Food MR 2016

XII International Conference
on the Applications
of Magnetic Resonance
in Food Science

June 07 – 10, 2016, Karlsruhe/Germany

KIT Karlsruhe Institute of Technology

NMR ProPro

MRI Max Rubner-Institut

cvua Karlsruhe
Chemisches und Veterinär-untersuchungsamt Karlsruhe

GVT Forschungs-Gesellschaft Verfahrens-Technik e.V.

AMPERE

Baden-Württemberg
REGIERUNGSPRÄSIDIUM KARLSRUHE

Organizing Committee

G. Guthausen (Chair), Karlsruhe Institute of Technology (KIT)
M. Bunzel, Karlsruhe Institute of Technology (KIT)
T. Kuballa, Chemical and Veterinary Investigation Agency (CVUA) Karlsruhe
B. Luy, Karlsruhe Institute of Technology (KIT)
M.J. Rist, Max Rubner Institut (MRI)
H.P. Schuchmann, Karlsruhe Institute of Technology (KIT)

Organizer:
Forschungsgesellschaft Verfahrens-Technik e.V. (GVT), Frankfurt/Main, Germany
Under the auspices of
Groupment Ampere, ETH Zürich, Laboratory of Physical Chemistry, Zürich, Switzerland

CONFERENCE SCOPE

Dear Colleagues,

Welcome to the 13th International Conference on Magnetic Resonance in Food in Karlsruhe, Germany. The series of conferences started 24 years ago and was continued as a biannual meeting. The last conferences were held in Cesena, Italy (2014), Wageningen, the Netherlands (2012), and Clermont-Ferrand, France (2010). This year, the conference is hosted for the first time in Germany.

The conference is focused on Magnetic Resonance and its application to foods with most recent advances in the technical developments as well as innovative applications and new insights into food systems being highlighted. The conference starts with three tutorials on Tuesday, June 7 to welcome newcomers as well as experienced researchers interested in refreshing their knowledge or broadening their expertise beyond their own research fields. Tutorial topics are chemometric data processing, new pulse sequences mainly in liquid state NMR, and MRI and diffusion tools for the investigation of food structure.

The scientific program, which will start on Wednesday, June 8 in the morning, covers the different aspects of Magnetic Resonance in Foods such as low and high field approaches, diffusion methods, and imaging. More than 35 oral presentations, including three plenary and five invited talks, will be complemented by more than 55 poster presentations. An overview about current developments and applications will be given.

In addition, on Wednesday evening, there will be a round table discussion on quantitative NMR. The contributions of all conference participants in terms of questions, remarks, and future prospects are most welcome. A form to submit questions in advance is included in your conference documents.

The conference dinner will take place on Thursday evening, June 9 at “Schalander” in close proximity to the Hoepfner brewery. The event is sponsored by Bruker – thanks a lot! The state of Baden-Württemberg is greatly acknowledged for providing the conference facilities at the Regierungspräsidium in Karlsruhe where the local organizers welcome you. Several companies sponsored the conference making it affordable to young scientists, too, which is highly appreciated. We wish you a pleasant and fruitful stay, good discussions, and new insights into the fascinating topic of Magnetic Resonance in Foods.

The organizing committee,

Gisela Guthausen (Chair)

Mirko Bunzel

Manuela Rist

Thomas Kuballa

Burkhard Luy

Heike Schuchmann

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PROGRAMME OVERVIEW

Tuesday, June 7	Wednesday, June 8	Thursday, June 9	Friday, June 10
	09:00 **Conference Opening** 09:10 **NMR Development** *Chair: B. Luy*	09:00 **MRI and Diffusion I** *Chair: J.M. Bonny*	09:00 **Application/Foodomics II** *Chair: M. Spraul*
	10:45 Coffee Break, Posters	10:35 Coffee Break, Posters	10:30 Coffee Break, Posters
	11:10 **From Method Development to Application** *Chair: S.B. Engelsen*	11:00 **MRI and Diffusion II** *Chair: J.M. Bonny*	11:00 **Application/Foodomics III** *Chair: D.W. Lachenmeier*
12:00 **Registration**	12:20 Lunch, Posters	12:20 Lunch, Posters	12:00 **Closing Remarks**
	13:30 **Low Field NMR and Other Techniques I** *Chair: J. van Duynhoven*	13:30 **Application/Foodomics I** *Chair: M. Bunzel*	
14:00 **Welcome** 14:10 **Tutorials** *Chair: F. Capozzi*	15:20 Coffee Break, Posters	14:45 Coffee Break, Posters	
	16:00 **Low Field NMR and Other Techniques II** 16:40 **Method and Application** *Chair: A. Fereira*	15:30 **Company Tours** → Bruker → Max Rubner-Institut → Hoepfner Brewery	
17:30 Welcome Mixer	17:40 Finger Food, Posters		
18:30 **Meeting of Scientific Committee** *Chair: J. van Duynhoven*	19:00 **Discussion Session: Quantitative NMR** *Chair: D.W. Lachenmeier*	19:00 Conference Dinner SCHALANDER (HOEPFNER BREWERY)	

Tuesday Afternoon, June 7	
12:00	**Registration**
14:00	**Welcome**
Tutorials, *Chair: F. Capozzi*	
14:10	Introduction to Multivariate Data Analysis for NMR Spectral Data ***W. Kessler***
15:10	Fast Data Acquisition Methods ***W. Bermel, B. Luy***
16:10	Choice of MRI Methods for the Investigation of Various Food Materials ***D. Gross**, V. Lehmann, T. Oerther, K. Zick, S. Schuhmann*
16:40	Technical and Practical Aspects of PFG Diffusion Experiments with respect to Food Applications ***K. Zick***
17:30	Welcome Mixer, EXHIBITION HALL
18:30	**Meeting of Scientific Committee**, *Chair: J. van Duynhoven*, LECTURE HALL

Wednesday Morning, June 8	
NMR Development, *Chair: B. Luy*, LECTURE HALL	
09:00	Conference Opening
09:10	**Plenary:** Microscale NMR Detectors Enable Mass-Limited Spectroscopy ***J.G. Korvink***
09:55	**Invited:** NMR Analysis of Food Extracts through *para*Hydrogen Hyperpolarization ***M. Tessari***
10:25	Structure and Dynamics of D-Fructose and Related Amadori Derivatives ***M. Kaufmann**, C. Mügge, L.W. Kroh*
10:45	Coffee Break, Poster Presentations, EXHIBITION HALL
From Method Development to Application, *Chair: S.B. Engelsen*, LECTURE HALL	
11:10	**Invited:** Diffusion and Multiple-Quantum NMR: Increased Resolution for Enhanced Characterisation of Mixtures ***S. Caldarelli***
11:40	Molecular Mapping of the Amino Acid Perturbated Metabolome of *S. Cerevisiae* by means of a HPLC-NMR Offline Sliced Metabolomics Approach ***R. Hammerl**, O. Frank, T. Hofmann*
12:00	Analysis of the Compositional Changes in Muscular Tissue Thermally Processed by Quantitative Nuclear Magnetic Resonance Spectroscopy (q-NMR) ***D. Pitoux**, M. Bria, V. Achterberg, D. Lioger, H. This*
12:20	Lunch, Poster Presentations, EXHIBITION HALL

Wednesday Afternoon, June 8	
Low Field NMR and Other Techniques I, *Chair: J. van Duynhoven*, LECTURE HALL	
13:30	**Invited:** Examples of Low Field NMR in Factory Process and High Pressure Process Environments *M.N. Martin, T.R. Wong, M.J. McCarthy,* ***M.P. Augustine***
14:00	A New 2D T_1-T_2 (IR-FID-CPMG) Method for the Characterization of Food and their Transformation ***C. Rondeau-Mouro****, R. Kovrlija, S. Moussaoui*
14:20	Characterisation of Emulsions by PFG-NMR ***G.H. Sørland***
14:40	Use of Temperature-Controlled Low Field ^{1}H NMR to Study Changes during Simulated Baking of a Flour-Water Model System ***G.M. Bosmans****, J.A. Delcour*
15:00	Low-Field RheoNMR: New Combination of Rheology and TD-NMR to Correlate Mechanical Properties with Molecular Dynamics in Soft Matter *V. Räntzsch, M.B. Özen, K.-F. Ratzsch, G. Guthausen,* ***M. Wilhelm***
15:20	Coffee Break, Poster Presentations, EXHIBITION HALL
Low Field NMR and Other Techniques II, *Chair: A. Fereira*, LECTURE HALL	
16:00	TD-NMR as a Method to Determine and Characterize the Water-Binding Capacity of Whey Protein Microparticles *J.P.C.M. Peters, F.J. Vergeldt,* ***H. Van As****, H. Luyten, R.M. Boom, A.J. van der Goot*
16:20	Characterization of Red and White Cocoyam (*Xanthosoma Sagittifolium*) Roots, Flours and Starches during Heating by Low Field NMR ***M. Gudjónsdóttir****, A.A. Boakye, F.D. Wireko-Manu, I. Oduro*
Method and Application, *Chair: A. Fereira*, LECTURE HALL	
16:40	Rapid and Quantitative Assessment of Early Lipid Oxidation in Mayonnaises during Shelf-Life by ^{1}H-NMR ***D. Merkx****, S. Hong, A. Ermacora, J. van Duynhoven*
17:00	Automatized Determination of Ingredients in Non-Alcoholic Beverages with NMR ***S. Ackermann****, K. Dolsophon, T. Thongpanchang, I. Ruge, H. Reusch, D.W. Lachenmeier, M. Bunzel, T. Kuballa*
17:20	Time-Course Evolution of Bioactive Compounds Thermally Treated in Water ***L. Le Falher****, C. Doyen, V. Faugeras, D. Lioger, F.X. Deolarte, H. This*
17:40	Finger Food, Poster Presentations, EXHIBITION HALL
19:00	**Discussion Session: Quantitative NMR**, *Chair: D.W. Lachenmeier* *Experts: T. Schönberger, M. Spraul*, LECTURE HALL

Thursday Morning, June 9	
MRI and Diffusion I, *Chair: J.M. Bonny*, LECTURE HALL	
09:00	**Plenary:** MR Measurements of Phase Transitions Molecular Dynamics in Gels: PGSE MR, MRI and Relaxation Correlations ***J.D. Seymour***
09:45	**Invited:** Physicochemical Characterisation of Multiple W/O/W Emulsions by NMR Diffusometry and Relaxometry ***P. van der Meeren**, L Vermeir*
10:15	NMR Diffusometric Droplet Sizing in Emulsions with Murday-Cotts and Regularization Methods ***J.-H. Sommerling**, A.J. Simon, A. Haber, M. Johns, G. Guthausen, G. Leneweit, H. Nirschl*
10:35	Coffee Break, Poster Presentations, EXHIBITION HALL
MRI and Diffusion II, *Chair: J.M. Bonny*, LECTURE HALL	
11:00	Characterisation of Gel Networks by NMR Nanoprobe Diffusometry *D. de Kort, F. Hoeben, E. Schuster, N. Loren, L.Z. Hohlbein, L. Zuidgeest, M. Emondts, H. Janssen, S. Han, H. Van As, **J. van Duynhoven***
11:20	Use of Multiparametric MRM in Monitoring of the Ham Dry-Curing Process *F. Bajd, M. Škrlep, M. Čandek-Potokar, J. Vidmar, I. **Serša***
11:40	Flow Behaviour of Fat Crystal Dispersions: A Rheo-MRI View ***T. Nikolaeva**, D. de Kort, Voda, H. Van As, J. van Duynhoven*
12:00	Visualisation of Fouling Layer Formation and Flow in Ceramic Hollow Fiber Membranes Using MRI ***F. Arndt**, S. Schuhmann, G. Guthausen, S. Schütz, H. Nirschl*
12:20	Lunch, Poster Presentations, EXHIBITION HALL

Thursday Afternoon, June 9	
Application/Foodomics I, *Chair: M. Bunzel*, LECTURE HALL	
13:30	Kinetic Analysis of the Metabolism of Food Protective Cultures by *In Vitro* NMR and Chemometrics *P. Ebrahimi, F.H. Larsen, H.M. Jensen, F.K. Vogensen,* ***S.B. Engelsen***
13:45	NMR-based Metabolomics to Assess Fruit Quality *P. Schuster, P. Eisenmann, C. Mack, B. Luy, S. Kulling, M. Rist, C. Weinert,* ***C. Muhle-Goll***
14:00	Metabolic Responses of Clams, *Ruditapes Decussatus* and *Ruditapes Philippinarum*, to Short-Term Exposure to Lead and Zinc ***V. Aru****, G. Sarais, F. Savorani, S.B. Engelsen, C. Marincola*
14:15	^{1}H NMR Spectroscopy – A Tool for Authenticity Control of Wine ***R. Godelmann***
14:30	SPE-NMR: Revival of an Old Technique for the Analysis of Wine and Juice ***M. Godejohann****, Y. Jaradat, M. Spraul*
14:45	Coffee Break, Poster Presentations, EXHIBITION HALL
15:30	**Company Tours** → Bruker → Max Rubner-Institut → Hoepfner Brewery
19:00	Conference Dinner, SCHALANDER (HOEPFNER BREWERY)

Friday Morning, June 10	
Application/Foodomics II, *Chair: M. Spraul*, LECTURE HALL	
09:00	**Plenary:** Routine Application of NMR Spectroscopy in Official Food Control **D.W. *Lachenmeier***, *T. Kuballa*
09:45	**Invited:** Metabolomic Investigations of Health Effects of Dairy Products ***M.R. Clausen***, *H. Zheng, B. Amer, C.C. Yde, T. Kastrup Dalsgaard, H.C. Bertram*
10:15	Characterization of Juices from Ancient Danish Apple Cultivars by ^{1}H NMR-Based Metabolomics ***N. Iaccarino***, *C. Varming, M.A. Petersen, F. Savorani, A. Randazzo, S.B. Engelsen*
10:30	Coffee Break, Poster Presentations, EXHIBITION HALL
Application/Foodomics III, *Chair: D.W. Lachenmeier*, LECTURE HALL	
11:00	Untargeted Analyses of Cowpea Seeds (*Vigna Unguiculata*) Using ^{1}H qNMR Combined with Chemometrics and Solid State NMR ***E.G. Alves Filho***, *L.M.A. Silva, F.H. Larsen, E.S. de Brito*
11:15	^{1}H NMR Metabolite Profiling of Guarana Seeds (*Paullinia Cupana*) from Different Geographic Regions of Brazil ***L.M.A. Silva***, *G.S. Silva, K.M. Canuto, E.S. de Brito, R.M. Jesus*
11:30	Honey-Profiling with NMR ***J. Missler***, *G. Beckh*
11:45	Classification of the Botanical Origin of Honey by ^{1}H NMR in Combination with Chemometric Methods and New Data Fusion Approaches ***N. Gerhardt***, *P. Weller, S. Rohn, M. Ohmenhaeuser, T. Kuballa*
12:00	**Closing Remarks**

LIST OF POSTERS

NMR Development, EXHIBITION HALL, D1-D5	
D1	CLIP-ASAP-HSQC for Fast and Accurate Extraction of One-Bond Couplings from Isotropic and Partially Aligned Molecules *J. Becker,* ***B. Luy***
D2	CLIP-COSY: A Clean In-Phase Experiment for the Rapid Acquisition of COSY-Type Correlations *M.R.M. Koos,* ***J.D. Haller****, B. Luy*
D3	Residual Dipolar Coupling-Accelerated Molecular Dynamics for Structural Elucidation of Small Molecules with Increasing Flexibility ***P. Tzvetkova****, U. Sternberg, T. Gloge, A. Navarro-Vázquez, B. Luy*
D4	Cross-Linked Poly(ethylene Glycol) Diacrylate – A Universal Alignment Medium for the Measurement of Residual Dipolar Couplings ***T. Gloge****, P. Tzvetkova, L. Barner, J. Peters, B. Luy*
D5	Elucidation of *Maillard* Reaction Pathways by means of the Carbon-Bond Labeling Technique (CABOLA) *O. Frank, M. Hegmanns, T. Hofmann*
Low Field NMR and Other Techniques, EXHIBITION HALL, L1-L9	
L1	Rapid Method to Measure T_1 of Food Products in Single Scans ***L.A. Colnago****, T. Bueno Moraes, T. Monaretto*
L2	Starch Retrogradation Investigated by 1D and 2D NMR *R. Kovrlija, E. Goubin,* ***C. Rondeau-Mouro***
L3	Studies of the Retrogradation Process of Starch in Gels by Using Low Field NMR Method ***H.M. Baranowska****, M. Sikora, M. Krystyjan, A. Dobosz, P. Tomasik, E.M. Kutyła-Kupidura*
L4	Bread Staling: TD-NMR Study via T_1-T_2 2D Maps *E. Curti, E. Carini, E. Vittadini, M.F. Cobo, T. Bocher, H. Todt*
L5	Pasta Cooking: TD-NMR Study via T_1-T_2 2D Maps *E. Curti, E. Carini, E. Vittadini, M.F. Cobo., T. Bocher, H. Todt*
L6	A Combined Rheology and TD NMR Approach for Determining Water Distribution in Protein Blends *B. Dekkers, D.W. de Kort, K.J. Grabowska, B. Tian,* ***H. Van As****, A.J. van der Goot*
L7	The Moisture and Oil Distribution in Tobacco ***T. Li****, Y. Zhang, P. Yang*

L8	Study of the Moisture Equilibrium of Tobacco by Using Spin-Echo Single Point Imaging Sequence ***Y. Zhang**, T. Li, P. Yang*
L9	Correlating Crystallization Kinetics and Rheological Properties of Polyethylene Using a Newly Developed Low-Field RheoNMR Combination ***M.B. Özen**, V. Räntzsch, K.-F. Ratzsch, G. Guthausen, N. Kavak, P.-K. Dannecker, M.A.R. Meier, M. Wilhelm*
Method and Application, EXHIBITION HALL, A1-A12	
A1	Quantitative ^{1}H-NMR to Assist the SNIF-NMR Analysis ***R. Popescu**, O.R. Botoran, D. Costinel, R.E. Ionete*
A2	PFG-NMR Analysis of Organic Acids in Oil/Water Emulsions *N. Decourcelle, S. Guégan, F. Courand, J.-F. Le Page, A.G. Mathot, O. Couvert, I. Leguérinel, **C. Rondeau-Mouro***
A3	Improved Methods and Tools for Identification of Mixture Components by NMR ***G. Rheinwald**, S. Golotvin, S. Pol, P. Wheeler, B. Pautler, T. Salbert*
A4	Proton Quantitative Nuclear Magnetic Resonance Analysis (^{1}H q-NMR) of Various Extracts of Raw and Thermally Processed ("Roasted") Coffee (*Coffea arabica* L.) Beans: Influence of the Extraction Process *G. Nord, E. Hamon, D. Aoudé-Werner, H. This*
A5	Determination of Fish Oil Quality by ^{1}H NMR Spectroscopy and Multivariate Statistics ***E. Giese**, O. Winkelmann, S. Rohn, J. Fritsche*
A6	^{1}H NMR Spectroscopy and Chemometrics Evaluation of Non-Thermal Processing of Orange Juice ***E.G. Alves Filho**; F.D.L. Almeida, R.S. Cavalcante, E.S. de Brito, P.J. Cullen, J.M. Frias, P. Bourke, F.A.N. Fernandes, Sueli Rodrigues*
A7	NMR Metabolomic Investigation of *Calligonum Azel* Maire ***M. Bannour**, A. Khadhri, D.W. Lachenmeier, T. Kuballa, S. Smiti, B. Hanchi*
A8	Quantitative *In-Situ* NMR to Characterize Protein Oxidation and its Dynamics ***G. Pagès**, A. Morisse, P. Gatellier, E. Martineau, P. Giraudeau, J.-M. Bonny*
A9	Quantitative HSQC-NMR Screening of Feruloylated Arabinoxylan Side Chain Profiles in Cereal Grains ***R.R. Schendel**, U. Schmitt, M. Bunzel*
A10	A 2D-NMR-Spectroscopic Profiling Approach to Analyse Structural Elements of Neutral Pectic Side Chains *D. Wefers, **M. Bunzel***
A11	Liquid and Solid-State ^{1}H, ^{13}C and ^{11}B NMR Analysis of Magnesium Fructoborate Complex: Chemical Structure, Identification and Stability Study ***B. Nemzer**, J. Edwards*

A12	Identification and Characterization of Ca and Mg Different Sugar Borate Esters Using Multi Nuclear Liquid and Solid-State NMR ***B. Nemzer**, J. Hunter, J. Edwards*
MRI and Diffusion, EXHIBITION HALL, M1-M6	
M1	A Framework for Nucleus Density Quantitative Mapping Corrected for B_1-Errors ***J.-M. Bonny**, S. Clerjon*
M2	Understanding Meat Crust Formation: Validate Mathematical Models from Quantitative Microscopic MRI ***S. Clerjon**, S. Portanguen, A. Kondjoyan, J.-M. Bonny*
M3	Magnetic Resonance Imaging to Monitor the Curing of Century Eggs *C. Hickling, A. Hogg, **R. H. Morris***
M4	Magnetic Resonance as a Tool to Assess Moisture Content in Potatoes for Frying Processes ***E.R. Dye**, M.I. Newton, R.H. Morris*
M5	MRI Study of Staling Process in White Bread: Effect of Bread Improver ***A. Traoré**, L. Linossier, S. Chapron*
M6	Water Diffusion in Biofilms with Different Physical Structures ***M.P. Herrling**, J. Weisbrodt, H. Horn, S. Lackner, G. Guthausen*
Application/Foodomics, EXHIBITION HALL, F1-F20	
F1	Food Matrix Description and Stability: A New Perspective from Foodomics ***A. Trimigno**, G. Picone, C. Pineda-Vadillo, D. Dupont, A. Bordoni, F. Capozzi*
F2	NMR Studies of the Quality-Deteriorating Wooden Breast Syndrome in Chicken ***H.C. Bertram**, U.K. Sundekilde, M.K. Rasmussen, P. Brandt, J.F. Young*
F3	Characterization and Identification of Biomarkers from Deterioration in Freshwater Fish by NMR and Chemometrics ***L.M. Lião**, V.S. Pinto, I.S. Flores*
F4	Extensive Regulation of Diurnal Transcription and Metabolism by Glucocorticoids *B.D. Weger, M. Weger, **B. Görling**, C. Gobet, M. Yildiz, C. Keime, G. Poschet, B. Jost, N. Krone, R. Hell, T. Akcay, T. Güran, F. Gachon, B. Luy, T. Dickmeis*
F5	Rapid Identification of Imitation Cheese and Imitation Ice Cream Based on Vegetable Fat Using NMR Spectroscopy and Chemometrics ***R. Brendel**, T. Kuballa, D.W. Lachenmeier, R. Godelmann, C. Andlauer, Y.B. Monakhova*
F6	Classification of the Botanical Origin of Honey by ^{1}H NMR in combination with Chemometric Methods and New Data Fusion Approaches ***N. Gerhardt**, P. Weller, S. Rohn, M. Ohmenhaeuser, T. Kuballa*

F7	Definition of Monofloral and Polyfloral Honeys Based on NMR Metabolomic Profiling ***E. Schievano**, C. Finotello, J. Uddin, S. Mammi, L. Piana*
F8	Characterization of Lignin Structures of Plant Based Foods by 2D-NMR Spectroscopy ***J. Schäfer**, M. Bunzel*
F9	Longitudinal Metabolic Profiling during Growth and Storage of Apples from Different Production Systems Studied by ^{1}H HR-MAS NMR ***M. Vermathen**, M. Marzorati, G. Diserens, D. Baumgartner, C. Good, F. Gasser, P. Vermathen*
F10	Untargeted NMR Spectroscopic Analysis of the Metabolic Variety of Apple Cultivars ***P. Eisenmann**, M. Ehlers, C. Weinert, M. Rist, B. Luy, C. Muhle-Goll*
F11	Variation of Blueberry's Metabolic Profile: The Influence of Ambient and Genetic Factors ***A.P. Sobolev**, D. Capitani, N. Proietti, M. Delfini, S. Carradori, F.R. De Salvador, L. Mannina*
F12	Fingerprint Profile by ^{1}H NMR and Chemometric Analysis of Freeze-Dried Açaí Berry Pulp ***T. da Conceição Alves**, A.G. Ferreira, M. do Socorro Padilha de Oliveira, R. de Andrade Mattietto*
F13	Study of Lipoxigenase Enzyme Activity in Common Beans by NMR and UV Spectroscopies ***L.M. Lião**, A.K. Silva, P.Z. Bassinello, A.C. Lanna*
F14	Authentication of Saffron (*Crocus Sativus* L.) Using ^{1}H NMR Spectroscopy ***S. Schumacher**, S. Mayer, C. Sproll, T.Kuballa, D.W. Lachenmeier*
F15	HR-MAS NMR Spectroscopy on the Quality Control of Green Tea ***A. Barison**, M. de Fátima Costa Santos*
F16	Investigation of the Impact of UV-C Treatment on Grape Must Using Untargeted NMR Spectroscopy ***L.A. Kromm**, K.Briviba, M.R. Stahl, T.Kuballa, D.W. Lachenmeier*
F17	Whisky Analysis through the Application of NMR Metabolomic Techniques ***N. MacKinnon**, C. Trautwein, J.G. Korvink*
F18	Nontargeted NMR Analysis to Detect Hazardous Substances Including Methanol in Unrecorded Alcohol from Russia ***T. Hausler**, M. Neufeld, J. Rehm, T. Kuballa, D.W. Lachenmeier*
F19	Classification of Italian Vinegar by Foodomics Approach ***G. Picone**, M. Sacco, A. Trimigno, F. Capozzi*
F20	HR-MAS NMR as Technique to Monitor *In-Vivo* Growth and Real-Time Fermentation Patterns of *Saccharomyces Cerevisae* ***C. Trautwein**, M.V. Meissner, J. Höfflin, J.G. Korvink*

EXHIBITORS

The following companies will present their products during the industrial exhibition:

Bruker BioSpin GmbH

Anvendt Teknologi AS

Mestrelab Research, S.L.

Niumag Analytical Instrument Corporation

LOT-QuantumDesign GmbH

Nanalysis Corp.

Spinlock

COMMITTEES

Scientific Committee

Peter Belton	University of East Anglia – UK
Jean-Marie Bonny	INRA, Clermont-Ferrand – FR
Francesco Capozzi	University of Bologna – IT
John van Duynhoven (MR-Food representative of Groupement AMPERE)	Wageningen University - NL
Søren Balling Engelsen	University of Copenhagen – DK
Antonio Ferreira	Federal University of São Carlos – BR
Gisela Guthausen	Karlsruhe Institute of Technology – DE
Manfred Spraul	Bruker BioSpin GmbH – DE
Graham Webb	Royal Society of Chemistry – UK

Organizing Committee

Mirko Bunzel	Institute of Applied Biosciences Department of Food Chemistry and Phytochemistry Karlsruhe Institute of Technology, Germany
Gisela Guthausen	Pro^{2}NMR at the Institutes for Mechanical Process Engineering and Mechanics and for Biological Interfaces 4, Karlsruhe Institute of Technology, Germany
Thomas Kuballa	Chemical and Veterinary Investigation Agency (CVUA) Karlsruhe, Germany
Burkhard Luy	Institute of Organic Chemistry, Institute for Biological Interfaces 4 – Magnetic Resonance Karlsruhe Institute of Technology, Germany
Manuela J. Rist	Max Rubner-Institut Department of Physiology and Biochemistry of Nutrition Karlsruhe, Germany
Heike P. Schuchmann	Institute of Process Engineering in Life Sciences Section I: Food Process Engineering Karlsruhe Institute of Technology, Germany

CONFERENCE GENERAL INFORMATION

Venue

The conference will be held at the building of the Regierungspräsidium in Karlsruhe:

Meidingersaal
Karl-Friedrich-Str. 17 (Rondellplatz)
76133 Karlsruhe

The sessions will be held in the LECTURE HALL.

Posters will be presented in the EXHIBITION HALL, authors should be present during coffee and lunch breaks.

The industrial exhibition will take place in the EXHIBITION HALL.

Registration and Help Desk

The registration and help desk will be located near the entrance of the building. It will open on Tuesday, June 7, 12:00 and will be open during the conference hours.

Internet Access

WLAN is available for all attendees. Information on WLAN access will be provided at the help desk.

Drinks and Food

Drinks and food will be provided in the EXHIBITION HALL during coffee and lunch breaks.

Also the “Welcome Mixer” on Tuesday evening 17:30 will be served in the EXHIBITION HALL.

All attendees are invited to the Conference Dinner by Bruker. Please see page 21 for details on the location of the restaurant SCHALANDER.

MEIDINGER HALL REGIERUNGSPRÄSIDIUM KARLSRUHE

RP Karlsruhe (www.rp-karlsruhe.de)
Karl-Friedrich-Str. 17 (Rondellplatz)
poststelle@rpk.bwl.de
☎ 0721 926-4010 or 4060

Public transport

Tramlines towards “Marktplatz“ as well as bus line 10 from central station Karlsruhe (rail replacement service) towards “Ettlinger Tor”
The visitors’ entrance is located at the building site Karl-Friedrich-Straße.

Arrival by car

A8/A5 until exit Karlsruhe-Mitte, continue along the ”*Südtangente*” (K9657) towards Rheinhafen/Landau, exit (2) central station (*Hauptbahnhof*) or A5 until exit Karlsruhe-Durlach, continue along B10 towards city centre.

Car parks nearby

- Erbprinzenstraße 2
- Friedrichplatz 7
- Kreuzstraße 13
- Karstadt, Zähringerstraße

If you arrive by car, please note:
Due to extensive construction work in connection with the underground railway, you will have to expect impairments in the city area of Karlsruhe.

Excursions

Three parallel excursions will take place on Thursday afternoon 15:30, June 11.

Bruker

Up to 50 participants of the conference are invited to visit the former head quarter of Bruker where NMR spectrometers and applications are developed and built.
Transport to Bruker by bus.

Max Rubner-Institut

MRI is the Federal Research Institute of Nutrition and Food in Germany with its head office in Karlsruhe. Here in Karlsruhe, the departments of Nutritional Behaviour, Physiology and Biochemistry of Nutrition, Food Technology and Bio Process Engineering, and Safety and Quality of Fruit and Vegetables are located. Up to 45 persons are welcome to visit the institute.
Haid-und-Neu-Straße 9, Karlsruhe
Tram station: Karl-Wilhelm-Platz (Tram: 4, 5)

Hoepfner Brewery

Historically, local and private breweries could be found everywhere in Germany. One of them is Hoepfner in Karlsruhe. You are invited to visit the Hoepfner Brauburg.
Haid-und-Neu-Straße 18, Karlsruhe
Tram station: Karl-Wilhelm-Platz (Tram: 4, 5)

Each tour will be accompanied by members of the organizing team. The members of the organizing team will wait for you in the EXHIBITION HALL at 15:30 after the Thursday afternoon coffee break. Please watch out for signs of the excursion you want to join.

Conference Dinner

Bruker invites you to the Conference Dinner on Thursday, June 9, starting at 19:00. The Conference Dinner will be held in the Restaurant SCHALANDER (Hoepfner Brewery).

SCHALANDER, Hoepfner Burghof
Haid-und-Neu-Straße 18
76131 Karlsruhe
http://www.hoepfner-burghof.de/en/

The Restaurant is located in the **Hoepfner Brewery** and very close to the **Max-Rubner-Institut**. Participants joining these two excursions can walk to the restaurant. Participants joining the excursion to **Bruker** will be brought to the restaurant by bus. Maps of the location of the restaurant will be provided at the help desk.

Guidelines for Oral and Poster Presentations

Oral Presentations

The official conference language is English.

The time slots for the presentations are 20 min (15 + 5) and 15 min (12 + 3), respectively. The reduced time slots for oral presentations in the “Application/Foodomics”-sessions are due to the high number of abstracts in this field.

Projector and laptops are available. For a smooth flow, it would be highly appreciated if you could use this equipment and accordingly upload your presentation at latest in the break before your presentation. Please contact the technical staff in the LECTURE HALL in this respect.

Oral contributions are invited to contribute to the conference proceedings, which will be open source articles by IMPublications. Please contact Gisela Guthausen if you are interested in contributing an article to this special issue (gisela.guthausen@kit.edu).

Poster Presentations

Poster boards of approximately 1.00 m width and 2.50 m height are available on site. The format of the poster should be A0 and portrait.

Posters are sorted according to the topics and marked with a number. Please mount your poster on the board according to your number and hang it up during the morning coffee break on Wednesday, June 7 at the latest. Poster sessions are scheduled during the breaks until afternoon coffee break on Thursday. Some referees will walk around to find the candidates for the poster awards. Therefore, we would like to ask all authors to remain close to their posters for possible questions and discussions from participants and referees.

Poster Awards

Two prizes for the best posters, sponsored by Wiley-VCH, will be awarded. The awards are endowed with a one-year free subscription to the European Journal of Lipid Science and Technology.

The two best posters will be selected by an independent jury.

Sponsors

We gratefully acknowledge the contributions of the following sponsors to the conference MR in Food 2016:

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Useful Information

Public Transport in Karlsruhe
Karlsruhe has a public transportation system and can easily be reached by train.
To plan a specific journey, please visit http://en.kvv.de/ in the city area or German Rail for connections outside the city area http://www.bahn.de/p_en/view/

Taxi
From Karlsruhe main station, you can take a taxi (approx. €10).

Airports
The nearest airports are

Frankfurt:
International airport with most connections, about 1 hour to Karlsruhe via the ICE, hourly train connections.
The long-distance train station is located on level 0 of Terminal 1 of the airport. Once you get there, take a train to Karlsruhe main station (Hauptbahnhof) (for exact times of departure, please refer to the train schedule of German Rail). [duration approx. 1h]

Stuttgart:
International airport, about 90-100 minutes via Stuttgart train station (tram connection) and to Karlsruhe via the IC, hourly train connections.
Take tram line S2 or S3 to Hauptbahnhof Stuttgart, then change to a train to Karlsruhe main station (Hauptbahnhof) (for exact times of departure, please refer to the train schedule of German Rail). [total duration approx. 2 h]

Karlsruhe/Baden-Baden:
Airport with mostly regional connections.
The Baden-Airpark-Express line will take you to Karlsruhe main station (Hauptbahnhof).
Alternatively, you can take a taxi from the airport to Karlsruhe (approx. €40).

Weather
Karlsruhe has a temperate climate (although it is one of the warmest places within Germany). In June, it is generally warm and sunny but it can also be unpredictable and showers are not uncommon.

Currency
Germany's currency is Euro - EUR. Symbol for Euro is €.

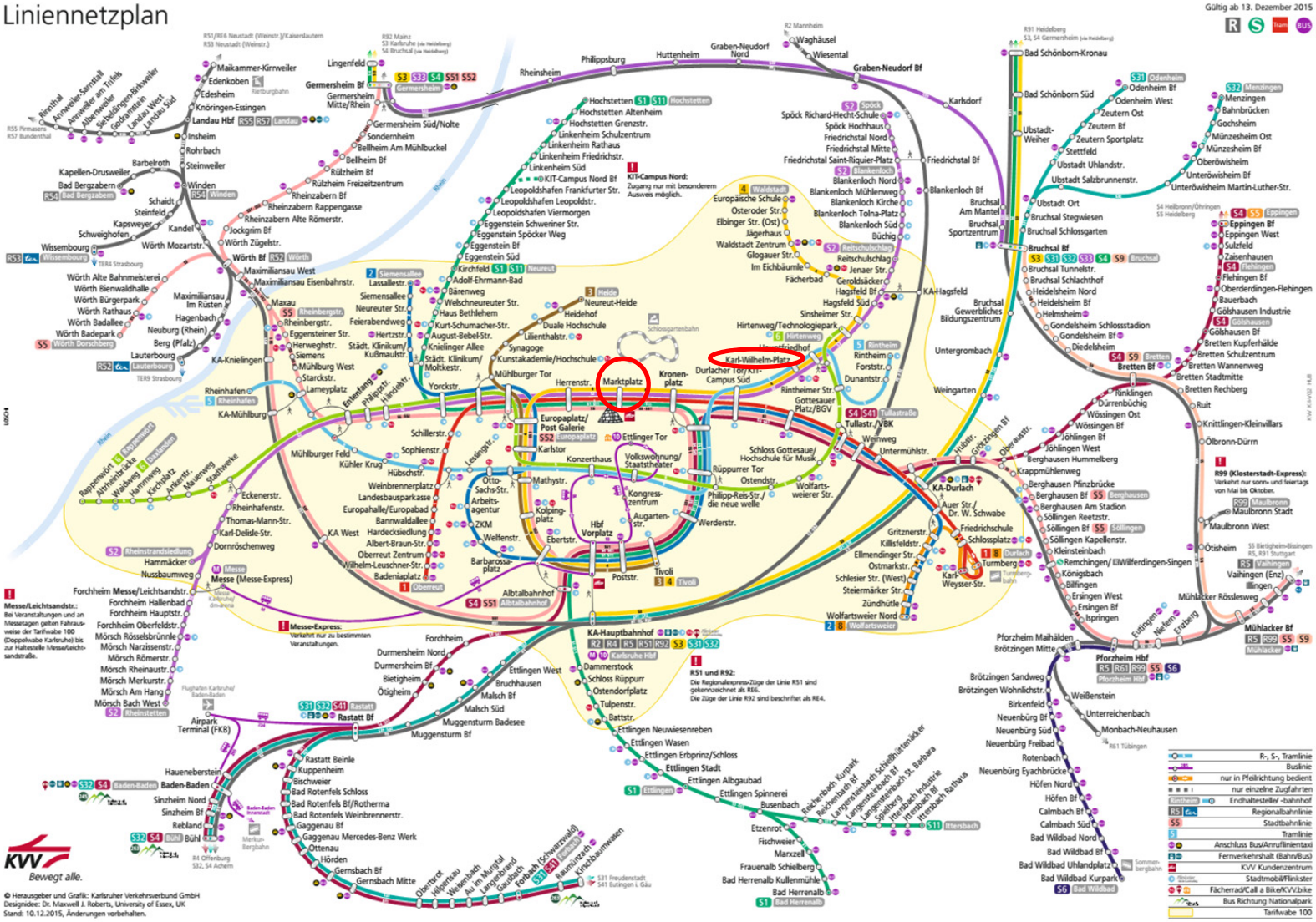
Electricity
The electricity in Germany is 220-240V/50Hz and accommodates a common European plug. Adaptors can be purchased in the major electrical shops and in airports.

Smoking Ban
There is a smoking ban in Germany in public places which includes bars, restaurants and public transport.

Time Zone
The time zone in Germany is GMT +1. German Summer Time is GMT +2:00 from the last Sunday in March until the last Sunday in October

LOCAL TRANSPORTATION

https://www.kvv.de/fileadmin/user_upload/kvv/dokumente/netz/liniennetz/2016/2015-12_L0SCHI_WEB.pdf



ABSTRACTS LECTURES

Tuesday, June 7, 14:10 – 15:10

Introduction to Multivariate Data Analysis for NMR Spectral Data

Waltraud Kessler
ISTI Multivariate Datenanalyse, Steinbeis-Hochschule Berlin

NMR spectroscopy is certainly the analytical methodology that provides the most information about a molecule. Food contains a great variety of components and thus a great number of resonances, originating from many different compounds. This type of complex data can be hard to summarize and interpret without appropriate tools and require sophisticated strategies for data evaluation. Multivariate projection methods like principal component analysis (PCA) and partial least squares regression (PLS-R) are capable of projecting the information contained in these high dimensional data down into low dimensional spaces. This allows easy interpretation of complicated structures. Thus NMR spectral information and multivariate methods can be used in the context of food surveillance. How this can be achieved will be demonstrated in the tutorial using examples for identifying pine nuts, for the analysis of alcoholic beverages and for validating nutrition labeling of milk.

Tuesday, June 7, 15:10 – 16:10

Fast Data Acquisition Methods

W. Bermel[1], B. Luy[2]
[1]*Bruker Biospin GmbH, Am Silberstreifen 4, 76287 Rheinstetten, Germany*
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The length of multidimensional NMR experiments is often determined by the required resolution in the indirect dimension(s) rather than by the signal-to-noise of the signal that yields the desired information. As a consequence, people have thought about methods to speed up NMR experiments, usually on the expense of signal intensity. Several approaches will be introduced and compared:

Non uniform sampling: Only a subset of the data points of the indirect dimension(s) is acquired. The missing points are reconstructed by appropriate mathematical algorithms (Compressed Sensing, MultiDimensional Decomposition, Maximum ENTropy).

Projection spectroscopy: Rather than recording a full multidimensional experiment, only 2D projections are acquired for a set of projection angles. From these the chemical shifts of the peaks in all dimensions can be extracted.

Hadamard spectroscopy: Instead of a chemical shift evolution in a time dimension, signals at known chemical shifts are selectively excited. From these known shifts a full spectrum can be reconstructed.

Rapid pulsing: Ultrafast 2D NMR in a single scan and extensions to the Ernst-angle approach in 2D experiments are two topics that allow the fast acquisition of spectra. The general ideas and limitations with respect to applicability will be discussed.

Tuesday, June 7, 16:10 – 16:40

Choice of MRI Methods for the Investigation of Various Food Materials

Dieter Gross[1], Volker Lehmann[1], Thomas Oerther[1], Klaus Zick[1], Sebastian Schuhmann[2]
[1]*Bruker Biospin GmbH, Rheinstetten Germany*
[2]*Karlsruhe Institute of Technology, Karlsruhe Germany*

Magnetic resonance imaging (MRI) or NMR microscopy is used to study foods from liquids of different viscosities and complexities to solid materials, from raw pure components or mixtures, during processing, to the uncooked or cooked end products. The physico-chemical food properties at their different stages have a strong impact on the possibilities to be studied by MRI. The most common properties used to achieve image contrast in MRI are the spin density, the T_1, T_2 and T_2^* relaxation, the translational diffusion, the chemical shift and the kind of nucleus in the objects under study. This tutorial shows various applications mainly tested as feasibility studies to evaluate the possibilities and limits of MRI to visualize spatially resolved properties of food at various stages. Some typical examples deal with wetting of raw food materials during processing, liquid uptake of cereals, drying of fruit, cooking of pasta and potatoes, bread dough evolution, glutamate distribution in tomatoes and others. These examples will be discussed with respect to the imaging methods of choice.

Tuesday, June 7, 16:40 – 17:10

Technical and Practical Aspects of PFG Diffusion Experiments with Respect to Food Applications

Klaus Zick
Bruker BioSpin GmbH, Rheinstetten Germany

Pulsed field gradient (PFG) diffusion NMR, also called PGSE (pulsed gradient spin echo) NMR, has wide applications in food science. This talk focuses on some technical aspects of this technique. Technical background information is useful for understanding the method and helping avoiding artefacts due to technical problems.

The core technology is the gradient coil design. The talk shall explain the basic reasons why high-end gradient technology is required and what the basic principles are. The second part is covering convection, a frequently seen problem in PFG diffusion NMR mainly in solution. Convection is a coherent flow driven by a temperature gradient. In PFG diffusion experiments convection usually increases the apparent diffusion coefficient and can therefore spoil the results of diffusion experiments. This part of the talk mainly wants to trigger awareness to the convection problem. The last part of the talk touches the topic q-space imaging used to characterize emulsions and gels in the context of food.

Wednesday, June 8, 09:10 – 09:55

Microscale NMR Detectors Enable Mass-Limited Spectroscopy

J.G. Korvink
Karlsruhe Institute of Technology, Institute of Microstructure Technology, Germany

Numerous ideas motivate the development of miniaturized NMR hardware, yet a common thread is the need to consider the application very carefully, in order to render the measuring instrument practicable, and of course to meet the need of extracting the desired signal from the sample. Additional constraints are imposed by available miniaturization technologies, since only a subset of these lead to assemblies that are suitable for insertion into an NMR magnet.
In my group we are dedicating extensive effort to build very small bespoke NMR detectors [4,5], both for applications in spectroscopy, as well as for imaging. On this adventurous road we are discovering many of the limitations of microfabrication technologies, and also some of the misconceptions about the appropriate scaling laws, such as the way detectability scales with dimension. In the same process, my grad students and postdocs are inventing new manufacturing technologies and procedures that are gradually overcoming the technical limitations that we encounter in miniaturization. This is simplifying the application of small detectors, mainly because we are focusing on methods of mass fabrication, which brings down the per sensor cost, and encourages experimentation. Our approach is holistic, in the sense that we are co-developing design software, manufacturing processes, and experimental protocols.
In the talk I will describe a range of our microscale NMR subsystems, including electronics [2], hyperpolarisation with SABRE and DNP, microcoils for MAS, MACS and MRFM [4,5], in-field electronics for phased microarrays, and numerical design tools for transport modelling, resonator modelling, and coil field tuning [1,3,7]. I will also cover our ongoing work to simplify micromanufacturing, towards achieving reliable mass fabrication. The focus of my talk will be on the micro-engineering of these small systems, where I will show results from our design-build-test cycles. I will also illustrate my talk briefly with a few results from the applications, which include C. elegans metabolomics, and brain slice and organ microimaging [6], and which require the hyphenation of other techniques, such as sample nurturing, or organism detection, and optical imaging.

[1] M. Jouda et al, Circuit level simulation of MRI receive chain using excitation derived from images, *Concepts in Magnetic Resonance Part B* (in print)
[2] M. Jouda et al, Implementation of an in-field CMOS frequency division multiplexer for 9.4 T magnetic resonance applications, Int. J. Circ. Theor. Appl. 2014
[3] M. Kudryavtsev et al, A Compact Parametric Model of Magnetic Resonance Micro Sensor," Proc. EuroSimE 2015.
[4] R.C. Meier et al, Microfluidic integration of wirebonded microcoils for on-chip applications in nuclear magnetic resonance, Journal of micromech. microeng., 24(4) 2014
[5] N. Spengler et al, Micro-fabricated Helmholtz coil featuring disposable microfluidic sample inserts for applications in nuclear magnetic resonance, Journal of micromech. microeng., 24(3) 2014
[6] K. Göbel et al, Phased-array of microcoils allows MR microscopy of ex vivo human skin samples at 9.4 T, Skin Research and Technology, 21(1) 2014
[7] P.T. While, J.G. Korvink, Designing MR Shim Arrays With Irregular Coil Geometry: Theoretical Considerations, IEEE Trans. Biomed. Eng., 61(6) 2014.

Wednesday, June 8, 09:55 – 10:25

NMR Analysis of Food Extracts through *para*Hydrogen Hyperpolarization

Marco Tessari
Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

NMR spectroscopy is one of the most powerful techniques to simultaneously obtain qualitative and quantitative information in chemical analysis. Despite its versatility, the applications of NMR in the study of complex mixtures, such as food extracts or biofluids, are often limited by the insensitivity of the technique, further aggravated by the poor signal dispersion in ^{1}H spectra. Recent advances in *para*Hydrogen induced hyperpolarization have proven to address both these limitations for specific classes of compounds [1-3]. We have recently applied this technique to the detection and quantification of target analytes in the low-micromolar concentration regime: a few applications to food extracts will be presented.

[1] Eshuis, N.; Hermkens, N.; van Weerdenburg, B. J. a; Feiters, M. C.; Rutjes, F. P. J. T.; Wijmenga, S. S.; Tessari, M. *J. Am. Chem. Soc.* **2014**, *136* (7), 2695–2698.
[2] Eshuis, N.; van Weerdenburg, B. J. A.; Feiters, M. C.; Rutjes, F. P. J. T.; Wijmenga, S. S.; Tessari, M. *Angew. Chemie Int. Ed.* **2015**, *54* (5), 1481–1484.
[3] Eshuis, N.; Aspers, R. L. E. G.; van Weerdenburg, B. J. A.; Feiters, M. C.; Rutjes, F. P. J. T.; Wijmenga, S. S.; Tessari, M. *Angew. Chemie Int. Ed.* **2015**, *54* (48), 14527–14530.

Wednesday, June 8, 10:25 – 10:45

Structure and Dynamics of D-Fructose and Related Amadori Derivatives

Martin Kaufmann[1], Clemens Mügge[2], Lothar W. Kroh[1]
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[2]Humboldt University of Berlin, Department of Chemistry, NMR Facility, Brook-Taylor-Straße 2, D-12489 Berlin, Germany

Amino acids such as L-alanine and L-proline are known to influence the kinetics of sugar degradation reactions for already more than 100 years. [1] Kinetic studies of sugar systems have shown that D-fructose related Amadori compounds show much higher reactivity than D-fructose itself. [2] With the aim of finding structure-reactivity relationships that explain the observed differences between ketoses and Amadori compounds, we elucidated the isomeric structures of various D-fructose derivatives. In doing so, it could be shown that structures as well as isomeric composition are not much influenced by C-1 substituent of D-fructose. It was therefore assumed that altered reactivities may result from different dynamics of isomerisation. [3] Applying ^{13}C selective saturation transfer NMR spectroscopy, thermodynamic activation parameters of isomerisation could be determined that correlate with molecular stability of different D-fructose derivatives. All results could be explained mechanistically.

[1] Maillard LC. Action des acides aminés sur les sucres. C R Acad Sci. 1912;154:66-68.
[2] Brands CMJ, van Boekel MAJS. Kinetic Modeling of Reactions in Heated Monosaccharide-Casein Systems. J Agric Food Chem. 2002;50:6725-6739.
[3] Kaufmann M, Mügge C, Kroh LW. Theory of the milieu dependent isomerisation dynamics of reducing sugars applied to D-erythrose. Carbohydr Res. 2015;418:89-97

Wednesday, June 8, 11:10 – 11:40

Diffusion and Multiple-Quantum NMR: Increased Resolution for Enhanced Characterisation of Mixtures

Stefano Caldarelli
Aix Marseille Université, Centrale Marseille CNRS, iSm2 UMR 7313, 13397 Marseille, France

Analysis of complex mixtures calls for high-resolution NMR methods capable of lifting ambiguities in the speciation of the sample composition. A key aspect of NMR is the possibility of spreading the spectral complexity over several dimensions. On the other hand, this enhancement is counterweighed by dramatic increases of the experiment duration.

This talk will illustrate strategies that our group is pursuing to find optimal experimental conditions in both resolution and timeframes for the NMR characterization of mixtures. An experiment that has shown intriguing potential is homonuclear multiple-quantum NMR. Particularly, a molecular fragment consisting of *n*-coupled protons provides the simplest correlation, a single line, in the *n*-quantum spectrum. Moreover, fragments with fewer than n protons are filtered out of the spectrum, with further simplification. Thus, analysis of a series of multiple-quantum spectra allows the annotation of a large number of spin systems, which eventually can be combined to provide full molecules. This Maximum-Quantum (MaxQ) protocol has allowed to resolve the spectra of highly overlapping signals, [1] as the ones stemming from the aromatic regions of phenolic molecules, for instance. [2]

Possible ways of achieving acceleration of Multiple-Quantum or other nD methods in the case of mixtures can be achieved either by multiplex (“ultrafast”) or non-uniform sampling (NUS) approaches. We shall provide some insight into the criteria of choices of the UF and NUS parameterization, particularly in light of the concentration and chemical shift ranges typically encountered in mixtures. [3-6]

Finally, improvements in mathematical approaches not based on FT can help disentangling more efficiently overlapping signals. Examples on the popular DOSY mixture analysis will be shown. [7]

[1] Reddy MGN, Caldarelli S. Demixing of Severely Overlapping NMR Spectra through Multiple-Quantum NMR. Anal Chem. 2010;82(8):3266-9.
[2] Reddy GNM, Caldarelli S. Maximum-quantum (MaxQ) NMR for the speciation of mixtures of phenolic molecules. Chem Commun. 2011;47(14):4297-9.
[3] Le Guennec A, Dumez J-N, Giraudeau P, Caldarelli S. Resolution-enhanced 2D NMR of complex mixtures by non-uniform sampling. Magn Reson Chem. 2015;53(11):913-20.
[4] Guennec AL, Giraudeau P, Caldarelli S, Dumez J-N. Ultrafast double-quantum NMR spectroscopy. Chemical communications (Cambridge, England). 2015;51(2):354-7.
[5] Andre M, Piotto M, Caldarelli S, Dumez J-N. Ultrafast high-resolution magic-angle-spinning NMR spectroscopy. Analyst. 2015;140(12):3942-6.
[6] Le Guennec A, Giraudeau P, Caldarelli S. Evaluation of Fast 2D NMR for Metabolomics. Anal Chem. 2014;86(12):5946-54.
[7] Toumi I, Torresani B, Caldarelli S. Effective Processing of Pulse Field Gradient NMR of Mixtures by Blind Source Separation. Anal Chem. 2013;85(23):11344-51.

Wednesday, June 8, 11:40 – 12:00

Molecular Mapping of the Amino Acid Perturbated Metabolome of *S. Cerevisiae* by means of a HPLC-NMR Offline Sliced Metabolomics Approach

Richard Hammerl, Oliver Frank, Thomas Hofmann
Lehrstuhl für Lebensmittelchemie und molekulare Sensorik,
Technische Universität München, Lise-Meitner-Str. 34, 85354 Freising

Metabolome investigations by means of mass spectrometry are often limited in structure elucidation of unknown and new metabolites. An innovative automated method for the analysis of quantitative and qualitative changes in the metabolome in biological systems is presented by coupling high performance liquid chromatography and ^{1}H-NMR spectroscopy. This process is demonstrated with *Saccharomyces cerevisiae* as selected microorganism in a fermentation batch in the presence and absence of Tyrosine as nitrogen source.

A preparative HPLC separation step with a subsequent ^{1}H-NMR analysis of the obtained subfractions enabled the identification of 33 metabolites, including three compounds that have not been earlier reported in yeast. For comparison of relative metabolite concentration ratios, ^{1}H-NMR spectra of the subfractions were used to calculate so called “NMR buckets” which are further used for sample comparison. Moreover, absolute metabolite concentrations were determined by the ERETIC 2 (Electronic REference To access *In vivo* Concentrations) tool based on the PULCON (PULse length based CONcentration determination) methodology within an error in the quantitation of 1.5 ± 0.2 %. Finally, human sensory analysis of identified metabolites showed a significant kokumi enhancing activity of *N*-(1-oxododecanyl)-tyrosine above a taste threshold concentration of 145 µmol/L (in model broth) and a pronounced bitter taste above 480 µmol/L (in water).

Wednesday, June 8, 12:00 – 12:20

Analysis of the Compositional Changes in Muscular Tissue Thermally Processed by Quantitative Nuclear Magnetic Resonance Spectroscopy (qNMR)

Daisy Pitoux[1,2], Marc Bria[3], Victor Achterberg[1,2], Delphine Lioger[1], Hervé This[2,4]
[1]*INNIT, 76 rue de la pompe, 75116 Paris, France*
[2]*Groupe de gastronomie moléculaire, Inra-AgroParisTech International Centre for Molecular Gastronomy, F-75005, Paris, France*
[3]*Université Lille 1, Sciences et Technologies, Plateforme RMN, F-59655 Villeneuve d'Ascq, France*
[4]*UMR GENIAL, AgroParisTech, Inra, Université Paris-Saclay, 91300 Massy, France*

In this study, data generated by ^{1}H NMR spectroscopy were used to evaluate the effect of thermal processing on the concentration of water-soluble metabolites in a muscular tissue. Unprocessed and thermally processed (200 °C, 1 hour) beef pieces (Bos Taurus, longissimus dorsi) were analysed. The study includes a comparison of different approaches, for which the extraction steps were limited. The first two approaches analysed non treated samples without [1] or with high-resolution magic-angle spinning (HR-MAS) [2] NMR spectroscopy. Finally, a classic method based on metabolites extraction and liquid-state NMR [3] is presented. Data analysis led to a quantitative determination of the compounds significantly affected by thermal treatment such as amino acids, sugars, lactate.

[1] Weberskirch L, Luna A, Skoglund S, This H. Comparison of two liquid-state NMR methods for the determination of saccharides in carrot (Daucus carota L.) roots. Anal Bioanal Chem. 2011 Jan;399(1):483–7.
[2] Ritota M, Casciani L, Failla S, Valentini M. HRMAS-NMR spectroscopy and multivariate analysis meat characterisation. Meat Sci. 2012 Dec;92(4):754–61.
[3] Daykin CA, Foxall PJD, Connor SC, Lindon JC, Nicholson JK. The Comparison of Plasma Deproteinization Methods for the Detection of Low-Molecular-Weight Metabolites by 1H Nuclear Magnetic Resonance Spectroscopy. Anal Biochem. 2002 May;304(2):220–30.

Wednesday, June 8, 13:30 – 14:00

Examples of Low Field NMR in Factory Process and High Pressure Process Environments

Michele N. Martin, Tricia R. Wong, Michael J. McCarthy, Matthew P. Augustine
Departments of Chemistry and Food Science and Technology, University of California Davis, Davis, CA 95618

Traditional high field liquids and solids NMR spectroscopy have enjoyed much success in the study of food. As food is a complex mixture, the ongoing challenge is the recovery of high resolution NMR spectra for selected components. Operation with a lower magnetic field often precludes the measurement of high resolution NMR spectra but offers the ability to accomplish experiments that either require higher sample volumes, complicated, non-standard sample geometries, or electrically noisy, non-laboratory, actively working, factory process environments.

These difficulties are presented in the study of tomato paste spoilage. Here high resolution low field NMR was first used to determine that ^{1}H T_1 and T_2 values directly report on tomato paste spoilage. These facts were used to develop a single-sided NMR sensor and pulse sequences to detect tomato paste spoilage in sealed non-ferrous metal lined, 1,000 L, 1 ton bins in less than 4 min/bin. Recent improvements in portability, sample throughput rate, and attenuation effects due to non-ferrous metal packaging will be described.

Conventional high pressure food processing environments offer similar challenges for NMR spectroscopy. Here either pipes or autoclaves with food product at pressure or custom designed NMR probes made primarily of non-ferrous metal for strength to prevent implosion are used. Recent NMR experiments involving aqueous phase electrolyte solutions at pressures up to 2 GPa, a factor of 4 greater than commercial high pressure food processors, indicate that equilibrium constants and hence pH is pressure dependent, dropping by ca. 1 unit for every 2,000 bar of applied pressure. Moreover experiments on the same electrolyte solutions and food products up to 1.8 GPa, a factor of 2 greater that the freezing pressure for water, indicate that water does not freeze on the timescale of hours – days. The implications of these measurements on the high pressure food processing industry and recent low field NMR results on solutions and food at high pressure will be described.

Wednesday, June 8, 14:00 – 14:20

A New 2D T_1-T_2 (IR-FID-CPMG) Method for the Characterization of Food and their Transformation

C. Rondeau-Mouro[1], R. Kovrlija[1], S. Moussaoui[2]
[1]*IRSTEA, UR TERE, 17 Avenue de Cucillé, CS 64427, F-35044 Rennes, France*
[2]*IRCCyN, CNRS UMR 6597, 1, rue de la Noë, BP 92101, F-44321 Nantes Cedex 03, France*

By acquiring the FID signal in two-dimensional TD-NMR spectroscopy, it is possible to characterize mixtures or complex samples composed of solid and liquid phases. We have developed a new sequence for this purpose, called IR-FID-CPMG [1], making it possible to correlate spin-lattice T_1 and spin-spin T_2 relaxation times, including both liquid and solid phases in samples. We have demonstrated also the potential of a new algorithm for the 2D inverse Laplace transformation of IR-FID-CPMG data based on an adapted reconstruction of the maximum entropy method [2], combining the standard decreasing exponential decay function with an additional term drawn from Abragam's FID function [3,4]. The results show that the proposed IR-FID-CPMG sequence and its related inversion model allow accurate characterization and quantification of both solid and liquid phases in multiphasic and compartmentalized systems, as for instance starchy products. As long as samples contain a moderate liquid content, this method can be applied to monitor structural changes during a particular process, such as heating. The implementation of FID acquisitions in 2D not only resolves short T_2 relaxation times related to strong dipolar interactions in solid phases, but also considers the NMR signal of each component whatever its physical state, making possible the quantification of molecules using the area of the relaxation time peak. Another advantage of the IR-FID-CPMG method concerns its ability to distinguish between solid phases having different T_1 relaxation times. It permits also to demonstrate some cross-relaxation phenomena. This is the case of many samples containing highly hydrophilic molecules like proteins or polysaccharides that display, with water, chemical exchanges and dipolar interactions.

[1] C. Rondeau-Mouro, R. Kovrlija, E. Van Steenberge, S. Moussaoui, Two dimensional IR-FID-CPMG acquisition and adaptation of a maximum entropy reconstruction Journal of Magnetic Resonance in press (2016).
[2] E. Chouzenoux, S. Moussaoui, J. Idier, F. Mariette, Efficient Maximum Entropy Reconstruction of Nuclear Magnetic Resonance T_1-T_2 Spectra, Ieee Transactions on Signal Processing 58 (2010) 6040-6051.
[3] A. Abragam, The principle of Nuclear Magnetism Clarendon Press:Oxford (1961).
[4] W. Derbyshire, M. van den Bosch, D. van Dusschoten, W. MacNaughtan, I.A. Farhat, M.A. Hemminga, J.R. Mitchell, Fitting of the beat pattern observed in NMR free-induction decay signals of concentrated carbohydrate-water solutions, Journal of Magnetic Resonance 168 (2004) 278-283.

Wednesday, June 8, 14:20 – 14:40

Characterisation of Emulsions by PFG-NMR

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The determination of droplet size distributions in biological material, as margarine, is one of the most successful low field NMR applications currently in use. It applies the method proposed by Packer et.al in 1972 [1], where the oil signal is assumed to be removed by applying an inversion sequence prior to the diffusion experiment. A log normal distribution of the droplet size distribution is assumed and this is fitted to a dataset describing restricted diffusion of the water trapped inside the droplets. The approach presented here does not assume an oil signal decaying with single time constant in T_1 (or T_2), but a significant difference in the relaxation times and/or a difference in the root mean squared displacement at a predefined observation time [2]. As the T_2 distribution resulting from a CPMG experiment is used to find the droplet size distribution, there is no assumption made for the shape of the distribution. The acquisition time is short, the order of a minute, which makes it possible to study the separation processes of an emulsion into a separated water and oil phase, for example due to an increasing temperature.

[1] Packer KJ., Rees C., Pulsed NMR studies of restricted diffusion. I. Droplet size distributions in emulsions. Journal of Colloid and Interface Science. 1972; 40(2):206-218.
[2] Sørland GH. Dynamic Pulsed-Field-Gradient NMR, Springer Verlag; 2014

Wednesday, June 8, 14:40 – 15:00

Use of Temperature-Controlled Low Field ^{1}H NMR to Study Changes during Simulated Baking of a Flour-Water Model System

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Wheat based foods typically contain proteins and carbohydrates that undergo changes during the heating and cooling steps in their production. However, it is still poorly understood how constituent transitions impact water mobility and how these changes relate to textural properties of the final product. Conventional techniques are used to study changes in starch and protein properties *in situ* and online (during the heating and cooling steps) on a molecular and macroscopic scale. However, there is need for ways to study changes in constituent properties and related water distribution *in situ* and online on intermediate length scales to further understand their impact on final product quality. A state of the art technique in this respect is temperature-controlled low field proton nuclear magnetic resonance (^{1}H NMR). The objective of this study was to online investigate changes in proton mobility with ^{1}H NMR of a flour-water model system, representative for the production of complex wheat based foods such as bread or cake, and to relate these changes to molecular and macroscopic properties as studied by differential scanning calorimetry (DSC, internal starch phenomena) and rapid visco analysis (RVA, starch swelling behavior, gelatinization and gelation), respectively. It was found that the changes observed with DSC and RVA as well as related water mobility coincide with pronounced changes in proton distributions. It is concluded that online low-field ^{1}H NMR is very useful for *in situ* monitoring changes occurring on multiple length scales that are related to product properties. The obtained knowledge will be valuable for developing strategies for use of additives that improve product quality.

Wednesday, June 8, 15:00 – 15:20

Low-Field RheoNMR: New Combination of Rheology and TD-NMR to Correlate Mechanical Properties with Molecular Dynamics in Soft Matter

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Rheology, the science of flow phenomena, provides access to the mechanical properties of soft matter, while TD-NMR is a useful technique for characterization of the molecular dynamics. To achieve greater insight into the interplay of these domains, especially with regard to the effects of shear, it is desirable to combine these two methods in one setup. Here we present a low-field RheoNMR set-up based on a portable 30 MHz NMR unit that was integrated into a commercial high-end strain-controlled rheometer. This unique combination can simultaneously conduct a full rheological shear characterization (*G'*, *G''*, $|\eta^*|$, FT-Rheology: $I_{3/1}$, Q_0) [1] while monitoring molecular dynamics *in-situ* via ^{1}H TD-NMR for temperatures from -15 – +210 °C [2]. Possible applications include the measurement of quantitative composition in crystallizing soft matter (fats, polymers, etc.) and multiphase systems during the application of shear, e.g. shear-induced crystallization. To display the possibilities of this new technique, studies on the crystallization of polymers are presented.

[1] Wilhelm M. Fourier-Transform Rheology. Macromol Mater Eng. 2002 Feb; 287(2):83-105.
[2] Räntzsch V, Wilhelm M, Guthausen G. Hyphenated low-field NMR techniques: combining NMR with NIR, GPC/SEC and rheometry. Magn Reson Chem. 2015; published online. doi:10.1002/mrc.4219.

Wednesday, June 8, 16:00 – 16:20

TD-NMR as a Method to Determine and Characterize the Water-Binding Capacity of Whey Protein Microparticles

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Water-binding capacity (WBC) is commonly measured with a centrifugation method in which a sample is hydrated in excess water and the pellet weight after centrifugation defines the WBC. When a dispersion is being analyzed, here containing whey protein microparticles (MPs), the pellet consists of swollen particles and water between the particles. These two water domains in MP pellets were distinguished using TD NMR. This distinction showed that an increase in WBC from 2 to 5.5 g water/g dry matter was mainly due to an increase in water between the MPs. Besides, it was found that TD NMR-measurements could be used to provide accurate values of the amount of water in both water domains in MP pellets. This makes TD NMR therefore a more accurate method to determine the WBC of the whole pellet than weighing the pellet after centrifugation.

Wednesday, June 8, 16:20 – 16:40

Characterization of Red and White Cocoyam (*Xanthosoma Sagittifolium*) Roots, Flours and Starches during Heating by Low Field NMR

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Cocoyams are important root and tuber staples in West African communities, but limited information exists on their physicochemical and processing characteristics. In this study low field proton relaxation analysis was used to characterize the water distribution and gelatinization behaviour during cooking of red and white cocoyam roots, as well as water dispersions of their corresponding processed flours and purified starches (conc. 1-12%).

Up to four fast-interacting water populations were observed in the roots, identifying water associated with starch (T_{2a}≈1.5 ms), water interacting with the cell walls (T_{2b}=5-10 ms), water in the cytoplasm (T_{2c}=13-54 ms), and water in vacuoles/extracellular water (T_{2d}=51-246 ms). 1-2 conc. dependent populations were observed in the flour and starch dispersions. T_{21} in the flours and starches was more sensitive towards starch swelling and gelatinization, while T_{22} was more sensitive towards water expelled from the matrix at temperatures above gelatinization (approx. 80°C in the roots, and 75°C in the starch and flours). Shorter relaxation times observed in the white variety, and a higher proportion of more restrained water, indicated that this variety was slightly more sensitive towards forming a gel and that it held a higher proportion of water after gelatinization. This is believed to relate to differences in the starch characteristics of the two varieties, including a higher amylose/amylopectin ratio in the white roots. Furthermore, the study showed that the roots have much wider potential than their current utilization.

Wednesday, June 8, 16:40 – 17:00

Rapid and Quantitative Assessment of Early Lipid Oxidation in Mayonnaises during Shelf-Life by ^{1}H-NMR

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Unilever R&D Vlaardingen

Lipid oxidation is one of the most important reasons for the compromised shelf life of food emulsions. Here we can discern a primary oxidation phase (hydroperoxidisation by a radical mechanism) followed by secondary oxidation (further degradation of these hydroperoxides). It is of great interest to monitor the formation of primary oxidation products over time to gain kinetic and mechanistic information about the oxidation process. Here a major bottleneck is the quantitative assessment of hydroperoxides with molecular specificity at the early stages of lipid oxidation. Hence we exploited the unbiased and quantitative nature of ^{1}H NMR for detecting fatty acid specific oxidation products in mayonnaise, a food emulsion that is particularly oxidation-prone. We first implemented and validated an efficient and robust procedure to produce samples where the ^{1}H NMR signals of lipid peroxides can be observed in a well resolved and reproducible manner. [1] Lipid hydroperoxide concentrations in mayonnaises at short shelf-life are low and hard to detect against the abundant background of non-oxidized lipids. Hence we implemented band-selective ^{1}H-pulse sequences to (semi-) quantify hydroperoxide concentrations. We can determine concentrations of oleic, linoleic and linolenic hydroperoxides at levels corresponding to Wheeler-POV value < 0.5. We demonstrate the quantitative assessment of these lipid hydroperoxides on mayonnaises with/without antioxidant during a shelf life test. The method revealed differences in time- and fatty acid-dependent lipid hydroperoxide concentrations.

[1] Skiera, C, Steliopoulos, P, Kuballa, T, 1H-NMR Spectroscopy as a New Tool in the Assessment of the Oxidative State in Edible Oils. J Am Oil Chem Soc (2012) 89; 1383-1391

Wednesday, June 8, 17:00 – 17:20

Automatized Determination of Ingredients in Non-Alcoholic Beverages with NMR

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Nuclear magnetic resonance spectroscopy (NMR) is an efficient tool for qualitative and quantitative determination of different ingredients in non-alcoholic beverages. The minimal sample preparation makes it a highly qualified technique. Here, the sample preparation requires only 600 µL degassed soft drink, 70 µL of 0.1 % of TSP-*d4* in D_2O (for referencing and locking) and 100 µL of phosphate buffer.

This study shows that it is possible to quantify 11 compounds from differing substance classes e.g. sugars, sweeteners, organic acids, vitamins and alcohols within one measurement. An automated MatLab routine was used for integration and quantitative calculation which is based upon the PULCON-Principle (Pulse Length Based Concentration Determination) [1].

The method was validated for three different types of soft drinks, including a beverage with high sugar content (matrix 1), a diet product (matrix 2) and an energy drink (matrix 3).

Recovery rates were between 85 and 106%. The limits of qualification (LOQ) varied in the range of 7 mg/L (lactic acid) to 3 g/L (sucrose) due to different content in matrix.

A comparison of already established methods showed the suitability for the use in routine analysis of non-alcoholic beverages.

[1] Wider G, Dreier L. Measuring Protein Concentrations by NMR Spectroscopy. J Am Chem Soc. 2006 Mar 1; 128 (8): 2571-6.

Wednesday, June 8, 17:20 – 17:40

Time-Course Evolution of Bioactive Compounds Thermally Treated in Water

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During thermal treatments of food ingredients, bioactives compounds such as vitamins, in particular, water solubles ones, are heated in an aqueous media, the cytosol.

In order to study chemical modifications of bioactive compounds during thermal processes, we modelled the intracellular environment of cells of plant or animal tissues by heating isolated organic compounds in water.

In particular, we explored the reactivity of a wide range of isolated vitamins, amino acids and saccharides such as L-ascorbic acid, L-cysteine or sucrose in refluxed water for up to 96 h.

For such studies, the time-course evolution of the compounds was followed by *in situ* quantitative proton nuclear magnetic resonance spectroscopy (*is*q ^{1}H NMR), since it is a fast and non-invasive method, without any extraction process.

Thursday, June 9, 09:00 – 09:45

MR Measurements of Phase Transitions Molecular Dynamics in Gels: PGSE MR, MRI and Relaxation Correlations

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This talk will address research on molecular dynamics in gels and polymer solutions using magnetic resonance (MR) measurements, including MR imaging (MRI), multidimensional relaxation correlation/exchange and displacement time dependent diffusion methods. The transport of solvent in natural and manufactured gels is of importance in a broad range of applications, ranging from food science to biomedicine. Biomolecular hydrogels are a material in which a hierarchy of length and time scales are important in controlling material structure and transport related material function. The transport and distribution of water in alginate solutions and gels made from O-acetylated and non-acetylated alginates from microbial genetic variants demonstrate the impact of biomolecular structure on water dynamics and distribution. In diffusion front reaction gelation of alginates by cations, molecular dynamics during spontaneous mesoscale structure formation of capillaries is measured using MRI. The mass transport of the water and polymer during this capillary formation is modeled using concepts from critical phase transition dynamics combining thermodynamics and transport phenomena. Phase transitions during solvent evaporation drying of biopolymer solutions (*e.g*. HPMC) are important in food science and pharmaceutical production processes. Displacement time dependent PGSE MR and relaxation time correlations to study molecular dynamics of phase transitions during solvent drying provide unique data on gel mesh size and connections between gelation and glass transitions.

Thursday, June 9, 09:45 – 10:15

Physicochemical Characterisation of Multiple W/O/W Emulsions by NMR Diffusometry and Relaxometry

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Multiple emulsions are emulsions whereby the dispersed phase is an emulsion on itself. Thus, W/O/W emulsions contain an aqueous phase with droplets which consist of water droplets in oil. These W/O/W emulsions are typically prepared in a 2-step process, whereby a W/O emulsion is emulsified into an external water phase. Using this technology, concentrated emulsions can be prepared with a lower caloric content, which opens interesting perspectives for light food applications.

In this presentation, the applicability of both high- and low-resolution NMR for the characterisation of multiple emulsions will be demonstrated. An important characteristic is the droplet size distribution of the internal water droplets, which can be realized by NMR diffusometry of either the water molecules or of an entrapped tracer, such as tetramethylammonium chloride. The difference between the results obtained by both approaches points towards the effect of water transport through the oil phase, which can be minimized by appropriate measurement conditions. As part of the internal water may be released during the second homogenization step, the determination of the yield (i.e. the ratio of the amount of internal water in the final W/O/W emulsion to the amount present in the primary W/O emulsion) is another quality criterion, which may be derived from either NMR relaxometry (using a paramagnetic probe) or diffusometry. The developed methodology enables to investigate the evolution of the internal water droplet size during storage, which may gradually change by Ostwald ripening. In addition, the effect of changing environmental conditions, such as osmotic stress, may be quantified.

Thursday, June 9, 10:15 – 10:35

NMR Diffusometric Droplet Sizing in Emulsions with Murday-Cotts and Regularization Methods

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NMR diffusometry allows to acquire droplet size distributions (DSD) of emulsions, using pulsed field gradient experiments. The signal decay correlates usually with the diffusion coefficient as described by Stejskal-Tanner. In the case of DSD, different approaches are known to deduce DSD from the experiments, differing in the mathematical approach with according constraints, limitations and processing speeds. In this work several approaches were evaluated and compared, one being the Murday-Cotts (MC) approach assuming a lognormal distribution and another being the regularization, using a generalized cross validation (GCV) [1]. As model system pharmaceutical emulsions containing squalene oil, water and phospholipids as emulsifier were chosen. The influence of droplet diffusion due to Brownian motion was considered additionally, estimating the movement according to the Stokes-Einstein law. The effects of droplet movement were investigated by measurements at different temperatures, small droplet sizes and switching continuous and dispersed phase, enabling to discriminate effects of droplet movement itself and molecular diffusion inside the droplets, leading to different DSD. Further on the ability of MC and regularization to display multimodal distributions was compared.

[1] Hollingsworth KG, Johns ML, Measurement of emulsion droplet sizing using PFG NMR and regularization methods. J. Colloid Interface Sci. 2002; 258:383-389

Thursday, June 9, 11:00 – 11:20

Characterisation of Gel Networks by NMR Nanoprobe Diffusometry

Daan de Kort[1,2], Freek Hoeben[2,3], Erich Schuster[4], Niklas Loren[4], Johannes Hohlbein[1], Lonneke Zuidgeest[1,2,6], Meike Emondts[5], Henk Janssen[2,3], Songi Han[5], Henk Van As[1,2], John van Duynhoven[1,2,6]
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Food gels comprise percolating and tortuous biopolymer networks that are notoriously difficult to describe at the sub-µm scale in a quantitative manner. Sub-µm structural information can be obtained from the self-diffusion behavior of nanoparticles through these networks that nicely complements microscopy techniques. We designed and synthesized a suite of spherical nanoparticles with defined diameters in the 3-30 nm range that were made inert (by PEGylation) and functionalized with spectroscopic labels (CF^{19}_3, TEMPO) in order to observe their mobility by ^1H and ^{19}F PFG NMR, and Overhauser Dynamic Nuclear Polarization (ODNP). This approach was applied to both homo- and heterogeneous polymer networks and provided average network descriptors (^1H, ^{19}F PFG NMR) as well as evidence of sub-µm network heterogeneity and local differences in water diffusivity (ODNP). Optical ensemble (FRAP, FCS, RICS) and single particle tracking (TIRF) diffusometric techniques applied to dye-labelled nanoparticles validated the gel network structural descriptors derived from PFG NMR nanoprobe diffusometry.

Thursday, June 9, 11:20 – 11:40

Use of Multiparametric MRM in Monitoring of the Ham Dry-Curing Process

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Dry-cured ham of a Mediterranean type is characterized by dry salting, absence of smoking and long ripening time. An efficient quality control during its processing is essential for providing its optimal textural, volatile and sensorial traits relevant for customer acceptability. Among the most important factors influencing final properties of dry-cured ham products are moisture and salt distribution, which also determine enzymatic activity during proteolysis and lipolysis. In the study, differences among four different Kraški pršut dry-cured ham sample groups were assessed by a novel multiparametric magnetic resonance microscopy (MRM) approach based on ADC, T_1 and T_2 mapping [1]. In the approach the maps were analysed by 1D ADC, T_1, and T_2 distributions as well as by 2D paired ADC-T_1, ADC-T_2 and T_1-T_2 distributions. The approach was efficient in discrimination among the examined sample groups that differed by anatomical position (biceps femoris vs. semimembranosus muscle) and by the applied processing protocol (high vs. low salting). The discrimination is based on different moisture contents and different water micro-environments that affect diffusion and relaxation properties of water in the tissue. Due to the discriminating potential of the MRM approach, the approach could be exploited as a complementary method to conventional chemical and textural analyses for dynamical monitoring of the moisture content during ham processing.

[1] Bajd F. et al. Food Chem. 2016; 197: 1093-1101.

Thursday, June 9, 11:40 – 12:00

Flow Behaviour of Fat Crystal Dispersions: A Rheo-MRI View

Tatiana Nikolaeva[1], Daan de Kort[1], Adrian Voda[2], Henk Van As[1], John van Duynhoven[1,2]
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Fat crystal networks are abundant in many food products and critically determine their macroscopic properties [1]. The behaviour of fat crystal networks under shear is however poorly understood [2]. This impedes rational design and engineering of fat-based food materials with enhanced shelf-life stability and sensorial quality. This can be overcome by establishing relationships between shear conditions, and the growth and disruption of multi-length scale fat crystal networks. We used rheo-MRI and rheology to understand mechanical properties of fat crystal networks and their flow behaviour under shear. Thus, the time-dependent yield stress behaviour was characterized in fat crystal dispersions. The yield stress behaviour of these dispersions clearly manifested itself by the presence of distinct shear banding in the Couette geometry as visualized by Rheo-MRI velocimetry. The yield stress behaviour could be reduced by pre-shear treatments; this was reflected by more invading shear bands in the velocimetric profiles. The transient disruption of fat crystal networks under shear could be visualized in a non-invasive manner by time-dependent Rheo-MRI velocimetry. The steady state flow behaviour of fat crystal dispersions was compared in Couette and cone-plate geometries.

[1] Marangoni A.G., Acevedo N., Maleky F., Co, E. et al. Structure and functionality of edible fats. Soft Matter. 2012;8:1275–1300.
[2] Hartel RW. Advances in food crystallization. Annu Rev Food Sci Technol. 2013;4:277-92. PMID: 23464574.

Thursday, June 9, 12:00 – 12:20

Visualisation of Fouling Layer Formation and Flow in Ceramic Hollow Fiber Membranes Using MRI

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Membrane filtration is known to be a major process in food processing. The main applications of membranes in this field are in diary, followed by beverage industry (1). As in other membrane applications one of the main tasks is the reduction of membrane fouling, which is due to the accumulation of mainly colloidal substances on the membrane surface (2). Filtration processes with ceramic hollow fiber membranes were investigated with respect to fouling layer formation and flow in the membrane lumen using MRI. In addition to the filtration data describable by a conventional cake filtration model, MRI was used to elucidate the influence of operating conditions and feed composition on the fouling layer structure time and spatially resolved. For this purpose, the polysaccharide sodium alginate was used as model foulant. To overcome the lack of contrast between alginate and surrounding water, different approaches were pursued e.g the addition of specific contrast agents.

[1] Daufin G, Escudier JP, Carrere H, Berot S, Fillaudeau L, Decloux M. Recent and emerging applications of membrane processes in the food and dairy industry. Food and Bioproducts Processing. 2001;79(C2):89-102.
[2] Membrane processing dairy and beverage applications. In: Tamime AY, editor. Chichester, West Sussex; Wiley-Blackwell; 2013.

Thursday, June 9, 13:30 – 13:45

Kinetic Analysis of the Metabolism of Food Protective Cultures by *In Vitro* NMR and Chemometrics

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Biopreservation is a safe and ecological approach to preserve food products, which has gained increased attention in recent years. Insight into the metabolism of food protective cultures can definitely lead to more efficient biopreservation systems. In this context, NMR spectroscopy can be particularly helpful as it allows *in vitro* investigations and kinetic analysis of the metabolism of the cultures used in for example yoghurt production. This paper will demonstrate an efficient analytical protocol developed for the kinetic analysis of *in vitro* NMR measurements of Lactic acid bacteria (LAB) [1] that play an important role in the food industry as protective cultures, and also as starter cultures to manufacture fermented food. The protocol includes guidelines for the different parts of the experiment, from sample preparation over data acquisition and preprocessing to the extraction of the metabolic kinetic profiles. The analytical protocol is applied to an experimental design with two LAB strains (*Lactobacillus rhamnosus* DSM 20021 and *Lactobacillus plantarum subsp. plantarum* DSM 20174), two initial pH levels (pH_i 6.5 and 5.5), two levels of glucose concentration (2.5 and 0.25 g/l), and two batch fermentation replicates. Reference deconvolution was introduced as a very effective solution for enhancing the quality of *in vitro* NMR measurements of cells, and MCR-ALS was used to extract the metabolic profiles from the processed time-series NMR data. The protocol allowed for detailed kinetic analysis of 11 major metabolites that are involved in the glycolysis, pyruvate catabolism, amino acid catabolism and cell energy metabolism of the bacteria. The developed analytical protocol facilitates simple and easy investigation of different fermentation factors, such as new strains, cohabitations, new substrates and deleterious metabolites, as well as temperature and pH, and thus have great potential for biopreservation studies, as well as to studies that are related to the application of LAB for enhancing the sensory properties of food products.

[1] P. Ebrahimi, F.H. Larsen, H.M. Jensen, F.K. Vogensen & S.B. Engelsen, Real-time metabolomics of lactic acid bacteria during fermentation as monitored by in vitro NMR and chemometrics, *Metabolomics* (2016), in press.

Thursday, June 9, 13:45 – 14:00

NMR-Based Metabolomics to Assess Fruit Quality

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The metabolome, the sum of all metabolites, varies with many factors like the genetic species, environment or disease. Metabolome analysis can also be used in quality control by generating unique fingerprints of different species or the developmental state of an organism. NMR spectroscopy, one of the main techniques employed in metabolomics studies, can analyze hundreds of components and their variation between different samples in a few minutes/hours with high accuracy and low effort of sample preparation. This qualifies it as a potentially interesting technique to assess authenticity and quality of food. Here, we present examples to demonstrate the potential of NMR-based metabolomics for quality control of important crops.

In the case of tomatoes, four genotypes cultivated in two different regions could be unambiguously identified on the basis of their metabolome. Accompanying experiments showed that the higher levels of chlorogenic acid in a yellow cultivar led to increased resistence to alternaria colonisation. By analysing the metabolome of Kiwi fruit, ripening stages could be identified. Acid:sugar ratios as well as specific metabolites changed with time and were characteristic for each stage. Flesh or peel metabolome was analysed separately for a wide variety of apple cultivars. All cultivars could be unambiguously identified not only on the basis of acid and sugar contents, but also the polyphenols, discussed as potential health promoting substances, varied substantially.

Thursday, June 9, 14:00 – 14:15

Metabolic Responses of Clams, *Ruditapes Decussatus* and *Ruditapes Philippinarum*, to Short-Term Exposure to Lead and Zinc

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[4]*Department of Applied Science and Technology – Polytechnic University of Turin, Italy*

In this study, a NMR-based metabolomics approach was applied to investigate and compare the biochemical responses of the clams *Ruditapes decussatus* and *Ruditapes philippinarum* to 48 hours lead nitrate ($Pb(NO_3)_2$) and zinc chloride ($ZnCl_2$) exposure. These bivalves are widely distributed around the globe and represent one of the main products of the Italian aquaculture industry [1].

^{1}H NMR spectra of the aqueous fraction of clams, extracted according to the Folch method [2], were analysed by Principal Component Analysis (PCA) to search for valid metabolic signatures for metal exposure. The results of the PCA pointed out a remarkable species-specific metabolic response upon metal exposure. In particular, metal treated *R. decussatus* ware mainly characterized by higher levels of organic osmolytes (such as betaine, taurine and hypotaurine) while it decreased the relative amount of free amino acids. On the contrary, *R. philippinarum* metabolic response was mainly characterized by larger amounts of amino acids (branched chain amino acids, threonine, tyrosine and phenylalanine) while it declined the level of organic osmolytes. Metabolite-Metabolite Correlation Analysis (MMCA) was further applied in order to achieve deeper insights into the impact of heavy metal pollution on clams' metabolic fingerprint. A higher number of strong (Pearson's) correlations was observed, in both species, upon lead exposure with respect to the zinc one. In particular, the more concerted action of the metabolites following lead exposure suggests a detrimental effect of wider extension on clams' metabolome probably due to its noxious nature. These findings show that NMR-based metabolomics has the required sensitivity and specificity for the identification of a biomarker contour [3] to be used for marine quality control.

[1] FAO, *The state of world fisheries and aquaculture*, vol. 2014. 2014.
[2] J. Folch, M. Lees, and G. H. S. Stanley, "A simple method for the isolation and purification of total lipids from animal tissues," *J Biol Chem*, vol. 226, no. 1. pp. 497–509, 1957.
[3] R. Bro, M. H. Kamstrup-Nielsen, S. B. Engelsen, F. Savorani, M. A. Rasmussen, L. Hansen, A. Olsen, A. Tjønneland, and L. O. Dragsted, "Forecasting individual breast cancer risk using plasma metabolomics and biocontours," *Metabolomics*, vol. 11, no. 5, pp. 1376–1380, 2015.

Thursday, June 9, 14:15 – 14:30

^{1}H NMR Spectroscopy – A Tool for Authenticity Control of Wine

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In recent years, the great potential of the ^{1}H NMR spectroscopy was recognized for qualitative and quantitative food analysis. This method combines quantitative and structural information with minimum sample preparation, high sample throughput, fast spectra acquisition, low costs per sample, and good reproducibility. NMR gives twice information in one experiment: targeted and non-targeted analysis. In *targeted analysis* within a few minutes about 60 quantitative ingredients and authenticity relevant parameters are evaluated simultaneously applying "WineScreener^{TM}" methodology. In a validation study for 32 wine ingredients (sugar, acids, alcohol, glycerol, higher alcohols, phenols, amino acids, etc.) specifity, selectivity, linearity, detection and quantification limit, repeatability, comparability, coefficient of variation and recovery according to DIN 32645 were calculated by manual integration of the NMR signals and compared with the results of the fully automated "WineScreener^{TM}" [1]. For the purpose of *non-targeted analysis* a commercial database of at present more than 10.000 wines worldwide has been established. To test the applicability of this database a second independent database was created – the test database. In the case of grape varieties eleven varieties were tested with a proper forecast probability of 92%.

The possibility of establishing NMR spectroscopy including databases for official wine surveillance in Europa and worldwide will be discussed.

[1] Godelmann R, Völker D, Validation studies for multicomponent quantitative NMR (qNMR) in wine using ^{1}H NMR, Accred Qual Assur, submitted

Thursday, June 9, 14:30 – 14:45

SPE-NMR: Revival of an Old Technique for the Analysis of Wine and Juice

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Solid phase extraction (SPE) is well known for compound enrichment and clean-up of complex aqueous samples in many analytical applications, e.g. in environmental or pharmaceutical analytical chemistry. It is often used as a sample pre-treatment technique in separation science followed by gas- or liquid chromatography.

It can also be used as a sample enrichment tool for NMR (nuclear magnetic resonance) mixture analysis as shown for the first time in an environmental application [1].

Here, we demonstrate the use of an automated SPE-NMR system for the analysis of wine and juice. The separation of matrix components (sugars and small organic acids) from the secondary metabolites of the plant in addition to the sample enrichment step allows save identification of grape- and fruit type in many cases. Both, targeted and untargeted investigation of samples is possible with the use of NMR.

[1] M. Godejohann, A. Preiß, K. Levsen, K.-M. Wollin und C. Mügge. Determination of polar organic Pollutants in aqueous samples of former ammunition sites in lower Saxony by means of HPLC/photodiode array detection (HPLC/PDA) and proton nuclear magnetic resonance spectroscopy (1H-NMR). Acta hydrochim. Hydrobiol. 1998 Nov; 26, 330-37.

Friday, June 10, 09:00 – 09:45

Routine Application of NMR Spectroscopy in Official Food Control

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Nuclear magnetic resonance (NMR) spectroscopy is gaining more and more importance in mixture analysis with a large application field in food analysis. In this plenary lecture, we will summarize our experience with routine applications of NMR spectroscopy in governmental food control. Our first routine applications have been developed for beverages, which can be measured with a very simple and time-efficient sample preparation. For example, it has been possible to detect microbial beer spoilage and to check the German beer purity law. In wine analysis, NMR is unique in providing a comprehensive prediction of the grape variety as well as the simultaneous quantitative determination of 56 compounds from the same spectrum. In the field of alcohol-free beverages, we have established an automated processing of spectra that allows controlling the legal limits for various compounds including some preservatives, food additives and sweeteners.

For solid foods, an aqueous or solvent extract has to be prepared for measurement with liquid probes, while we found the measurement using solid state NMR currently not feasible for routine control purposes. Examples for solid foods include the verification of the labelling of Arabica and Robusta coffee species, the determination of rice type (Basmati), the authentication of saffron, the detection of melamine in milk powders, or the detection of pine nut species that may cause taste disturbances.

In conclusion, NMR spectroscopy was judged as suitable for the rapid routine analysis of samples in official food control and the application range will be extended to further matrices in the future.

Friday, June 10, 09:45 – 10:15

Metabolomic Investigations of Health Effects of Dairy Products

Morten Rahr Clausen[1], Hong Zheng[1], Bashar Amer[1], Christian Clement Yde[1], Trine Kastrup Dalsgaard[1], Hanne Christine Bertram[1]
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Milk has been known for a long period as a source for bioactive components and there are an increasing number of observations that indicate an association between dairy intake and an improved human health. Therefore, we have investigated the effects of dairy products and milk derived macronutrients in humans on adiposity and blood lipids and we combined that with metabolomic analysis of bio-fluids in order to elucidate how dairy products affect metabolic health.

Firstly, our results show that the effect of dairy on metabolic health is multifaceted and derives from several sources. Hence our NMR- and MS-based metabolomics studies indicated that that whey proteins and medium chain fatty acids induced weight loss through loss of energy in the urine and an increase in fatty acid oxidation. Furthermore, processing of milk into cheese may have beneficial effects on metabolism. Our data indicate that cheese consumption alter the gut metabolome to contain higher amounts of short chain fatty acids, which may have led to beneficial effects on blood lipid content.

In this presentation we will discuss how NMR based metabolomics contribute to the understanding of the effects of dairy products on metabolism and how different analytical techniques can corroborate each other.

Friday, June 10, 10:15 – 10:30

Characterization of Juices from Ancient Danish Apple Cultivars by ^{1}H NMR-Based Metabolomics

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[2]*Department of Food Science, University of Copenhagen, Denmark*
[3]*Department of Applied Science and Technology, Polytechnic University of Turin, Italy*

In this work a NMR-based metabolomics approach was applied, for the first time, to chemically characterize apple juices of over 200 old Danish cultivars. The study is the result of a collaboration with 'Pometet', an experimental orchard and gene bank of the University of Copenhagen that hosts the national and international collection of fruit genotypes. It is part of a project that aims at promoting the utilisation of ancient Danish apple cultivars for niche products since they may have unique flavour qualities that can be attractive in juices.

High-field proton NMR spectroscopy was applied for samples characterization. 1D ^{1}H NMR spectra were acquired to determine the metabolic fingerprint of the juices, while 2D homonuclear experiments were acquired for assignments purposes. A total of 26 metabolites were quantified by using Bruker's Spin Generated Fingerprint (SGF) Profiling ™ [1]. Early and late harvest cultivars were included in the study in order to evaluate the influence of the picking time on the juice chemical composition. Principal Component Analysis (PCA) was employed to explore the whole NMR spectral dataset seeking for valid metabolic signatures related to different harvesting time. Remarkably, some patterns were found that pointed towards discrimination between cultivars with respect to harvesting time and year. Partial Least Squares Discriminant Analysis (PLS-DA) was further applied in order to identify the metabolites responsible for the observed trend. The carbohydrates sucrose and glucose, as well as malic and chlorogenic acids, turned out to be the main responsibles for cultivars discrimination. In particular late cultivars were found to be richer in sucrose than the early ones. The results clearly confirm the ability of NMR-based metabolomics to comprehensively survey the metabolic composition of fruit juices, enabling the formulation of precisely characterized niche products using special cultivars.

[1] M.Spraul, B. Schütz, P. Rinke, S. Koswig, E. Humpfer, H. Schäfer, M. Mörtter, F. Fang, U.C. Marx, A. Minoja, "NMR-Based Multi Parametric Quality Control of Fruit Juices: SGF Profiling", Nutrients , vol. 1, pp. 148-155, 2009.

Friday, June 10, 11:00 – 11:15

Untargeted Analyses of Cowpea Seeds (*Vigna Unguiculata*) Using ^{1}H *q*NMR Combined with Chemometrics and Solid State NMR

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The ultimate aim of this study was to apply a non-targeted chemometric analysis of NMR data to investigate the variability of organic compounds in nine different cowpea seeds, without any complex pre-treatment. [1] Furthermore, an additional analysis was performed to investigate rigid and mobile components in the seeds cotyledon using solid-state NMR.

The ^{1}H NMR analysis coupled to chemometrics appointed the Tvu 382 cowpea variety as that with the lower raffinose and stachyose contents. This fact is in agreement with the aim of the breeding program to produce cowpea varieties that contain lower quantities of these oligosaccharides. Additionally, niacin (vitamin B3) was detected in a range from 0.8 to 1.5 mg/g. The ^{13}C CP and SP/MAS NMR spectrum showed that the cotyledon of the cowpea comprised a truly rigid portion made of starch as well as a soft portion made of amylose, fatty acids and protein, beyond to present that the hydration process affects the dynamics of the cowpea regarding the C6 and C4 resonances showing that these carbons are easily accessible for water. The variable contact time experiment showed the presence of lipid-amylose complexes and, therefore, suggesting that the Tvu 233 and Tvu 382 are softer seeds.

[1] Liao, LM, Alves Filho, EG, Silva, LMA, Choze, R, Alcantara, GB, & Bassinello, PZ. Quantification of oligosaccharides from common beans by HR-MAS NMR. In: Magnetic Resonance in Food Science, pp. 47-53: The Royal Society of Chemistry: 2011.

Friday, June 10, 11:15 – 11:30

^{1}H NMR Metabolite Profiling of Guarana Seeds (*Paullinia Cupana*) from Different Geographic Regions of Brazil

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Guarana is an Amazonian fruit whose seeds are rich in caffeine, being therefore used in energetic drinks. Nowadays the Bahia state is the national leader in the production of guarana. However, the market price of the seed from Amazon is higher because the guarana producers negotiate directly with the processing industries which are situated exclusively within the state. In the present work, seeds obtained from the major producing regions of Brazil (Amazonas and Bahia) were studied through a non-target approach by means of NMR coupled to chemometrics. The principal component analysis (PCA) from ^{1}H NMR dataset distinguished the seeds regarding the geographical origin. The major metabolites that contributed to the discrimination of the seeds were caffeine, catechin, epicatechin and the fatty acids. The seeds from Bahia presented higher contents of caffeine, catechin, and epicatechin while those from Amazonas exhibited higher content of fatty acids (oil). Indeed, ANOVA test of the HPLC-measured caffeine content (an official analytical method) corroborated the findings revealed by the NMR analysis. These results demonstrate that the NMR metabolic profiling with chemometric analysis can be a useful tool to identify the geographical origin of guarana seeds.

Friday, June 10, 11:30 – 11:45

Honey-Profiling with NMR

Jane Missler, Gudrun Beckh
Quality Services International GmbH

Authenticity of honey has become an important issue for the honey industry in the past years. To ensure quality and authenticity of honey, it needs to be tested with several different methods. Classical ways of testing mostly focus on the presence of a certain marker compound. The absence of a marker compound does not necessarily mean that a honey is not adulterated.

The Honey-profiling developed by QSI, Bruker and AINuMed is based on comparison of an entire NMR-spectrum with a database, including the quantification of specific substances that occur at certain concentrations. More than 4,000 samples have been analysed with classic analyses so far to ensure their suitability for the database. The samples are acquired from more than 50 countries and more than 20 botanical varieties, like Acacia, Linden, Manuka.

The NMR analysis combined with the multivariate statistics is used to check unknown samples for their authenticity and gives information on adulteration, processing steps and also on geographical and botanical origins.

The recipes for syrup production used for adulteration are ongoing changed in a way, that they will not contain specific marker compounds anymore. Therefore a range of syrup samples are collected and adulteration experiments were conducted to get more information about the adulteration process.

Friday, June 10, 11:45 – 12:00

Classification of the Botanical Origin of Honey by ^{1}H NMR in Combination with Chemometric Methods and New Data Fusion Approaches

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[2]*Institute of Food Chemistry, Hamburg School of Food Science, University of Hamburg*
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[4]*Chemical and Veterinary Investigation Agency (CVUA) Karlsruhe, Germany*

The authentication of the botanical origin of honey is particularly challenging, since the composition not only depend on the botanical provenance, but also on factors such as geographic area, soil types, climatic conditions or even on storage quality. Hence, an analytical approach covering a multitude of parameters in parallel on the one hand, paired with strong discrimination power on the other hand is required here. Targeted analysis methods for marker substances commonly fail here, as quite often there simply are no characteristic substances present. In this context, non-targeted honey analysis by ^{1}H-NMR spectroscopy, combined with multivariate statistical analysis was applied as a powerful tool for quality assessment, which provides fast, simple and low-cost per analysis screening of honey samples. The NMR fingerprint of a honey sample is processed by means of chemometric techniques, typically by principal component analysis (PCA). A second approach is the low-level data fusion of orthogonal data, obtained from multiple spectroscopic techniques, e.g. NMR and FT-MIR, in order to increase the discriminative power. This was performed in custom MATLAB routines by combining non-targeted analyses of honey samples by ^{1}H-NMR and FT-MIR.

ABSTRACTS POSTER PRESENTATIONS

D1

CLIP-ASAP-HSQC for Fast and Accurate Extraction of One-Bond Couplings from Isotropic and Partially Aligned Molecules

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We present the CLIP-ASAP-HSQC experiment that allows the detection of ω_2-coupled 2D spectra in 25 seconds or less and from which $^1J_{CH}$-couplings can be determined with high precision. The experiment combines the previously published ASAP-HSQC designed for fast acquisition with the commonly used CLIP-HSQC which allows the measurement of couplings in the direct dimension without artefacts from incomplete coherence transfer. For best possible robustness of the pulse sequence, broadband excitation, inversion and refocusing pulses derived from Optimal Control Theory (OCT) are used. The performance is demonstrated on three test samples including partially aligned molecules. Besides other structural NMR parameter the detection of RDCs is highly valuable for structure determination. Therefore speeding up the acquisition is desirable especially when dynamic processes are observed. Fastest 2D experiments can in principle be obtained in a single scan using gradient-encoding imaging-type schemes - and the approach has already been applied to the measurement of RDCs - but the method faces severe limits in terms of resolution, accessible bandwidth and sensitivity. In contrast spectra obtained from the CLIP-ASAP-HSQC can be recorded with no compromises. The extraction of couplings is evaluated in comparison to the best available CLIP-HSQC sequence for the three test samples.

D2

CLIP-COSY: A Clean In-Phase Experiment for the Rapid Acquisition of COSY-type Correlations

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The COSY-experiment is one of the oldest 2D NMR experiments; yet it is still invaluable for the assignment of signals in a homonuclear spin system as it only shows coherences between directly coupled spins, peaks of high explanatory power. The signal build-up in the conventional COSY (DQF-COSY), however, is dependent on t_1, starting at zero intensity. This leads to the well-known anti-phase line shape and high acquisition time in the indirect dimension. We present a clean in-phase COSY (CLIP-COSY) which reduces the required experiment time and yields simple in-phase cross-peaks.

Another essential and widely used pulse sequence for determination of spin systems is the TOCSY-experiment where polarization is transferred to every spin within the system. Different mixing sequences for the transfer are well known (DIPSI, MOCCA, MLEV), however, they are associated with high power consumption. Average Hamiltonian Theory shows that the Perfect Echo sequence provides a method for low power broad-band planar mixing which can be used for the TOCSY-experiment.

D3

Residual Dipolar Coupling-Accelerated Molecular Dynamics for Structural Elucidation of Small Molecules with Increasing Flexibility

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Time averaged molecular dynamics simulations with orientational constraints (MDOC) can be performed based on residual dipolar couplings (RDCs). The full tensorial calculation performed contrasts to other approaches for RDC analysis, where an alignment tensor is calculated for a sterically fixed orientational model, and makes the approach in principle very suitable for the structural analysis of molecules.

The MDOC protocol is implemented in the program COSMOS. We demonstrate here the applicability of this methodology for a set of organic molecules with different degrees of flexibility: from rigid models to flexible compounds using $^{1}D_{CH}$ couplings as constraints. The run is monitored for the correspondence of experimental (imported) and calculated data and the overall temperature of the MD simulation. Here, we present our results obtained within the evaluation process for some test molecules with increasing flexibility: norcamphor, staurosporine and spiroindene and oidiolactone B.

D4

Cross-Linked Poly(ethylene Glycol) Diacrylate – A Universal Alignment Medium for the Measurement of Residual Dipolar Couplings

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The measurement of residual dipolar couplings (RDCs) requires an appropriate weak partial alignment in a so-called alignment medium. For small molecules two types of alignment media are commonly used to align solutes: liquid crystalline phases and stretched polymer gels. A major drawback of both media is the limited applicability to various solvents. However, previous work with cross-linked poly(ethylene glycol) gels (PEG) has shown that a large range of solvents can be covered with this polymer network. Corresponding gels are formed from linear PEG either by irradiation with γ-rays and accelerated electrons, or by derivatization of their terminal hydroxyl groups followed by chemical cross-linking.

Here, we show that the bisacrylated derivative, poly(ethylene glycol) diacrylate (PEG-DA), can easily be cross-linked to yield homogeneous gels. These are equally applicable in a stretching or compressing apparatus or by direct swelling in NMR tubes to provide uniaxially anisotropic phases. Due to their broad compatibility to solvents and their inherent homogeneity, PEG-DA gels allow extraction of RDCs with small line widths for almost any class of small organic molecules.

D5

Elucidation of *Maillard* Reaction Pathways by means of the Carbon-Bond Labeling Technique (CABOLA)

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Beside aroma and taste the formation of color is one of the most important attributes of the *Maillard* reaction between reducing carbohydrates and amino acids in thermally processed foods. Due to the complexity of this reaction and the tremendous number of reaction products formed, the knowledge about the chemical nature of these colorants is rather fragmentary. For this purpose the so called CABOLA (carbon-bond-labeling) technique in combination with ^{13}C-NMR analysis was applied. *Maillard* model reaction mixtures of glucose/alanine with 5% of [$^{13}C_6$]-glucose were carried out to follow the joint transfer of several ^{13}C atoms *en bloc* into chromophores. This labelling strategy offers the possibility to obtain ^{13}C-^{13}C couplings and is able to show which structural moieties originate from different glucose molecules [1]. As an example 3-(1,2-dihydroxy)-5-(5-(hydroxymethyl)furan-2-yl)-1-oxo-2,3-dihydro-1H-pyrrolizine-6-carboxylic acid, could be identified successfully and its formation pathway could be confirmed to run via two intact C6 carbon skeletons as well as a C3 carbohydrate fragment by isotopomeric pattern analysis.

[1] Frank O, Hofmann T, Reinvestigation of the chemical structure of bitter tasting Quinizolate and Homoquinizolate and studies on their Maillard-Type formation pathways using suitable 13C-labeling experiments. J Agric Food Chem. 2002; 50:6027-36.

L1

Rapid Method to Measure T_1 of Food Products in Single Scans

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T_1 and T_2 measurements in low-field NMR have been widely used in food science. T_2 can be measured in a few seconds using a single scan method based on the CPMG pulse sequence. T_1 measurement is less used because the available methods require multiple scans and, as a consequence, long experiment times. We have introduced several continuous wave free precession (CWFP) sequences to measure T_1 and T_2 simultaneously and in a single scan [1]. However, for these measurements, it is necessary to determine the intensity of the FID signal at about 10 us after the pulse that is not possible in several low-field instruments, due to the longer dead time. In this article we present a rapid method to measure T_1 based on the CWFP method, named "CWFP-T_1" pulse sequence that does not depend on FID amplitude. CWFP- T_1 sequence uses one 180^o pulse followed by a train of small flip angle pulses (generally 5 or 10^o) separated by a time interval similar to other CWFP sequences, smaller than T_2*. The T_1 value is measured directly by the exponential adjustment of the signal obtained with CWFP-T_1 sequence. This sequence has been used to measure T_1 in food samples such as vegetable oils, meat, and fresh fruits. The great advantage of this method is that the T_1 measurement can be performed in a few seconds, similarly to T_2 measurement with CPMG.

[1] Monaretto T., Andrade F. D., Moraes, T.B. Moraes, Souza, A. A, DeAzevedo, E. R., Colnago,L. A, , J. Magn. Reson. 2015, 259, 174–178.

Acknowledgments: FAPESP (grant 2014/22126-9), CNPq, and CAPES.

L2

Starch Retrogradation Investigated by 1D and 2D NMR

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Starch retrogradation has been extensively investigated mainly due to its detrimental effect on the sensory and storage qualities of many starchy foods; however, this phenomenon has proved to be desirable for some of them [1]. The association of linear amylose molecules occurs rapidly in the first stage of retrogradation, whereas slow increase in the degree of crystallinity and gel firmness, exudation of water (syneresis), and the appearance of B-type crystallites should be ascribed to the long-term amylopectin retrogradation. The time-domain Nuclear Magnetic Resonance (TD-NMR) allows obtaining qualitative and quantitative description of these processes. This method was commonly used to study complex wheat starch-based systems, such as bread [2,3]. On the other hand, the retrogradation of starches having different origins than wheat was rarely investigated [4]. Therefore, the potato starch, waxy maize starch, and wheat starch, all hydrated at 50% (wet basis), were heated from 20 to 90°C, cooled to 20°C, and subsequently stored for 3, 7, and 14 days at the same temperature in order to investigate and compare their retrogradation ability. These three types of starch were chosen due to their different composition (amylose/amylopectin ratio) and crystalline unit packing (A- and B-type X-ray diffraction patterns). The NMR signal (20 MHz) was always acquired at 20°C, in one dimension (T_1 and T_2) as well as in two dimensions (T_1-T_2), at the onset of heating, after the cooling step, and during the storage. NMR measurements including the novel 2D approach using IR-FID-CPMG sequence [5] were interpreted in terms of changes in the starch and water dynamics in relation with solid content changes due to starch retrogradation.

[1] Wang S, Li C, Copeland L, Niu Q, Wang S. Starch Retrogradation: A Comprehensive Review. Comprehensive Reviews in Food Science and Food Safety. 2015;14(5):568-85.
[2] Curti E, Bubici S, Carini E, Baroni S, Vittadini E. Water molecular dynamics during bread staling by nuclear magnetic resonance. LWT-Food Science and Technology. 2011;44(4):854-9.
[3] Bosmans GM, Lagrain B, Fierens E, Delcour JA. The impact of baking time and bread storage temperature on bread crumb properties. Food chemistry. 2013;141(4):3301-8.
[4] Farhat I, Blanshard J, Mitchell J. The retrogradation of waxy maize starch extrudates: Effects of storage temperature and water content. Biopolymers. 2000;53(5):411-22.
[5] Rondeau-Mouro C, Kovrlija R, Van Steenberge E, Moussaoui S. Two dimensional IR-FID-CPMG acquisition and adaptation of a maximum entropy reconstruction. Journal of Magnetic Resonance. 2016.

L3

Studies of the Retrogradation Process of Starch in Gels by Using Low Field NMR Method

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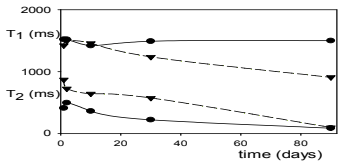
Retrogradation occurs in the starch-water system after the cooling process. This phenomenon depends on the reorganization of the molecules of biopolymers [1]. Methods of studying the starch retrogradation can be conveniently classified as macroscopic techniques (mechanical or textural changes) and molecular - NMR. The latter show changes in the conformation of the starch polymer or mobility of water [2,3]. The aim of the study was analysing a retrogradation process in corn and potato starch gels. The measurements of the relaxation times T_1 and T_2 were performed during a 90 days by using a NMR spectrometer operating at 15 MHz.



Changes of relaxation times in starch gels: ▼ potato, ● corn

The obtained results shown that molecular dynamic of water in different starch gels is determined by amylose/amylopectin contents. In corn starch gel the relaxation parameters were constant. The significant restrict of the molecular dynamic of water is observed. The potato starch gel was characterized by monotonically decrease of the relaxation times values.

Potato starch shows a higher tendency towards retrogradation. Starches containing more linear molecules of amylose have a higher water binding process and form a stable double helix structure.

[1] Narpinder S, et. al., Food Chem. 81, 219-231, 2003
[2] Baranowska H.M., et al., J. Food Eng., 109 (4), 685-690 2012
[3] Karim A.A et al., Food Chem. 71, 9-36, 2000

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L4

Bread Staling: TD-NMR Study via T_1-T_2 2D Maps

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1D NMR has been extensively used to study bread staling and showed water molecular migration and redistribution between bread components (starch and gluten), decreased water availability, amylopectin recrystallization and increased rigidity [1-3]. In this work characterization of bread was addressed with Time Domain (TD)-NMR via T_1-T_2 bi-dimensional maps, in an attempt to resolve structural features not observable by 1D TD-NMR [4-5]. White (W) and gluten enriched (15%, flour basis, G) breads were analysed during 7 days of storage for hardness, Texture analysis; moisture content - MC, frozen water – FW and recrystallized amylopectin, 1D TD-NMR [RD 3s; T_2 (4000 echoes, tau 0.04 ms) and T_1 (20 data points, tau 0.01-5000 ms)] distributions of relaxation times and 2D TD-NMR [(T_1-T_2; T_1: 150 points, tau 1: 0.1ms; tau increment factor: 1.08; T_2 tau CPMG: 0.0567 ms, T_2 data points: 3000)] (Bruker the minispec mq20). Fresh breads had similar MC (40% g water / 100 g sample), hardness (~0.66 N) but different FW (55 vs 63%, in W and G, respectively). At day 7, G had higher MC, FW, it was softer and had comparable retrograded amylopectin to W. Four ^{1}H T_2 populations (A, B, C, D) were observed. During storage pop A decreased in both samples and T_{2C} decreased only in W. One T_1 population was observed in W and G (T_1 – 40-200 ms range) with no change during storage. 2D T_1-T_2 reflected the multi-exponential 1D T_2 behaviour, with correspondent T_2 relaxation times for each population, and T_1-T_2 map changed to a lesser extent in G than in W. 2D T_1-T_2 also indicated a multi-exponential behaviour in T_1, that was not indicated by 1D T_1 (mono-exponential).

[1] Bosmans GM, Lagrain B, Ooms N, Fierens E, Delcour, J. Biopolymer interactions, water dynamics and bread crumb firming. J Agric Food Chem. 2013 Apr 30;61(19):4646-54.
[2] Curti E, Carini E, Tribuzio G, Vittadini E. Bread staling: effect of gluten on physico-chemical properties and molecular mobility. LWT-Food sci technol. 2014 Nov 30;59(1):418-25.
[3] Sereno NM, Hill SE, Mitchell JR, Scharf U, Farhat IA. Probing water migration and mobility during the ageing of bread. In Farhat IA, Belton PS, Webb GA, editors. Magnetic Resonance in Food Science: From Molecules to Man. UK: RCS Publishing; 2007. P. 88-95.
[4] Hills BP Relaxometry: Two-Dimensional Methods. In: Harris R, Wasylishen R, editors. Encyclopedia of Magnetic Resonance. 2009. Available from http://onlinelibrary.wiley.com/book/10.1002/9780470034590/
[5] Van Duynhoven J, Voda A, Witek M, Van As H. Time-domain NMR applied to food products. Annu Rep NMR Spectro. 2010 Dec 31;69:145-97.

L5

Pasta Cooking: TD-NMR Study via T_1-T_2 2D Maps

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Pasta cooking is a complex process that implies water absorption and diffusion in the pasta matrix, starch gelatinization and coagulation of the protein network [1-3]. Pasta cooking has been previously investigated by 1D TD-NMR and MRI to collect information about water mobility parameters, and mechanical properties of cooked pasta, also in presence of additional ingredients [4-5]. In this work pasta cooking was investigated with Time Domain (TD)-NMR via T_1-T_2 bi-dimensional maps, in an attempt to resolve molecular features not observable by 1D TD-NMR [6-7]. Wheat semolina dry pasta was cooked in boiling water (up to 14 minutes) and analyzed for moisture content (MC, 105°C), starch gelatinization (DSC, 25-120°C, 5°C/min), 1D TD- NMR mobility [RD 3s; T_2 (4000-8000 echoes, tau 0.04 ms) and T_1 (20 data points, tau 0.01-4000/9000 ms) distributions of relaxation times], and 2D TD-NMR [(T_1-T_2; T_1: 150 points, tau 1: 0.1ms; tau increment factor: 1.08; T_2 tau CPMG: 0.0567 ms, T_2 data points: 5000)] (Bruker the minispec mq20). Pasta MC increased from 5 (0 min, raw) to 60 (14 min, overcooked) % g water / 100 g sample. 1D TD-NMR indicated the presence of two resolved T_1 populations at short cooking times, that became not resolved at longer cooking times (T_1 1-1000 ms range). Overlapped 1D TD-NMR T_2 populations were observed over cooking (T_2 0.01-1000 ms range). 2D TD-NMR maps indicated a more complex T_1 pattern and a different protons distribution characterized by a different time range, and more resolved T_2 peaks, in particular at longer cooking times as compared to 1D TD-NMR results.

[1] Del Nobile MA, Massera M. A method to evaluate the extent of residual deformations in dry spaghetti. Journal of food engineering. 2002 Dec 31;55(3):237-45.
[2] Nobile MA, Buonocore GG, Panizza A, Gambacorta G. Modeling the spaghetti hydration kinetics during cooking and overcooking. Journal of food science. 2003 May 1;68(4):1316-23.
[3] De Noni I, Pagani MA. Cooking properties and heat damage of dried pasta as influenced by raw material characteristics and processing conditions. Critical reviews in food science and nutrition. 2010 Apr 9;50(5):465-72.
[4] Curti E, Carini E, Diantom A, Cassotta F, Najm NE, D'Alessandro A, Vittadini E. Effect of Glycerol and Gluten on Mechanical Properties and ^{1}H NMR Mobility of Cooked Pasta. Food Biophysics. 2015 Dec 1;10(4):474-80.
[5] Bernin D, Steglich T, Röding M, Moldin A, Topgaard D, Langton M. Multi-scale characterization of pasta during cooking using microscopy and real-time magnetic resonance imaging. Food Research International. 2014 Dec 31;66:132-9.
[6] Hills BP Relaxometry: Two-Dimensional Methods. In: Harris R, Wasylishen R, editors. Encyclopedia of Magnetic Resonance. 2009. Available from http://onlinelibrary.wiley.com/book/10.1002/9780470034590/
[7] Van Duynhoven J, Voda A, Witek M, Van As H. Time-domain NMR applied to food products. Annu Rep NMR Spectro. 2010 Dec 31;69:145-97.

L6

A Combined Rheology and TD NMR Approach for Determining Water Distribution in Protein Blends

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We present a combined TD NMR and rheology approach to quantify the water distribution in a phase separated protein blend. The approach forms the basis for a new tool to assess the microstructural properties of phase separated biopolymer blends, making it highly relevant for many food and non-food related applications**.** First, we determine the relaxation rate of absorbed water, and the viscoelastic properties of the separated phases as function of the water content. Next, the same properties are measured for the protein blends. Finally, predictions for water distribution obtained from rheological experiments are made via the polymer blending law, and compared to a more direct assessment of the water distribution with TD NMR relaxometry. In this study, the protein blend consists of soy protein isolate (SPI) and vital wheat gluten (WG). We demonstrate that predictions for water distribution are similar for both TD NMR and rheological measurements. It turns out that water does not distribute homogenously over the phases. Independent of the SPI and WG ratio, more water is absorbed by the SPI phase relative to the WG phase, which largely determines the resulting rheological properties of the blends.

L7

The Moisture and Oil Distribution in Tobacco

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The water and oil distribution of tobacco has a significant impact on industrial manufacturing. However, the proton distribution of tobacco remains largely unknown. In the present study, the proton distribution of tobacco was measured before and after dehydration. The fraction disappeared after hot air drying was assigned to moisture, and the T_2 relaxation time of moisture fraction was in the range of 0.1 to 1.0 ms. The oil fraction, located in 10-100 ms, was almost unchanged after hot air drying. In order to explore the details of moisture fraction, two-dimension (2D) T_1-T_2 correlation spectrum was carried out. 2D spectrum revealed that different moisture fractions could be identified in T_1-T_2 correlation spectrum, although they could not be distinguished in T_2 spectrum.

L8

Study of the Moisture Equilibrium of Tobacco by Using Spin-Echo Single Point Imaging Sequence

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The equilibrium of water and essence in tobacco plays an important role in the efficiency of tobacco processing. It is well known that the fluid diffusion in tobacco is mainly determined by the fluid gradient between adjacent layers. In the present study, a non-destructive, multifaceted NMR method was applied to monitor the water and essence diffusion continuously. The moisture and essence content of different layers were expressed as signal intensity of corresponding layers, and the diffusion speed between adjacent layers was also calculated. Several conclusions can be obtained : 1) The initial diffusion speed of essence was significantly faster than that of water 2) After the first 10 min, the diffusion of essence gradually slowed down. 3) Compared with essence, the diffusion of water was a relatively stable and lasting process. The diffusion speed 4) Both water and essence could not reach to the layer which is 2 cm away from the glass tube bottom (fluid source) in 30 min.

L9

Correlating Crystallization Kinetics and Rheological Properties of Polyethylene Using a Newly Developed Low-Field RheoNMR Combination

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The newly developed unique low-field Rheo-NMR setup consists of a permanent 0.7 T magnet (30 Hz proton resonance) combined with a commercial high-end strain-controlled rheometer (Rheometrics / TA ARES) to enable simultaneous measurements of the full rheological shear behavior (*G'*, *G''*, LAOS, $I_{3/1}$, FT-Rheology [1]) and development of crystallinity [2]. In this study both commercial high density polyethylene (HDPE) with nucleating agent and a model synthesized HDPE with different M_w but the same polydispersity, were investigated to evaluate crystallization temperature, additives and applied shear effects on crystallization. PE model system used to interpret the behavior of semicrystalline foods, e.g. fat or carbon hydrates.

[1] Hyun, K., Wilhelm, M., Klein, C. O., Cho, ., K. S., Nam, J.G., Ahn, K. H., Lee, J. S., Ewoldt, R. H., McKinley, G. H., "A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS)", *Prog. Polym. Sci.*, 2011, 36, 1697.
[2] Räntzsch, V., Wilhelm, M., Guthausen, G., "Hyphenated low field NMR techniques: combining NMR with NIR, GPC/SEC and rheometry", *Magn. Reson. Chem.*, 2015, DOI 10.1002/mrc.4219.

A1

Quantitative ^{1}H-NMR to Assist the SNIF-NMR Analysis

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Determining the botanical origin of food is an important issue in the food industry. One of the most reliable methods to identify the source of a product is by measuring the distribution of deuterium in a targeted molecule (e.g. ethanol in alcoholic beverages, acetic acid in vinegars, etc.). For this purpose certain terms must be met: the compound is extracted from the food matrix and the concentration in the extract must be known with good accuracy, since the value is used to calculate the isotopic results [1,2]. The paper presents an alternative method of measuring the concentration of the target molecule in the extract by ^{1}H-NMR, value that will be used in determining the deuterium distribution by SNIF-NMR (Site-Specific Natural Isotope Fractionation studied by Nuclear Magnetic Resonance).

[1] Bauer-Christoph C, Wachter H, Christoph N, Roβmann A, Adam L. Assignment of raw material and authentication of spirits by gas chromatography, hydrogen- and carbon-isotope ratio measurements. Z Lebensm Untrers Forsch A. 1997; 204:445-452;
[2] OIV Resolution OENO 71-2000. Wine vinegar - Authentication via FINE-NMR and other isotopic methods. 2000.

A2

PFG-NMR Analysis of Organic Acids in Oil/Water Emulsions

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Organic acids are widely used as hurdles to inactivate foodborne pathogens or spoilage microorganisms in food industry. Their inhibitory effect on bacterial spores is based on their lipophilic character by affecting membrane integrity of spores (van Melis *et al.*, 2012). Yet, the composition and the structure of foodstuffs have also an effect on the microorganism growth. Thus, with the aim of increasing product shelf-life and improve their safety, it is also important to understand the relationships between food structure/composition and inhibitors. Our objective was to evaluate the mobility and the partition of organic acids in model emulsions by measuring their self-diffusion coefficients using Pulsed Field Gradient-Nuclear Magnetic Resonance (PFG-NMR) spectroscopy. Emulsions were prepared with mineral oil mixed with distilled water using sonication, and were stabilized by Tween80 and Span80. Oil content was either 35 % (v/v) or 50 % (v/v) and each emulsion was studied in the presence of organic acid (acetic, lactic and hexanoic) at two pH levels (pH 5.5 and pH 6, reached by organic acid addition). Quality and stability of emulsions were characterized by multiple light scattering. Results showed that whatever the pH of the emulsions, the diffusion coefficient of the organic acids decreased when the oil/water ratio increased: rise of pH increased amount of undissociated forms (-COOH) which may be trapped in oil phase, and/or it may also occur a structure effect on diffusion coefficient. Furthermore, in 35 % (v/v) oil emulsion at pH 5.5 hexanoic acid showed lower values of D/D0 with pH decrease in comparison to AA and LA. Thus, specificity in the diffusion among organic acids was observed due to their different solubility in oil phase which depends on both pka and logP. Finally, in this latter emulsion, fraction of HA showed a completely restricted mean displacement and therefore may be trapped in oil droplets.

A3

Improved Methods and Tools for Identification of Mixture Components by NMR

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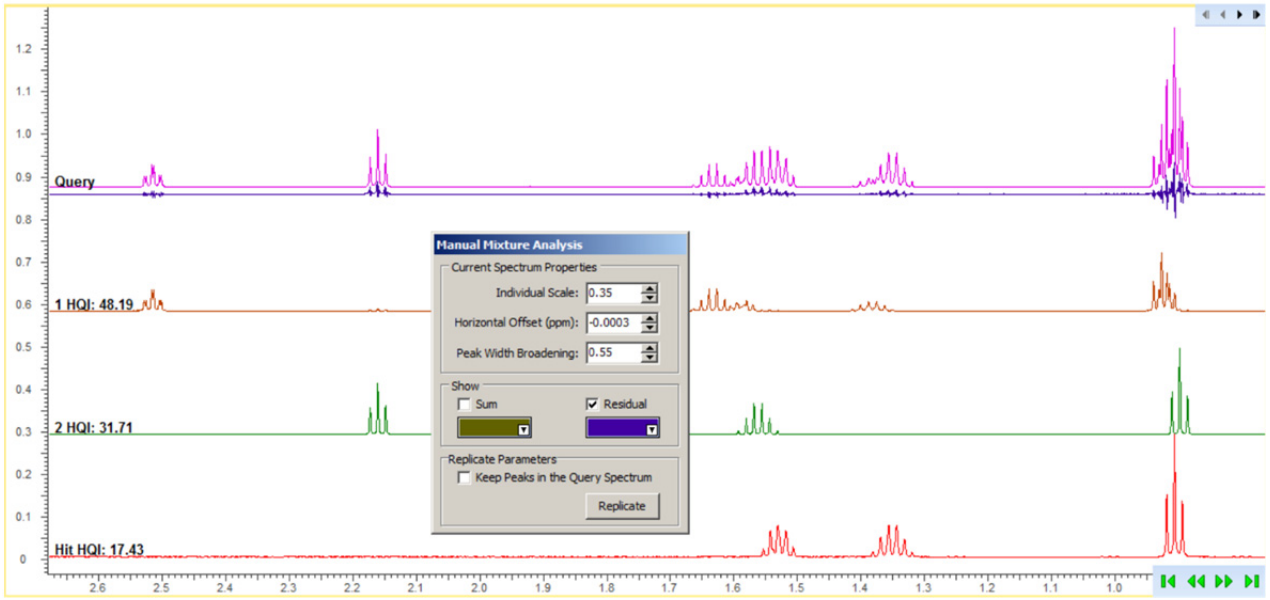
It is a common requirement in the preparation and analysis of many products to be able to easily identify and quantify the different components in mixtures of varying complexity. Specific examples include beverages, flavorings, drug formulation and counterfeit detection, as well as various consumer products [1,2]. A wide variety of analytical techniques have been applied to address this need which often depends on sample characteristics such as FT-IR, Raman spectroscopy, GC-MS & LC-MS. Nuclear Magnetic Resonance (NMR) spectroscopy offers a non-destructive approach that is information rich.

The analysis of NMR spectra can pose certain problems, not the least of which is the overlap of signals. Interpretation becomes more difficult through manual methods as the number of components grows and overlap increases. Various capabilities have been introduced over the years to assist with analysis, including database construction and query, deconvolution (peak fitting) and automated multiplet analysis. As the use of these methods increases, it becomes necessary to create an integrated tool-box to make this sort of work more consistent, accurate, and fast. Here we present a toolset to efficiently identify components in 1D NMR datasets can be coupled with integrated DOSY analysis and advanced databasing. This implementation will allow for the analyst to work more effectively and allows for a better overall understanding the composition of mixtures by NMR.



[1] Simpson et al., J. Chem. Edu. 2009, 86, 360.
[2] Wuet al., J. Magn. Reson. A 1995, 115, 123.

A4

Proton Quantitative Nuclear Magnetic Resonance Analysis (^{1}H q NMR) of Various Extracts of Raw and Thermally Processed ("Roasted") Coffee (*Coffea arabica L.*) Beans: Influence of the Extraction Process

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Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool to investigate food composition. For that purpose liquid extraction is often used, whose performances are highly dependent on the solvent and the extraction protocol. Particularly for polar extracts, signal discrepancies can be expected between deuterated and non-deuterated solvents in relation to hydrogen bonds. Therefore the relevance of both types of solvents should be assessed in light of the extraction protocol used.

In this work, various extraction protocols of water-soluble compounds contained in coffee (*Coffea arabica L.*) beans were investigated using proton quantitative nuclear magnetic resonance spectroscopy (^{1}H q NMR). Extractions performed during one hour with D_2O and H_2O on raw ("green") and thermally processed ("roasted") beans according to three methods were compared: at room temperature (1) with or (2) without sonication and (3) by heating under reflux at solvent boiling point. The relative intensities of several resonance signals (caffeine, trigonelline, sucrose, formate and acetate) served as basis for comparison. This allowed determining for both types of coffee the influence of solvent nature and extraction procedure on the extraction yields of these compounds.

A5

Determination of Fish Oil Quality by ^{1}H NMR Spectroscopy and Multivariate Statistics

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Fish oil dietary supplements have become increasingly popular, which is mainly due to their high content of the health promoting omega-3 fatty acids. However, these polyunsaturated fatty acids are extremely prone to oxidation. The traditional methods to determine fat quality parameters such as peroxide value (PV), anisidine value (AnV) and acid value (AV) are time-consuming, work- and solvent-intensive and require high amounts of sample [1–3]. ^{1}H NMR spectroscopy is an alternative non-destructive method that can provide comprehensive information within a short period of time and with little effort [3–7]. The aim of this study was to develop and validate models for the prediction of PV, AnV, AV as well as the content of total omega-3 fatty acids, DHA and EPA in fish oil. Data evaluation was based on ^{1}H NMR spectra in combination with PLS regression and artificial neural networks (ANN). No study has yet been published in which the oxidation level of edible oils as measured by the aforementioned parameters was predicted from NMR spectra by PLS regression or ANN.

[1] EFSA BIOHAZ. Scientific Opinion on Fish Oil for Human Consumption. Food Hygiene, including Rancidity. EFSA J. 2010 Oct;8(10):1874.
[2] Shahidi F, Zhong Y. Lipid Oxidation: Measurement Methods. In: Shahidi F, editor. Bailey's Industrial Oil and Fat Products. New York (USA): John Wiley & Sons, Inc.; 2005.
[3] Skiera C. ^{1}H NMR spectroscopic determination of deterioration marker compounds in fats and oils. Ph. D. Thesis. Würzburg (Germany): Julius Maximilian University of Würzburg; 2013. Available from: Universitätsbibliothek Würzburg: OPUS.
[4] Malz F. Quantitative NMR in the Solution State NMR. In: Holzgrabe U, Wawer I, Diehl B, editors. NMR Spectroscopy in Pharmaceutical Analysis. Oxford (UK): Elsevier; 2008.
[5] Standal IB. Use of NMR spectroscopy in combination with pattern recognition techniques for elucidation of origin and adulteration of foodstuffs. Ph. D. Thesis. Trondheim (Norway): Norwegian University of Science and Technology; 2009. Available from: NTNU Open.
[6] Dais P, Hatzakis E. Quality assessment and authentication of virgin olive oil by NMR spectroscopy: A critical review. Anal Chim Acta. 2013 Feb;765:1-27.
[7] Guillén MD, Ruiz A. High resolution ^{1}H nuclear magnetic resonance in the study of edible oils and fats. Trends Food Sci Tech. 2001 Sep;12(9):328-338.

A6

^{1}H NMR Spectroscopy and Chemometrics Evaluation of Non-Thermal Processing of Orange Juice

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This study evaluated the effect of atmospheric cold plasma and ozone treatments on the key compounds in orange juice by NMR and chemometric analysis. The juice was directly and indirectly exposed to atmospheric cold plasma field at 70 kV for different treatment time (15, 30, 45 and 60 s). For ozone processing different loads were evaluated. The Principal Component Analysis has shown that the groups of compounds are affected differently depending on the processing. The ozone was the processing that more affected the aromatic compounds and atmospheric cold plasma processing affected more the aliphatic compounds. However, no significant changes were verified by quantitative analysis in the orange juice as a whole, despite of the variations observed in chemometric analysis. NMR data and chemometrics were suitable to follow quality changes in orange juice processing by atmospheric cold plasma and ozone. This fact is important because it was especially useful to evaluate both non-thermal processes and to indicate that these processes could be applied to orange juice without compromising its composition. To our knowledge, this is the first time that NMR and chemometrics were applied to evaluate the effect of non-thermal processing in foodstuffs.

[1] Alves Filho, EG; Almeida, FDL; Cavalcante, RS; de Brito, ES; Cullen, PJ; Frias, JM; Bourke, P; Fernandes, FAN; Rodrigues, S. ^{1}H NMR spectroscopy and chemometrics evaluation of non-thermal processing of orange juice. Food Chemistry. 2016; 204:102-107.

A7

NMR Metabolomic Investigation of *Calligonum azel* Maire

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In the context of establishing plant NMR metabolomics, nuclear magnetic resonance (NMR) spectroscopy provides a fast and simple screening of initially unknown compounds. It is considered as a complementary technique for the identification and quantification of compounds in plants and also as the most suitable technique for this task [1]. In this study NMR spectroscopy is applied for the first time on *Calligonum azel* Maire, a plant from the Tunisian desert, which has been rather poorly studied for its chemical composition in general. For sample preparation, Soxhlet extraction was applied on leaves and roots of *C. azel* using two solvents, acetone and methanol. 600 µl of extract was adjusted to a concentration of 10 mg/ml. Two aqueous extracts of the same material were also prepared (200 mg/ml), mixed with buffer and TSP solution (10 mg/ml) for metabolomic evaluation using BBIOREFCODE 2 database (Bruker, Rheinstetten, Germany).

[1] Ferry-Dumazet H, Gil L, Deborde C, Moing A, Bernillon S, Rolin D, Nikolski M, de Daruvar A, Jacob D. MeRy-B: a web knowledgebase for the storage, visualization, analysis and annotation of plant NMR metabolomic profiles. *BMC Plant Biol.* 2011; 11:104.

A8

Quantitative *In-Situ* NMR to Characterize Protein Oxidation and its Dynamics

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To preserve food quality, it is critical to limit the oxidation processes. The evolution of meat colour or the development of rancid taste in oils are two examples of oxidative processes degrading the food quality. The reaction of oxygen (or its derivatives) with metal ions naturally present in food (*eg.* iron) forms free radical reactive oxygen species (ROS). These ROS are the main factors of food oxidation. The aim of this work is to evaluate the intakes of quantitative *in situ* NMR to understand and characterize the oxidation mechanisms.

Our preliminary work focussed on the evaluation of some amino acid mixtures as models of protein oxidation. Due to NMR signal overlaps, recording 2D NMR spectra is indispensable to isolate NMR signals from targeted amino-acids. However, these experiments are time-consuming and not adapted to chemically evolving media. To address this limitation, we developed tailored hybrid methods based on ultrafast 2D NMR. The spectrum recording time decreased from ~30 min for a classical pulse sequence to a few minutes only with the ultrafast method. This approach allows the real-time monitoring of chemical evolutions in such complex mixtures. Using this quantitative approach, we observed a fast oxidation for the histidine while threonine and lysine oxidization kinetics were significantly slower. Our analytical approach offers a promising tool to monitor oxidation processes in food products.

A9

Quantitative HSQC-NMR Screening of Feruloylated Arabinoxylan Side Chain Profiles in Cereal Grains

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Feruloylated arabinoxylans are a major component of whole grains' dietary fiber complex. Their xylan backbones are substituted with both monosaccharidic and oligosaccharidic feruloylated side-chains (FSC). Increased FSC quantity and complexity (degree of polymerization of sugar moiety) potentially reduce feruloylated arabinoxylans' enzymatic digestibility/fermentability. We have developed and validated a straightforward HSQC-NMR screening method enabling routine semi-quantitative FSC profile comparison of cereal grain materials. The three most abundant FSC in cereal grains were isolated in preparative quantities as standard compounds for method development, and the method was validated for precision, accuracy, linearity, and limits of detection and quantification. For application to cereal grain materials (insoluble fiber from maize, wheat, oats, and wild rice), FSC were semi-selectively released (50 mM TFA, 2 h, 100°C) and, following C18-SPE clean-up, were measured in DMSO-*d*6. Individual FSC were quantified via volume integration of unique signals and internal calibration curves. The determined FSC concentrations showed good correlation to a previously published LC-DAD-MS/MS method [1], and sample handling time was reduced.

[1] Schendel RR, Meyer MR, Bunzel M. Quantitative profiling of feruloylated arabinoxylan side chains from graminaceous cell walls. Front Plant Sci. 2016 Jan;6:1-11.

A10

A 2D-NMR-Spectroscopic Profiling Approach to Analyse Structural Elements of Neutral Pectic Side Chains

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The structure of plant cell wall polysaccharides has a significant impact on the physiological and technological properties of plant-based foods. In dicotyledonous plants pectins are often the quantitatively dominant polysaccharides with the neutral pectic side chains arabinans and galactans being discussed as key components. However, due to multiple branching positions and varying side chains the analysis of these polymers remains challenging. By using conventional methods of carbohydrate analysis, information about ester-linked substituents and the anomeric configuration of the monosaccharides is lost due to unselective chemical hydrolysis. Thus, the aim of this study was to develop a NMR-based profiling approach to obtain additional information about complex structural elements. Arabinans and galactans were solubilized from insoluble cell wall preparations by selective enzymatic cleavage, while soluble polysaccharides could be analysed directly. Due to severe signal overlap in the proton spectra, an HSQC-experiment was chosen to analyze the arabinan and galactan structures. Specific HSQC-marker signals were identified by using previously isolated and characterized standard oligosaccharide compounds. The different relative signal intensities of the marker signals were taken into account by the determination of relative response factors. The developed approach allows for a time efficient, semiquantitative estimation of the different arabinan and galactan structural elements and provided a more detailed insight into polysaccharide structures than conventional methods.

A11

Liquid and Solid-State ^{1}H, ^{13}C and ^{11}B NMR Analysis of Magnesium Fructoborate Complex: Chemical Structure, Identification and Stability Study

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Magnesium Fructoborate is natural plant mineral complex that is marketed as a nutritional supplement with potential health benefits for conditions linked to inflammation and cardiovascular conditions. The product is a magnesium fructoborate complex formed by the reaction of boric acid with fructose and magnesium carbonate. Liquid and solid-state ^{13}C and ^{11}B NMR was utilized to establish a baseline for product quality and to establish a robust testing method for both identification and quantification of the mono-complex and the di-complex present in the product, as well as free borate and free fructose that is present in the finished product. Liquid-state ^{11}B, ^{13}C, and ^{1}H NMR was performed on a Varian Mercury 300MVX NMR spectrometer equipped with a 5mm Varian ATB Probe at resonance frequencies of 96.14 MHz (^{11}B), 75.36 MHz (^{13}C) and 299.67 MHz (^{1}H), respectively. Solid-State ^{13}C (50.30 MHz), ^{11}B (64.17 MHz) NMR spectra were obtained on a Varian UnityPlus-200 NMR spectrometer equipped with a Doty Scientific 7mm Supersonic CP-MAS probe. The effect of varying the molar ratio of the complex components was studied by ^{11}B and ^{13}C NMR to establish the relative amounts of free borate, free fructose, and mono-/di-complex present in the products formed by the manufacturing recipe changes. Finally, an NMR based product stability study was performed to monitor molecular level stability of the complex at temperature ranging from 35-70^{o}C with exposure lasting from 2-18 hours.

A12

Identification and Characterization of Ca and Mg Different Sugar Borate Esters Using Multi Nuclear Liquid and Solid-State NMR

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Different sugar borate esters (SBE) are found in fruits, vegetables, nuts and legunes and they are naturally absorbed by animal cells. Fructose and glucose borate esters are most common SBEs. In food they serve as soluble borate with potential health beneficial effects. The samples used foor this study are magnesium and calcium sugarborate complexes formed by the reaction of boric acid with different sugars (fructose, glucose, galactose, mannose and sucrose) and magnesium or calcium carbonate. Liquid and solid-state ^{13}C and ^{11}B NMR was utilized to establish a baseline for product quality and to establish a robust testing method for both identification and quantification of the mono-complex and the di-complex present in the product, as well as free borate and free sugar that is present in the finished product. Liquid-state ^{11}B, ^{13}C, and ^{1}H NMR was performed on a Varian Mercury 300MVX NMR spectrometer equipped with a 5mm Varian ATB Probe at resonance frequencies of 96.14 MHz (^{11}B), 75.36 MHz (^{13}C) and 299.67 MHz (^{1}H), respectively. Solid-State ^{13}C (50.30 MHz), ^{11}B (64.17 MHz) NMR spectra were obtained on a Varian UnityPlus-200 NMR spectrometer equipped with a Doty Scientific 7mm Supersonic CP-MAS probe. The effect of varying of the complex components was studied by ^{11}B and ^{13}C NMR to establish the relative amounts of free borate, free sugar, and mono-/di-complex present in the products formed by the manufacturing recipe changes.

M1

A Framework for Nucleus Density Quantitative Mapping Corrected for B_1-Errors

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The quantification of nucleus density (ND) by magnetic resonance imaging (MRI) is of major importance for many applications, and particularly in food science (e.g. moisture or salt content). Nevertheless, ND mapping techniques are underemployed, mainly due to the lack of reliability on the obtained ND estimates. Bias is due to the inhomogeneity in the sample to be imaged of both transmit and receive radiofrequency fields. These B_1-related inhomogeneities should be taken into account because their effects cumulate, and bias the image intensities in a multiplicative way. The problem is badly conditioned so that even a small B_1 deviation could induce large errors in ND estimation.

Assuming equal spatial distributions of transmit and receive radiofrequency fields, we introduced a generic B_1 correction approach consisting in (i) mapping the transmit B_1 field in the presence of the sample, (ii) inferring the bias field and (iii) correcting the ND map using the calculated bias field. Because acquiring ND and B_1 maps require long acquisition times to prevent T_1-contamination, we developed a method to reconstruct both maps from the same radiofrequency-spoiled gradient echo MRI data. This approach was supplemented by a theoretical framework which allowed predicting the quality of the corrected ND maps in terms of residual bias and spatially-varying uncertainties. By this way, we can readily optimise the different steps required for ND mapping as well as the accuracy over a wide range of radiofrequency field variations. This global approach dedicated to the high-precision mapping of ND by MRI was validated on various simulated and experimental datasets.

M2

Understanding Meat Crust Formation: Validate Mathematical Models from Quantitative Microscopic MRI

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During cooking, meat crust is where both flavour and carcinogenic compounds are formed. To control crust formation, water content profiles were collected by quantitative proton density (PD) magnetic resonance imaging (MRI) on samples cooked under different temperatures [1]. Beyond its high resolution, MRI was chosen for its non-destructive nature.

After cooking, tubes containing meat cylinders were filled with gelatine to reduce artefacts at the crust interface, detect crust beginning and provide an internal reference. Experiments were performed at 400 MHz on a Bruker Avance system equipped with an actively shielded gradient coil for micro-imaging. Multi-slice single-echo spin-echo images (0.15×1×1 mm) were acquired at eight short echo-times (4 to 11 ms). After mono-exponential fitting, quantitative PD “z”-profiles were computed, averaged on the whole sample and normalized to the gelatine intensity. If x,y-B_1-errors were mitigated by such 2D integrations, those along the z-direction were neglected thanks to the large PD differences between crust and cooked meat.

Profiles show that crust was a fully dried area. Crust formation appeared after 40 and 20 min of heat treatment at 124 and 210 °C, respectively. Lower temperature regimes led to a gradual water loss in the first 3 mm, but without any crust formation. Afterwards these profiles were used to refine and validate mathematical models, which predict crusting. It emphasizes that quantitative MRI is a unique approach for linking the numerical modelisation to real complex processes.

[1] Portanguen S, Ikonic P, Clerjon S, Kondjoyan A. (2014) 10.1007/s11947-014-1321-y

M3

Magnetic Resonance Imaging to Monitor the Curing of Century Eggs

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The century egg is a well-known Chinese delicacy, which is produced by curing duck eggs in an alkaline solution for a number of weeks. This process preserves the eggs significantly and results in a physical composition radically different to that found with traditional cooking methods with a transparent yellow to golden coloured gel instead of the familiar white gel. This protein assembly based gelation has been studied to determine the mechanism by which it is produced [1] as well as its physical and optical properties. The process has not however previously been monitored whilst it occurs. In this work, we observe the gelation of the egg yolk and white using various magnetic resonance imaging measurements. The rate of gelation of the interior of duck and chicken eggs is monitored using this technique and in combination with measurements of the natural porosity of the egg shells, rate of propagation of the gelling is determined. It is also possible to produce a similar gelling effect on eggs which have been boiled, resulting in similar final properties. This process is also monitored using the same technique to investigate the influence of the inherent self-diffusion of the egg proteins on the rate of gelling.

[1] E. Eiser, C. S. Miles, N. Geerts, P. Verschurenc and C. E. MacPheed. *Molecular cooking: physical transformations in Chinese 'century' eggs*. Soft Matter, 2009, 5, 2725–2730

M4

Magnetic Resonance as a Tool to Assess Moisture Content in Potatoes for Frying Processes

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Fried sliced potatoes, known as crisps or chips, are a popular product throughout the world. It has been known for some time that during their production industrially, controlling the final oil content requires prior knowledge of the dry solids of the potatoes to modify the temperature and frying time [1]. It is most common to determine the dry weight of the batch of potatoes based on a small sample of each batch to undertake optimisation of the frying process. In preliminary experiments, we have found evidence that this is not representative of the batch as a whole.

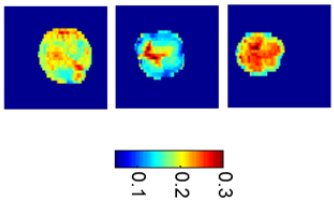

Figure.1 - T_2^{eff} map of three potatoes of the same breed.

We present an investigation into the processes to determine the properties of potatoes using magnetic resonance relaxation measurements. Imaging is performed on large batches of potatoes using a Bruker 2.35 T small animal imaging system (Bruker, Billerica, MA, USA). This preliminary study will lay the groundwork for the development of an online process monitoring device to allow better determination of the water content of incoming potatoes to allow online adjustment of frying time and temperature. Fig.1 shows T_2^{eff} maps of 3 potatoes from the same batch showing the wide range of moisture distribution within them.

[1] Lee, Y. et al.Process for preparing low oil potato chips. US Patent 4,721,625, 1985

M5

MRI Study of Staling Process in White Bread: Effect of Bread Improver

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Magnetic resonance imaging (MRI) and T_2 relaxometry were used to study water distribution and mobility in fresh white bread and their change during storage up to 17 days. The effect of bread improver to increase the softness during shelf life was analyzed.

A homogeneous spatial distribution of water as probed by proton signal intensity was observed in fresh samples at the really early stage (day of production). Both samples displayed similar T_2 relaxation times in the crumb. By 7 days of storage, these T_2 decreased for the control sample while being unchanged for the improved bread. Meanwhile an increased signal intensity of the crust in the control sample indicated a higher water migration from the crumb to the crust, whereas the inverse was observed in the improved sample. The relationship between these water state and mobility and the staling rate in both samples was discussed.

M6

Water Diffusion in Biofilms with Different Physical Structures

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Biofilms are of high interest in the context of food safety due to their ability to e.g. host pathogens. Therefore, many outbreaks of diseases are associated with biofilm formation. The biofilm formation on surfaces, such food-contact surfaces, is influenced by the mass transfer of substrates [1,2]. Biofilms can show various structures with smooth, rough, fluffy, porous or compact texture which drive the fluid-structure interaction [3]. Therefore, we performed NMR water diffusion measurements in biofilms exhibiting different physical structures (compact and fluffy) to better understand their functionality. Results show that the water diffusion in biofilms is hindered and significantly slower (20–30%) than free water. This is proved by the decay of the diffusion coefficients with increasing diffusion time (Δ). However, the was no clear correlation between biofilm structure parameters (e.g. density, organic carbon content) and the water dynamics in biofilms exhibiting different physical structures.

[1] Kumar CG, Anand SK. Significance of microbial biofilms in food industry: a review. International Journal of Food Microbiology. 1998;42(1-2):9-27.
[2] Srey S, Jahid IK, Ha SD. Biofilm formation in food industries: A food safety concern. Food Control. 2013;31(2):572-85.
[3] Flemming H-C, Wingender J. The biofilm matrix. Nature Reviews Microbiology. 2010;8(9):623-33.

F1

Food Matrix Description and Stability: A New Perspective from Foodomics

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The so-called "matrix-effect" on the added ingredients of enriched food is of fundamental evaluation. [1,2]. In addition, matrix' stability might also play an important role in the interaction between the fortifying ingredients and the hosting food.

^{1}H-NMR spectroscopy was employed to profile the molecular composition of the aqueous phase of bioactive-enriched food matrices and their control counterparts. Pancakes, both with or without the addition of DHA (docosahexaenoic acid) combined with anthocyanins (AC), were evaluated during their shelf-life in four time points.

This research work develops an algorithm capable to assess the stability of the two different food matrices (enriched or not), based on the comparison of the whole NMR spectral profiles. The results show how the two matrices develop different shelf-life behaviours during the selected storage points, displaying a different release of compounds.

[1] Turgeon SL, Rioux LE. Food matrix impact on macronutrients nutritional properties. Food Hydrocolloids. 2011 Dec; 25 (8):1915-1924
[2] Mc Clements DJ. Enhancing nutraceutical bioavailability through food matrix design Current Opinion in Food Science. 2015 Aug; 4:1-6

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° **311876: Pathway-27**.

F2

NMR Studies of the Quality-Deteriorating Wooden Breast Syndrome in Chicken

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Globally there is an increasing demand for poultry meat, which can be ascribed to its attractive nutritional profile. Concomitantly, commercial chicken production is facing increasing challenges with high incidences of abnormalities observed in chicken breast muscles. The abnormalities are characterized by pale and bulging areas of substantial hardness and are referred to as wooden breast. The high incidences of wooden breast has been ascribed to efficient breeding work, which has led to progressive improvements to produce fast-growing broilers with a high proportion of breast meat [1]. Recently it was revealed that management factors also have significant impact [2], but the exact underlying physiological mechanisms involved in the induction and progression of the muscle abnormalities are far from cracked. In addition, the specific impact on technological traits of the meat remains to be identified. We demonstrate how the application of multiple NMR techniques including high-resolution magic angle spinning spectroscopy and proton NMR relaxometry can gain insight into biochemical and biophysical changes in chicken muscle tissue defined as wooden breast.

[1] Petracci M, Mudalal S, Soglia F, Cavani C. Worlds Poultry Sci. J. 2015; 71, 363-373.
[2] Bailey RA, Watson KA, Bilgili SF, Avendano S. Poultry Sci. 2015; 94:2870–2879.

F3

Characterization and Identification of Biomarkers from Deterioration in Freshwater Fish by NMR and Chemometrics

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Changes in metabolic profile of three Brazilian freshwater fish species (*Oreochromis niloticus, Lutjanus cyanopterus and Pseudoplatystoma corruscans*) using qNMR and chemometrics, were evaluated. A total of six different fish samples with no viscera and bowels was stored at -18 °C and subjected to thawing and refreezing cycles to evaluate metabolite profile variations caused for this process. The metabolite analysis of polar extracts (water) were performed by ^{1}H NMR. The identification of biomarkers from degradation process was obtained by correlation between NMR data and principal component analysis (PCA). Metabolites such as inosine, free amino acids and biogenic amines are biological markers identified and related to a loss of nutritional value, which can be used to express the fish storage time. Using the measurement with electronic reference (ERETIC) were determined variations in inosine, inosine monophosphate, hipoxantine, lactate, dimethylamine, trimethylamine and Creatine/ Phosphocreatine contents. The method provide fast results and allows the understanding of the processes that lead to nutritional loss of fish caused by thawed and refrozen process. Although prohibited, this process is often used by dealers, especially in large supermarkets.

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F4

Extensive Regulation of Diurnal Transcription and Metabolism by Glucocorticoids

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[8]*Plateforme Biopuces et séquençage, IGBMC, 1 rue Laurent Fries, Parc d'Innovation, 67400 Illkirch, France*
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Metabolic diseases are suspected to be linked with altered daily patterns in hormone levels. Here we examine how adrenal glucocorticoid hormones contribute to daily patterns of transcriptome and metabolism in zebrafish with NMR spectroscopy, RNS-seq and HPLC. We found changes in metabolic pathways like glutaminolysis and citrate cycle that could be rescued by constant, non-rhythmic glucocorticoid treatment. Additionally, we could highlight metabolic pathways that potentially contribute to morbidity and identify similarities to patients with glucocorticoid deficiency.

F5

Rapid Identification of Imitation Cheese and Imitation Ice Cream Based on Vegetable Fat Using NMR Spectroscopy and Chemometrics

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Vegetable oils and fats may be used as cheap substitute for milk fat to manufacture imitation cheese or imitation ice cream. The consumer may be deceived if such imitate products are marketed without adequate labeling. In this study, 400 MHz ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy is used in the context of food surveillance to validate the labeling of milk products. Using principal component analysis (PCA), imitate products can be easily detected. In both cheese and ice cream, a classification according to the type of raw material (milk fat, plant fat) was possible. The loadings plot shows that imitation products are distinguishable by differences in their fatty acid ratios. Furthermore, a classification according to the types of cheese (Edamer, Gouda, Emmentaler, Feta) was possible. Quantitative data regarding composition of the investigated products can also be predicted from the same spectra using partial least squares (PLS) regression. The models obtained for 13 parameters in cheese (R^2 0.75-0.95) and 17 parameters in ice cream (R^2 0.83-0.99) (e.g., fatty acids and esters) are suitable for a screening analysis. NMR spectroscopy was judged as suitable for the rapid routine analysis of dairy products based on milk or on plant fat substitutes.

F6

Classification of the Botanical Origin of Honey by ^{1}H NMR in combination with Chemometric Methods and New Data Fusion Approaches

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The authentication of the botanical origin of honey is particularly challenging, since the composition not only depend on the botanical provenance, but also on factors such as geographic area, soil types, climatic conditions or even on storage quality. Hence, an analytical approach covering a multitude of parameters in parallel on the one hand, paired with strong discrimination power on the other hand is required here. Targeted analysis methods for marker substances commonly fail here, as quite often there simply are no characteristic substances present. In this context, non-targeted honey analysis by ^{1}H-NMR spectroscopy, combined with multivariate statistical analysis was applied as a powerful tool for quality assessment, which provides fast, simple and low-cost per analysis screening of honey samples. The NMR fingerprint of a honey sample is processed by means of chemometric techniques, typically by principal component analysis (PCA). A second approach is the low-level data fusion of orthogonal data, obtained from multiple spectroscopic techniques, e.g. NMR and FT-MIR, in order to increase the discriminative power. This was performed in custom MATLAB routines by combining non-targeted analyses of honey samples by ^{1}H-NMR and FT-MIR.

F7

Definition of Monofloral and Polyfloral Honeys Based on NMR Metabolomic Profiling

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A remarkably precise, simple and objective definition of monofloral and polyfloral honey based on NMR metabolomics is presented. The spectra of organic extracts of more of 1000 samples of 17 botanical origins were used to derive one-*vs*-all OPLS-DA classification models. The predictive components of the statistical models were used to classify a honey as monofloral or polyfloral and also to reveal the principal and the secondary floral origins present in a sample of honey [1]. This is a novel feature with respect to the methods present in the literature that are able to confirm the authenticity of monofloral honeys but not to characterize a mixture of honey types. This result descends from the peculiar features of the chloroform spectra that show diagnostic resonances for almost each botanical origin, making these NMR spectra suitable fingerprints. The reliability of the method was tested with additional 120 samples and the class assignments were compared with those obtained by traditional analysis. The two approaches are in excellent agreement in identifying the floral species present in honeys and in the botanical classification.

[1] E. Schievano, C. Finotello, J. Uddin, S.Mammi, L. Piana. Objective Definition of Monofloral and Polyfloral Honeys Based on NMR Metabolomic Profiling. **2016,** *J. Agric. Food Chem.*,. DOI: 10.1021/acs.jafc.6b00619

F8

Characterization of Lignin Structures of Plant Based Foods by 2D-NMR Spectroscopy

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Next to indigestible polysaccharides, lignin is part of the dietary fiber complex. Especially lignified fibers are suggested to reduce colon cancer risk by adsorbing carcinogens such as heterocyclic aromatic amines, depending on both lignin content and structure [1,2]. A detailed structural characterization of lignin structures is thus required to evaluate potential health benefits of lignified dietary fiber.

Lignin polymers are most complex and their compositions vary between plant species, cell types, and plant maturation stage. Solution-state 2D-NMR is a suitable tool to characterize the structures of the whole polymer. Using HSQC experiments both monomeric composition and linkage type distribution can be determined. In addition, linkage types can be structurally characterized by identifying the involved monomers using additional HMBC experiments. 2D-NMR based lignin characterization is commonly used for wood and grass samples by analysing whole cell wall material, which is a simple and rapid way to screen these materials without prior fractionation of the cell walls [3]. However, application of the whole cell wall approach on low lignified samples, such as plant based foods, is challenging due to the high matrix content which often prevents the identification of lignin based signals. Therefore, the isolation of lignin polymers is still recommended to characterize lignin structures of plant based foods. [4]

[1] Funk, C.; Weber, P.; Thilker, J.; Grabber, J. H.; Steinhart, H.; Bunzel, M., Influence of lignification and feruloylation of maize cell walls on the adsorption of heterocyclic aromatic amines. *J. Agric. Food Chem.* **2006**, *54*, 1860-1867.
[2] Funk, C.; Braune, A.; Grabber, J. H.; Steinhart, H.; Bunzel, M., Model studies of lignified fiber fermentation by human fecal microbiota and its impact on heterocyclic aromatic amine adsorption. *Mutat. Res.* **2007**, *624*, 41-48.
[3] Mansfield, S. D.; Kim, H.; Lu, F.; Ralph, J., Whole plant cell wall characterization using solution-state 2D NMR. *Nat. Protoc.* **2012**, *7*, 1579-1589.
[4] Bunzel, M.; Ralph, J., NMR characterization of lignins isolated from fruit and vegetable insoluble dietary fiber. *J. Agric. Food Chem.* **2006**, *54*, 8352-8361.

F9

Longitudinal Metabolic Profiling during Growth and Storage of Apples from Different Production Systems Studied by ^{1}H HR-MAS NMR

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Different plant protection strategies and storage conditions in agricultural apple production may have a considerable impact on the quality of the final fruit products. This in turn may be reflected in the metabolic profile of the apples. Direct application of ^{1}H High Resolution Magic Angle Spinning (HR-MAS) NMR spectroscopy to apple pulp is a powerful tool for obtaining a mostly unaffected metabolic profile [1].

In the current study we have investigated Golden Delicious apples grown under three different production systems, i.e. organic (BIO), low-input (LI) and integrated (IP) production. Fruit samples were harvested at different times during fruit development on the tree. In addition, apples picked at optimal harvest time were studied before and after controlled atmosphere (CA) storage.

^{1}H HR-MAS NMR based metabolomic analysis of the apple pulp samples revealed metabolites distinguishing BIO apples from LI and IP production. Discrimination was best at optimal harvest time and possible but diminished after storage. The longitudinal metabolic changes taking place during growth and storage are discussed in detail.

[1] Vermathen, M. et al. *J. Agric. Food Chem.* 2011, 59, pp. 12784-12793.

F10

Untargeted NMR Spectroscopic Analysis of the Metabolic Variety of Apple Cultivars

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Metabolome analyses by NMR spectroscopy can be used in quality control by generating unique fingerprints of different species. Hundreds of components and their variation between different samples can be analyzed in a few minutes/hours with high accuracy and low effort of sample preparation. Here, apple pulp or peel extracts of a variety of apple cultivars were studied to assess what is better suited to discriminate between the different varieties. Cultivars comprised mainly newly bred varieties or ones that were brought onto the market in recent years. All were cultivated in a pesticide-reduced environment.

All cultivars could be unambiguously identified both in pulp and peel extracts. The cultivars varied not only in acid and sugar concentrations, but also the polyphenols, discussed as potential health promoting substances, varied substantially. If the main sugar metabolites were omitted from the analysis, the discriminative power of the method increased substantially.

F11

Variation of Blueberry's Metabolic Profile: The Influence of Ambient and Genetic Factors

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In the present study metabolic profiles of four different blueberry cultivars collected during two consecutive years (2014 and 2015) were analysed by NMR and chemometrics. PCA and TCA analyses have shown that the samples were grouped according to the cultivar, indicating the genetic factor as the main responsible for metabolic profiles discrimination. Although less important, the year is the second factor responsible of the differentiation between samples. The influence of genetic factor on the content of glucose, fructose, quinic acid, alanine, asparagine, glutamine and isoleucine was observed, whereas the year has influenced the level of citric and malic acids, aspartic acid, glutamic acid, sucrose, and 3-O-α-L-rhamnopyranosyl quercetin.

F12

Fingerprint Profile by ^{1}H NMR and Chemometric Analysis of Freeze-Dried Açaí Berry Pulp

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Pulp of açaí berry is very consumed in the north region of Brazil especially in Belém city (Pará state) and also in the southwest of Brazil. We report here the fingerprinting profile obtained by ^{1}H NMR for açai fruits genetically modified by Embrapa Amazonia Oriental cultivated in controlled agronomic conditions and also for commercial açaí pulp sold in Belém city. The fruits were collected at different seasons in the years 2014/2015, the pulp was freeze dried in the same day and the methanolic extracts were obtained in quintuplicate. ^{1}H NMR spectra were acquired in a Bruker AVANCE III 9.4 T equipment at 300 K using a 5 mm BBI probe head (with ATMA® and using SampleXpress™). PCA was carried out in the ^{1}H NMR data using AMIX® software. The study showed that there is strong similarity between samples of açaí pulp genotypes freeze dried and the commercial ones. It was possible to observe tendencies in the distribution of periods of fruits genotype collection and also in the commercial açaí pulp. Some commercial samples showed higher concentration of unsaturated lipid compounds than genotype samples and only one point it was not possible to distinguish period 2014/2015. Probably they buy açaí fruit very often and do not keep stockpile. Of the 31 genetically modified açaí palm trees, only five genotypes showed chemical different characteristics in the fruit and these fruits have higher concentration of unsaturated lipids and carbohydrates. The signs in the carbohydrate region are probably sugars attached to phenolic compounds such as anthocyanins and other flavonoids.

F13

Study of Lipoxigenase Enzyme Activity in Common Beans by NMR and UV Spectroscopies

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Oxidative rancidity is an important process of food spoilage caused by enzymatic oxidation of lipids. This process can change flavor and color, and lipoxygenases are the most responsible for this. There are several studies for lipoxygenase activities in soybean, however, little is known about the activity of this enzyme in beans. In this context, we use NMR and UV to evaluate the lipoxygenase action in five bean Brazilian cultivars: Madrepérola, BRS Estilo, CNCF, BRS Pontal and Pinto Beans, stored in different time and temperature conditions. This information will be used to define the best conditions for beans storage.

UV analyses demonstrated that enzymes have your activity increased with course of time. The highest activities were: BRS Estilo > Madrepérola > Pinto Beans > CNFC > BRS Pontal. On the other hand, the storage in different temperatures influenced only Madrepérola > Pinto Beans > BRS Pontal. NMR data demonstrated that increasing of enzyme activity results in decreasing of fatty acids content. This is in agreement with UV results. NMR spectra demonstrated that diallylic hydrogens signal of linolenic acid have disappear after 5 minutes of lipoxygenase action. We can also percept signals for new compounds, like citric acid, demonstrating degradation products. This information was corroborated by HR-MAS NMR analyses of *in natura* bean grains where fatty acid contents decrease during storage time.

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F14

Authentication of Saffron (*Crocus Sativus* L.) Using ^{1}H NMR Spectroscopy

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Saffron, the dried stigmata of the plant *Crocus sativus* L., is a spice used for colouring and flavouring food. It is considered to be the most expensive spice, which can be explained by the laborious way the stigmata have to be harvested. There is a considerable profit to be made by adulterating saffron, e.g. by mixing it with other saffron plant materials such as flower petals and styles or other colouring plants such as safflower or turmeric. Another way of adulteration is to use artificial colours to falsify deteriorated natural material or complete imitation using coloured paper. Fifteen saffron samples (mostly from internet trade) presented to the CVUA Karlsruhe in 2015 were analysed using ^{1}H NMR for the saffron-specific colouring agents, but also using non-targeted principal component analysis. Thirteen samples were found by NMR to consist of natural saffron material (as validated by microscopic analysis), but one sample was additionally (and illegally) coloured with tartrazine (E102). Two samples (from the African market) were complete frauds (coloured paper), and 8 samples had to be objected because of offences against food labelling requirements. NMR has been proven to be of higher versatility and specificity to detect saffron adulteration compared to traditionally applied techniques such as UV/VIS spectrophotometry or thin-layer chromatography. The non-targeted spectral “fingerprinting approach” is specifically advantageous to detect food fraud with previously unexpected substances.

F15

HR-MAS NMR Spectroscopy on the Quality Control of Green Tea

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Tea is the most popular health beverage widely consumed in the world, after water. It is obtained through infusions from the leaves of *Camellia sinensis* (L) Kuntze (Theaceae) [1]. Historically, tea has been used in Chinese traditional medicine for more than a thousand years due to its health benefits. Regarding the types of tea, green tea is one of the most consumed, mainly in Japan and China as well as in United States, Canada and Europe. The high consume of green tea is due to its biological properties, including antiaging and antitumoral, which is associated to its greatest content of polyphenols. Therefore, there is the need for the quality control of green tea to warranty its health properties, once powdered leaves are in general sold as green tea around the world. In this way, several approaches has been developed to access green tea authenticity and geographical origin, including solution ^{1}H NMR spectroscopy [1,2]. Although, most of them are quite laborious, time and chemical consuming. In this work, green tea authenticity was accessed by means of HR-MAS NMR data, acquired directly from the samples. It was found that the leaves of *C. sinensis* have a single ^{1}H HR-MAS NMR profile that could be used to recognize true green tea.

[1] Engelhardt UH. Chemistry of Tea. In: Reedijk J, Editor. Reference Module in Chemistry, Molecular Science and Chemical Engineering. Oxford, Elsevier; 2013. p1-29.
[2] Heyman HN, Meyer JJM. NMR-based metabolomics as a quality control tool for herbal products. *South Africa J Bot*. 2012; 82:21-32.

F16

Investigation of the Impact of UV-C Treatment on Grape Must Using Untargeted NMR Spectroscopy

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UV-C treatment of grape must or wine is a promising approach to control the growth and activity of microorganisms during the winemaking process. This method is independent from the addition of sulfur dioxide, however, it may affect the chemical composition of the must or wine. Especially constituents like polyphenols are able to absorb UV-C light, providing potential targets for UV-C induced modifications. Chemical alterations of grape must components in consequence of UV-C treatment can be monitored by untargeted NMR spectroscopy. In this work, we study the changes of metabolic fingerprints of grape must induced by UV-C at different doses needed to ensure microbial safety.

F17

Whisky Analysis through the Application of NMR Metabolomic Techniques

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Beverage analysis utilizing magnetic resonance techniques has already been established, most notably in the cases of fruit juice [1-3], beer [4,5], and wine [6-8]. The results obtained from such analyses are useful for determining quality, authenticity, and even origin of the product. In the case of whisky, traditional chemical analyses for product characterization were established decades ago [9]. Quantities including alcohol content, general chemical content (acidity, esters, aldehydes, tannins, fusel oil), specific chemical content (furfural), and sample properties (pH, solids content, colour) were measured, with acidity and ester content correlating most strongly with the age of the whisky [9]. With the recent development of advanced mixture analysis methods, particularly driven by the metabolomics field, and taking inspiration from the beverage analysis work [1-8], we undertook a pilot study with the aim to determine the applicability of modern metabolomic NMR techniques in distinguishing not only whisky age, but also origin and flavour characteristics. While the sample size is small (12 commercial whiskies), there are hints that characteristics can be distinguished through statistical analyses of water soluble small molecule 1H NMR data. With these preliminary results, we believe there is justification to pursue whisky analysis in greater detail, including optimization of the NMR sample preparation protocols and correlation of the traditional chemical analyses with NMR-derived statistical models. As in the cases of fruit juice, beer, and wine, these results would be critical in ensuring authenticity and quality in the global market.

[1] Spraul M, et al., Magnetic Resonance in Chemistry. 2009;47(S1):S130.
[2] Spraul M, et al., Nutrients. 2009;1(2):148.
[3] Cuny M, et al., Analytical and Bioanalytical Chemistry. 2008;390(1):419.
[4] Rodrigues JE, et al., Magnetic Resonance in Chemistry. 2011;49:S37.
[5] Almeida C, et al., Journal of Agricultural and Food Chemistry. 2006;54(3):700.
[6] Weekley AJ, et al., Journal of Magnetic Resonance. 2003;161(1):91.
[7] Laghi L, et al., Food and Nutrition Sciences. 2014;05(01):52.
[8] Godelmann R, et al., Journal of Agricultural and Food Chemistry. 2013;61(23):5610.
[9] Scherl B. Industrial & Engineering Chemistry. 1949;41(3):534.

F18

Nontargeted NMR Analysis to Detect Hazardous Substances Including Methanol in Unrecorded Alcohol from Russia

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Nuclear magnetic resonance (NMR) spectroscopy is applied for the analysis of alcoholic products in the context of health and safety control. A total of 74 samples of unrecorded alcohol (i.e., illegally or informally produced alcohol or surrogate alcohol such as cosmetic, medicinal or industrial alcohol which are consumed as alcoholic beverages in marginalized populations) were collected in Novosibirsk and nearby cities. For sample preparation, only addition of buffer in a water/ethanol mixture is required as single step. To detect potentially harmful samples, a nontargeted approach based on principal component analysis (PCA) was applied. The PCA scores plot clearly shows two conspicuous samples with highly divergent scores from the rest of the samples. These samples were antifreeze fluids containing alarming proportions of methanol, with concentrations of 26% and 48%, respectively. Both products were bought in regular retail sale and were claimed as “not containing methanol” on the labels. Furthermore, the occurrence of formic acid (1.1 g/100 g) was observed in some of the alcohol-containing medicinal products. The major advantage of NMR over conventional methods is the fact that it not only provides the same quantitative data for specific compounds, but also allows a fast and simple nontargeted screening analysis for initially unknown or unexpected compounds.

F19

Classification of Italian Vinegar by Foodomics Approach

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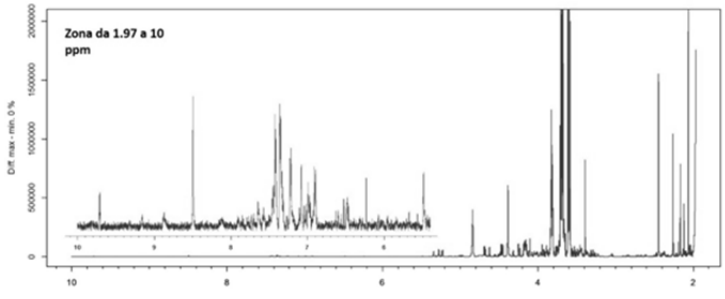

Nuclear Magnetic Resonance (NMR) is known to be a suitable technique for the development of affordable applications focused on food authenticity and traceability. As the method is fast, reliable and reproducible in obtaining the molecular profiles of biological samples, it is largely used in different field, from clinical to nutritional studies and for food science. In this last case, the coupling of the spectral data to the multivariate analysis provides a robust set of parameters, mainly patterns of metabolites, reported in literature to be helpful in the assessment of the origin of some product, e.g. oil, wine and tomato, both in terms of geographic site and of production technology. The research work, conducted in collaboration with one of the most important Italian producer of vinegar, describes a distribution map of the overall molecular compositions of a preliminary set of wine vinegar samples produced with different wines, in three factories and a range of storage times and conditions. The study is aimed at exploring the natural variability of composition of vinegar, in order to drive the production towards products with most optimal nutritional quality. 65 samples of vinegar have been analyzed, whose technological origin has been directly guaranteed by the producer, which is interested in defining its production with unequivocal molecular fingerprints. The results have interestingly shown that some clustering occurs depending on technological processing and factory of production.

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F20

HR-MAS NMR as Technique to Monitor *In-Vivo* Growth and Real-Time Fermentation Patterns of *Saccharomyces Cerevisae*

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Yeast (*Saccharomyces cerevisiae*) was not the only first microorganism to by systematically used by mankind, it also continues to be one of the most important ones. Its roles in food industry (alcohol fermentation and bakery) and biofuel production are indisputable. Among the microorganisms (e.g. bacteria) that ferment substrates to ethanol, *S. cerevisae* is of special robustness (tolerating a wide pH range and high ethanol levels) and less susceptible to infection and substrate composition. Even though many techniques exist to study alternative substrates, fermentation progress or modified yeast strains, yet to date we lack a nondestructive technique which allows to monitor the growth and fermentation process of *S. cerevisae* for different substrates *in-vivo* and in real-time. This is where high-resolution magic angle spinning (HR-MAS) could fill the gap. Originally designed for solid-state NMR this technique recently gains more and more interest for *in-vivo* studies of intact small-size organisms. In our work we investigated the five most common brewing sugars upon their metabolisation by *S. cerevisae* in a 25 µL insert of a 4 mm HR-MAS rotor at 500 MHz high-field NMR (Bruker Avance III). We showed different time-dependent metabolite kinetics and ethanol yields for monosaccharides (glucose, fructose), dissacharides (maltose, saccharose) and the trisaccharide maltotriose under identical conditions, underlining the potential and benefit of HR-MAS NMR for research and industrial application.