CNR Italy) |
| 9:30  | **Conventionally vs. Organically Produced Eggs: Differentiation with NMR**  
   S.M. Ackermann, D.W. Lachenmeier, T. Kuballa, M. Bunzel |
| 9:50  | **Revisiting the Isotope Analysis of Vanillin by Anisotropic $^2$H NMR: an Original Tools against the Counterfeiting of Food Aroma?**  
   T. Texier-Bonniot, P. Berdagué, R. Robins, G. Rémaud and P. Lesot |
| 10:10 | **Targeted and non-targeted $^1$H-NMR based Methods for Authenticity and Quality Control of Food**  
   A. Steck |
| 10:30 | Coffee break, Posters                                                                            |
| 11:00 | **Foodomics and Food Chemistry**  
   *Chair:* A. Ferreira  
   **Balsamic vinegar affects the digestion of carbohydrates and proteins in food, assessed by NMR spectroscopy applied to in vitro models**  
   E. Urbinati, G. Picone, M. Di Nunzio, A. Bordoni, F. Capozzi |
| 11:20 | **$^{13}$C-NMR-based isotopomics for food authentication**  
   G. Hajjar, T. Rizk, S. Akoka, J. Bejjani |
| 11:40 | **Identification of roasting markers of Coffea arabica L. seeds in coffee beverage through NMR fingerprinting and chemometrics**  
   L. Febvay, D. Aoudé-Werner, E. Hamon, R. Recht, V. Viraswami, H. This |
| 12:30 | Excursion, picnic                                                                                |
| 19:30 | Conference dinner                                                                                 |
### Friday, Sept. 21

<table>
<thead>
<tr>
<th>Time</th>
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<th>Speaker(s)</th>
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<tr>
<td>9:00</td>
<td><strong>Foodomics and food chemistry</strong></td>
<td><em>Chair: F. Capozzi</em></td>
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<tr>
<td></td>
<td><strong>Invited speaker</strong></td>
<td>Fast quantitative 2D NMR methods for the analysis of complex mixtures in food science</td>
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<td><strong>P. Giraudeau</strong> (Univ. Nantes France)</td>
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<tr>
<td>10:00</td>
<td><strong>NMR metabolomics: a useful tool in aquaculture feed development</strong></td>
<td>C. Deborde, B. Madji Hounoum, M. Maucourt, D. Jacob, F. Terrier, G. Corraze, F. Médale, B. Fauconneau, A. Moing</td>
</tr>
<tr>
<td>10:20</td>
<td><strong>Salmon metabolomics: metabolic profiling of plasma and fecal samples by NMR reveals biomarkers of gut condition in farmed salmon</strong></td>
<td>V. Aru, B. Khakimov, E. Chikwati, A.J. Torres, A. Krasnov, T Kortner, Å Krogdahl, S Balling Engelsen</td>
</tr>
<tr>
<td>10:40</td>
<td><strong>Can the human urinary metabolome predict risk-of-poverty status? An inter European study.</strong></td>
<td>Al Trimigno, B Khakimov, S. Balling Engelsen</td>
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<tr>
<td>11:00</td>
<td><strong>Closing remarks</strong></td>
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<td>11:30</td>
<td><strong>Coffee break</strong></td>
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End
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<th>NMR/MRI development and signal processing</th>
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<tbody>
<tr>
<td>1 Quantitative $^{13}$C INEPT Method for the Detection of Fatty Acid Composition of Vegetable Oils.</td>
<td>Lei Chen, Hongbing LIU, Huili LIU</td>
</tr>
<tr>
<td>2 MRI flow cell development to monitor in-situ and in-real time dissolution of porous food products.</td>
<td>Gert-Jan Goudappel, Theo Blijdenstein, Adrian Voda</td>
</tr>
<tr>
<td>3 NMRProcFlow: A graphical and interactive tool dedicated to 1D spectra processing for NMR-based metabolomics.</td>
<td>D. Jacob, C. Deborde, A. Moing</td>
</tr>
<tr>
<td>4 Signature Mapping (SigMa): A new semi-automatic tool for rapid processing of urine and blood 1D 1H-NMR metabolomics data.</td>
<td>Bekzod Khakimov, Alessia Trimigno, Violetta Aru, Søren Balling Engelsen</td>
</tr>
<tr>
<td>6 Can CEST contrast image gluten network?</td>
<td>Charbel ASSAF, Guilhem PAGES, Jean-Marie BONNY</td>
</tr>
<tr>
<td>7 Selective oil-phase rheo-MRI velocity profiles to monitor heterogeneous flow behaviour of oil/water food emulsions.</td>
<td>M.R. Serial, Tatiana Nikolaeva, Frank Vergeldt, Henk Van As, John van Duynhoven</td>
</tr>
<tr>
<td>8 Quantification of water sorption in starch-glycerol extrudates by MR micro-imaging.</td>
<td>C. Rondeau-Mouro, R. Kovrilija</td>
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<thead>
<tr>
<th>Food physics</th>
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<tbody>
<tr>
<td>9 An Investigation of Water/Bovine Milk Interactions with κ-carrageenan Using Fast-Field Cycling NMR Relaxometry and Viscosimetry.</td>
<td>Malgorzata Fiorek-Wojciechowska</td>
</tr>
<tr>
<td>10 Characterization of different cultivars of European Olea L. using MRI techniques</td>
<td>N. Funicello</td>
</tr>
<tr>
<td>11 Diffusion in different polysaccharide gels.</td>
<td>D. Wefers, L. Bitenc, M. Bunzel, G. Guthausen</td>
</tr>
<tr>
<td>12 Increasing the value of cod head by-products by LF-NMR</td>
<td>Maria Guðjónsdóttir, Elisa Viðarsdóttir, Hildur Inga Sveinsdóttir, Magnæa G. Karlssdóttir, Sigurjón Arason</td>
</tr>
<tr>
<td>14 NMR relaxation and oxygen permeation studies on protein-sugar matrices conditioned at different humidities.</td>
<td>Jens Meissner, Nikolaus Nestle, Emma Thompson, Eduard Schreiner, Fangfang Chu</td>
</tr>
<tr>
<td>16 Contrast enhanced proton MRI study of potato tubers subjected to electroporation process.</td>
<td>M. Suchanek, Z. Olejniczak</td>
</tr>
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<td>17 Low-resolution NMR relaxometry, diffusometry and profilometry on salad dressing and mozzarella upon storage time.</td>
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Rennes is a green city that co-exists peacefully with Mother Nature. Home to a patchwork of parks and gardens, such as the renowned Parc du Thabor, Rennes’ answer to Central Park, the Parc des Gayeulles, the banks of the river Vilaine with its ponds and towpaths, and the many green spaces within the city walls, nature is everywhere you look in Rennes. Go from city bustle to untouched countryside in a matter of minutes. To visit Rennes is to step back in time, soaking up the city’s past through its monuments, characters and key moments, from the Parlement court and the Great Fire of 1720 to the Odorico mosaics, half-timbered houses and bloody alleyways that were once serial killer Hélène Jegado's haunts. A fresh take on Brittany and its heritage, a place where stories and legends are recounted, memories that will stick in your mind for years to come...

The congress will take place to the conference convention named Couvent des Jacobins at the following address:

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TUTORIALS

Tutorials on Monday, 17th of September 2018, 14:00 – 17:30
These sessions are opened to the congress participants.

1. MRI hardware: bridging the gap between theory and images
   Hervé SAINT-JALMES – LTSI, Université de Rennes, INSERM U1099 & Centre Eugène Marquis, Rennes; PRISM

   This tutorial will provide an introduction to the hardware architecture of a Magnetic Resonance scanner, focusing on the magnetic and electromagnetic fields needed to polarize, manipulate and localize nuclei in the sample of interest.

2. Measurement uncertainties in quantitative MRI
   Guylaine COLLEWET – MRI-Food, UR OPAALE, IRSTEA Rennes; PRISM

   The objective of this tutorial is to provide an overview on the subject of measurement uncertainties in the context of quantitative MRI measurements. It will give some clues to answer questions such as: What are the precision and the accuracy of the results? For a model-based method, which model parameters most influence the quality of the results? How can the optimal protocol be defined? The talk will cover considerations from image acquisition steps to the post-processing stage.

3. Fat quantification with MRI
   Florence FRANCONI – MINT INSERM U1066 CNRS 6021, Université d’Angers, Angers; PRISM

   MR technique offers the opportunity to non-invasively separate fat from water signal. This tutorial will provide an overview of methods to quantify fat with MRI, from T1 based or frequency selective methodologies to chemical shift induced imaging. Underlying principles, advantages and confounding factors will be presented.
PLENARY CONFERENCES
Developments in Rheo-NMR

Petrik Galvosas

MacDiarmid Institute for Advanced Materials and Nanotechnology,
SCPS, Victoria University of Wellington, New Zealand

For over 25 years, Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI) techniques have been used to study materials under mechanical deformation [1]. Collectively these methods are referred to as Rheo-NMR [2]. In many cases it provides spatially and temporally resolved maps of NMR spectra, intrinsic NMR parameters (such as relaxation times) or motion (such as diffusion or flow). Therefore, Rheo-NMR is complementary to conventional rheological measurements.

This lecture will review the development of Rheo-NMR including recent advances [3, 4]. Furthermore, it will highlight the potential of Rheo-NMR and where it contributed substantially in the past to the understanding of complex fluids under deformation and flow. This may cover the early detection of shear stress in Rheo-NMR applications [5], temporal fluctuations in wormlike micelles [6], the detection of diffusion under shear flow [7] or the influence of different shear geometries on complex fluid flow [8]. The lecture will also include a review of Rheo-NMR applications in food sciences [9-12] and discuss possible opportunities for Rheo-NMR in the future.

References
Optimized signal processing methods for NMR signal modelling and MRI data analysis for the estimation for relaxation times distributions

Saïd Moussaoui

Ecole Centrale de Nantes, LS2N UMR CNRS 6004, 44321 Nantes Cedex 3, France

Processing data sets resulting from MRI or NMR measurements requires the setting of adequate signal models encoding the physical information and the development of appropriate mathematical computing techniques for estimating the quantities of interest. For instance, the reconstruction of relaxation time distributions (T1, T1 or T1-T2) from NMR relaxometry signals reduces to a numerical inversion of a Laplace transform, which is known to be an instable (ill-posed) inverse problem. The solving of such kind of problems is performed by means of statistical inference methods and numerical computing techniques allowing to ensure convergence of the algorithms and to handle large amount of data matrices. In this communication, this signal processing pipeline will be illustrated through two examples: the first case-study is the inversion of a two-dimensional Laplace transform for the estimation of T1-T2 distributions from CPMG and FID data sets. The second example is the fitting of multi-exponential relaxation times from magnitude MRI data sets and their exploitation for tissue composition analysis.

References:


Network formation and structure in polysaccharides gels studied by gradient NMR

Shingo Matsukawa\textsuperscript{1} and Qiuhua Zhao\textsuperscript{2}

1)Department of Food Sci. & Tech, Tokyo University of Marine Sci. & Tech.
2)School of Chemistry & Molecular Engineering, East China Normal University

For the study of the molecular mobility and network structure, NMR measurements give useful information; NMR relaxation times are related to the segmental motion of polysaccharide and the diffusion coefficient indicates the mobility of whole of molecule. Moreover, the network structure is evaluated by the measurement of probe diffusion\textsuperscript{1-4)}. The network structure affects the physical property and the texture, and also affects the diffusion of taste component and taste. Therefore, the investigation of the network structure is also important for the taste of food gels.

In this presentation, studies on network structures in polysaccharide gels by using gradient NMR will be introduced. The network structures were evaluated from the diffusion coefficients of polymer added as a probe. The echo signal intensities of the polysaccharides were also used.

References

Specific developments and applications of MRI and NMR to plant quality

Henk Van As

Lab of Biophysics and MAGNetic resonance research FacilitY (MAGNEFY), Wageningen University, Stippeneng 4, 6708 WE Wageningen, NL

Modern plant breeding needs to increase agricultural productivity under climate changes while decreasing the ecological footprint. Therefore, there is a strong need to characterize plant genotypes in relation to dynamic environmental (stress) conditions based on photosynthesis, water use efficiency and plant performance. This requires an approach that couples information from different organ and tissue levels and function, while considering the variables that affect these biological systems from cell to organism. Intact plant MRI allows the study of photosynthesis and long distance transport (source-sink relations) in an integrative way [1].

Plant products like seeds, and fruits and vegetables (F&V) are good sources of several essential nutrients, the intake of which has been associated with a wide range of beneficial health effects. A number of strategies are active to raise the daily intake: quality control of fresh, stored and processed F&V, convenience in preparing (e.g. drying and dehydration shortly before consumption, conserving texture of the original product as much as possible) and the use of plant materials processed in such a way that a meat structure develops with the firmness and fiber structure of a steak.

The use of proton TD-NMR and (rheo-)MRI relaxometry, diffusometry and flowmetry for the above mentioned applications will be reviewed and discussed. The NMR parameters are particularly sensitive to water status, transport processes, the subcellular distribution of water in plant tissues (and exchange between them!), metabolite contents and to membrane permeability/integrity and as such to food (micro)structures, water holding capacity and distribution of water in the different components [2]. The consequences for quantitative NMR/MRI will be discussed [3].

Reference

New and improved pulse sequences for measuring food quality by low field NMR

Luiz Alberto Colnago\textsuperscript{1}, Tatiana Monaretto\textsuperscript{2} Rodrigo Henrique Garcia\textsuperscript{2}

\textit{1-Embrapa Instrumentation Center, São Carlos, SP, Brazil, 2-Institute of Chemistry of São Carlos, USP, São Carlos, SP, Brazil}

Recent improvements in low-field NMR sequences based on continuous wave free precession (CWFP) regime and time-reversal will be presented. The improvement in single shot method to measure longitudinal relaxation time (CWFP-$T_1$)\textsuperscript{1}, was the enhancement of the signal to noise ratio (SNR) by processing the data with several types of low pass filter. Savitzky-Golay's and Wavelet show the best results with highest SNR enhancement and minimal signal distortion. The two-pulse time-reversal sequence, used to refocus dipolar interaction in solids, was improved by the optimization of the rf power of the first pulse. The length of the first pulse has to be set to a time twice the dead time and to an odd multiple of 90° pulse. We observed that is not necessary to adjust the pulse to an odd multiple of 90° pulse but is necessary to use high rf power, equivalent to a bandwidth higher than 50 KHz. This new sequence, named radiofrequency optimized solid echo (ROSE) refocus dipolar echoes with higher intensity than the ones obtained with sophisticated magic sandwich echo (MSE) sequence. Applications of these sequences in heterogeneous and solid food products will also be presented.

Reference:


Acknowledgments: FAPESP, CNPq and CAPES (Brazilian agencies) for financial support
The potentiality of NMR based metabolomics in food science and food authentication assessment

R. Consonni, L.R. Cagliani

Institute for Macromolecular Studies, NMR laboratory, National Research Council, Via Corti 12, 20133 Milan, Italy

In the last years there was an increasing interest on NMR spectroscopy, whose application experienced an exponential growth in several research fields, particularly in food science. NMR was born as the elective technique for structure elucidation of molecules and nowadays is largely adopted to investigate complex mixtures. In the era of the “omics” techniques, NMR was rapidly enrolled as one of the most powerful methods to approach metabolomics studies. Its use in analytical routines, characterized by rapid and reproducible measurements, would provide the identification of a wide range of chemical compounds in the mixture under investigation simultaneously, revealing potential markers, disclosing sophisticated frauds or addressing the geographical origin. The great economic value of high quality or guaranteed foods demands highly refined characterization tools to protect consumers and the productions of valuable foods. This scenario suggests metabolomics as a privileged approach for the modern analytical studies in the next decades. The large potentiality of NMR techniques is here presented through specific applications and using different techniques also focused on authentication process on different food products, like Traditional Balsamic vinegar of Modena, tomato paste, roasted coffee, honey and saffron.

References

Fast quantitative 2D NMR methods
for the analysis of complex mixtures in food science

Patrick Giraudieu

Université de Nantes, CNRS, CEISAM UMR 6230, 44322 Nantes Cedex 03, France
Institut Universitaire de France, 75005 Paris, France

NMR spectroscopy is a powerful analytical tool in many areas of food science, thanks to its ability to provide structural, dynamic and quantitative insights in a non-destructive fashion. However, one-dimensional (1D) $^1$H spectroscopy, the most widespread approach, is strongly limited by the numerous peak overlaps that prevent the accurate quantification of food mixture components. This limitation can be overcome by multi-dimensional NMR, and particularly by 2D NMR, albeit at the cost of a longer experiment time and of several specificities associated with the use of multi-pulse sequences.

In the last few years, we developed an ensemble of fast and quantitative 2D NMR approaches for the accurate analysis of complex mixtures [1,2]. These methods combine accelerated 2D pulse sequences such as ultrafast NMR with analytical chemistry methods such as external calibrations or standard additions. They provide efficient solutions for the accurate quantification of targeted compounds in mixtures, but also for the untargeted analysis of large sample collections.

We will illustrate the potential of these fast quantitative 2D NMR methods in the area of food science. Recent examples of targeted quantification include the analysis of energy drinks [3] or the monitoring of metabolite concentrations during the development of tomato [4]. We will also introduce a workflow that we developed for untargeted lipidomics by fast 2D NMR, which was applied to a chemical food safety issue [5]. Beyond these studies that were carried out at high magnetic field, we will also illustrate the potential of fast 2D NMR methods that we recently implemented on a benchtop spectrometer [6], opening new perspectives for the high-throughput profiling of food samples [7].

References


Acknowledgement

The author thanks support from the ANR, the IUF, from the Région Pays de la Loire via the RFI Food 4.2 Program, as well as the CORSaire metabolomics platform. Colleagues from the CEISAM laboratory (EBSI team) are warmly acknowledged.
ABSTRACTS OF THE LECTURES
High field micro MRI velocimetry to obtain quantitative local flow curves of food dispersions with transient yield stress behaviour

Tatiana Nikolaeva¹, Frank Vergeldt¹, Henk Van As¹, John van Duynhoven¹,²

¹ Laboratory of Biophysics, Wageningen University, Wageningen, The Netherlands

² Unilever Discover Vlaardingen, Vlaardingen, The Netherlands

Micro MRI velocimetry (rheo–MRI) is a non-intrusive technique that allows a direct and quantitative view on spatially resolved (local) flow behaviour of complex fluids. For food dispersions it offers unique opportunities to study structure formation and degradation under shear, where conventional rheological measurements often provide ambiguous outcomes. Rheo-MRI velocity profiles are commonly obtained in the Couette geometry, which consists of concentric cylinders with a gap in between them. By measuring the applied torque on the inner cylinder at standard rheometer the local stress can be determined, since the stress distribution over the gap is well known. Combining this information with local shear rates over the gap obtained from the rheo-MRI velocity profiles allows to construct a local flow curve [1].

We constructed a set of Couette geometries with 1, 2.5 and 4 mm gap sizes that can be mounted in a conventional rheometer and in a standard micro-MRI probehead of a wide bore 7 T system (¹H NMR frequency of 300 MHz). The high field enabled rapid recording of velocity profiles with high signal to noise and a spatial resolution of 50 microns, but also introduced artefacts due to chemical shift dispersion. Furthermore, artefacts due to subtle mechanical instabilities became apparent. The signatures by which these artefacts can be recognized will be described, as well as circumvention strategies. A good match was found between global and constructed local flow curves for Newtonian (Silicon oil) and simple yield stress (Carbopol) fluids. Based on local flow curves we monitored network formation of fat crystals dispersed in oil under shear. The local yield stress as a function of time was estimated based on the Herschel–Bulkley equation. Time- and position - dependent local viscosity changes were obtained based on the local flow curves.

Detection of robust group-level fMRI brain responses to food tastes

Mélodie Angeletti\textsuperscript{1,2}, Sylvie Clerjon\textsuperscript{1}, Jonas Koko\textsuperscript{2}, Jean-Marie Bonny\textsuperscript{1}

\textit{1 AgroResonance, UR370 QuaPA - INRA, 63122 Saint-Genès-Champanelle, France}

\textit{2 Université Clermont Auvergne, CNRS, LIMOS, F-63000 Clermont-Ferrand, France}

Despite its severe technical constraints, which still preclude normal eating conditions, fMRI based on BOLD contrast has been used with success to elucidate many mechanisms of coding and integration, mostly directly in the human eater (Bonny \textit{et al.}, 2017). Further progress is however needed to improve the sensitivity and specificity of the activation maps obtained. For this purpose, a key aspect is to replace food images, which are most often used (Yeung \textit{et al.}, 2018), by real food stimuli in liquid form.

With such manner, repetitive jaw movements and swallowings introduce complex motion artifacts in the MR images which may be stimulus-dependent, and thus further detect as brain activations.

Here, original data obtained at 3T with several real food stimuli are presented. Motion-related effects are predominantly seen in voxels close to tissue boundaries and are highly variable across-subjects depending on how the subject performed the task lying in the magnet. A correction strategy has been developed to censor image volumes acquired during periods of high-motion. Then, by using modern approaches for detecting spatial patterns of activity (Angeletti \textit{et al.}, 2018), common brain regions of the gustatory network have been found between subjects which are elicited at specific times of the paradigm. This suggests that most of the motion-related artifacts can be ruled out by our analysis pipeline which allows to perform sensitive and specific task-based fMRI studies with real food stimuli in liquid form.

References


A robust and prior knowledge independent method to interpret non-negative least squares (NNLS) $T_2$ relaxation results

Guilhem Pagès, Amidou Traoré, Jean-Marie Bonny

AgroResonance, UR 370 QuaPA, INRA, F-63122 Saint-Genés-Champanelle

The fitting of an NMR signal decay in a weighted sum of exponentials is an ill-posed problem, i.e. different sets of relaxation times and amplitudes will lead to the same least-squares distance between the model and the experimental noisy data. To analyze such data, the classical pipe consists in performing a non-negative least squares (NNLS) algorithm combined with a regularization to smooth the $T_2$ distribution. However, a critical step of this approach deals with the choice of the operator and then of the corresponding regularization parameter which significantly affects the $T_2$ distribution. These parameters are usually chosen based on the operator experience as well as prior knowledge on the sample.

In this work, we propose to analyze NNLS results without regularization to circumvent these drawbacks. Our approach is based on the analysis of NNLS outputs by cumulative distribution functions (cdf) and not by probability density functions (pdf) as it is usually done. This concept is validated in different simulations for which the true $T_2$ distributions are built from discrete to continuous functions. Simulation results showed that the $T_2$ amplitude measured at a plateau of the cdf is unbiased and (almost) independent of both the decomposition basis and the signal-to-noise ratio. This observation allows to quantitatively interpret the NNLS inversions, especially when the true distribution is continuous. We suggest that NNLS by itself suffices in many situations, provided that cdf plateau can be discernable. The degrees of freedom to adjust in the method are then limited to the decomposition basis. To exemplify, this pragmatic and fruitful approach is applied on real NMR data obtained by spectroscopy and imaging.
Fruit tissues classification from MRI multi-exponential T2 maps

Christian El Hajj\textsuperscript{1,2,3}, Guylaine Collewet\textsuperscript{1,2}, Maja Musse\textsuperscript{1,2} and Saïd Moussaoui\textsuperscript{3}

1. Irstea, UR OPAALE, 17 Avenue de Cucillé-CS 64427, F-35044 Rennes, France
2. Univ Bretagne Loire, France 3. LS2N-ECN, Nantes, France

Water status in vegetal cells can be studied using their multi-exponential T2 relaxation times and their associated amplitudes $I_0$. Multi T2 and $I_0$ maps are firstly assessed from multi-spin echoes MRI images using a spatially regularized estimation algorithm accounting for the Rician noise\textsuperscript{2}. Afterwards, K-means clustering is applied in order to regroup in the same class all the voxels having similar T2 and $I_0$ values. Figure 1 represents a classification result obtained on a tomato, with a 512 multi-spin echoes sequence ($\Delta$TE=6.5 ms) on a 1.5T MRI. A tri-exponential T2 model and 4 classes are used to study the distribution of T2 values and intensities inside each class. $I_0$ values in function of their corresponding T2 values are plotted for each class. The tissues structure of the fruit can be observed, each class representing a tissue with different T2 and $I_0$ distribution.

References:


Figure 1: Results of the clustering algorithm, applied on the tri-exponential relaxation parameters estimated from MRI of a tomato.
Self-diffusion studies on cocoa butter using PG-NMR and FFC-NMR

Ladd Parada, M. ⁠¹, Vieira, J. ², Povey, M. ¹, Ries, ME. ³

¹School of Food Science and Nutrition, University of Leeds, Leeds, LS2 9JT, UK
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Cocoa butter (CB) is a key ingredient in chocolate; hence, its crystallisation behaviour has been studied for decades⁠¹. However, little has been done to understand how it behaves when molten, especially in terms of diffusion. This is highly relevant as studies in the molten state can help unravel the mechanisms through which pre-nucleating structuring occurs.

Consequently, in this project we compared the diffusion coefficients of CB at different temperatures ranging from 25 to 100 °C, both on heating and cooling, using the FFC-NMR technique as proposed by Kruk, et al. ² Measurements were also performed using the standard method of PG-NMR to validate the obtained results. Interestingly, rather than an Arrhenius behaviour a Vogel-Fulcher-Tamman³ trend was observed, which is frequently seen in glass-forming structures such as polymers. Additionally, FFC-NMR was used to monitor CB once it was cooled down to 22 °C and held isothermally for two hours. Differences were observed in the region between 0.01 and 0.63 MHz, indicating that these are the most sensitive frequencies to study structuring. These results suggest that FFC-NMR is a valid technique not only for diffusion measurements, but also for monitoring the crystallisation processes.

References

Increasing water solubility with decreasing droplet size limits the use of water NMR diffusometry in submicron W/O-emulsion droplet size analysis

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When the droplet size distribution of W/O-emulsions is determined using water NMR diffusometry, water exchange through the oil phase can lead to erroneous (overestimated) results. However, it is generally accepted that measuring at lower temperature avoids this issue.

In this work, it was examined whether measuring at lower temperature leads to satisfactory results when (sub)micron sized water droplets are present. It was shown that from a certain droplet size downwards, the increased water solubility resulted in water exchange at the W/O-interface which led to the observation of free water diffusion through the oil phase. As a further consequence, low-resolution PFG-NMR based on water diffusion is incapable of accurately determining the droplet size distribution of these samples. On the other hand, the use of an oil insoluble marker in the water phase extended the application window of PFG-NMR diffusometry towards smaller droplet sizes. However, high-resolution equipment is required in the latter case.

Summarizing, our results revealed that low-resolution NMR diffusometry could only be used for supermicron W/O-emulsions. Alternative techniques are needed when (sub)micron sized water droplets are present. In this respect, $T_2$-relaxometry was shown to be capable of detecting differences in droplet size distribution between W/O-emulsions, especially when the droplets were submicron in size.
Low field NMR for quality monitoring of 3D printed surimi from cod byproducts: Effects of the pH-shift method compared to conventional washing

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With the implementation of 3D food printing there can be reduction in food waste and utilization of seafood byproducts. In the current study low field Nuclear Magnetic Resonance (LF-NMR) translational relaxation and chemometric analysis was used to investigate the printability and characteristics of surimi pastes from cod byproducts as affected by different processing methods (the pH-shift method vs. conventional washing), addition of salt (0, 1.5 and 3%), length of cold storage (0, 4 and 7 days) until 3D printing, and steam cooking.

The analysis revealed 2-3 water populations in the 3D printed samples. The salt concentration had a significant increasing effect on all relaxation times of the pH-shift processed samples, indicating a salting in effect. No such effect was observed in the conventionally washed samples, until at salt concentrations above 3%. Cooking, on the other hand, had a decreasing effect on the $T_{21}$ relaxation time and its corresponding apparent population ($A_{21}$), which can be correlated to protein denaturation during the cooking process and subsequent loss of water from the cells and pores to the extracellular space. This decreasing trend in $T_{21}$ was slightly stronger in the pH-shift samples than in the conventionally washed samples, indicating slightly more protein denaturation during cooking in the pH-shift processed samples. However, proportionally more water was lost from the restricted population $A_{21}$ to the less restricted water population $A_{22}$ in the conventionally washed samples during cooking. Increasing the salt concentration to 3%, seemed to have a protective effect towards this exchange of water between the $A_{21}$ and $A_{22}$ populations in the conventionally washed samples, while such effects were more subtle in the pH-shift treated samples. Similar trends in the relaxation parameters were observed after 4 and 7 days of storage as well, although the intermediate population $A_{22}$ seemed to be most affected by the processes.

Overall LF-NMR turned out to be an effective quality monitoring tool for the physicochemical changes occurring in the 3D printed samples. Although the analysis did not show any preference between the two processing methods, it can be concluded that increasing the salt content had a preserving effect on the surimi gels, as well as printing of fresh raw materials can be recommended.
What can NMR learn us about how to make a healthy hotdog sausage?

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Consumers’ awareness that diet influences our health is growing, and an increasing demand for healthier food choices has therefore emerged. At the same time consumers are rather conservative and prefer well-known foods (Hoek et al., 2011), which makes it relevant to introduce minor modifications to enhance the nutritional value of existing and traditional foods. The hotdog represents a common and popular fastfood, and the hotdog was in fact the first type of fastfood introduced in Denmark. A hotdog sausage typically contains about 20-25% saturated fat and the content of dietary fiber is diminishing. We decided to investigate if we could improve the nutritional profile of a hotdog sausage while maintaining attractive sensory attributes through partial replacement of fat with rye bran fiber. To ensure satisfactory technological and functional properties, collagen protein was also introduced at various levels to the sausage recipes, and NMR relaxometry was applied to elucidate the impact on the intrinsic water mobility and distribution. In conclusion, our NMR relaxometry study revealed a high ability of collagen to create distinct water-protein interactions in complex meat-based matrices, thereby confirming that collagen is a useful functional ingredient in the manufacturing of healthier meat products undergoing fat reduction/ replacement.

References

Relating crystal properties to water exchange kinetics in W/O/W double emulsions by low resolution $^1$H-NMR-diffusometry

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Low resolution pulsed field gradient $^1$H-NMR-diffusometry was used as a means to evaluate the oil phase permeability in water-in-oil-in-water (W/O/W) double emulsions. These emulsions are comprised of oil globules containing internal water droplets, which are dispersed in a continuous aqueous phase. An internal and external water phase are thus identified, which are characterized by restricted and free water diffusion, respectively. In the event of water transport between the water compartments, $^1$H-NMR-diffusometry offers a fast and nondestructive tool to assess this extra-droplet water exchange in W/O/W emulsions by evaluation of the impact of the diffusion delay time (Δ-value) on the diffusion echo decay. Knowledge about the oil phase permeability is crucial to better understand the retention and release mechanism for encapsulation applications of W/O/W technology. The aim of this study was therefore to unravel the impact of the crystal properties on the barrier function of the solid fat in W/O/W double emulsions. A tempering protocol (i.e. successive heating and cooling of partly melted fat), with three different cooling rates (10°C/min, 1°C/min, 0.1°C/min), was used to alter the fat crystal properties in the W/O/W emulsion. Different techniques revealed that tempering resulted in larger crystals with decreasing cooling rate, while the solid fat content and polymorphic form remained similar. The NMR diffusion curves revealed that the tempered samples with decreasing cooling rates showed increasing extra-droplet water exchange. Hence, the larger the crystal size, the more water exchange, which suggests that the permeability of the oil phase of a W/O/W double emulsions decreases with decreasing crystal size.
Utilization of FFC Relaxometry to Differentiate Frankfurters Made of Different Meat Sources

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In Turkey, using mixture of meats of different animal kinds in the formulation of sausage products has been illegalized to prevent adulteration. Adulteration in food products is usually analysed by PCR which might take some time. As an alternative method to identify adulteration, NMR relaxation and NMRD profiles could be used as fingerprints to differentiate different sausage products.

In this study, it was investigated to determine the characteristics of frankfurters made of different meat sources (chicken, turkey, beef and pork) by using FFC NMR relaxometry. Chicken, turkey and beef frankfurters chosen from the same brand were purchased from a local supermarket in Turkey, while samples produced with pork was procured from a supermarket in Portugal. The study was conducted in both undried and dried frankfurters to determine the effect of moisture on measurements and compare the results obtained from dried treatments to the values of undried samples. Drying process was accomplished by lyophilisation.

In the study, a wide range of frequencies were applied to differentiate the sausage products by the help of three different NMR instruments working at different frequencies. FITTEIA software was used to analyse the data. In the Fast Field Cycling (FFC) instrument, numerous frequency values below 1 MHz and between 1 MHz and 8.9 MHz were tested to obtain NMR dispersion curves (Figure 1). Furthermore, 60 MHz and 300 MHz were also applied in different instruments and the data from all these instruments were merged on the dispersion curves.

According to the results, there were slight differences between $T_1$ values of the frankfurters particularly in lower frequencies and it was inconvenient to differentiate the products. However, in higher frequencies, the frankfurter samples seemed to be easily distinguished through chemometric studies. $T_1$ values for the undried samples were higher than the dried treatments probably due to the effect of moisture.

![Figure 1. T1 values of different sausage samples obtained at different field frequencies](image-url)
TD-NMR to assess the application of heat-treatment on sheep milk and curd

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Heat treatments are commonly applied in cheese production and, beyond affecting milk microflora, they may result in physico-chemical modifications of its components, consequently affecting the final product quality¹. In this work Time-Domain Nuclear Magnetic Resonance (TD-NMR) is applied to determine the effect of heat treatments on the relaxation behaviour of milk proton pools. To this end, fresh milk was daily provided by a local producer during the entire lactation period (December-July). Heat-treated milk was produced by soaking a 10mm NMR tube in hot water (72°C) for 15 (M15) and 20 seconds (M20) while shaking. At least 5 samples of Raw milk (R), M15 e M20 were analysed on a daily basis. Raw-milk curds (RC) were produced by heating 500 ml of milk to 38°C and adding 500 μl of rennet. Curds from heat-treated milk (HC) were produced by previously heating the 500 ml samples to 72°C (15 seconds holding time). RC and HC were acquired in triplicate every day. Milk pH was measured daily. ¹H T₂ and T₁ relaxation curves for milk (T₂: 8000 echoes, tau 0.05 ms; T₁: 20 data points, tau 1-12000 ms) and curds (T₂: 8000 echoes, tau 0.05 ms; T₁: 20 data points, tau 1-10000 ms) were obtained with a benchtop instrument (the minispec mq20, Bruker). A CONTIN Bruker software was used to obtain the distributions and the characteristic relaxation times (population peak maximum) of the detected proton populations.

Milk: ¹H T₁ showed one main population relaxing in the 600-1800 ms range, whose characteristic T₁ times were generally shorter in M15 and M20 than in R. ¹H T₂ distributions indicated the presence of a prevalent population relaxing in the 70-160 ms range (a minor population relaxing at 150-200 ms was also detected in T₂ and attributed to milk fat). Characteristic T₂ times of the main population were generally shorter in M15 and M20 than in R.

Curd: ¹H T₁ showed one population in the range 50-1500 ms, whose characteristic T₁ times were comparable between RC and HC. ¹H T₂ distributions indicated the presence of two populations, relaxing in the 10-25 and 25-65 ms ranges, respectively. Characteristic T₂ times were generally shorter in HC than in RC, mainly for the fastest relaxing population.

The results of this work indicate the potentiality of TD-NMR as a valid tool to detect changes undergone by milk protons during heating.

References

NMR study of fresh cut escarole: influence of temperature and storage time on leaf structure and water repartition

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Consumption of fresh-cut vegetables has rapidly increased over the past decades. Among salads, escarole is one of the most popular varieties. Specific packaging limits gas exchange and consequently water loss and bacterial respiration, increasing in this way the relatively short shelf life of salads. The quality of the raw material has also a great impact on the shelf life of the fresh-cut salads. It is determined by the growing conditions, cooling and transport of the salads and finally by the conditions of the storage before transformation (duration and temperature). These steps can be at the origin of the quality loss, as they induce modifications of tissue structure and consequently the leaf textural changes. Therefore investigating the impact of storage conditions before processing on the structural changes of leaves is important in order to improve the shelf life of fresh cut salads. In this study, we investigated by measurements of transverse NMR relaxation times the impact of storage duration and temperature on complex leaf structure. The storage duration (maximum 12 days) and temperatures (4, 7, 10, and 12°C) have been chosen according to the real conditions registered in a factory. We showed that during the first week, the temperature did not have significant impact on the multi-exponential relaxation times measured on leaves. During the second week, changes in the water status and distribution inside the leaf tissue were observed by NMR before any changes in the visual aspect of salad. These changes were more important for the higher storage temperatures. The present study confirmed the sensitivity of NMR relaxometry for monitoring water changes in leaves during salad storage.

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Real-Time dynamical monitoring of plants status in normal and stress conditions: from Low Fields NMR in laboratory to compact NMR in planta

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Keywords: radio frequency antenna, transportable NMR setup, NMR climatic chamber, NMR relaxation and imaging, eco-physiological biomarkers, biotic and abiotic stresses in plant

Today, understanding how plants respond to water stress is essential to meet the challenge of developing new cultivars and new irrigation strategies, consistent with the maintenance of crop productivity in the context of global change. In this context, the study of plant-water relations is of central interest for modeling plant and organ responses to biotic and abiotic constraints. Paradoxically, there are very few direct and non-invasive methods to quantify and measure the level and the flow of water in plants.

For this purpose, we report on the development of an innovative methodology based on Nuclear Magnetic Resonance relaxometry and imaging at low and high magnetic fields, respectively, to study the water contents, the phloem and xylem transport in sorghum plants. The combination of these approaches allows us to seek new eco-physiological biomarkers and to design experiments in the laboratory and even in field conditions¹.

One particular interesting result concerns the investigation of the spatial distribution of water in stems (knot and inter knot) from T1 and T2 MRI 3D images. The modification of the NMR relaxation parameters during dynamic diurnal cycle will be presented in normal and abiotic stress conditions. A direct application could permit to extract eco-physiological biomarkers which allow to explore and model water fluxes during heat and water stresses and analyze their impact on the development of young reproductive organs.

Finally, we present some developments achieved for the optimization of homogeneity of static field⁴, RF antenna, and NMR sequences in order to build a complete portable NMR device working at 336kHz, with the versatility and thermal conditions to maintain the plant intact.

References

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Multiscale NMR analysis of apple thermal denaturation

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Microstructure evolution of foods during cooking is difficult to assess because of the need of sensitive non destructive technique. To study such phenomena in apple, we undertook MRI, quantitative NMR and mechanical experiments at key temperatures of the cooking process (45, 50, 53, 60 and 70°C). MRI measurements were performed at 9.4 T with a 30mm diameter ¹H volume coil. We acquired 10 SE images at different TE (4.5 to 200ms), with a single echo per acquisition for preventing refocusing errors (TR=3000ms, voxel vol. 1mm³ isotropic, duration 32min) to map T2 assuming a monoexponential decrease. NMR CPMG acquisitions, 90°-x-[τ-180°y-τ-(echo)]ₙ, were also carried out (τ=500µs and n=128). Data were fitted using non-negative least squares algorithm fed with a decomposition basis made of 200 T2 logarithmically-spaced from 1ms to 1000ms. In parallel, we performed puncture tests with a 2mm diameter flat end needle descending at 1mm/min until the strain reached 70%. Both T2 maps and quantitative NMR show a dramatic change in T2 values between raw and cooked parenchyma at a transition temperature of around 50°C. This change can be interpreted by the filling of pores after thermal permeabilization of the cell membranes. The effective T2 obtained by imaging is sensitive to internal magnetic field gradients, due to susceptibility differences (Van As et al., 1997). Then, this T2 is shorter than the CPMG’s bulk T2 in the porous material (before 50°C) and it dramatically increases when the pores are filled. The resistance to a mechanical stress also displays a sharp decrease, for a slightly higher temperature of 53°C. This temperature shift supports the hypothesis of a complex thermal denaturation of the plasmalemma, first releasing vacuolar water before being structurally affected (Bourles et al., 2009). This work emphasizes the interest of multiscale relaxation studies for studying thermal denaturation of food products. CPMG allows resolving multiple T2 compartments in the whole sample whereas imaging is sensitive to heterogeneities.

References
In situ measurement of deposit layer formation during skim milk filtration by MRI

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Filtration and separation via membranes are key processes in food processing technologies. One major application of membrane filtration is in the dairy industry, aiming for the separation of different proteins in milk [1]. The various chemical components of milk possess different physio-chemical properties and can be used most effectively in further food processing if they are separately available and remain in their native state. Microfiltration of skim milk allows a fractionation of the milk proteins casein and whey by size. During the filtration process, a deposit is formed on the membrane surface mainly by micellar casein proteins. Membrane pore blockage by whey proteins and fouling layer formation during the membrane filtration occur [2]. The retained deposit layer consisting of proteins negatively affects the yield of the significantly smaller whey protein fraction (approx. 2 nm) that are supposed to permeate the membrane.

Skim milk filtration and the deposit layer formation was measured time and spatially resolved by in situ MRI [3]. The nature of the fouling layer was investigated during dead-end filtration in ceramic hollow fiber membranes. MRI was used to clarify the influence of operating conditions on the separation and filtration mechanisms which are responsible for fouling layer growth. It is known that filtration parameters such as transmembrane pressure and feed velocity are spatially dependent which makes also the deposit layer formation spatially dependent. The results obtained by MRI measurements were analyzed for a detailed description of a skim milk filtration process.

Methods to Probe Baking with Unilateral Low-Field NMR

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Since several years, the MRIFood team (IRSTEA, France) has developed NMR and MRI techniques to monitor the baking process in bread with the aim of elucidating the transfers of matter and energy in it and the transformation of its constituents (Lucas et al., 2012, Rondeau-Mouro et al., 2015). Within this frame of work, new methods have been developed recently using a low-field unilateral NMR sensor (Perlo et. al., 2005) to probe the transfer of water during this process. As a proof of validation, a 3.5 mm thick sample of dough has been used. It was placed within a homemade thermal control device that takes advantage of the open geometry of the NMR sensor. The device bakes the dough and measures the temperature of the sample. Acquisition of the NMR signal was performed in a 130 um thick slice (the sensitive volume of the sensor) that can be displaced within the sample using a lifting mechanism for the sensor. By this way, profiles of the water content along time could be obtained after temperature-dependent corrections. The “evaporation–condensation–diffusion” mechanism, regarded as responsible for the internal increment of water content in the loaf during baking (De Vries et al., 1989), has been explored in the interpretation of these profiles. Furthermore, insight into the transformation of constituents in dough (starch gelatinization) could be won by the local measurement of the longitudinal relaxation and the coefficient of self-diffusion. Disentanglement of both mechanisms for the evolution of the magnetization could be achieved using a modified saturation-recovery pulse sequence.


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NMR to understand complex food properties

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Many food products can be considered as complex materials having various phases. For example, ice cream consist of 7 phases, including different water phases. Different water phases can occur in materials having different biopolymers, such as protein and carbohydrates, at high concentration. The properties of those phases depend on the exact amount of water present in that phase, and thus the division of the water between the phases. We discovered that TD-NMR is a very useful tool to understand water binding in a multiphase system.

Processing is applied to alter the properties of a food product. Those changes in properties can be related to changes in properties of the phases. Also here, TD-NMR turns out to be a very important tool to understand the effect of heating, shearing, freezing or cooling on water distribution and water-holding capacity (WHC) of food samples.

Whey and plant-based proteins, such as pea, lupin, soy, wheat gluten an their blends, were analyzed (Dekkers \textit{et al.}, 2016, 2018; Peters \textit{et al.}, 2017). Besides, other novel plant-based ingredients, such as rapeseed or sunflower, are nowadays being studied.

Results showed that heating and shearing may not affect soy protein isolate (SPI) and wheat gluten (WG) blends (Dekkers \textit{et al.}, 2018), and variations in water binding are dependent on particles deformability and their ability to bind interstitial water (Peters \textit{et al.}, 2017).

In next research, we will focus on the role of fat in plant-based food samples. For this purpose, both classic and novel plant-based ingredients will be studied with NMR.


Using NMR and MRI to characterize dry cat food physical properties

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Comprehensive studies on cat’s gustative, aromatic and textural perceptions are of huge importance in conceiving new pet food products. Indeed, it has been shown that beside taste, smell and, somesthesia, dry cat food palatability can be strongly influenced by the textural and structural properties of the kibble.

Cat kibbles are roughly composed of a “core” extruded matrix (textured expensed solid matter) coated with fat and palatants in liquid or powder form. These ingredients, that bring sensorial elements to the kibbles, also modify the matrix physical properties. Studying the interactions that occur at the surface of the kibble is thus of particular importance to have a deeper understanding of mechanisms that drive palatability.

Most of the methods traditionally used to describe the physical aspect of kibbles, like apparent density measurement, optical or electronic microscopy, tend to be either destructive and/or gives a literally superficial or too narrow picture of the cat kibble structure.

In that study, two non-destructive methods using NMR signal were successfully used to study the interactions between the ingredients applied in top coating and the kibble matrix:

1) low-field Nuclear Magnetic Resonance allowed to monitor the transfers of water - brought by a liquid palatant or by direct spraying - from the surface to the core of the kibble. It also gave a more global picture of the behavior of macro-components of the matrix such as fat and the dry matter.

2) 2D - Magnetic Resonance Imaging was used on whole kibbles to follow the penetration of the topical fat inside the kibble via the superficial porosity. It allowed having an overview of the behavior of the fat at a limited depth of around 600µm.

These preliminary trials showed that NMR and MRI methods can be successfully used to characterize dry cat food structure. Though they still need to be optimized to better suit the specificities and complexity of dry pet food, they already bring valuable information that complements the physical data obtained with classical techniques.

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The Application of Low Field NMR in food quality analysis and monitoring

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Low field nuclear magnetic resonance technology, including NMR and MRI, is emerging in the 20th century. Compared with other method, the technology is not destructive and invasive, and provide a wealth of information, real-time, rapid measurement, and can realize dynamic, online process monitoring.

It is well known that LF-NMR has widely used in dynamic monitoring food quality change. Besides these conventional applications, it is worth that Niumag Corporation has achieved the world’s first microwave vacuum drying (MVD)-NMR device for dehydrated vegetable research[1], A$_2$ value can be measured online during drying process, at the same time, the moisture content can be calculated through a formula fitting. Likewise, it is available for combined LF - NMR conjunction with temperature and pressure system for in situ, online analysis of samples. LF-NMR is also used in combination with nanotechnology for rapid detection of pathogenic bacteria, viruses and other biomolecules[2]. In the field of nutrition and health, the research of obesity, nutrition research, diabetes and other metabolic diseases based NMR is a hotspot[3]. LF-NMR provides a precise, non-anesthetics, non-destructive, stress-free measurement of lean tissue, fat, and fluid in live mice. Please visit our website for more information: www.nmranalyzer.com

References


Conventionally vs. Organically Produced Eggs: Differentiation with NMR

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Both the European and global organic food markets are growing fast, and there is also a rising demand for organic chicken eggs. Consumers are willing to pay higher prices for organic eggs produced in an animal appropriate environment considering animal welfare. Strict labelling requirements do not prevent chicken eggs from being a subject of food fraud. Conventionally produced (barn/free-range) eggs can easily be mislabeled as organic eggs. Especially since the demand for organically produced chicken eggs is likely to exceed supply in the future mislabeling appears to be a realistic scenario. Therefore, there is a need for analytical methods that are suitable to classify eggs as being either conventionally or organically produced.

Nuclear magnetic resonance spectroscopy in combination with multivariate data analysis is a suitable tool to screen eggs according to the different systems of husbandry. Sample preparation is based on a fat extraction method previously reported by Folch et al. [2], which, however, required optimization for its application to freeze dried egg yolk. Samples were analyzed using typical q-NMR parameters. In total, 288 chicken eggs (194 barn/free-range eggs and 94 eggs from organic farms) were used to build and validate the prediction model.

A non-targeted approach was used for the analysis of the $^1$H NMR data. Principle component analysis was applied followed by a linear discriminant analysis (PCA-LDA) and Monte-Carlo cross validation. The results showed that the prediction model allowed for the correct classification of about 90% of the organic eggs (Figure 1).

References

Revisiting the Isotope Analysis of Vanillin by Anisotropic $^2$H NMR: an Original Tools against the Counterfeiting of Food Aroma?

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The evaluation of the site-specific, natural isotopic composition of (bio)-compounds in food products is a continuous challenge for the authentication/determination of their origins. Historically, $^2$H SNIF-NMR$^\text{®}$ based on the quantitative, natural abundance deuterium (NAD) NMR in isotropic organic solvents has been exploited for various authentication issues [1,2].

In this work, we exploit the analytical potential of NAD 2D-NMR in lyotropic liquid crystals for revisiting the ($^2$H/$^1$H) isotope information of vanillin, one of the most used food aroma. Compared to SNIF-NMR$^\text{®}$ protocol, the NAD NMR gives access to all order-sensitive NMR interactions such as the $^2$H residual quadrupolar couplings ($^2$H-RQCs) [3]. In case of vanillin, the spectral discrimination of all aromatic monodeuterated isotopomers becomes possible on the basis of $\delta^{\text{max}}$($^1$H) and $^2$H-RQCs [3,4], thus leading for the first time to the complete experimental determination of the relative distribution of ($^1$H/$^2$H) ratios in the aromatic ring.

From the analysis of their isotopic profile, we demonstrate how the determination of ($^1$H/$^2$H) fractionation on all aromatic positions provides a new analytical tool for distinguishing between biological and synthetic origins of the aromatic core [4].

Targeted and non-targeted $^1$H-NMR based Methods for Authenticity and Quality Control of Food

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Food supply networks continue to grow in scale and complexity, and deliberate food fraud, driven by the prospect of economic gain, is an emerging risk alike. High-priced food products, but also those with high volume of sales, have turned out to be most vulnerable to adulteration.

The emergence of more and more sophisticated food analysis techniques has dramatically forced back overt falsifications, but is inevitably a trigger to subtilize adulteration methods. The key to profile food quality economically, and increase the detection rate of "smart" adulterations is a fast and efficient analytical technique which is able to cover the range from whole matrices down to single compounds.

Due to its unique "all-in-one" capabilities, high-resolution $^1$H-NMR spectroscopy, combined with multivariate statistical chemometrics, is the screening methodology of choice for food quality and authenticity control.$^{1,2}$

As $^1$H-NMR is intrinsically quantitative, only one quantification reference for all NMR-detectable components in a mixture is required. Yielding targeted quantification of selected compounds as well as untargeted fingerprinting in a single run, NMR is a specific and holistic method likewise. Its supreme reproducibility enables worldwide lab-to-lab spectra comparison and collective database buildup. Unlimited data re-processing is given and allows to apply future statistical algorithms, re-modelling of more or different parameters, or retrospective quantification of mixture components not in the focus of interest at present.

Our portfolio of fully automated and ISO-17025 accredited food profiling methods covers fruit juice$^3$, wine$^{4,5}$ and honey screening at present, and further methodologies are under development.

The principles behind this NMR methodology as well as recent applications are presented.


Balsamic vinegar affects the digestion of carbohydrates and proteins in food, as assessed by NMR spectroscopy applied to in vitro models

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Usually, digestion of foods is investigated without considering the reciprocal interference among the different components of a meal, which could be exerted either at the substrate or at the enzymatic level. Such underestimation affects the assessment of the actual bioaccessibility, and then the bioavailability, of nutrients and other bioactive compounds. For this reason, the effect of excipient ingredients and condiments must be correctly considered in the studies dedicated to the evaluation of the digestion steps contributing to the nutritional value of foods consumed in a meal.

The aim of this study was to evaluate the impact of balsamic vinegar of Modena IGP on the digestibility of some illustrative foods. The foods included in the study were bresaola [1], Parmesan cheese [2] and boiled potatoes [3].

The three different food products were digested in vitro according to Minekus et al., 2014 [4]. Digestions were conducted under the same conditions and quantities of food, either in presence of vinegar or acetic acid, as well as in absence of vinegar as the control system. The resulting digestion fluids were analysed by nuclear magnetic resonance (NMR) and by Bradford protein assay. While NMR allows detection of soluble peptides of whatever size, and proteins released during digestion, the Bradford method is used to measure the concentration of proteins and large peptides (>2kDa), even if scarcely soluble. Thus, the two methods provide a complementary picture of the digestion process, allowing a more complete evaluation of the different effects exerted by vinegar on the digestion of proteins and starch, depending on the food.

Vinegar seems to have an enzyme-specific and matrix-specific action on the digestion of food products: in potatoes, vinegar inhibits pancreatic amylase, whilst in Parmesan cheese, but not in Bresaola, it causes a greater protein digestion, justified by a different supramolecular structure of the food matrix.

Acknowledgement:
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References
C-NMR-based isotopomics for food authentication

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Food industry is a fertile ground for fraud and adulteration. NMR emerged as a powerful analytical tool for food authentication. It is used for metabolomic analysis and position-specific isotopic measurements of target molecules, such as lipids. Their isotopic fingerprint and metabolomic profile are influenced by the geographical and botanical or animal origins of the matrix, weather conditions, and, in the case of products of animal origin, the animal’s nutrition.

In a previous work, Lebanese olive oils were classified according to their sub-regional origins using 1H [1] and 13C [2] NMR of triglycerides. The aim of the present work is to be able to use other lipid fractions, such as cholesterol and phospholipids, in order to avail of the complete isotopomic profile of the lipid fraction. 27 isotopic variables can be calculated from the 13C NMR spectra of cholesterol due to the presence of 27 carbon sites. On the other hand, the analysis of phospholipids enable to distinguish between sn-1 and sn-3 carbons of the glycerol backbone. In this respect, egg yolk was chosen as a model matrix, being easy to handle and rich in lipids. The extraction procedure was optimized to avoid isotopic fractionation and to permit a precision (per mil) required for isotopic 13C NMR.

Egg samples from different Lebanese traditional and industrial farms were collected, and triglycerides, phospholipids, and cholesterol were isolated. The pulse sequence (adiabatic INEPT sequence [3]) and deconvolution procedure of 13C NMR spectra were optimized in order to reach the desired high precision. 13C NMR spectra were recorded on a 500 MHz spectrometer, and peak areas were obtained from curve fitting, carried out in accordance with a Lorentzian-Gaussian mathematical model using at least five parameters for each peak: position, height, linewidth, phase and Gaussian-to-Lorentzian ratio. The determined peak areas were used as descriptors in the construction of multivariate models for the classification of egg samples according to their origin or to the corresponding farming system.

References


Acknowledgment

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Identification of roasting markers of *Coffea arabica* L. seeds in coffee beverage through NMR fingerprinting and chemometrics

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Roasting of *Coffea Arabica* L. seeds gives rise to chemical reactions that produce more than 800 different compounds. Some are responsible for the desired organoleptic properties for which the beverage called “coffee” is known. In the industry, the roasting profile is thus key to influence the composition of roasted coffee beans and the subsequent flavour of the beverage. The impact of roasting on the chemical composition of coffee has been the subject of numerous studies, including by NMR spectroscopy. However, the roasters and the roasting profiles applied in these studies are often far from real industrial conditions. In our work, the effect of two critical technological parameters of the roasting process on coffee beverage were investigated by NMR fingerprinting, namely the "development time" (i.e. the period of time after the "first crack", a characteristic noise due to seed disruption) and the final roasting temperature. Seeds were roasted at pilot scale according to 5 industrial roasting profiles and extracted in D\(_2\)O. The extracts were analyzed by \(^1\)H NMR experiments. The obtained NMR spectra were compared using (i) quantitative analysis of main signals by successive orders of magnitude and (ii) recent chemometric tools (Sparse PLS). This allowed to identify compounds which may serve as markers of realistic development times and final roasting temperatures.
NMR metabolomics: a useful tool in aquaculture feed development

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Objective: In a context of limited marine resources and continuous development of aquaculture, developing aquafeeds with a reduced content of fish-ingredient is a real challenge. NMR metabolomic profiling was chosen to characterize the content in small hydrosoluble molecules of three experimental feeds for trout: a plant-based (P), a fish-based (M) and a commercial-like (C) feed which have been tested in a long-term fish nutrition experiment. Along the last month of the experiment, pellets of the three feeds were sampled at different times: 0, 2 and 4 weeks after their preparation to assess the stability of their composition.

Methods: Feed extracts were prepared by a hot ethanol/water series solid-liquid extraction\textsuperscript{[1]}. After evaporation, extracts were solubilized in deuterated buffer solution and pH–adjusted. Quantitative \textsuperscript{1}H-NMR spectra were acquired on a Bruker AVIII 500 MHz spectrometer with an ATMA BBI 5-mm probe. The main compounds were identified by comparison with spectra of commercial compounds, and validated with specific acquisition and/or by spiking the samples. Spectra processing and compound concentration calculations were performed with NMRProcFlow\textsuperscript{[2]} tool.

Main results: More than 30 water-soluble compounds were identified and quantified. Numerous compounds showed significant differences between the three feeds, some of them being specific of either fish or plant-based feed. The stability of these compounds during storage of the feed for one-month was assessed successfully. The larger changes were observed in the M and the C feeds compared to the P feed.

Conclusion and perspectives: The \textsuperscript{1}H-NMR-based compositional differences of the feed could explain part of the differences in feed intake by fish between P vs M feed. The feed effect on fish will be studied using \textsuperscript{1}H-NMR profiling of fish plasma and tissues. NMR metabolomics is a useful tool for aquaculture feed characterization and fish nutrition studies.

References

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We warmly thank the technical staff at the INRA experimental facilities of the fish farm (Donzacq, France). This work was funded by European project ARRAINA Advanced Research Initiatives for Nutrition & Aquaculture (FP7-KBBE-2011-5 N°288925) and MetaboHUB project (ANR-11-INBS-0010).
Salmon metabolomics: metabolic profiling of plasma and fecal samples by NMR reveals biomarkers of gut condition in farmed salmon

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The fish immune system is intimately related to the microbiome and functionality of the gastrointestinal tract. Optimal intestinal and digestive functions have been demonstrated to be essential prerequisites for the production of a healthy and robust fish. Occasionally, the aquaculture industry reports compromised gut function in farmed salmons and early research suggests that the increasing levels of plant ingredients in feeds can be an important contributing factor.

This work applies for the first time an untargeted NMR metabolomics approach to investigate the metabolome of plasma and fecal (pyloric caeca and distal intestine) samples obtained from 120 smolts. The salmons were collected from 6 different farming sites in Norway in December 2017. Histological examination of the intestinal tissues was carried out to determine the health status of the fish. Plasma samples and fecal extracts were measured by \(^1\)H-NMR spectroscopy. Standard operating procedures (SOPs), developed for the high-throughput analysis of human plasma samples, were applied for the first time to analyze salmon plasma. Several metabolites were identified including cholesterol, \(\omega-3\) fatty acids (i.e. eicosapentaenoic and docosahexaenoic acids), phospholipids (i.e. phosphatidylycerine and phosphatidylethanolamine), organic acids (i.e. lactic acid) and amino acids (i.e. alanine and phenylalanine). Amongst the identified metabolites, lactic acid was found to be particularly abundant in the plasma of salmons with gut inflammation. The analysis of the fecal samples evidenced similar metabolic composition for pyloric caeca and distal intestine specimens. In particular, amino acids (i.e. methionine), organic acids (i.e. lactic acid) and sugars (i.e. \(\beta\)-glucose) were found to be the main components of the fecal samples.

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A large subset of the European population lives at risk-of-poverty [1]. This group, characterized by a low income, differs in age, culture and ethnicity among the different EU countries, and could be facing nutritional deficiencies due to bad dietary habits, related to their socio-economic status.

In this study, the human urine metabolome of people at risk-of-poverty (ROP) was compared to that of affluent (AFF) subjects through the employment of 600 MHz proton \(^1\)H-NMR spectroscopy. A total of 1391 subjects were recruited in five EU countries (United Kingdom, Finland, Italy, Lithuania and Serbia), obtaining 2732 urine samples, which were explored using multivariate data analysis. ANOVA-Simultaneous Component Analysis, also called ASCA [2], is employed to partition the study design effects. ASCA revealed that most of the urinary variation was due to gender and “country of origin” effects (ethnicity and cultural food habits). However, the economic status was proven to display a weak effect, which in the more homogeneous Lithuanian cohort was more pronounced. The level of the common metabolites citrate and hippurate proved to be amongst the most powerful biomarkers of ROP which in turn can be linked to nutritional deficiencies and poor dietary habits in the ROP population.

References

Quantitative $^{13}$C INEPT Method for the Detection of Fatty Acid Composition of Vegetable Oils

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Fatty acid composition of edible vegetable oils has commonly been determined by GC or GC-MS. The cumbersome methyl esterification treatment must be performed in these methods. Since it doesn’t need complicated sample pretreatment and has the advantages of fast, effective and high reproducibility, NMR has been applied for the quality detection and authentication analysis of vegetable oils. Quantitative $^{13}$C NMR spectroscopy has been employed to detect fatty acid composition of vegetable oils. However, due to the lower sensitivity and long $T_1$ relaxation time, it takes much longer time to obtain quantitative results with inverse gated $^1$H decoupled $^{13}$C NMR experiments. In order to enhanced signal intensity and faster repetition rate the polarization transfer techniques were introduced into $^{13}$C quantitative NMR, such as Q-DEPT+ and Q-INEPT-CT.

In this study, an improved quantitative $^{13}$C INEPT method (Quantitative Refocused INEPT with Adiabatic Pulses, Q-RINEPT-AP) was employed to detect vegetable oils and analyze fatty acid composition. In the method, an optimized delay set (including 8 pairs of polarization transfer and refocusing delay time) was cycled to achieve uniform signal enhancement for different types of $^{13}$C groups across a broad range of $^{1}J_{CH}$ coupling constants (115 - 170 Hz). Adiabatic inversion (Crp60.05.20.1) and refocusing (Crp60comp.4) sequences were used to overcome the inhomogeneity of $B_1$ field and the offset effect. As shown in Fig.2, the Q-RINEPT-AP experiment requires less time and number of scans to achieve similar signal-to-noise ratio compared with the quantitative inverse-gated-decoupling $^{13}$C experiment employing a 45° pulse. The different species of vegetable oils demonstrated different characteristic resonances from a variety of fatty acid in $^{13}$C NMR spectra. The specific fatty acid composition was calculated using the integral values of the corresponding resonances ($\text{C}_{9}$ for oleic, $\text{L}_{10}$ or $\text{L}_{12}$ for linoleic, $\text{Ln}_{15}$ or $\text{Ln}_{16}$ for linolenic, C-3 for all fatty acid as a reference). Tab.1 shows that results obtained by Q-RINEPT-AP were agreement with those from GC. It indicates that quantitative $^{13}$C INEPT method is simple and feasible for fast and accurate determination of fatty acids of vegetable oils.

![Q-RINEPT-AP pulse sequence.](image1)

![A quantitative inverse-gated-decoupling $^{13}$C spectrum (A) compared to Q-RINEPT-AP spectrum of soybean oil. The total measurement times were 180 min and 13 min for (A) and (B), respectively.](image2)

Tab.1. Fatty acid composition determined by NMR and GC

<table>
<thead>
<tr>
<th></th>
<th>Q-RINEPT-AP</th>
<th>GC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O L Ln Ln S</td>
<td>O L Ln</td>
</tr>
<tr>
<td>Rape</td>
<td>48.2 19.2 8.6 24.0</td>
<td>47.6 19.5 8.0 24.9</td>
</tr>
<tr>
<td>Soybean</td>
<td>21.4 52.7 6.2 19.7</td>
<td>21.3 52.8 6.7 19.2</td>
</tr>
<tr>
<td>Corn</td>
<td>28.0 53.2 - 18.8</td>
<td>27.7 52.7 0.5 19.6</td>
</tr>
<tr>
<td>Olive</td>
<td>78.0 4.5 - 16.8</td>
<td>76.3 4.5 0.6 16.8</td>
</tr>
</tbody>
</table>

(O, Oleic; L, Linoleic; Ln, Linolenic; S, Saturated fatty acid)

MRI flow cell development to monitor in-situ and in-real time dissolution of porous food products

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Many food products and ingredients are stored in dry form until meal preparation. Consumer appreciation of such products is for a major part determined by their dissolution behaviour. Macroscopic assessment of dissolution behaviour provides only limited insight in mechanisms by which water enters porous food materials. For this purpose, an experimental MRI flow cell setup was designed and implemented on a Bruker 300 MHz NMR wide bore system for non-invasive μ-imaging of water ingress and dissolution.

Measurements can be performed in-real time and in-situ under consumer relevant convection and temperature (ambient to 95°C) conditions. Convection of water was achieved by continuous flow from a water reservoir of 5 litres with adjustable flow rate. Water ingress profiles were obtained using a Flash sequence and acquired as a 2D sample slice with a minimum achieved time resolution (including I/O handling) of 8 seconds. Water mobility (T2) maps were recorded in stop-flow conditions on a time average of 2 - 4 minutes.

The data were processed with home-written Matlab codes, which allowed for fast import, image intensity normalisation, background correction, rotation and ROI selection. The ingress profiles allowed to study the effect of porosity and swelling on water diffusion regimes in a wide range of food products. Examples will be provided of composite savoury products where porosity and presence of swelling ingredient can have a pronounced impact on water ingress and ultimately dissolution behaviour.
NMRProcFlow: A graphical and interactive tool dedicated to 1D spectra processing for NMR-based metabolomics

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Although metabolomics by 1D NMR spectroscopy has become a common approach, multiple challenges in spectra and data processing remain to be solved. Unlike techniques coupled with mass spectrometry, 1D NMR spectroscopy has only one dimension on which we can rely, and apart from very well-mastered and very reproducible use-cases, the implementation of 1D NMR spectra processing workflows within a Virtual Research Environment (VRE) and operating automatically in order to be widely used by non-expert users has not yet reached full maturity. Indeed, the expert eye is often required and even crucial to disentangle the intertwined peaks and the best way is to proceed interactively with a 1D NMR spectra viewer.

To fulfill this need, we have been developing NMRProcFlow\textsuperscript{[1]}, an interactive 1D NMR spectra processing (\textsuperscript{1}H & \textsuperscript{13}C) dedicated to metabolomics. It has been built by involving NMR spectroscopists eager to have a quick and easy tool that greatly helps spectra processing and that can be used also by new-comers. For each of the two major metabolomics approaches, namely Metabolic Fingerprinting and Targeted Metabolomics, the workflow covers all steps from spectral data up to data matrix output. Moreover, the possibility of visualising the experimental factor levels within the NMR spectra set through a spectral viewer makes the tool valuable to create links between the experimental design and subsequent statistical analyses, and thus facilitates interactions between biologists and NMR spectroscopists. In addition, NMRProcFlow allows experts to build their own spectra processing workflows, in order to become models applicable to similar NMR spectra sets, i.e. stated as use-cases.

NMRProcFlow handles Bruker, JEOL, Varian and nmrML formats. It is accessible online (http://nmrprocflow.org), or alternatively, a virtual machine for local installation can be downloaded.

Reference


Acknowledgment

We thank the worldwide community of NMRProcFlow users for their valuable feedback that has inspired relevant developments since its first official release in July 2016.
Signature Mapping (SigMa): A new semi-automatic tool for rapid processing of urine and blood 1D $^1$H-NMR metabolomics data

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The 1D $^1$H-NMR measurement of human urine and blood generates data that contain chemical information of about one hundred of the most abundant metabolites consistently present in both types of bio-fluids. Retrieving this metabolite information from the complex NMR spectra is a bottleneck of metabolomics studies dealing with hundreds and thousands of samples. The processing of NMR spectral ensembles of urine and plasma is challenged by three major problems: 1) the chemical shift of the same signal may change across samples due to differences in pH, ionic strength and/or deviations in sample preparation. This hampers signal alignment and identification; 2) signal overlapping caused by the complex metabolite cocktails present in the biofluids which in turn complicates signal deconvolution, quantification and identification; 3) baseline drifts, that occur due to matrix effects and/or deviations during the measurement, further complicate signal quantification. Currently, the NMR metabolomics world uses two different approaches to convert complex spectral data into an informative metabolite table. The first approach is based on processing one spectrum at a time and extract signals of known metabolites using prior knowledge and/or deconvolution techniques to extract signals of known and unknown spin systems. The second approach employs data mining techniques to process all samples simultaneously through signal alignment, baseline correction, and quantification of deconvoluted or binned signals. However, in the presence of the above-mentioned three major problems, both approaches are bound to fail when it comes to processing hundreds and thousands of NMR spectra of complex samples like urines.

This work demonstrates the development of the Signature Mapping (SigMa) approach for semi-automatic processing of urine and blood 1D $^1$H-NMR metabolomics data. SigMa converts a raw NMR spectrum into an informative metabolite table ready to be used for multivariate data analysis. The engine behind SigMa incorporates six major operations: 1) Referencing NMR spectra to the TSP signal at 0.0 ppm; 2) Identification of Signature signals of known metabolites and unknown spin-spin systems; 3) Iterative alignment of NMR spectral intervals of signature signals using iCoshift [1]; 4) Baseline correction and deconvolution of aligned signature signal intervals using Multivariate Curve Resolution (MCR) [2, 3]; 5) Binning complex spectral regions that do not contain signature signals (step 2); 6) Generation of the final metabolite table which contains the MCR scores of signature signals as well as bins of unsorted complex spectral regions.

The new SigMa approach offers a pragmatic rapid, reliable and user-friendly spectral processing for the NMR metabolomics world eliminating the omnipresent bottleneck. The MATLAB source code of SigMa is available at http://models.life.ku.dk/algorithms.

A new algorithm for wines authentication by joint $^1$H and $^2$H NMR spectroscopy

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A new methodology of cumulative screening by quantitative $^1$H and $^2$H NMR spectroscopy (CS-qNMR) is developed for the rapid control of natural wines authenticity. The algorithm includes three stages. Stage 1 – control the correspondence of the molecular composition of wines from qNMR $^1$H by content of the dominant (water, ethanol, glycerin) and some minor (other alcohols, organic acids and amino acids) components. Determination of total content of the all exchanging hydrogen atoms of fragments OH (the signal $^1$H with a chemical shift of 4.8 ppm), integral intensity of which is necessary for stage 2. Stage 2 – calculation the $^2$H isotope content for detection of water addition in wine from intensity of signal at 4.8 ppm in qNMR $^2$H spectrum using an internal or external standard with a known increased content of the $^2$H isotope. Calculated value is compared with value for tap water of interesting viticulture area. Official method (EU Regulation 555/2008) is based on analysis by IRMS the isotopic ratio $^{18}$O/$^{16}$O ($\delta^{18}$O ‰) of wine water after prolonged extraction by isotopic equilibration with CO$_2$ and the comparison this value with reference values from official wine data bank. Our method is much faster than the IRMS method. The measuring cycle takes 1 hour for one wine sample without any sample preparation (spectrometer NMR Jeol JNM ECA 600, sample tube 10 mm, measurement error ≤ 2 ppm). Stage 3 – detection adulteration of wine by addition exogenous sugar before fermentation. Our approach has some differences from official method SNIF-NMR. The main differences are the use of enriched $^2$H internal standard and measurement of integral intensities of all signals instead of height. It allows to reduce the time of the experiment and to measure the $^2$H contents for all fragments of the molecules of ethanol (CH$_3$, CH$_2$, OH). New algorithm was successfully tested for series white and red authentic wines of 2015, 2016 and 2017 yields from Krasnodar region – the main producer of natural wine in Russia.

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Can CEST contrast image gluten network?

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Non-coeliac gluten sensitivity (NCGS) is a major issue in our occidental countries. Unfortunately, the medical causes of this NCGS are unknown. One hypothesis to explain the development of the gluten sensibility deals with a longer and more complex gluten network leading to a lower digestibility. However, while the gluten is suspected to be responsible for the NCGS, it does not exist yet a non-invasive analytical method able to image the gluten network in food products.

The gluten network is made from the formation of disulfide bonds from thiols moieties. From a chemical point of view, it is dealing with an oxidation process and the loss of exchangeable protons. Chemical exchange saturation transfer (CEST) is an indirect metabolic contrast imaging the exchangeable protons [1]. While this method has been successfully applied to hydroxyl and nitrogen based moieties, the proof of concept on thiols functional groups has not yet been realized. In this presentation, we first demonstrate that thiol moieties are sensitive to CEST contrast. Then, we study the CEST effect obtained from dough products. Due to the presence of significant magnetization transfer effect of the immobile macromolecules, the CEST effect is not visible anymore in the experimental data. To extract the CEST effect from thiol moieties, our data were fitted with a 3-pool model [2].

We show that CEST might be an interesting contrast to detect gluten network. However, to obtain a reliable imaging method of the baking products, it will be important to limit the macromolecule magnetization transfer compared to the CEST effect.


Selective oil-phase rheo-MRI velocity profiles to monitor heterogeneous flow behaviour of oil/water food emulsions

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Rheo-MRI is becoming an established technique in food soft matter research. Since NMR imaging (MRI) allows to acquire velocity profiles of the sample during shear, it is possible to determine the structure and rate of deformation of the material non-invasively\textsuperscript{1}. In the past years, rheo-MRI has been successfully applied to the characterization of multi component food materials, in particular to assess their behaviour as shear thinning yield stress fluids. The velocity and density profiles obtained by rheo-MRI allow for unambiguous recognition of shear banding and non-local properties.

In the current work we have addressed the study of non-linear flow of oil/water and mayonnaise systems by means of rheo-MRI in a standard micro-MRI probehead of a wide bore 7 T system ($^1$H NMR frequency of 300 MHz). At this high magnetic field oil/water food emulsions display well resolved NMR spectra with a 3.5 ppm separation between the main oil and water peaks. This provided the opportunity to specifically record the local density and velocity of the oil droplet phase. We have modified the standard spin-echo sequence to measure flow by adding chemical selective signal suppression pulses. In this way, suppression of the signal of the continuous water phase allowed to obtain rheo-MRI velocity profiles of the oil droplet phase with high signal to noise ratio. This approach was successfully applied to mayonnaises with distinct shear thinning yield stress properties.

Quantification of water sorption in starch-glycerol extrudates by MR micro-imaging

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Starch is widely used in controlled release systems because it is a high purity biocompatible and biodegradable material, which can be easily metabolized in the human body [1]. The ingress of water in starch is therefore of great interest because of its relevance for the formulation of controlled release materials. Over the past decades, the magnetic resonance micro-imaging technique (MRµI) has proven to be an extremely reliable tool for measuring the water ingress during sorption and swelling of polymers used in a wide range of fields (food, pharmaceutical formulations, medical implants etc.) [2]. However few studies present quantitative measurements when the sample of interest changes over time or in case of a long acquisition time. In this domain, two challenges have to be overcome: the introduction into the probe of a phantom as a reference signal and the guarantee that this signal is stable over the experiment duration while some conditions such as temperature and/or the moisture are varied. For that, we implemented a dedicated experimental set-up to generate a virtual phantom (ViP) signal in images [3]. We will present its advantages and application to monitor the water sorption of a potato starch blend containing 20% glycerol that was shown to have interesting properties for biomedical applications. The relationships between the water rotational mobility (using T2 maps) and the water transport diffusion (using proton density maps) were analyzed. The rate constants for water diffusion and the starch swelling extracted from the proton density images showed that starch-glycerol blends exhibited a Fickian diffusion (type I) behavior at first step of the water uptake (400min). This kinetic revealed that the water concentration gradient was the driving force for its diffusion into the extrudate while glycerol was released into the surrounding aqueous phase. With time, the water intake of the starch-glycerol extrudates was slower due to the competition between the crystallization of starch and penetration of the water [4].


An Investigation of Water/Bovine Milk Interactions with κ-carrageenan Using Fast-Field Cycling NMR Relaxometry and Viscosimetry

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The dynamical properties of κ-carrageenan gels in water and bovine skimmed milk was investigated with $^1$H Fast Field Cycling (FFC) NMR relaxometry accompanied with viscosity measurements. $T_1$ values were measured using SpinMaster FFC-2000 produced by Stelar Srl (Mede, Italy) in the range of 4 kHz-30 MHz (referring to $^1$H Larmor frequency). The viscosities of the systems under investigation were controlled using DV3T Brookfield viscometer equipped with UL Adapter.

While spin-lattice relaxation of aqueous carrageenan gels is almost frequency independent regardless of temperature and concentration, gels with milk reveal large dispersion. The log-log plot of the relaxation rate dispersion profile of bulk milk reveals a nearly linear region (the power-law dependence) from 30 kHz to 30 MHz with a plateau at low frequencies. Relaxation get faster with increasing polysaccharide content denoting that overall dynamics in the system slows down.

So-called quadrupolar maxima arise at 1.5-3 MHz range even for liquid milk samples. For rigid milk gels (with carrageenan concentration above 0.5%) another set of quadrupolar maxima emerge at low frequencies. These two triplets indicate $^1$H-$^{14}$N interactions modulated by slow dynamics; their position allows to calculate quadrupolar coupling constants and asymmetry parameters describing local fields.

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Characterization of different cultivars of European Olea L.

using MRI techniques

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The olive tree (Olea europaea L.) is a typical Mediterranean plant, particularly adapted, therefore, to temperate regions characterized by long and dry summer seasons. It is an evergreen arboreal plant of medium development (4 - 8 meters height). The fruit of the olive tree is a drupe of variable weight (between 0.5 and 20 g), formed by epicarp, mesocarp, endocarp and more internally from the seed. The quantitatively most important components of the fresh fruit are water (40-70%) and fatty substances (6-25%), mainly contained in the mesocarp. The fruit can be used both for extraction oil and for direct consumption. The oil is mainly present in the pulp (16-25% of the fresh weight) and limited in the almon of the olive drupe (1-1.5% of the fresh weight). The quality and yield of olive oil changes significantly depending on the cultivar considered. In this study, Magnetic Resonance Imaging (MRI) was used to characterize several olive cultivars of region Campania-Italy (Pisciottana, Coratina, Frantoio, Locale). The main advantages of MRI techniques are: simple sample preparation, non-invasive and non-destructive analysis, overall evaluation of the characteristics of the fruit. The MRI experiments were performed with a Bruker ASCEND™ 300 MHz wide bore 89 mm spectrometer with a MicWB40 microimaging probe. T$_2$ and T$_1$ maps for each cultivar have been produced using Multi-Slice Multi-Echo and Inversion Recovery sequences respectively. From the maps we can extract the T$_1$ and T$_2$ histograms. Through a PCA analysis (Principal Component Analysis), it has been possible to characterize the different cultivars.

References

Diffusion in different polysaccharide gels

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The textural properties of gel-based foods are mostly influenced by gelling agents, which immobilize water and other low molecular weight compounds in a three-dimensional network. Besides gelatin, polysaccharides of various origins and with very heterogeneous structural composition are the most important gelling agents. Structural differences between the polysaccharides result in various mechanisms by which polysaccharide chains form three-dimensional networks. Widely established mechanisms are (cation induced) aggregation of helices, ionic cross-linking via divalent cations, or covalent cross-linking. Depending on the type and structural composition of the polysaccharide and the production conditions of the gel, significant variations in regards to gel strength as well as diffusion properties of small molecules and ions may be observed. Diffusion processes are essential to understand transport and retention phenomena in this class of food systems, because they are thought to influence product parameters like texture, sensory and storage properties. Geometric hindrance, chemical exchange processes and adsorption are parameters that are usually used to describe differences in the diffusion in gels on the microscopic level [1]. In this preliminary study, NMR spectroscopy was used to assess the diffusion properties of small molecules and ions in well characterized polysaccharide gels of varying structural composition and gel formation mechanisms.

Alginate was used as a commonly used gelling agent, which is cross-linked by divalent cations described within the “egg-box” model. In contrast, carrageenans, agar, and agarose form thermo-reversible gels, which result from the (cation dependent) aggregation of polysaccharide helices. To investigate covalently cross-linked gels, pectins were extracted from sugar-beet pulp and cross-linked by oxidation of ferulic acid residues.

It was already demonstrated that the effective \textsuperscript{1}H diffusion coefficients, determined by pulsed field gradient stimulated echo (PFG-STE) NMR [2], depend on diffusion time. This dependence can be described within the model of tortuosity, i.e. geometric hindrance of diffusion and thereby by a limitation of the mean free path length. If so, the diffusion coefficient is also a function of the swelling degree, which is accessible by varying the polysaccharide-to-solvent ratio. Another significant parameter is the size of the diffusing moiety, which should reflect the geometric hindrance. Adsorption and chemical exchange processes were addressed by exploring hetero-nuclei concerning relaxation, spectral and diffusion properties.

First experiments showed the influence of the above mentioned parameters, i.e. of diffusion time, swelling degree, size of diffusing moiety, and electrostatic interactions. Results of \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{23}Na NMR experiments gave some insight into the mechanisms, which determine diffusion in food gels.

References

Increasing the value of cod head by-products by LF-NMR

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The present project investigated the physical and chemical properties of various different parts of Atlantic cods’ head (brain, eyes, gills, cheek, and tongue) with the aim of promoting further development of valuable by-products from Atlantic cod (Gadus morhua). Cod heads of different sizes were collected in two different seasons (May and November) and analyzed by low field NMR, as well as traditional physical and chemical analysis for reference.

The obtained NMR relaxation curves were analyzed with principal component analysis (PCA) to give an overview of the spectral data (Figure 1). The PCA revealed a clear difference between the eyes and brain compared to the more muscle based tissues in the cheeks, tongue and gills. Discrete fitting of the relaxation data showed that the brain and eyes generally showed dominating populations of freely moving water with low restriction or interactions to macromolecules. The amount of water in the eyes got proportionally more restricted with increasing fish size. Differences within the tongue, cheeks and gills between seasons or size of the fish were more subtle. The shortest relaxation times were observed in the gills. However, the muscle based tissues in the gills, tongues and cheeks all had dominating populations with relaxation times below 100 ms, referring to water within the myofibrils, as well as intramuscular lipids.

The analysis clearly indicated that the water and lipid distribution and characteristics were very dependent on the part of the head analyzed, which gives good reason of further investigations and utilization of each part of the head individually.

Figure 1. PCA of NMR relaxation data. All data was maximum normalized prior to analysis and the samples were marked and colored according to the part of the head that they were taken from.
Monitoring the Fermentation of Kefir Milk with Magnetic Resonance Imaging

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Kefir, Kephir or Búlgaros is a fermented milk product originally from the Caucasus Mountains. A small quantity of a bacterial starter, termed a grain, is added to animal milk which is then left overnight to undergo fermentation at room temperature. The resulting product is similar to a thin yoghurt which is slightly sour. The starter grains themselves are complex both from a compositional viewpoint with a structure similar to that of a cauliflower floret, and also from a biological viewpoint with a great diversity of bacteria and yeasts making up the grain. Throughout the fermentation process, the grains can be seen visibly to produce gas bubbles which in some cases lead to the grains rising to the surface. The initial trapping of these bubbles makes traditional fermentation rate measurements as a function of time challenging and offers an exciting opportunity for MRI. In this study, we investigate strategies to maximize the rate of the fermentation process and to yield a more consistent result. It is not well known if the colony of microorganisms is consistent throughout the matrix of the grain or if they are mainly constrained to the surface. If they are found in good quantity throughout, then mechanical processing to expose more of the inner structure should increase the fermentation rate. If however they are found mostly at the surface, then the rate of fermentation should be largely unchanged by breaking up the grains. To determine the influence of this on the process, the initial focus of this study is to investigate different grain sizes from crushed through to clusters over 2cm in diameter. The experiments are undertaken on a 1.5T Siemens Avanto whole body clinical MRI scanner with an automatic patient table. The milk fermentation takes place in a flask initially in the isocentre of the magnet where it is imaged once every minute (Fig 1a.). The aperture of the flask is piped to an upturned, water filled cylinder to capture the carbon dioxide which is produced during fermentation. Every 10th minute of the experiment, the patient table is automatically moved, to bring the upturned cylinder into the isocenter where it is then imaged (Fig 1b.). In this way, an automated experiment is produced, allowing overnight monitoring of the fermentation process. High resolution images of the Kefir milk allow monitoring of the site of production of the gas bubbles (hypointensities), changes in the size of the grains as the microorganisms reproduce and the rate of coagulation of the milk, which is in many respects a better measure of the production rate. We hope that these experiments will improve the commercial production of Kefir by aiding the standardization and understanding of the process.

Figure 1. a) Left hand side, images of evolving kefir grains (30 minutes, 4 hours, 8 hours) and b) the corresponding CO₂ produced trapped in upturned cylinder used to measure fermentation.
NMR relaxation and oxygen permeation studies on protein-sugar matrices conditioned at different humidities

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Many food ingredients including vitamins and other micronutrients as well as aroma substances and pigments are degraded over time by atmospheric oxygen. This degradation is a major limiting factor for shelf-life of many food and feed products, especially for powder formulations. In addition to the use of packaging materials offering a high permeation barrier towards oxygen, the matrices used in the actual powder formulation can also contribute to reduced oxygen-induced degradation.

Many of these materials come with sufficiently low oxygen permeability on dry state but with increasing moisture content the barrier properties deteriorate considerably. The present approach to study the oxygen permeation properties of such materials are permeation measurements on films conditioned at different humidity. This is a rather time-consuming approach and requires careful production of defect-free macroscopic films of the polymer mixtures to be studied.

In order to gain insights into the impact of moisture on molecular dynamics inside the matrix materials and to reduce the need for permeation measurements at different moisture conditions, we are exploring the use of NMR relaxation studies and molecular dynamics simulations using LAMMPS as a predictive tool for oxygen permeation properties under different conditions.

In our contribution, we will present moisture dependent studies of NMR and permeation properties and simulation results for various matrices composed of proteins and sugars and discuss observed correlations and open questions.
Assessing the Effect of pH and Boiling Time on the Crust Formation of Boiling Water Bagels Using Magnetic Resonance Imaging

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Traditional bagels, sometimes referred to as water bagels since they are directly boiled for a period in water to induce enhanced gelatinization of the crust, have been a staple bread product since their alleged invention in the 17th Century. The number of recipes for production of traditional water bagels is uncountable with each family or baker having their own variations on the same theme. The point of greatest contention between these conflicting recipes is the inclusion of ingredients within the boiling water and the strength or gluten content of the flour. Historically, commercially produced bagels are produced with very strong bread flour (14%) and boiled in alkali water containing lye, or sometimes baking powder, to increase the rate of protein gelatinization. To the best of the author’s knowledge, this production of bagels as a process is not well documented in the scientific literature, and there are no studies utilizing MRI to investigate the gelatinization process, despite it being an ideal tool. The final product, once baked depends extensively on this process with regard to organoleptic properties and color. In this work, we systematically vary the pH of the boiling solution in both directions from neutral using acetic acid or sodium hydroxide before undertaking imaging during the boiling process of bagels produced with different flours, in a 1.5T Siemens Avanto MRI scanner. Once imaged, the bagels are baked and textural analysis undertaken to assess the elasticity of the final crust. The live imaging of the boiling process allows us to determine the rate of crust formation as a function of pH to find an optimum concentration and time for a given crust thickness and elasticity. An example of the rate of crust gelatinization as a function of time for strong and very strong flour is shown in Figure 1. The spin echo imaging is conducted in a reduced cross section of the ring of proved and retarded dough to allow for the maximum spatial and temporal resolutions. It is hoped that an improved understanding of the relationship between pH and boiling time and the resulting crust thickness, elasticity and color will allow for improved understanding of bagel production and may feed into commercial production methods.

Figure 1. Left hand side shows cross sectional images of the bagel at the start (top) and end (bottom) of the experiment, showing the formation of the crust. Right hand side shows the normalised (to starting point) plot of the integral over the crust region, showing increased gelatinization as a function of boiling time.
Contrast enhanced proton MRI study of potato tubers subjected to electroporation process.

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A new method of assessing the effects of high voltage pulsed electric field (PEF) applied to potato tubers is proposed. The low-field proton MRI with the contrast agent affecting the local $T_1$ relaxation time is used to monitor the distribution and transport dynamics of paramagnetic ions within the sample. The magnitude of PEF was sufficient to cause an irreversible damage to the cell membranes. After the PEF treatment the samples were soaked in an aqueous salt solution (0.2% CuSO$_4$), and the distribution of paramagnetic ions was monitored for 98 hours. The MRI profiles confirmed the rapid increase in the non-selective ions flow within the potato tissue. The transport speed was estimated to be about 0.1 mm/h. Comparing to the direct analysis of tissue changes resulting from the increased migration of naturally occurring ions, the $T_1$ weighted images showed significantly higher sensitivity. Therefore, the low field contrast enhanced proton MRI was proven to be an effective and relatively inexpensive method in the examined application.

References:

Low-resolution NMR relaxometry, diffusometry and profilometry on salad dressing and mozzarella upon storage time

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Oil-in-water emulsions (e.g. mayonnaise and salad dressings) and mozzarella might undergo physicochemical changes as a function of storage time. In the case of low-fat O/W emulsions, water sedimentation might occur, which was measured using low-resolution $^1$H 1D NMR profilometry (Hahn spin echo), before it was visible with the naked eye. Water sedimentation might be slowed down using different thickeners. The resulting change in viscosity of the water phase was measured using NMR T$_1$-relaxometry, whereas an optimal thickener concentration was determined upon measurement of the oil droplet size distribution using pfg-NMR diffusometry (PGSTE).

The state of water in freshly produced cheese evolves rapidly upon storage, which was measured using NMR T$_2$-relaxometry (CPMG) and pfg-NMR diffusometry (IRPGSTE). Upon addition of D$_2$O, which exchanged with water within the cheese, valuable information was given regarding its water relaxation time. ($^1$H and $^{23}$Na) 1D NMR profilometry was also applied as a non-destructive method for measurement of the water and salt gradient in brined mozzarella upon storage, which was found to slowly diminish upon storage. Knowing the presence of a gradient is important towards e.g. sampling for chemical analysis.
Quantitative magnetic resonance imaging of peach fruit during development

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Quantitative magnetic resonance imaging was performed to investigate peach quality traits during fruit development. The MRI measurements of multi-exponential relaxation times and apparent microporosity were studied in relation to the variations in biological parameters. The aim was to identify the MRI parameters that best describe variations in structure and composition of fruit tissues during development.

Peach fruits were harvested at four developmental stages during the cell enlargement period (54, 61, 95 and 119 days after flowering). Two contrasted fruit loads were applied at the tree scale in order to induce variations in peach size and chemical composition. MRI imaging of the 5-mm median fruit plane were performed at 1.5T (Avanto, Simens) with the 0.8²mm² spatial resolution. Relaxation parameters were estimated from the 256-echo multi spin echo sequence with ΔTE=6.5ms, TR=10s. $T_2^*$ used for apparent microporosity estimation [1] was measured with multi gradient echo sequence with TE1=2.27ms, ΔTE=1.6ms, TR=5s. After MRI measurements, fruit density was estimated from mass and volume measurements. Then following parameters were measured on the pericarp samples taken from the outer and inner pericarp regions: water and osmotic potentials, water, soluble sugar and acid contents and cell size (measured after enzymatic dissociation).

The results showed the tissue evolution and setting up of the pericarp heterogeneity in terms of water status and distribution at the cell level and microporosity. The changes in vacuole-related transverse relaxation rates were mostly explained by the cell size. The impact of cell solute composition and water relation on relaxation times will be also discussed.

References:


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NMR approach to evaluate impact of nitrogen supply on the senescence process of Brassica napus leaves under field conditions

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During leaf senescence, improved remobilization of nutrients from old leaves to growing organs may represent an adaptive response of Brassica napus plants to the decrease in nitrogen (N) input. Therefore characterization of the natural genotypic variability of leaf remobilization efficiency should allow providing relevant information for crop improvement. It has been recently demonstrated that NMR transverse relaxation times can be used to monitor leaf senescence process through senescence associated cell and tissue structural modifications [1-2]. The impact of N deficiency on these changes has also been demonstrated on Brassica Napus plants grown under controlled conditions [3]. The aim of the present work was to investigate by NMR a plant response to nitrogen fertilization under field conditions.

Two genotypes of winter oil seed rape (Brassica napus, cv Aviso and Express) with different tolerance to N deficiency were assessed. A mobile NMR lab [4] was brought into the field allowing NMR measurements without plant uprooting. Transverse relaxation times were measured on leaf discs cut from the leaves of each leaf rank of the plant studied. A CPMG sequence with a 90°-180° pulse spacing of 0.2ms and 64 averages were used. The genotypic response to N depletion was evaluated through dry mass production and seed yield.

The results obtained in two different genotypes showed that despite a great variability of the macro and micro environmental factors, the NMR relaxation provided robust indicators of the structural changes that occurred during leaf development. The pattern of these changes differed between genotypes in lower N regime due to their different responses to the decrease in N input. This study presents an important step toward the use of NMR relaxometry for field phenotyping of nitrogen fertilization response.

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In situ measurement of molecule mobility in mucilage polysaccharide gels from the seeds of different species

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On imbibition the seeds of certain species form a polysaccharide hydrogel, termed mucilage. In \textit{Arabidopsis thaliana} and \textit{Camelina Sativa}, this mucilage is composed of 2 layers, the outer being water-soluble while the inner is tightly attached to the seed surface. Determining the macromolecular properties of mucilage polymers in the inner mucilage layer can only be achieved \textit{in situ} as detaching the polysaccharides involves breaking them either by physical or enzymatic methods, which alters or eliminates their structure. It has already been shown that the physicochemical properties of mucilage polysaccharides affect accessibility and mobility of molecules within the hydrogel. In order to compare inner mucilage properties between species, we have developed methods that can be applied to intact seeds. We have used low-field nuclear magnetic resonance (NMR) spectroscopy to characterize water uptake and mobility in \textit{Arabidopsis thaliana} intact seeds based on T\textsubscript{2} relaxation times (Saez-Aguayo et al. Plos Genetics, 2014). In imbibed seeds, five T\textsubscript{2} components were identified which could be assigned to protons of various water populations with different mobility and ratio depending on their localization in seed tissues and mucilage layers. Analysis of the evolution of signal amplitudes for the different components allowed the water transfer rates between different compartments to be determined. Calculation of water content for each compartment confirmed that even after 24 h of imbibition, approximately 40\% of water associated with wild-type seeds was trapped outside in mucilage. Surprisingly, despite released mucilage being an excellent hydrogel, it did not increase the rate of water uptake by internal seed tissues and is more likely to play a role in retaining water around the seed. In order to localize the different tissues and the inner mucilage layer, we analyzed \textit{Camelina sativa} seeds which are bigger making possible their characterization by magnetic resonance micro-imaging and this is compared to analysis of mucilage properties using fluorescent recovery after photobleaching (FRAP).

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Combining flow-MRI method and modelling approach to assess water fluxes in tomato plant architecture

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Water and carbon status throughout growth and development are tightly controlled by the plants and they are key components of their response to environmental stresses. In order to predict the plant behavior under contrasting environments, many biophysical functional-structural plant models have been developed, describing the network of source and sink organs as well the transport of resources within this network (Baldazzi \textit{et al.}, 2013). However, local endogenous resource availability and transport within intact plants are difficult to measure because only a few non invasive techniques exist. Yet Nuclear Magnetic Resonance (NMR) spectroscopy, relaxometry and Imaging (MRI) methods are available to study cell water balance, cell-to-cell, phloem and xylem transport in large potted plants (Van As, 2007). The objective of this study is to estimate, in a non invasive way, xylem and phloem fluxes in the plant architecture and to measure their short-term variations in well-irrigated plants. The work focuses on tomato, a model plant for fleshy fruits and the second fruit consumed worldwide. In order to measure water flows, we used a novel flow-MRI method taking advantage of inflow slice sensitivity (Buy \textit{et al.}, 2018). This method involves the slice selectivity in the context of a multi slice spin echo sequence. Two sequences such as a given slice is consecutively inflow and outflow sensitive are performed, allowing slow flow sensitive imaging.

We applied this method to estimate water fluxes in the main stem of a tomato plant, and at the abscission zone, close to the fruit, where the pedicel breaks at fruit maturity. The experiments have been performed on a Agilent MRI scanner working at 9.4T. Two \textsuperscript{1}H MRI probes (tuned at 400MHz) have been designed to fit the different regions of interest: an openable saddle-coil for the stem and an Helmholtz coil for the abscission zone. We followed the diurnal evolution of the water fluxes up to three consecutive days. We compared these measurements to the predictions of an integrated functional-structural model of tomato plant, able to map the local supply of resources and its variation within the plant architecture (Baldazzi \textit{et al.}, 2013; Najla \textit{et al.}, 2009). Results will boost our capacity to integrate and validate both approaches and to go beyond the limits of current approaches in plant ecophysiology.


Low field NMR relaxation for early detection of water deficiency in *Nicotiana tabacum* leaves

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Drought limits harvest in numerous crops worldwide and climatic models predicts that this issue will grow in the next decade. Water stress has a negative impact at different levels of the plant: limiting growth and photosynthesis, creating oxidative stress... New methods are investigated including early water stress detection method for a better water management in field and greenhouses in order to save water and prevent drought. Among the new phenotyping methods, low field NMR spectroscopy appears promising because this technique has been shown to be able to follow leaf development and to detect nitrogen deprivation in oilseed rape. This method provides an unique way for the characterization of the leaf water status at the tissue level through T2 relaxation spectra. Therefore the goal of this study is to demonstrate the sensitivity of the low field NMR relaxation to monitor the water stress of plant. Using tobacco plant as model, this study focuses on the early detection of mild water stress on leaves as this organ is very sensitive to stress. The effect of foliar biostimulant against water stress has also been studied. Three treatments have been examined: control, stressed (80 % of the field capacity), and stressed plants treated with foliar biostimulant (TIMAC SL28). For each treatment, two leaves from different ranks (4 and 8), depicting two developmental stages, were characterized through NMR and physiological measurements (relative water content, osmotic potential, Chlorophyll content...). The stress was applied from 28 days after sowing to harvest and measurements were done 42 and 57 DAS. The two leaf ranks studied had different NMR T2 spectra, confirming the ability of NMR to describe developmental stage of the tobacco leaf. For the 4th leaf rank, at 42 DAS physiological measurements were the same whatever the treatments while NMR signals associated to water in vacuoles were already affected by the slight water deficit. The result proved the sensitivity of NMR relaxation to detect slight water stress induced changes occurred in leaf tissues. Moreover, NMR results showed that foliar application of the biostimulant limited the negative consequences of drought.
Evaluation of different texture algorithms-regressors combinations to determine Iberian loin characteristics by MRI

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The use of MRI-computer vision to determine physico-chemical characteristics of loin is being proposed as an alternative to the traditional analysis. These techniques are laborious, use solvents and involve the destruction of the meat pieces, while MRI is a non-destructive technique, and also non-invasive and innocuous.

Usual MRI-computer vision methodology consists of texture algorithm for MRI analysis and data mining for data analysis. The present study aims giving a step forward, being its main objective to evaluate different frequencial and statistical methods and new regression methods to predict quality features of Iberian loins.

In this work, 5 fresh and 5 dry-cured Iberian loins were used, which were scanned on a MRI device with a low magnetic field (ESAOTE VET-MR E-SCAN XQ 0.18 T) applying spin echo sequences. The images were analyzed by applying frequentencial texture methods (gabor filter [1], Daubechies filter and double-tree complex Wavelet [2]) and statistical methods (Sum and Difference Histograms, Local Binary Patterns, Fractals and Co-occurrence Matrix). In total, 7 feature vectors were used: daub4, dtcwt, gni, msdhc, mlbp, mfs and mcoms [3]. Then, physico-chemical analysis for evaluating moisture and lipid content, water activity and instrumental color (L, a *, b *) were carried out. Then, a database was constructed with computational and physico-chemical data. Finally, 10 regressors [3] were applied on this database: svr, gamboost, rqlasso, enet, Boruta, bagEarth, extraTrees, elm_kernel [4], dlkeras [5] and lm to predict the physico-chemical parameters as a function of texture features [6]. Seventy combinations of feature vector - regressor were applied (the 10 regressors on the 7 feature vectors) for prediction each physico-chemical characteristics of loin, computing the coefficient $R^2$. Best results were: for moisture, $R^2=0.97828$ with mfs-extraTrees; for water activity, $R^2=0.99154$ with gni-elm_kernel; for the L color coordinates, $R^2=0.86167$ with msdh-svr; for color *a $R^2=0.82514$ with mfs-Boruta; and for color *b, $R^2=0.55110$ with gni-rqlasso; for lipid, $R^2=0.75074$ with mlbp-gamboost; and for the lipid in dry matter, $R^2=0.39543$ with the combination of gni-svr. Each quality parameter shows a different combination as the best, not being able to find a common one. For that, the Friedman ranking [7] was applied, which shows msdh-dlkeras as the best option. This combination achieved acceptable correlations ($R>0.25$) for 6 in 7 characteristics of the loin.

In conclusion, although it is difficult to find a common-best combination of texture method and regressor that allows the prediction of all physical-chemical features of Iberian loin, the use of msdh-dlkeras could be proposed, since this combination achieved acceptable correlations for most characteristics.


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Best combination of MRI sequences-3D texture algorithms-regression techniques to predict quality parameters of loin

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Magnetic Resonance Imaging (MRI) and computer vision techniques have emerged as ones of the alternative methodologies to the physico-chemical analysis of meat products, since this technique is non-destructive, non-invasive, non-intrusive, non-ionizing and innocuous. Several studies have pointed out the influence of i) the MRI acquisition sequence, ii) texture algorithms to analyse MRI, and iii) the technique of data analysis, on the accuracy of the results [1] [2] [3].

The aim of this work was to evaluate combinations of different MRI acquisition sequences, 3D texture algorithms and advance regression methods to predict quality features of Iberian loins. In this work, 10 Iberian loins (5 fresh and 5 cured) were scanned on a low-field MRI device (ESAOTE VET-MR E-SCAN XQ 0.18 T), using three T1 sequences: Spin Echo (SE), Gradient Echo (GE) and Turbo 3D (T3D). Then, reconstruction and interpolation techniques were applied on MRI images, obtaining a 3D MRI image for each loin, which were analyzed by three classical texture algorithms adapted for 3D MRI of loins (GLCM3D, NGLDM3D, GLRLM3D) [3]. Besides, moisture, water activity, lipid content and instrumental color (L, a *, b *) of loins were analyzed by physico-chemical analysis. Then, 28 regressors [4] was applied on a database constructed with computational and physico-chemical data. Thus, the prediction of each physico-chemical characteristics of fresh and dry-cured loins was carried out by 252 combinations of MRI acquisition (sequences (3), 3D texture algorithm (3) and regressor (28)), which was evaluated by means of $R^2$. In addition, *p*-value was calculated for comparing physico-chemical and predicted values.

Results have shown a different best combination for each characteristic: SE-dlkeras-NGLDM3D for moisture, $R^2=0.9735$; GE-grnn-GLRLM3D for water activity, $R^2=0.9839$; SE-svr-GLRLM3D-svr for L color coordinate, $R^2=0.82406$; GE-GLCM3D-M5 for color *a*, $R^2=0.84557$; SE-GLRLM3D-svr for color *b*, $R^2=0.5777$; GE-GLCM3D-elm-kernel for lipid content, $R^2=0.68053$. No significant differences ($p>0.05$) have been found between physico-chemical values and predicted ones for all analyzed parameters of loins, as can be observed in figure 1 for moisture and lipid content of dry-cured loins. This shows the accuracy of this methodology.

![Figure 1. Percentage of moisture and lipid of dry-cured loins by means of chemical analysis (●) and predicted by MRI-computer vision (○).](image)

In conclusion, physico-chemical characteristics of fresh and dry-cured loins can be predicted by MRI, applying 3D texture algorithms and advance regressors, but it is difficult to set a common best combination of MRI acquisition sequence-3D texture algorithm-regressor for prediction all parameters of loins.


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Multimodal imaging of dough and fat layers in Danish pastry for revisiting the mechanisms of bubble growth

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Puff, Danish pastries and croissants are characterized by a unique alveolar structure with large, eye-shaped bubbles nearly aligned horizontally. These bubbles increase in number with that of fat layers. This is commonly explained by the impervious barrier represented by fat layers. Likewise, it is believed that pronounced fat fragmentation results in lower gas retention in the dough layers and the disappearance of these typical bubbles. The aim of this study was to revisit these mechanisms, through image analysis.

Proving of a real sized Danish pastry was monitored by MRI (1.5 T) to visualize dough and fat layers. The number of fat layers was varied from 4 to 12, the latter being relevant to the lower range used on an industrial scale. A new method of quantification of the three components, gas, gas-free dough and fat, in partial volume was applied to these MRI images. Complementary visualization of fat and dough layers was performed by CLSM applied just before proving and after pastry staining. CLSM image analysis permitted to count the number of fat fragments, and measure their length and thickness.

The MRI method estimated accurately in each voxel the proportion of gas with a maximal bias of 5%. Large bubbles (> 0.5 mm) could be visualized in dough layers but they were not elongated at this step of processing contrary to bubbles typical of Danish pastry once baked. The eye-shaped bubbles were visualized in fat layers. This explained that, at the beginning of the proving, the fat layers, which thus include small bubbles not distinguishable with the MR resolution, appeared thicker than those measured by CLSM just after lamination. The number of bubbles growing in fat layers increased more rapidly than that of fat layers, with a contribution to overall inflation rather low at this processing stage (10%). Finally, large, undetectable portions of fat (40±13 mm equivalent to about 80 pixels in MRI images) were assigned to missing fat material and breaks in the layering, considered as undesirable by the bakers. Indeed, these void spaces represented 7.7% of the expected total length of fat layers in the MRI images, a proportion also reported from CLSM images obtained with a better spatial resolution. The number of eye-shaped bubbles was correlated with the number of fat fragments, giving a ratio of 5 of the widths of bubbles to fat fragments, suggesting that the finite dimensions of fat fragments in some way determined the final size of the eye-shaped bubbles.
Gluten-free bread baked under reduced pressure characterized by TD-NMR

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Based on spin-spin T2 relaxation time measurements, the time-domain NMR (TD-NMR) spectroscopy has been used to provide relevant information on the water and biopolymer motion and transfer in bread [1]. This technique permits to characterize molecular interaction and transformations in a non-invasive and non-destructive way, in real time during a process (heating, freezing, hydration ...). In bread, proteins of gluten when hydrated form a viscous mass that confers to the dough, structure, viscosity, mixing tolerance and gas holding ability [2]. On the other hand, starch, in presence of water and increasing temperature, undergoes a series of changes known as swelling, gelatinization and retrogradation that induce variations in water distribution, in starch structure and interactions between them [3]. This study aimed at understanding and ranking the contribution of these biochemical transformations that contribute to the crumb structure and the textural properties of bread prepared with a gluten free mix (Schär). The water transfers and the extent of starch gelatinization in crumb were studied by TD-NMR after the heating/cooling process of dough hydrated at 55% and 48% (wet basis). Two baking processes were compared, one at the atmospheric pressure while the other was carried out at reduced pressure (-20 kPa). Bread baking using partial vacuum results in greater oven-rise and greater gas fraction in the crumb, giving an increased softness of the crumb for a more pleasant mouthfeel. Under reduced pressure, the boiling point of water decreases but, until now, no study was conducted to check if this baking condition modifies or not the starch gelatinization and protein denaturation. By comparing rheological measurements (modulus of elasticity using a compression stress relaxation experiment) with TD-NMR data, it was shown that the crumb softness was mostly driven by the gas fraction while the biochemical changes (starch gelatinization, protein denaturation), monitored by TD-NMR, were little modified when dough was baked under partial vacuum.


Characterization of food products by two-dimensional-CWFP-$T_1$ sequence using low resolution NMR

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The correlations relaxation times and diffusion in food products have been measure in low-field NMR using two-dimension (2D) techniques. Most of these 2D techniques use the Carr-Purcell-Meiboom-Gill pulse sequence as direct dimension. Recently, we have introduced a 1D method to measured the longitudinal relaxation time ($T_1$), based on continuous wave free precession (CWFP) sequence using a very low flip angle ($5^\circ$ or $10^\circ$)$^1$. This sequence was named CWFP-$T_1$ and that was also used in new 2D sequences. In the 2D-CWFP methods the CWFP-$T_1$ was used as indirect (CWFP-$T_1$-CPMG) and direct (CPMG_CWFP-$T_1$) detection sequence to obtain $T_1$-$T_2$ correlation maps. The advantages and disadvantages of these 2D CWFP-$T_1$ methods over classical 2D sequences will be demonstrated in the analysis of fresh and processed food products.

References

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Measurement of physicochemical properties of food products in low field NMR using filtered CWFP-T$_1$ signal

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Low field NMR relaxometry has been widely used in the analyses of food products. However most of these measurements are based on single shot Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. Recently, we have introduced, single shot method to measured the longitudinal relaxation time (T$_1$), based on continuous wave free precession (CWFP) sequence using a very low flip angle ($5^\circ$ or $10^\circ$). This sequence called CWFP-T$_1$ uses less rf (radio frequency) power than CPMG, reducing sample heating and shows higher selectivity for sample with different T$_1$/T$_2$ ratios. One of the limitations of CWFP-T$_1$, when compared to CPMG, is its lower signal to noise ratio (SNR) due the use of low flip angles. To enhance SNR we have tested several low pass digital filters. Savitzky-Golay’s and Wavelet were the best filters that enhance S/N with minimal signal distortion. The advantages of filtered CWFP-T$_1$ signal in comparison with CPMG of analyses of fresh and processed food products will be demonstrated.

References

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Transient Effect Determination of Spin Lattice (TEDSpiL) Relaxation Time Changes with Continuous Wave NMR For Screening Milk Powder Solutions

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With the dominance of pulsed NMR techniques, continuous wave (CW) NMR has been consigned mainly to students experiments and use in commercial magnetometers. Whilst conceptually simpler, CW in practice can be challenging to reliably determine relaxation parameters even though hardware for CW can be an order of magnitude cheaper than a pulsed NMR system. CW usually involves sweeping the magnetic field through resonance at fixed frequency or sweeping the frequency through resonance at fixed field. In very homogeneous magnetic fields, the width of the resonance then gives a measure of $T_2^*$. For the measurement of $T_1$, Look and Locker [1] utilized a fixed frequency and gated sweep waveform they called a ‘tone burst’ where the sample was left aligned with the magnetic field, held off resonance before the start of the measurement. A number of cycles of the sweep coils follow during which each absorption trace was collected providing exponentially varying amplitudes with time constant $T_1$ until saturation was reached. More recently [2] it was shown that a variation on this technique using a marginal oscillator could be used to produce a parameter $T_x$ and that calibration samples could then be used to relate this to $T_1$. The use of inexpensive NdFeB magnets and low cost microcontrollers to perform this have also been reported [3] giving the potential of a relatively inexpensive, low power and portable system. This technique has the advantage of giving a $T_x$ value in under 5 seconds compared to several minutes for pulsed determination of $T_1$ with traditional low field hardware. Figure 1 shows the $T_x$ values for different skimmed milk powder concentrations in distilled water; this is consistent with the $T_1$ changes with concentration shown in recent work using pulsed NMR [4]. In this presentation we demonstrate that the parameter $T_x$ can be used to screen for changes in rehydrated milk from powders stored under challenging conditions experienced in transit.

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MRI-computer vision to monitor quality parameters of meat products: main achievements

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This work summarizes main achievements of a research line focused on analyzing meat products from Iberian pigs by Magnetic Resonance Imaging (MRI) and computer vision techniques. MRI-computer vision has emerged as an alternative to traditional and destructive techniques for determining physico-chemical and sensory characteristics of meat products, due to its non-destructive, non-invasive, non-intrusive, non-ionizing and innocuous nature.

The methodology can be divided in three stages: the MRI acquisition, the MRI analysis and the data analysis. Studies have been developed with Iberian hams and loins, moving forward in each stage.

First studies were carried out by using a high-field scanner (at the “Infanta Cristina” University Hospital) to acquire the MRI images of Iberian hams, which were analyzed by means of Active Contours [1], Region of Interest (ROI) [2], texture algorithms, and traditional statistical techniques. This achieved to estimate weight loss and time of processing of hams [3], classify hams as a function of pig feeding [4], and predict some sensory attributes of dry-cured hams [5].

First advance on this methodology was the application of data mining techniques, instead of traditional statistical techniques, attaining the prediction of the content of moisture, lipid and salt, the weight and most sensory attributes of Iberian hams [6-8].

Going on with the progress, the research group got a low-field scanner, which is cheaper than high field ones although they offer lower signal to noise ratio. Thus, several tests were carried out to configure the MRI acquisition of loins by using the new scanner. These MRI images of loins were initially analyzed by classic texture algorithms [9]. However, important advances have been performed for their analysis: the development of two fractal algorithms [9,10]; the application of interpolation and 3D reconstruction techniques to obtain 3D images of loins; the adaptation of the texture algorithms to analyze the obtained 3D images [11]; and the development of new 3D algorithms [12]. In these studies, data mining techniques have also been applied, getting the prediction of most physico-chemical and sensory characteristics of Iberian loin with high accuracy.

More recently, a high number of combinations of advance algorithms (for MRI analysis) and regressors (for data analysis) have been applied on previous MRI from Iberian hams and loins, not being possible to set a common methodology for both pieces. Besides, a realistic validation method has been implemented in these last studies [12].

Nowadays, the main task is being the optimization of the MRI acquisition of Iberian hams by using the low-field scanner as well as their analysis, to determine the quality parameters of this food non-destructively, being the further focus of this research line to automate the whole procedure.


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$^1$H NMR-based metabolomic for discrimination of high valuable Canastra’s cheese

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Canastra artisanal cheese is a typical Brazilian product of high economic importance to the region of Canastra saw at Minas Gerais state. The cheese is obtained from raw cow’s milk and starter specific microorganism culture, found only in the Canastra region. The economic value attributed to cheese is based in the consumer sensory perception. This study aimed to characterize parameters and to found biomarkers which are associated with the high quality Canastra’s cheeses, by NMR metabolomic analysis.

Fifty milligrams of the each cheese sample, stored in freezer at -80°C, were weighed and extracted with 800 μL of CDCl$_3$, centrifuged and supernatant were analysed by $^1$H NMR in quantitative conditions. The characteristic chemical shifts of fatty acid were representative for the statistical separation observed in the graph. The preliminary results show that use of $^1$H NMR spectroscopy in combination with multivariate data analysis proved to be a potential tool for metabolite fingerprinting of cheeses and for contrasting differences between cheeses of different producers.

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31P NMR assessment of the phosvitin-iron status in mayonnaise

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In mayonnaise, a critical ingredient is egg yolk, which is rich in phospholipids and proteins that act as emulsifiers [1]. One of the most abundant proteins in egg yolk is phosvitin, which is a phosphoprotein that effectively binds iron in its (ferric) Fe(III) state [2]. In hen egg yolk, the pH is 6.5, which enables a tight binding of the Fe(III)-phosvitin complex. However, in mayonnaises, the pH is typically between 3.5 and 4.0, which significantly reduces binding strength for Fe(III). Upon release from phosvitin, Fe(III) can form a redox couple with Fe(II) which can effectively catalyse lipid oxidation at the oil-water interface in mayonnaise [3]. This leads to rancid off-flavour and compromised shelf-life. Therefore, it is of great interest to map the Fe(III)-phosvitin binding status and Fe(II)-Fe(III) redox state in mayonnaises.

Fe(II) and Fe(III) have different magnetic properties: Fe(II) is diamagnetic, whereas Fe(III) is paramagnetic. Due to paramagnetic broadening, Fe(III) effectively quenches the 31P NMR signal of its complex with phosvitin. We exploited this effect to assess the Fe(III)-phosvitin loading and oxidation state by means of 31P NMR. This approach was first tested and validated in model phosvitin systems by liquid state 31P NMR, where we show that reducers and chelators have the hypothesized effect on the phosvitin signal. Moreover, we could quantify the Fe(III) loading of phosvitin. The approach was then expanded to whole mayonnaise, using MAS 31P NMR. Here we could semi-quantitatively assess the Fe(III) iron bound to phosvitin by comparing formulations with different amounts of chelators. Finally, we investigated the effect of reducers on the phosvitin signal, to assess the transition between the oxidative states of iron.

A Preliminary Investigative Study of Brazilian Exotic Fruits by NMR

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Due to the nutritional importance of exotic fruits found in the Brazilian Amazon region, the knowledge about their chemical composition is quite relevant not only for the local residents but also to export for other regions in Brazil or outside. Brazil is the third largest producer of fruits in the world, however, there are numerous Brazilian exotic fruits that are not very well known especially due to the lack of disclosure information and the little knowledge about the chemical composition, physical-chemical properties etc, of them. Thereby, the aim of this work was to investigate by liquid NMR experiments the chemical composition of six exotic Brazilian fruits: Abrico (Mammea americana), Bacuri (Platonia insignis), Camapu (Physalis angulata), Murici (Byrsonima crassifolia and Byrsonima verbascifolia), Tapereba (Spondias mombim) and Uxi (Endopleura uchi). Freeze-dried fruit pulp samples were redissolved directly in deuterated water (D₂O) and the solutions were analyzed. First, from quantitative data of ¹H NMR (qNMR) and database query and also from 2D NMR experiments. The following metabolites were identified / characterized: sucrose, α- and β-glucose, fructose, choline, asparagine, alanine, valine, ethanol, GABA and chiquimic, acetic, formic, citric, aspartic, latic, benzoic acids. After this, a comparison of 1H NMR spectra among the six fruits was performed employing the normalized absolute area of each signal identified/characteriz. It was noted that Camapu and Bacuri have higher sugars level, Camapu and Tapereba are richer in aminoacids and Uxi has more organic acids. In this way, a general idea about main metabolites of these fruits was obtained in this work which may be used to introduce others researches related to the investigated fruits.
Identification of Chemical Markers related to Processing Methods and Aging of Green Coffee Grain

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Scientific studies with gourmet coffees have advanced due to the increased demand for good quality differentiated coffees, giving them a high added value. In this way, the quality control of these products has become very important, since the decrease of their quality during the period of storage represents a great financial loss. Thus, the aim of this work was to use a chemometric approach using $^1$H NMR to evaluate specific chemical changes of green coffee beans in order to identify chemical markers related to processing and aging methods during their storage. In total, 443 $^1$H NMR spectra of methanolic extracts of green coffee beans were subjected to principal component analysis (PCA). Initially, two processing methods (wet and dry) were evaluated in which the coffee grains were dried inside endocarp and exocarp, respectively. From PCA the compounds trigonelline and caffeine were identified as possible chemical markers to differentiate these two methods of processing. These samples were evaluated after 3, 6, 9, 12 and 18 months of storage in paper packaging and, in the same way that previously described, it were identified glycerophosphocholine, phosphocholine and choline as chemical markers of aging of green coffee grain during the storage. Hence, the use of the $^1$H NMR spectroscopy and the chemometrics were efficient in identifying of chemical markers and their monitoring will contribute to improvement the product quality control.
NMR studies to explain the Influence of caffeine-polyphenol-melanoidin interactions on the bitter taste perception of coffee beverages (part I)

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Freshly brewed coffee is appreciated by consumers all over the world, because of its stimulating effect, its attractive aroma, and its characteristic taste centering on sourness and pleasant bitterness. Although multiple taste active molecules have been identified as coffee components, the sensory significance for coffee quality of one most abundant bitter compound, caffeine, is still unclear. In literature a caffeine-potassium-chlorogenate complex was reported which might influence the taste perception of caffeine.

Sensory experiments with non-roasted coffee brews showed that no bitter taste is perceivable, although the caffeine concentration in such a coffee exceeded its bitter threshold detection by a factor of more than 20 times. Adding concentrations of 1500 mg/L caffeine to a roasted decaffeinated coffee beverage revealed that none of the sensory panellists is able to distinguish between the decaffeinated beverage and the beverage supplemented with caffeine. ¹H NMR analysis of the caffeine supplemented beverage revealed a strong chemical shift difference of the signals of caffeine as well as of the aromatic resonances of the natural occurring chlorogenic acid derivatives in the spectrum. In addition, e.g. the methine proton of the caffeine showed a strong line broadening, whereas other major coffee compounds like N-methylpyridinium, trigonelline or formic acid showed neither chemical shift differences nor line broadening.

To gain more detailed insight into the molecular phenomenon explaining these effects, NMR titration experiments were performed with different binary mixtures of caffeine and chlorogenic acid. These experiments showed the formation of a strong π-π complex indicated by extreme chemical shift differences of the aromatic protons compared to the signals of single compounds. Calculation of the electron density of the aromatic constituents of this complex clearly indicate that caffeine as an electron deficient and chlorogenic acid as an electron rich aromatic system are well suited to form such a π-π complex and support the results obtained by NMR spectroscopy.

Sondheimer, E; Covitz, F.; Marquisee, M.J. Association of naturally occurring compounds, the chlorogenic acid-caffein complex; Archives of Biochemistry and Biophysics (1961), 93, 63-71.

Horman, I; Viani, R. The nature and conformation of the of the caffeine-chlorogenate complex of coffee; Journal of Food Science (1972), 37, 925-927.

Martin et al. The caffeine-potassium chlorogenate molecular complex; Phytochemistry (1987), 26, 273-279.
NMR studies to explain the Influence of caffeine-polyphenol-melanoidin interactions on the bitter taste perception of coffee beverages (part II)

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As already shown in Part I a non-roasted coffee infusion exhibited no bitter taste, although the caffeine concentration exceeds its bitter threshold more than 20 times. Moreover, the addition of 1500 mg/L caffeine to a roasted decaffeinated coffee infusion could not be perceived by a trained sensory panel, in a triangle test with a decaffeinated beverage without the addition of caffeine. In contrast to other major coffee constituents like trigonelline or N-methylpyridinium the ¹H NMR analysis of this caffeine supplemented beverage revealed a strong chemical shift difference of the signals of caffeine as well as of the aromatic resonances of the chlorogenic acid derivatives in the spectrum.

The analysis of the chemical shifts and the line shape of all signals (from caffeine and chlorogenic acid), showed that a part of the chemical shift difference could be explained by the formation of a caffeine-chlorogenic acid complex. The remaining shift difference, the line broadening and the influence on the bitter taste perception could not only be explained by the formation of this complex.

NMR titration experiments of caffeine solutions with increasing concentrations of coffee matrix showed a strong signal broadening as well as an up-field shift of methine and methyl protons of the caffeine. The isolation of the high molecular weight faction (melanoidins) from coffee and the addition to the caffeine-chlorogenic acid complex in natural concentrations led to a dramatic decrease of the bitterness of such a ternary mixture. This effect could be monitored by NMR, where beside the chemical shift differences of the small molecules a strong signal broadening caused by interactions of the caffeine-chlorogenic acid complex with the melanoidins was observable, indicating the formation of a caffeine-chlorogenic acid-melanoidin complex.

Sondheimer, E; Covitz, F.; Marquisee, M.J. Association of naturally occurring compounds, the chlorogenic acid-caffeine complex; Archives of Biochemistry and Biophysics (1961), 93, 63-71.

Horman, I; Viani, R. The nature and conformation of the of the caffeine-chlorogenate complex of coffee; Journal of Food Science (1972), 37, 925-927.

Martin et al. The caffeine-potassium chlorogenate molecular complex; Phytochemistry (1987), 26, 273-279.
Quantification of natural products in herbal supplements: a combined NMR approach applied on goldenseal

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Quantitative NMR (qNMR) providing an accurate and repeatable quantification of components together with an unambiguous identification is widely used as a powerful technique for identifying and quantifying compounds in complex mixtures.

In this study, we have applied a new developed quantitative 2D NMR approach called Q QUIPU\textsuperscript{1} in combination with 1D \textsuperscript{1}H NMR capable to access the concentration of three major alkaloids, berberine, hydrastine and canadine, in the root extract of goldenseal (\textit{Hydrastis canadensis}), one of the 20 most popular herbal supplements used worldwide. We highlight the complementarity of 1D and 2D quantitative NMR to accurately access the amount of alkaloids with different range of concentrations and stability within extracts. In particular, unstable natural products having non-overlapped signals like berberine could only be quantified by sensitive and fast 1D \textsuperscript{1}H, while overlapped signals of hydrastine and low intense ones of canadine could only be quantified with the recent 2D Q QUIPU HSQC.

Results obtained from this combined approach have led to a good accuracy as compared with coupled UPLC-MS/UV techniques. As opposed to MS, the qNMR can be applied directly on the matrices in the absence of further purification and does not rely on external calibration. This combined NMR approaches can be used and expanded to quantify other compounds in complex mixtures with a better sensitivity, and resolution, high precision, good accuracy, repeatability and reproducibility and in a less time consuming manner in different areas such as agricultural, food and agricultural or pharmaceutical products, where verification and quantification of components are necessary for product assessment and quality control.

Reference:

Free amino acids and majority metabolites as markers for the distinction between tender and tough beef using HR-MAS NMR


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An important point in beef quality is the tenderness, directly influenced by factors such as genetics, breed, age, animal handling, feeding, and the post-mortem handling of beef. Several studies have been done on beef chemical composition that directly affects the taste of the beef.1,2 In this context, this study evaluated the chemical composition of beef, looking for chemical markers for beef tenderness. For this, 30 beef samples were assigned as tender, intermediate or tough according shear force method. After this, raw beef were analyzed by NMR spectroscopy using an HR-MAS probe. The samples were disrupted and homogenized by a FastPrep®, and 15 mg were inserted into 50 μL rotor, and 35 μL of D₂O were added. The spectra were performed in duplicate, spun at 5 kHz and temperature was 28 °C. The main constituents from the spectra of the tender and tough groups were statistically compared by t-test. After the identification and quantification of the compounds in beef, t-test indicated that tender, intermediate and tough beef had different concentrations of some essential amino acids: tough group presented a higher content of methionine and valine, and a lower content of isoleucine. The correlation test was also used to verify if the compounds had correlation with each other, and it can be seen that the tough beef presented the most correlation, then the tender and finally the intermediate beef. The number of correlated compounds were 11, 6 and 4, respectively for each beef group. In addition to indicate which are the main metabolites responsible for the classification of beef tenderness, HR-MAS NMR also proved to be able to monitor the changes in the beef composition due to the reactions occurring during the cooking process.

References:

Acknowledgment: FAPEG, CNPq, FINEP
Monitoring the influence of meat-ripening through a combined proteomics and metabolomics study

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Meat proteins are exposed to the action of different proteases and peptidases during digestion. As a result, a broad range of low molecular weight (LMW) nitrogen compounds are potentially released and made free to diffuse to the absorption sites at the gastrointestinal tract [1,2]. However, the digestion process is also modulated by the supra-molecular organization of meat product, in turn affected by bio-technological production processing. Therefore, the complex network of molecular interactions and the compartmentalized matrix structure prevent, in a product specific manner, the free diffusion of nutrients in the digestion fluid, and modulate the consequent enzymatic attack by the digestion system. In this way, nutrient bioavailability and the final nutritional value of the meat product can be greatly modified. It is thus necessary, for the assessment of the quality of meat-based products, to study the bioaccessibility, as a precondition to bioavailability, of these molecules and their interaction with the food matrix [3]. The aim of this work was to investigate the effect of the transformation process in Bresaola, a model of cured and salted raw meat, on the release and bioaccessibility of peptides derived by simulated in vitro human digestion. To this aim, samples of in vitro digested Bresaola were investigated through different complementary techniques including in vitro biological and chemical assays, proteomic and metabolomic approaches [4]. At the end, a holistic view has been gained on the effect of the maturation time on the molecular profile of Bresaola digestion fluids, with special emphasis on some molecules with potential biological activity.

References

Evaluation of free amino acids and water distribution in broiler *Pectoralis major* affected by muscular abnormalities through by TD-NMR and HR-NMR


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Chicken meat is still one of the most consumed meat (compared to beef and pork) because it is considered healthier and not related to religious and cultural impediments.1 However, over the years some breast abnormalities such as wooden breast (WB), white striping (WS) and spaghetti meat (SM) have emerged and increased the economic loss for the poultry industry. In this context, this study aimed to evaluate free amino acids and water distribution as affected by main broiler breast abnormalities by using NMR spectroscopy.

For this purpose, 48 Pectoralis major muscles were classified by visual evaluation as Normal (NORM), WS, WB and SM and used for both TD-NMR and HR-NMR. Measurements of 1H NMR, 1D CPMG spectra were carried out on Bruker Avance III 600 using an BBI probe. In addition, TD-NMR measurements were carried out by Minispec Bruker PC/20, operating at 0.47 T using CPMG sequence pulse to assess T2 relaxation properties (water mobility and distribution). One-way ANOVA was performed to test the effect of muscular abnormalities and linear correlation analysis (Pearson’s coefficients) was performed among all variables.

According to the results, if compared with controls, abnormal samples presented higher intensity in the signal of extra-myofibrillar protons, as well as greater relaxation time $T_2$, indicating a lower water holding capacity. With the HR-NMR it was possible to notice that the abnormal samples had lower concentration of lactate, which agrees with the higher pH of these samples. IMP and hypoxanthine, produced through hydrolysis of adenosine triphosphate (ATP) and responsible for energy storage,3,4 also differed among the groups. Finally, content of free amino acids such as glutamine and methionine which are responsible for the meat taste was strongly modified by occurrence of muscle abnormality. Overall, the findings of the present study evidenced that TD-NMR and HR-NMR, providing a wide set of information concerning the sample, might be considered as promising technique to ascertain differences between normal muscles and those affected by muscle abnormalities.


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Semi-preparative isolation and high-level $^1$H NMR spectral assignment of black tea metabolites from urine by means of SPE-LC-MS-LC-MS-NMR

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A main bottleneck in the assessment of the bioactivity of phytochemical products such as tea is the identification of the derived metabolites as they enter circulation upon consumption [1]. Recently it was shown that by hyphenation of LC, SPE, NMR and MS, large-scale identification of tea polyphenol metabolites can be achieved [2]. However, this approach did not result in full $^1$H NMR spectral assignments, mainly due to lack of both 2D NMR data and non-overlapping, well-resolved spectra. This could be attributed to the relatively small amounts of impure metabolites that were isolated by LC-SPE [3]. We therefore implemented a SPE-LC-MS-LC-MS-NMR workflow for isolation, identification, and quantification of conjugated valerolactone metabolites from urine of tea consumers. Focus was on conjugated valerolactones, since these are considered as the bioactives that can explain the cardiovascular benefits of tea consumption. First, the urine was cleaned and pre-concentrated using an SPE method. For the first separation step 15 times 500 µL of the cleaned urine was injected on a preparative LC column. Seven different fractions with masses of different valerolactones were collected. These fractions were evaporated under N$_2$ flow. These fractions were reconstituted in 75 µL of the start gradient of the second LC separation step. For this second separation step an analytical column was used. In total, seven different fractions were collected. These fractions were evaporated under N$_2$ flow and afterwards these fractions were reconstituted in 190 µL methanol-$d_4$ and identified and quantified using 1D and 2D homo- and heteronuclear NMR, in combination with mass spectrometry. This resulted in the full spectral $^1$H NMR assignments of five conjugated valerolactones and sinapinic acid-3’-o-glucuronide, and the $^1$H NMR partial assignment of a valerolactone (MSI level = 2). These metabolites were collected in quantities of 1-10 µg and purities of 80-99%. In conclusion, the SPE-LC-MS-LC-MS-NMR workflow is suitable for isolating metabolites that occur at low, sub-µM concentrations in a concentrated biofluid such as urine. The workflow also provides an alternative for cumbersome and expensive de-novo synthesis of tea metabolites for testing in bioactivity assays or for use as authentic analytical standards in quantification by mass spectrometry.

References

Application of magnetic resonance for the analysis and assessment of the lipid fraction of green and roasted *Coffea Arabica* beans

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Approximately 15% of the mass of an Arabica coffee bean, *Coffea Arabica*, consists of lipids. This lipid fraction has a number of applications in the food, cosmetic, and pharmaceutical industries, and the effect of roasting on this important lipid fraction is not yet fully understood. The objective of this study is to employ multinuclear and multidimensional NMR spectroscopy as a rapid and reliable method for the quantitative analysis and evaluation of the non-polar, including unsaponifiable, fraction of *Coffea Arabica*, as well as employ MRI to visualize the coffee roasting process. Our results suggest that NMR can be a valuable tool for the determination of many compounds in coffee oil and can be used for quantifying the impact of the coffee roasting process. Green and roasted coffee beans, as well as spent coffee grounds, were analyzed for their lipid components. A number of gradient-selected two-dimensional NMR techniques were applied for a systematic two-dimensional analysis of the various components in coffee oil, including FA, terpenes, oxidation and hydrolysis products, caffeine, and sterols. Quantification was achieved by integration of the appropriate diagnostic signals in the NMR spectra using 2,6-Di-tert-butyl-4-methylphenol (BHT) as an internal standard (IS), as well as the PULCON method, which offers several advantages compared to IS. Bland-Altman analysis showed that PULCON and IS approaches are in a good agreement. Overall, it was found that the major fatty acids in coffee oil are linoleic, oleic, linolenic and saturated fatty acids. Targeted analysis showed that, with the exception of linolenic acid, only minor changes occur in the fatty acid profile during roasting. A statistically significant increase occurs in secondary oxidation products and free fatty acids after roasting. Additionally, 1,3-diacylglycerides significantly decrease with roasting due to their instability to hydrolysis. Untargeted analyses, namely PCA and OPLS-DA, revealed differences between green and roasted samples. MRI indicated significant morphological changes in coffee beans due to roasting, which may be responsible for these compositional variations. Finally, lipids extracted from spent coffee grounds can be successfully used as precursors for the production of bioplastics. Overall, NMR and MRI are effective tools to help monitor the coffee roasting process and quantify the changes that occur in coffee lipids during roasting.

References
