13th ASAC JungenanalytikerInnen-Forum
University of Natural Resources and Life Sciences
12th-13th May 2017 | BOKU Vienna
13th ASAC JunganalytikerInnen-Forum – Book of Abstracts

Edited by
Division of Analytical Chemistry
Department of Chemistry
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Forward

Dear colleagues,

It is a great pleasure to welcome you all to the 13th Austrian Society of Analytical Chemistry (ASAC) JunganalytikerInnen-Forum to be held at the University of Natural Resources and Life Sciences (BOKU) in Vienna between the 12th and 13th of May this year.

Thanks to the many interesting contributions from delegates and the generous support of our sponsors, we can look forward to some high-quality scientific content across the two day program. Moreover, there will also be ample opportunities to get to know fellow young scientists and discuss with some of the more experienced forum attendees during our lively social program which will include dinner at a local Heuriger on Friday evening and a farewell drink (“Fluchtachterl”) at the close of the forum on Saturday.

I wish you all many scientifically and socially rewarding experiences at this year’s forum!

Best regards,

Tim Causon
Organiser
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Program

Friday, 12th of May

13:00    Registration

13:30    Opening

13:45    “Impulsvortrag”
About multiplex experiments and a single scientist
Larissa Müller, Thermo Fisher Scientific, Bremen, DE

14:30    Coffee Break

Scientific Session I: Metabolomics
Session Chair: Michaela Schwaiger, University of Vienna

15:00    Artifacts caused by methanol extraction can lead to false interpretation of
metabolomics data
Claudia Sauerschnig, University of Natural Resources and Life Sciences

15:20    Development of a metabolomics method for the investigation of apparent
symbiosis
Yasin El Abiead, University of Vienna

15:40    Assessment of fully-wettable RPLC columns for LC-MS-based cellular
metabolomics
Le Si Hung, University of Natural Resources and Life Sciences

16:00    Assessment of relative matrix effects for a “dilute and shoot” multi-mycotoxin
LC-ESI-MS/MS method
David Stadler, University of Natural Resources and Life Sciences

16:20    Investigations of the uptake and metabolism of antidepressants in plants
Bernd Reichl, Johannes Kepler University Linz

16:40    Understanding the metabolism of the anticancer drug Triapine by application of
electrochemistry and liquid chromatography coupled to mass spectrometry
Karla Pelivan, University of Vienna

17:00    Integration of NMR-based metabolic phenotyping in basic and applied
biomolecular research
Sarah Stryeck, Medical University of Graz

18:30    Dinner at Heuriger Muth
Saturday, 13th of May

**Scientific Session II: Technology & Health**

**Session Chair: Florian Meischl, Leopold Franzens University Innsbruck**

09:00  New classes of NIR phosphorescent benzoporphyrin dyes for optical oxygen sensing and application in photonic materials
  *Peter W. Zach, Graz University of Technology*

09:20  Ultra-bright and highly photostable perylene indicator dyes for optical carbon dioxide and pH sensing
  *David Pfeifer, Graz University of Technology*

09:40  Metabolomics in tumour spheroids
  *Mate Rusz, University of Vienna*

10:00  Post-digestion stabilization of osmium enables quantitation by ICP-MS in cell culture and tissue
  *Matthias H.M. Klose, University of Vienna*

10:20  DNA vs. protein – capillary zone electrophoresis–mass spectrometry to characterize metallodrug binding preferences
  *Christian Artner, University of Vienna*

10:40  **Coffee Break**

**Scientific Session III: Environment**

**Session Chair: Lisa Emhofer, Johannes Kepler University Linz**

11:00  Spectral insights: multi-dimensional approach to evaluate the diagenetic status of skeletal remains for Sr isotope analysis
  *Anika Retzmann, University of Natural Resources and Life Sciences*

11:20  Arsenic’s low temperature volatilization pathway and its importance for the biogeochemical cycle of arsenic
  *Stefan Tanda, University of Graz*

11:40  Analytical characterization of macromolecular ice nuclei from birch pollen grains
  *Teresa Seifried, TU Wien*

12:00  Identification of oxidation products of lubricant and fuel components by combination of gas-phase isotope labelling combined with capillary gas chromatography mass spectrometry (GC-MS)
  *Marcella Frauscher, TU Wien*

12:20  Novel approaches in NIR-spectroscopy
  *Christian G. Kirchler, Leopold Franzens University Innsbruck*

12:40  Ca$^{2+}$-sensitive fluorescent indicator dyes for optical sensing
  *Lukas Tribuser, Graz University of Technology*

13:00  **Lunch**
Saturday, 13th of May (cont.)

Scientific Session IV: Food

Session Chair: David Steiner, University of Natural Resources and Life Sciences

13:50 Determination of micro- and macroelements in cashew (Anacardium occidentale) by inductively coupled plasma atomic emission spectroscopy
   Dora Hlebec, University of Zagreb, HR

14:10 Exploring the arsenic speciation in mushrooms
   Simone Braeuer, University of Graz

14:30 Identification and activity testing of volatile organic compounds (VOCs) found in different grapevine genotypes in response to downy mildew infection
   Valentina Lazazzara, University of Natural Resources and Life Sciences

14:50 Development, validation and application of an LC-ESI-MS/MS multi-analyte method for the quantification of Alternaria toxins in Austrian food commodities
   Hannes Puntscher, University of Vienna

15:10 Mineral oil hydrocarbons (MOH) in food - an analytical challenge
   Andrea Walzl, Graz University of Technology

15:30 Characterisation of aroma compounds in wines from fungus resistant grape varieties
   Dorothea Leis, Graz University of Technology

15:50 Close of the Forum

Farewell drink (“Fluchtachterl”)
   Provided by Josef Hartl, Weinbauer
Oral Presentation Abstracts
Artifacts caused by methanol extraction can lead to false interpretation of metabolomics data

Claudia Sauerschnig, Maria Doppler, Christoph Büschl, Alexandra Maria Simader, Rainer Schuhmacher

Center for Analytical Chemistry, Department of Agrobiotechnology (IFA-Tulln), University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad-Lorenz-Strasse 20, 3430 Tulln

In many metabolomics studies mixtures of methanol and water with or without addition of formic acid are used for sample extraction (1). As methanol has been shown to potentially cause artifacts during natural product isolation (2), we hypothesized that this might also be the case in metabolomics studies employing aqueous methanol as extraction solvent. Especially in untargeted metabolomics studies, where metabolites are unknown before analysis (and often remain unknown even after analysis) the formation of methanol-derived artifacts might be erroneously mistaken as true biochemical constituents.

In the present study wheat leaves were extracted with mixtures of acidified (0.1% HCOOH) aqueous methanol (native and labelled (C\textsubscript{2}H\textsubscript{3}OH)) and water and the resulting extracts were analysed with an HPLC-ESI-Q-Exactive HF Orbitrap instrument with polarity switching in the full scan mode immediately and after one week of storage at 10 °C, -20 °C or at -80 °C. Isotope assisted data processing was performed with MetExtract (3) and Thermo Xcalibur. Our study revealed that numerous methylated metabolites had already been formed during sample extraction. Moreover, we observed that storage of samples at 10 °C for several days, as can typically be the case during longer measurement sequences, lead to an increase in both intensity and number of methylated artifacts. In this presentation the isotope-assisted workflow for artifact detection and the characterisation of the methanol-derived reaction products will be discussed in detail.

References
Development of a metabolomics method for the investigation of apparent symbiosis

Yasin El Abiead\textsuperscript{a}, Petra Pjevac\textsuperscript{b}, Michaela Schwaiger\textsuperscript{a}, Evelyn Rampler\textsuperscript{a}, Holger Daims\textsuperscript{b}, Michael Wagner\textsuperscript{b}, Gunda Köllensperger\textsuperscript{a}

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\textsuperscript{b) Department of Microbiology and Ecosystem Science, University of Vienna, Althanstrasse 14, 1090 Vienna}

Metabolomics is a fast developing research field with many different possible applications. However, there are still many unsolved issues and pitfalls that restrict its potential in terms of reliability and explorative use. Within the presented work some of those topics were broached within the frame of a metabolomics study. To put it into biological context targeted and untargeted metabolomics approaches were utilised to investigate an apparent symbiosis between the ammonia oxidising archaea Nitrosospharea gargensis and a betaproteobacterium (1). For the sake of this monocultures as well as a co-culture of the organisms of interest were probed. In order to explore the samples as comprehensive as possible the technical advantages of high resolution mass spectrometry and different orthogonal separation techniques, namely high performance reversed phase chromatography and anion exchange chromatography were applied. Moreover, absolute quantification of a number of targeted analytes was achieved by the use of yeast-extracted \textsuperscript{13}C-labelled internal standards (2).

As limits of detection for small organic molecules are becoming lower and lower contaminations are also becoming more and more of an issue. This is especially true for untargeted metabolomics where contaminations can easily be misinterpreted for sample components or lead to other problems. In order to become more aware of the extensiveness of this problem the contamination potential of a number of lab materials was investigated.

References
Assessment of fully-wettable RPLC columns for LC-MS-based cellular metabolomics

Le Si-Hung, Tim J. Causon, Stephan Hann

Division of Analytical Chemistry, Department of Chemistry, University of Natural Resources and Life Sciences, Muthgasse 18, 1190 Vienna

Reversed-phase LC combined with high-resolution mass spectrometry (HRMS) is one the most popular methods for cellular metabolomics studies. Due to the difficulties in analyzing a wide range of polarities encountered in the metabolome, it is widely accepted that a single method with comprehensive metabolome coverage does not exist. Therefore, 100%-wettable reversed-phase materials are frequently used to maximize metabolome coverage within a single analysis. In this study, a comparison of several reversed-phase LC columns for metabolome analysis using such a dedicated workflow is presented. All columns were tested under the same analytical conditions on an LC-Time-of-Flight-MS (LC-TOFMS) platform using a variety of authentic metabolite standards and biotechnologically-relevant yeast cell extracts. A comprehensive assessment of the column’s performance for cellular metabolomics requires use of a full LC-HRMS workflow in order to reflect realistic study conditions used for cellular metabolomics. Data on total workflow performance including retention behavior, peak capacity, coverage, and software-based molecular feature extraction repeatability from these columns were presented with consideration for both non-targeted screening and differential metabolomics workflows using authentic standards and Pichia pastoris cell extract samples.
Assessment of relative matrix effects for a “dilute and shoot” multi-mycotoxin LC-ESI-MS/MS method

David Stadler, Rudolf Kriska, Michael Sulyok

Department of Agrobiotechnology (IFA-Tulln), Center for Analytical Chemistry, University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad Lorenz Str. 20, 3430 Tulln

In the recent years, the LC-ESI-MS/MS based multi-analyte approach has been demonstrated to be a powerful technique for the simultaneous determination of mycotoxins in food and feed.(1) One significant drawback of the ESI source is its high susceptibility to matrix effects (i.e. the decrease or - more rarely – the increase of the analytical signal of an analyte due to co-eluting matrix constituents). To obtain a robust LC-ESI-MS assay, matrix effects have to be minimized or compensated. For the presented method, sample clean-up needs to be kept at a minimum due to the chemical diversity of the targeted analytes. The use of stable isotopically labelled internal standards is not feasible because of limited availability and high costs. Therefore, the quantification of mycotoxins is increasingly based on the analysis of diluted crude extracts and external- or matrix-matched calibration.

In everyday practice the calibration curve is constructed from a single lot of a matrix. However, the degree of ion suppression for an analyte may vary in different lots of the same matrix, which is referred to as relative matrix effect. This effect has already been addressed in quantitative bioanalysis in the course of drug development, but remains unstudied for multi-analyte methods and unmentioned in the official guidelines (2).

This contribution provides a critical assessment of relative matrix effects for 70 mycotoxins and fungal metabolites in seven different matrices. Experiments to demonstrate the presence and absence of relative matrix effects are described. Furthermore, the influence of intra-matrix variability on the measurement uncertainty is discussed.

References
Investigations of the uptake and metabolism of antidepressants in plants

Bernd Reichl, Markus Himmelsbach, Lisa Emhofer, Christian Klampfl, Wolfgang Buchberger

Institute of Analytical Chemistry, Johannes Kepler University Linz, Altenbergerstrasse 69, 4040 Linz

Environmental contamination with pharmaceuticals has received growing attention in recent years. Several studies describe the presence of traces of drugs in water bodies and soils and their impacts on non-target organisms including plants (1, 2). Due to these facts investigations of the uptake and metabolism of pharmaceuticals in organisms is an emerging research area.

The present study demonstrates the analysis of three selected antidepressants (sertraline, clomipramine and trazodone) as well as metabolites and transformation products in a cress model (Lepidium sativum). Cress was cultivated hydroponically and irrigated with tap water containing 10 mg L\(^{-1}\) of the parent drugs. Employing an analytical approach based on HPLC coupled with quadrupole-time-of-flight or Orbitrap mass spectrometry in MS and MS\(^2\) mode, in total 15 substances were identified in the cress extracts. All three parent drugs were taken up by the cress and translocated from the roots to the leaves in specific patterns. In addition to this, twelve metabolite species were identified. They were generated by hydroxylation, demethylation, conjugation with amino acids or combinations of these mechanisms. Finally, the inclusion of control cultures in the experimental setup allowed for a differentiation of “true” metabolites generated by the cress and transformation products generated by plant-independent mechanisms.

References
Understanding the metabolism of the anticancer drug Triapine by application of electrochemistry and liquid chromatography coupled to mass spectrometry

Karla Pelivan\textsuperscript{a}, Lisa Frensemeier\textsuperscript{b}, Uwe Karst\textsuperscript{b}, Gunda Koellensperger\textsuperscript{c}, Bjoern Bielec\textsuperscript{a}, Petra Heffeter\textsuperscript{d, e}, Christian R. Kowol\textsuperscript{a, e} and Bernhard K. Keppler\textsuperscript{a, e}

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In anticancer chemotherapy α-N-heterocyclic thiosemicarbazones belong to the most effective ribonucleotide reductase inhibitors\textsuperscript{1,2}. With regard to the clinical practice, Triapine, the most prominent representative, showed promising activity against hematological diseases, but it failed against a variety of solid tumors\textsuperscript{3}. However, the underlying reasons are still vague. Therefore, it is of a high importance to get more insights into the pharmacokinetics and metabolism of Triapine.

Electrochemistry, coupled to liquid chromatography and mass spectrometry (EC/LC/MS), is a valuable tool in metabolism research for simulation of many oxidative liver reactions. Therefore, this method was compared to in vitro incubation with human liver microsomes (HLM). Additionally, metabolism reactions of Triapine were investigated in in vivo samples collected from treated mice and analysed by an optimized LC/MS method.

From the three-dimensional mass voltammogram of the EC/MS measurements, recorded by plotting mass spectra against the applied potential ramp, the oxidation products of Triapine were identified. Dehydrogenation, with an interesting ring-closure reaction, was the main oxidation reaction next to hydroxylations and dimer formations. Furthermore, LC-MS analysis of the different metabolites was applied to detect possible isomers. In addition, MS/MS measurements were conducted for structural elucidation. Complementary, in vitro incubations were performed with microsomes for metabolite generation under physiological conditions. Subsequently, they were separated and identified via LC/MS, which, in accordance with the EC/MS measurements, also revealed dehydrogenated and hydroxylated
species. Finally, the metabolic conversion of Triapine was investigated *in vivo*. LC/MS measurements of collected serum, liver, kidney and urine confirmed dehydrogenation and hydroxylation as the main metabolic reactions, although the number of different hydroxylated metabolites was much higher.

Taken together, the metabolism of the anticancer drug Triapine was elucidated for the first time by electrochemistry, *in vitro* and *in vivo*. The data show fast metabolic conversion of Triapine with an unexpected ring-closed metabolite, which will help to better understand the anticancer activity of this clinically investigated drug.

**References**

Integration of NMR-based metabolic phenotyping in basic and applied biomolecular research

Sarah Stryeck, Tobias Madl

Institute of Molecular Biology and Biochemistry, Medical University of Graz, Harrachgasse 21/III, 8010 Graz

Nuclear Magnetic Resonance (NMR) spectroscopy-based metabolic phenotyping provides a snapshot of the functional endpoint of complex biological networks and accurately describes the functional and physiological states of an organism. NMR provides access to unique structural information of metabolites, is quantitative and highly reproducible. Aiming at in-depth characterization of complex metabolite mixtures, the recent technological developments in the field of NMR-based metabolomics have opened up a wide range of research fields in biological, biomedical, environmental, agricultural, and nutritional research. In biomedical research, metabolomics has established itself as key technique for systems biology, disease diagnostics, and biomarker discovery.

We will present recent highlights of our own research projects which focus on the integration of NMR-based metabolic phenotyping in basic and applied biomolecular research. Along this line we will show how untargeted NMR approaches can provide systemic insight into complex signalling pathways in cells and in vivo model systems. Whereas most approaches provide a static snapshot of the functional and physiological state of an organism, we will show how flux analysis with isotope-labelled compounds can provide systemic insight into the dynamic processes of biological pathways.

Finally we will show how untargeted NMR-based metabolic phenotyping can be integrated in clinical studies and demonstrate the suitability of this approach for disease biomarker research. Through this, we aim to show that unprecedented opportunities will be opened up for the evaluation and exploration of the metabolome for markers of disease states and in understanding the diversity of metabolic pathways in a variety of organisms. The knowledge gained from this approach provides a ready link to genomic, transcriptomic, and proteomic information to achieve systems biochemical and mechanistic understanding of physiological and disease states in living cells and organisms.
New classes of NIR phosphorescent benzoporphyrin dyes for optical oxygen sensing and application in photonic materials

Peter W. Zach, Maximilian Maierhofer, Andreas Steinegger, Sergey M. Borisov, Ingo Klimant

Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, 8010 Graz

Oxygen is undoubtedly one of the most important and often measured analytes on earth. Although many different ways to measure oxygen exist, optical sensor technology has received much attention in the last decades due to the various advantages.

Most optical sensing systems developed for the detection of oxygen rely on the process of luminescence quenching of the indicator dye embedded in a polymer matrix by molecular oxygen. Phosphorescence of the complexes in the NIR makes them also attractive candidates for triplet-triplet-annihilation based upconversion (TTA), applicable in photovoltaics.

We present two different classes of benzoporphyrin complexes that can be obtained from cheap and commercially available chemicals in a convenient way, thus avoiding multi-step synthesis presented in the literature.

The first class, where electron-withdrawing groups combined with long aliphatic chains were attached in the β-β-pyrrole position, demonstrates excellent solubility in various organic solvents, high photostability and brightness and the possibility of excitation in the blue as well as in the red part of the spectrum with emission of fluorescence in the red part and phosphorescence emission in the NIR-region. Moreover the small singlet-triplet energy gap of these complexes is responsible for very efficient thermally activated delayed fluorescence with quantum yields up to 14% at 120 °C, enabling dual sensing and imaging of oxygen and temperature simultaneously with a single probe.

The dyes of the second class, in which the π-system is extended by intramolecular bridging via Scholl-reaction, show very interesting photophysical properties with (narrow) absorption bands in the red part of the spectrum and emission maxima ranging from 870 nm up to 995 nm. The new indicators are perfectly suitable as transducers for subcutaneous glucose monitoring with an enzymatic sensor, due to its long-wavelength emission which does not overlap with the oxygen reference sensor.
Ultra-bright and highly photostable perylene indicator dyes for optical carbon dioxide and pH sensing

David Pfeifer, Sergey M. Borisov, Ingo Klimant

Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, 8010 Graz

The determination of pH is an issue of great interest for a variety of applications belonging to biotechnological processes, marine science, diagnostics and many other fields. An alternative to the well-established electrochemical method is the determination with an optical sensor, which can be miniaturized, combined with fibre optics and features robustness against electrochemical interferences. For many applications e.g. measuring of biological samples the use of indicators with absorption/emission profiles in the red/near-infrared region are preferable because they feature many advantages such as less scattering background and lower auto-fluorescence of biomolecules. Optical solid state pH sensors typically consist of an indicator dye embedded into a proton permeable polymer matrix. Due to the carbonic acid equilibrium in water, a pH sensitive dye with a sufficiently high pKa value can feature sensitivity to carbon dioxide. For this concept, the basic (anionic) form of the dye is usually entrapped in an ethyl cellulose matrix as an ion pair with a quaternary ammonium cation. A gas permeable hydrophobic membrane is used as a protective layer.

We present new pH sensitive, laterally extended perylene bisimide dyes with high fluorescence quantum yields, high molar absorption coefficients and excellent photostability. A bathochromic shift in absorption and emission spectra to the red/near-infrared region of the electromagnetic spectrum and the pH sensitivity are both caused by the introduced phenyl-imidazol group in bay-region of the perylene core. Combined with an adequate reference material pH determination can be performed with a handheld phase fluorimeter by dual-lifetime referencing.

High obtained pKₐ values >9 of the new perylene dyes supplementary enable optical carbon dioxide monitoring in different dynamic ranges. Tuning of the sensitivity and the performance of the solid state sensor can be realized by variation of plasticizer concentration, humidity and modification of the chemical perylene structure.
Figure 1. Photographic image of sensor foil A: protonated (purple) and deprotonated (green) form of dye; B: pH sensitive absorption and corresponding pKₐ plot; C: miniaturized phase fluorimeter
Metabolomics in tumour spheroids

Mate Rusz\textsuperscript{a,b}, Michaela Schwaiger\textsuperscript{b}, Luis Galvez\textsuperscript{b}, Michael Jakupec\textsuperscript{a}, Gunda Koellensperger\textsuperscript{b}

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Metabolomics aims to measure small molecules from biological samples, thereby investigating the metabolism on a global scale and providing insights into multiple aspects of cellular physiology (1). As altered metabolism is a characteristic feature of cancer cells, eventually these changes might be exploited to improve cancer therapy (2).

LC-MS metabolomics platform has in principle high broad metabolite coverage and high sensitivity, which allows a comprehensive metabolomics analysis even for low-abundance metabolites. Unfortunately, sample preparation of adherent cell lines is usually extensive and represents the bottleneck in the overall analytical process. Therefore, there is a need for improvement of extraction protocols and combination of dedicated sample preparation steps to generate reliable data. In addition to testing several sample preparations, the application of diverse chromatographic separations is required.

In this work we investigated 3D tumour spheroids, which are an important model for cytotoxicity studies and drug discovery as they resemble closely the in vivo tissue (3). Since they consists of considerably lower number of cells than two dimensional cell cultures used for metabolomics studies, it is challenging to find reliable methods to profile their metabolome.

References
Post-digestion stabilization of osmium enables quantitation by ICP-MS in cell culture and tissue

Matthias H.M. Klose\textsuperscript{a,b}, Michaela Hejl\textsuperscript{a}, Petra Heffeter\textsuperscript{b,c}, Michael A. Jakupec\textsuperscript{a}, Samuel M. Meier\textsuperscript{a,b,d}, Walter Berger\textsuperscript{c}, Bernhard K. Keppler\textsuperscript{a,b}

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Cancer was still the 2nd most prominent cause of death worldwide in 2015 despite intense research efforts. Since the discovery of cisplatin, platinum-based anticancer agents developed into key therapeutic agents to cure cancer. However, together with sometimes severe side effects, resistance phenomena limit the applicability of this successful class of anticancer agents.

Thus, metallodrug discovery programs focused on other metals to circumvent these shortcomings and ruthenium-based drug candidates are among the most advanced and promising non-platinum anticancer agents. Very recently, osmium-based drugs attracted significant interest in inorganic drug discovery stages. They offer a broad range of oxidation states, known synthetic chemistry, but potentially novel mode of actions compared to both platinum and ruthenium anticancer agents.

Inorganic drug discovery relies heavily on analytical techniques to elucidate molecular reactivities, cellular accumulation studies \textit{in vitro} or organ distribution studies \textit{in vivo} (e.g. pharmacokinetics) and inductively coupled plasma mass spectrometry (ICP-MS) is vital for most of these studies. ICP-MS-based analytical platforms are well established for platinum and ruthenium anticancer therapeutics. However, similar methods for osmium are not reliable, nor robust because of the tendency of osmium to generate volatile OsO\textsubscript{4} species during the routine oxidative sample preparation. This characteristic hampered investigations on osmium-based compounds in a therapeutic context strongly.

We addressed this problem by developing complementary approaches for sample preparation of osmium-based drug candidates. Based on the work of Venzago et al.\textsuperscript{1}, who determined impurities of osmium in pharmaceuticals using a pressure vessel, we developed a reliable method for post-digestion osmium stabilization and optimized lysis and digestion...
conditions to quantify osmium in biological matrices. The approach was validated in spiked liver tissue by means of appropriate matrix and digestion controls. We show that the method may be successfully used for cellular accumulation studies and for determining total osmium content in organs from treated mice.

References
DNA vs. protein – capillary zone electrophoresis–mass spectrometry to characterize metallodrug binding preferences

Christian Artner\textsuperscript{a,b,c}, Hannah U. Holtkamp\textsuperscript{c}, Christian G. Hartinger\textsuperscript{c}, Samuel M. Meier\textsuperscript{b,d}, Bernhard K. Keppler\textsuperscript{a,b}

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It is generally accepted that the cytotoxic mode of action of cisplatin, one of the leading metal-based anticancer drugs, is based on its binding ability to DNA [1]. In the same way, for early ruthenium-based complexes DNA was believed to be the primary target for the therapeutic effect as well [2]. However, in recent years, it emerged that the therapeutic effect of ruthenium-based drug candidates may likely be caused by interaction with proteins rather than DNA, although the exact mechanisms of action are often not yet clarified and direct targets unknown. A fundamental question to be addressed in the discovery process is whether a metallodrug shows binding preference to DNA (oligonucleotide) or proteins in a competitive experiment and this cannot be determined by classical screening assays so far on a molecular level.

We developed a competitive binding assay, where a model protein, an oligonucleotide and a metallodrug were incubated together and analyzed with capillary zone electrophoresis hyphenated with different mass spectrometry (MS) methods. Firstly, online electrospray ionization (ESI) MS\textsuperscript{1} was used to identify intact biomolecule-metallodrug adducts. In a second experiment these adducts were fragmented by \textit{in-source} collision-induced dissociation ESI-MS to identify the specific binding site (nucleotide or amino acid). Finally, hyphenation with inductively coupled plasma MS gave quantitative as well as pseudo-kinetic information about the reactions of metal complex with the model protein and oligonucleotide.

References

Spectral insights: multi-dimensional approach to evaluate the diagenetic status of skeletal remains for Sr isotope analysis

Anika Retzmanna, Magdalena Blanzb, Johanna Irrgeherc, Andreas Ziteka, Jörg Feldmannb, Thomas Prohaskaa

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b) College of Physical Sciences, Department of Chemistry, Trace Element Speciation Laboratory Aberdeen (TESLA), University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland, UK
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Strontium isotopic analyses by either TIMS or MC ICP-MS of in vivo incorporated environmental signatures (aka ‘biosphere fingerprint’) in human and animal skeletal remains have been widely used in anthropology and archaeology to trace residential changes, mobility or living conditions. Often the in vivo isotopic signature in bone and teeth is distorted by cumulative physical, chemical and biological alteration during burial which leads to exchange and/or addition of strontium from the burial environment (soil, water) – referred to as diagenesis. A well-preserved biogenic Sr signal is crucial for a reliable evaluation of historic migration (paths) using 87Sr/86Sr-analysis. Thus, localizing biogenic areas and the spatial extent of diagenetic alteration is essential.

Herein we present the first results of the comparison between solubility profiling and bioimaging of archaeological bone to assess in vivo 87Sr/86Sr ratios of the biogenic material. Bioimaging was performed to spatially resolve the extent of diagenesis on bone cross-sections by simultaneous mapping diffusion profiles of 87Sr/86Sr ratios and the concentrations of Sr and elements of non biogenic origin (Ba, Pb, U) using laser ablation split stream ICP-QMS and MC ICP-MS (1).

Preliminary results show diffusion gradients of trace elements originating from the repository material along with a change in the Sr isotopic composition which can be related to diagenetic processes. In addition, measurements of the diagenetically altered bones were performed by near infrared hyperspectral imaging (NIR HSI). The preliminary results of the Principle Components Analysis of the HSI pictures already indicates differences correlated with the diagenetic changes identified by the biomapping.
References

Arsenic’s low temperature volatilization pathway and its importance for the biogeochemical cycle of arsenic

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Arsenic is ubiquitous in the environment and of special concern due to its varying toxicity depending on the chemical form and oxidation state the element is present. In the past, the determination of arsenic and its speciation was focused on ground and drinking water, soils, biota and food. Thus far only limited knowledge exists about arsenicals in our atmosphere. Seventy years ago Challenger wrote a comprehensive review about the biological methylation of arsenic by microorganisms. Since then it has been shown that a number of bacteria and fungi in soils are capable of forming four major volatile arsenic containing compounds, namely arsine and its methylated forms. These species are released into our atmosphere, in a process called the low temperature volatilization pathway of arsenic. Volatile arsenicals have a very reactive nature and can be easily oxidized in the atmosphere to their non-volatile species, subsequently found in atmospheric particulate matter.

Difficulties and challenges during sample collection and measurement of these volatile and particle-bound species call for sophisticated analytical methods. It is therefore hardly surprising that studies in the literature so far are often restricted to point sources (e.g. natural gas, landfill sites or hot springs).

We developed and optimized an analytical method for the sampling and determination of arsenic and its species (including total inorganic arsenic, methylarsonate, dimethylarsinate and trimethylarsine oxide) in 14 size-resolved classes of airborne particles with a diameter between 15 nm to 10 µm. An electrical low pressure impactor is used for sample collection combined with the subsequent analysis using liquid chromatographic separation and ICPQQQMS detection for lowest detection limits and interference-free measurements.

The combination of these techniques is now used to study the low temperature volatilization of arsenic by microorganisms and its contribution to the geochemical cycle of arsenic on a bigger scale.
Analytical characterization of macromolecular ice nuclei from birch pollen grains

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Clouds are important entities in the atmosphere as they influence the Earth’s radiation budget due to their ability to throw incoming sunlight back to space. Thus, they have a significant impact on global climate. Further, ice clouds are of central importance as they are able to reflect and scatter sunlight even more than liquid clouds (1). At high altitudes ice clouds can be formed through either homogeneous ice nucleation at temperatures below -38°C (just water molecules are involved) or heterogeneous ice nucleation above -38°C, where foreign aerosol particles catalyze the ice formation.

These particles are called ice nuclei (IN) and can be of biological origin, such as different bacteria, fungi, plankton and pollen of diverse plants. Recently, studies have shown that the concentration of biological IN increase during and after rainfall (2, 3). Pratt et al. investigated ice clouds over Wyoming (U.S.), where they saw that 33 % of all ice-crystal residues, measured by aerosol mass spectrometry, include biological particles (4). These studies and also others support the theory that biological ice nucleation plays an important role within atmospheric processes.

In 2001 and 2002 Diehl et al. discovered that birch pollen act as efficient IN (5, 6). In 2012 our working group showed that IN can be leached from pollen surfaces with water (7). We now present various analytical techniques which we are using for the characterization of the macromolecular IN from birch pollen. Steps to reduce sample complexity for identification of the corresponding macromolecule(s) will be presented. Methods applied are solid phase extraction (SPE), centrifugal filtration, capillary zone electrophoresis, chip-based capillary gel electrophoresis and liquid-chromatography-ESI-mass-spectrometry. Results from SPE experiments indicate that IN have amphiphilic properties. Subsequently, collected fractions were analyzed for ice nucleation activity.

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References

Identification of oxidation products of lubricant and fuel components by combination of gas-phase isotope labelling combined with capillary gas chromatography mass spectrometry (GC-MS)

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Thermo-oxidative stability of fuels and lubricants is of high relevance in technology in general. A novel approach combining tailor-made artificial alteration, gas-phase stable oxygen isotope labelling and mass spectrometry is presented to elaborate detailed knowledge on oxidation processes related to the mentioned materials. In particular, thermo-oxidative stability of oxygen-containing components and their involvement in oxidative degradation mechanisms on the molecular level can be revealed. The usefulness of the approach is demonstrated by the examples of fatty acid methyl esters (FAME, biodiesel) and ester-based base oil.

Artificial alterations of biodiesel model mixtures were performed in a modified rotating and pressurised vessel standardised for lubricant oxidation stability tests (RPVOT). Subsequently, they were analysed by capillary (GC-MS). Comparison of samples from alteration under isotope labelled $^{18}$O\textsubscript{2} atmosphere with those altered under common $^{16}$O\textsubscript{2} atmosphere enables the identification of the site of oxidative cleavage on the target molecules as well as differentiation of the oxygen’s origin in a degradation product – either from fuel components or atmosphere. Main degradation products were identified as hexanoic acid TMS ester, methyl-9-oxodecanoate and 9-methoxy-9-oxononanoic acid TMS (1).

In view of increasing stress of lubricants in engines, compressors, and gears thermo-oxidative stable base oils in combination with appropriate antioxidants (AO) are indispensable. The isotope labelling approach was applied to elaborate oxidation behaviour of esters and the influence of AO. Oxidation of a diester base oil revealed preferential cleavage to alcohols as 2-ethylhexanol or esters such as 2-ethylhexyl formic acid ester or 2-ethylhexyl 2-oxobutyl adipate. Based on these findings a general oxidation mechanism could be proposed. For blends containing AO, a remarkably longer alteration period was observed while producing similar oxidation products as without AO (2).
References

Novel approaches in NIR-spectroscopy

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The most outstanding advantage of near infrared (NIR) spectroscopy is the measuring process of samples itself since measurements operate non-invasive, fast and generally do not need sample preparation. This also justifies its easy handling and its chemical- and time-saving properties. In recent times the progress of the development of handheld/miniaturized NIR-spectrometers raises the attractiveness of using them as laboratory independent analytical systems. Nevertheless, these devices use different technologies than common benchtop spectrometers. This results in smaller accessible spectral regions and lower resolutions. Therefore, miniaturized NIR spectrometers have to be evaluated critically.

Two-dimensional correlation spectroscopy (2D-COS), quantum chemical calculations and determination of the multivariate limit of detection (mLOD) are used as novel approaches for sophisticated evaluation.

In recent studies 2D-COS unveiled qualitative discrepancies between the recorded spectra of miniaturized spectrometers to a benchtop device. Therefore, the rosmarinic acid (RA) content in rosemary leaves (Rosmarini folium) was determined via the establishment of partial least squares regression (PLSR) models. Quantum chemical calculation of the NIR spectrum of the complex phytopharmaceutical relevant molecule RA was performed. The theoretical spectrum showed good agreement with the experimental and therefore could be used for obtaining a better understanding of the main influences in the PLSR models (1). mLOD calculations for the determination of melamine in milk powder uncovered significant disparities between the different spectrometers (2).

Establishing these new approaches enabled the evaluation of the aforementioned applications and furthermore created new insights into the performances of miniaturized NIR spectrometers.
References


Ca$^{2+}$ - sensitive fluorescent indicator dyes for optical sensing

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The ocean chemistry has an extensive direct and indirect effect on organisms and their inhabitants. Ocean acidification directly relates to the production of CaCO$_3$. The acidification is creating an imbalance in the CaCO$_3$-formation, making the dissolution of formed CaCO$_3$ more likely. Hence, the measurement of free Ca$^{2+}$ in the sea is of great interest. Optical sensors provide certain advantages for this purpose (1).

In this contribution, the concept of ion sensing based on fluorescence quenching is presented. The fluorescent indicator dye consists of a BODIPY fluorophore linked to a recognition unit (receptor), leading to a fluoroionophore (FI). As receptor we utilized a chelating agent which is highly selective for binding Ca$^{2+}$ over other competing ions such as Mg$^{2+}$ or Na$^+$. The sensing mechanism is based on intramolecular quenching due to photo-induced electron transfer (PET). A tertiary amine on the receptor is responsible for emission enhancement in the presence of ions, due to the reduction in the PET effect (2).

The synthesis of the receptors for Ca$^{2+}$-ions and the modification of BODIPY will be shown. The new indicators were characterized in respect to their photophysical properties and their suitability as sensor materials by performing calibrations of the fluoroionophores in solution and after immobilization into polymer matrices. The latter yield a solid state sensing material, with which continuous measurements of seawater Ca$^{2+}$ concentrations are enabled. Different hydrogel polymer matrices were studied and the influence on the PET effect and complexation behaviour was investigated.

References
Determination of micro- and macroelements in cashew (Anacardium occidentale) by inductively coupled plasma atomic emission spectroscopy

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Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for the quantitative determination of essential and toxic elements in cashew. The seeds of cashew tree, rich in oil and distinctively flavoured, are used in South and Southeast Asian cuisine. In Western countries they are eaten mainly as a premium-quality protein-rich snack food. In a 100-gram serving, raw cashews provide 553 calories and they are rich sources of fats, protein, dietary fiber and dietary minerals (Cu, Mn, Mg, P) (2). Several studies have shown that cashew nuts consumption reduced cardiovascular risk and have big potential use for the prevention and treatment of coronary heart disease (1).

Whereas the organic compounds are well studied, there are only rare data on the mineral composition of the cashew. The ICP-AES method was used for the determination of selected elements. To determine the total amount of nutrients, the commercially available cashew were dried, homogenised and digested in a closed microwave assisted digestion system using nitric acid and hydrogen peroxide. The nutrients Ca, K, Na and Mg are present in the cashew (dried matter) at mg/g level, whereas the other elements are present in µg/g level. Thus cashew nuts are a good dietary source of essential metals in addition to the organic compound contained.

References

Exploring the arsenic speciation in mushrooms

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Fungi are important and indispensable parts of our environment. They have some quite unique characteristics, like the ability to accumulate unusually high amounts of various (trace) elements. Concerning arsenic, up to 2000 mg As/kg dry mass have already been reported (1). Furthermore, the arsenic speciation in mushrooms can be very different from other organisms of the terrestrial environment. In fact, many arsenic compounds that are otherwise typically present in marine samples have also been found in mushrooms, for example arsenobetaine or arsengocholine (1,2).

Although there is a huge variety of different mushrooms in our environment, only very few of them have been investigated concerning their arsenic species. Most of the work has been carried out in the 1990s, where instrumental limitations made the detection of trace levels of arsenic species very challenging, or even almost impossible.

In the present study around 100 different species of macrofungi were collected and investigated for their arsenic concentration and speciation with inductively coupled plasma mass spectrometry (ICPMS) and HPLC coupled to ICPMS. The total arsenic concentrations were sometimes extremely high, with up to several thousand mg/kg dry mass. The results on the arsenic speciation were even more interesting. Apparently, the variety of arsenic compounds that can be present in mushrooms is much bigger than it has been thought until now. Also the proportions of the arsenic species to each other can vary a lot between different fungi. Our findings will play an important role for understanding the geo-biochemical pathway of arsenic in our environment, but they also clearly show that a lot of work still has to be done in this context.

References

Identification and activity testing of volatile organic compounds (VOCs) found in different grapevine genotypes in response to downy mildew infection

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\textit{Vitis vinifera} is susceptible to several pathogens including \textit{Plasmopara viticola}, the causal agent of downy mildew (1). American grapevine species are resistant or tolerant to \textit{P. viticola} and breeding programs have introduced resistance traits to susceptible cultivars. Although grapevine resistance mechanisms against downy mildew have been widely characterized in resistant genotypes (1), the possible contribution of volatile organic compounds (VOCs) was not yet investigated. The aim of this work was the characterization of VOCs produced by resistant and susceptible grapevine genotypes in response to \textit{P. viticola} inoculation, in order to identify VOCs associated to grapevine resistance against downy mildew. The susceptible \textit{V. vinifera} cultivar Pinot noir, and the resistant genotypes Kober 5BB, SO4, BC4 and Solaris were grown under greenhouse conditions and they were subsequently inoculated with \textit{P. viticola}. Leaves were harvested immediately before (T0) and six days (T1) after inoculation, and the lower disease severity in resistant genotypes as compared with Pinot noir was confirmed. A headspace-solid-phase microextraction-gas chromatography-mass spectrometry (HS-SPME/GC-MS) approach was used to analyze VOCs from the five studied genotypes. GC-MS chromatograms showed specific VOC emission profiles of the four resistant genotypes as compared with Pinot noir at T1. VOCs specifically found in resistant genotypes were selected, and pure compounds were tested against \textit{P. viticola} sporangia by leaf disk assays. Particularly, four sesquiterpenes, one C5 aldehyde, one terpenoid, one alcohol and one heterocyclic compound were tested in liquid suspension with \textit{P. viticola} sporangia and significantly reduced downy mildew symptoms on Pinot noir leaf disks. Moreover, four of these VOCs were tested in air volume and displayed significant reduction of downy mildew symptoms demonstrating that VOCs could play an important role in the resistance against downy mildew by direct toxicity against \textit{P. viticola} sporangia.

References

Development, validation and application of an LC-ESI-MS/MS multi-analyte method for the quantification of *Alternaria* toxins in Austrian food commodities

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*Alternaria* toxins are secondary metabolites produced by black molds belonging to the fungal genus *Alternaria*. Both, pre- and post-harvest infestation of cereals, tomatoes and other fruits by these worldwide occurring plant pathogens can result in considerable economic losses due to crop spoilage. Additionally, food and feed products can be contaminated with *Alternaria* toxins, of which several compounds proved acute toxic, genotoxic, mutagenic and estrogenic effects \(1\). However, no maximum permitted levels for *Alternaria* toxins have been established to date. In order to evaluate, whether such regulatory guidelines would be necessary, further data on occurrence patterns and the toxicological potential of *Alternaria* toxins are required.

In this study, a new liquid chromatography tandem mass spectrometric method was developed to allow the simultaneous quantification of 17 *Alternaria* toxins in the following food matrices: wheat flour (Type 480), tomato sauce and sunflower seed oil. Analytes included are the most relevant parent toxins (derivatives of tetramic acids, dibenzopyrenes, perylene quinones and others), as well as some selected phase II metabolites of alternariol and its monomethyl ether (sulfates and glucosides).

Chromatographic separation was realized on a reversed phase HPLC column (C18, 2.7 µm) using a binary gradient elution. The mass spectrometer was operated in negative ionization and selected reaction monitoring (SRM) mode, including 2 parent to fragment ion transitions per analyte with optimized ion source and fragmentation parameters. The method validation was based on the artificial fortification of blank matrices, due to the lack of certified reference materials.

A survey on food products purchased from Austrian supermarkets was conducted to prove the method’s applicability and give first insights about *Alternaria* toxin contaminations.
patterns, comparing commodities of different commercial brands, product price ranges and agricultural production types (conventional and organic production).

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Mineral oil hydrocarbons (MOH) in food - an analytical challenge

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The analysis of mineral oil hydrocarbons contamination in food is an emerging issue in the last years. There are several sources for possible contamination throughout the whole production chain from raw material to the packed good.

The analysis of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) is a big challenge due to its really complex composition of unresolved and unidentified substances. Recently a proposed method uses a combination of LC directly coupled to a GC-FID system for the determination of the total amount of MOSH and MOAH. The advantage of the FID is the “identical” response to all classes of hydrocarbons, but it lacks on specific information (1). Even mass spectral detection deals with the problem of severe spectral and chromatographic interferences. Improved information can be generated by additional dimensions in separation by using multidimensional approaches of the preseparated fractions (two dimensional comprehensive GC×GC-MS and/or MDGC) (2).

Aim of this work is the development and application of new analytical approaches for the determination and further characterisation of MOH. In addition sources of mineral oil contamination in packed food and the influence of different materials used as functional barriers (examples given in (3)) will be investigated.

References

Characterisation of aroma compounds in wines from fungus resistant grape varieties

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Fungus resistant grape varieties (FRGs) are a cross of middle European \textit{vitis vinifera} varieties and American or Asian species. They are immune to some of the most common fungal diseases like mildew and grey rot. This immunity reduces the amount of plant protection agents needed for the cultivation. Even though FRGs have been available for a long time their cultivation is not very common. This is mainly a result of the consumers' preference for well-known and established varieties and certain sensory qualities of the FRGs wines.

The Department of Fruit Growing and Enology has a monitor programme for the suitability of some FRG varieties for the Styrian wine growing region. Different cultivars are fermented by single yeast strains in micro vinification for comparable results. Grape juices and wines were analysed for their aroma compounds by headspace based sample preparation techniques (SPME, Arrows) coupled to one and two dimensional gas chromatography with mass selective detection systems and GC-Olfactometry respectively. The main aim of this research is a basic characterization of the relevant varietal compounds of the selected varieties.

The results are compared with sensory trials from a trained expert panel. The results should be used to support local wine growers to select the varieties which are able to produce wines with the highest consumer acceptance.

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