Applied Analytical Chemistry (AAC)

Annual Report 2017

AAC
applied analytical chemistry

Applied Analytical Chemistry

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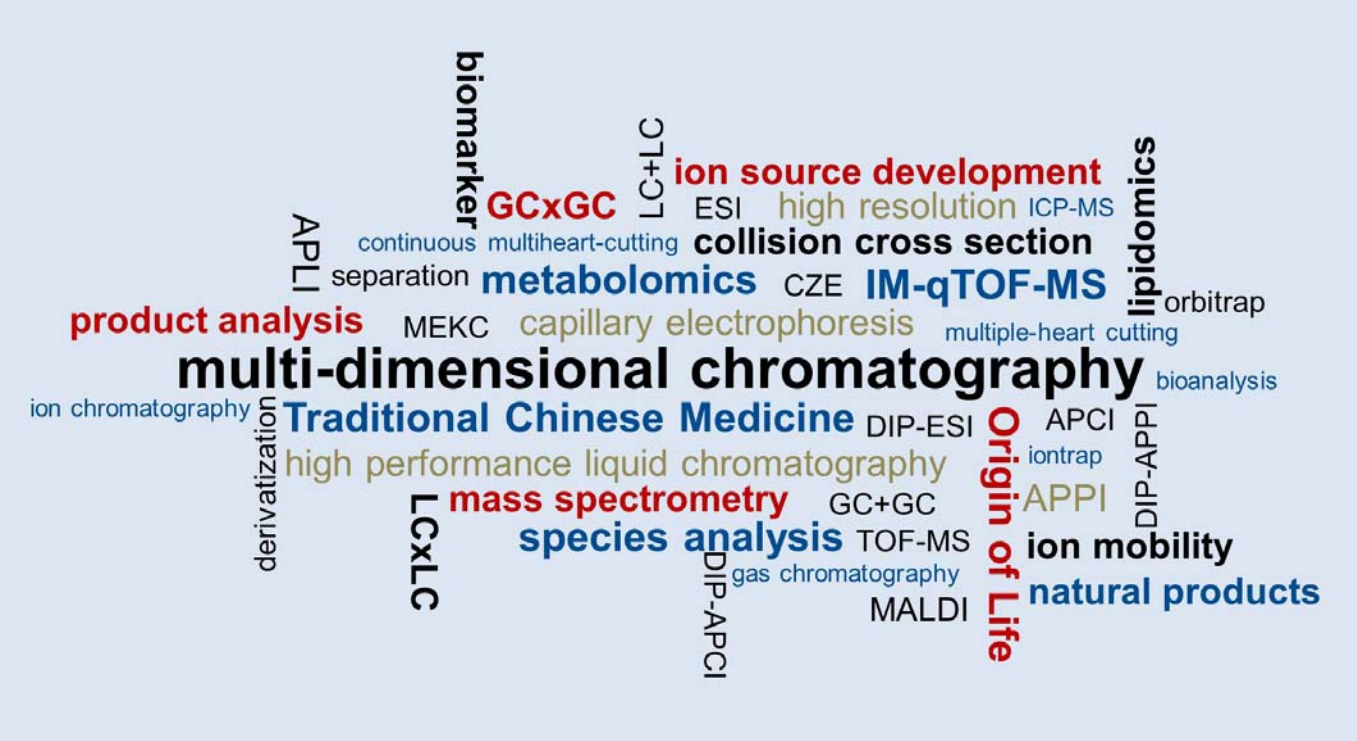

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Content

Applied Analytical Chemistry

The Applied Analytical Chemistry (AAC) is part of the Faculty of Chemistry at the University of Duisburg-Essen. The AAC exists since September 2012 with the main focus on the development of novel ion-sources for mass spectrometry, the non-target analysis of complex samples (e.g. metabolome) by multi-dimensional separation techniques in combination with ion mobility and high-resolution mass spectrometry and the metal(oid) species analysis by ICP-MS in combination with gas chromatography (GC), liquid chromatography (LC) or laser ablation.

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2017 was the fifth year of the Applied Analytical Chemistry research group at the University of Duisburg-Essen and a very successful one. Nine scientific papers in peer-reviewed journals, 13 posters at national and international conferences (two poster awards), several successful grants, strong industrial cooperations and all finished PhD students in job.

Many colleagues have contributed to an exciting year of research, teaching and last but not least to shouldering many other tasks.

This time I would like to thank especially Dr. Sven Meckelmann and Dr. Florian Uteschil, who were indispensable in organizing the research group and to manage all smaller and bigger problems in the labs.

During 2017 several new projects are started, e.g. development of a new GC-APCI ion source, LCxLC-MS for petrochemical products, µLC+LC-IM-qTOF-MS for Lipidomics and Proteomics, characterization of the metabolom of Pseudomonas aeruginosa etc.

In addition, many cooperations with colleagues from universities, hospitals and national and international industries were continued or started. Another very important event was the 7th Spring School "Industrial Analytical Chemistry", which took place at the University of Essen this year and was organized by the Section for Analytical Chemistry of the GDCh, Dr. Michael Arlt (Merck KGaA) and both analytical working groups at UDE (IAC, Prof. Dr. Torsten Schmidt´s group, and AAC, Prof. Dr. Oliver J. Schmitz´s group).

Nevertheless, in 2017 my group has, for the second time, organized the PhD seminar of the Working Group Separation Science of the Section for Analytical Chemistry of the GDCh in Hohenroda. Many thanks to Claudia Kowalczyk and Lin Gan for organizing this very successful and inspiring conference with more as 150 participants and 27 lectures.

As mentioned last year, it is also a pleasure and honour that the Permanent Scientific Committee of HPLC has commissioned us, Prof. Dr. Michael Lämmerhofer (University of Tübingen, Germany) and me, with the organization of the 51st International Symposium on High Performance Liquid Phase Separations and Related Techniques (HPLC 2021), which will be held from June 20 to 24, 2021 in Düsseldorf, Germany. It will be the fourth time that the HPLC symposium series will come to Germany, after Baden-Baden in 1983, Hamburg in 1993, and Dresden in 2009. This year we have launched the homepage (www.hplc2021.com) and started with advertising to make HPLC 2021 successful. Mark your calendar! We look forward to your participation.

I want to take this opportunity to thank all co-workers for their excellent work in 2017 as well as the many collaborators in and outside the University of Duisburg-Essen for pleasant and efficient collaborations.

In case you see possibilities for future collaborations, I would be happy to discuss them with you.

I wish you all the best, good health, happiness, and success for the year 2018.

Essen, December 8, 2017

Applied Analytical Chemistry – Staff

Regular Staff

Prof. Dr. Oliver J. Schmitz	Head
Dr. Martin Sulkowski	Senior Researcher
Dr. Sven Meckelmann	Senior Researcher
Maria Madani	Technician / Lab Assistant
Birgit Wöstefeld	Secretary

Post-Docs

Dr. Florian Uteschil

Ph.D. Students

University Duisburg-Essen	External
Ahmad Abu awwad	Susanne Brüggen
Dominik Brecht	Annika Doell
Amela Bronja	Wiebke Mehwald
Maxim Diel	Niklas Danne-Rasche
Lin Gan	Dinh Lien Chi Nguyen
Simeon Horst	Bing Peng
Julia Klein	Ruzanna Mnatsakanyan
Timo Köhler	
Claudia Kowalczyk	
Claudia Lenzen	
Junjie Li	
Christian Lipok	
Kristina Rentmeister	
Alexandra von Trotha	

M.Sc. Students

Dominik Brecht, Richel D Costa, Timo Köhler, Lukas Benedikt Maskow (external), Martin Meyer, Pratima Shrestha, Kristina Rentmeister, Harley Simpson

B.Sc. Students

Guest Scientists

Prof. Abdalla A. Elbashir (Karthoum University, Sudan)

Apprentices

Julia Banken, Miriam Brosch, Gina Paulus

Major News 2017

7th Spring School "Industrial Analytical Chemistry"

The 7th Spring School of Industrial Analytical Chemistry was organized by Prof. Dr. Oliver J. Schmitz and Prof. Dr. Torsten C. Schmidt (both from the University of Duisburg-Essen), the Section for Analytical Chemistry of the GDCh and the Industrieforum Analytik, headed by Dr. Michael Arlt (Merck KGaA, from 13 to 24 March 2017 at the University of Duisburg-Essen. The aim of this 10-day block event was to familiarize students with master's degrees in chemistry with analytical methods and questions that are of importance in industrial analysis. Lecturers from the chemical and pharmaceutical industries as well as from the manufacturer industry have discussed industrial-relevant analytical topics from the fields of methodology, process analysis, quality assurance and management as well as social skills and successful applications at industrial companies. The program was rounded off by excursions to analytical departments of Thyssen-Krupp and Evonik AG.

HPLC 2021 in Düsseldorf, Germany

It is a great pleasure to announce that the 51st International Symposium on High Performance Liquid Phase Separations and Related Techniques (HPLC 2021) will be held at June 20-24, 2021 in Düsseldorf, Germany. Prof. Michael Lämmerhofer from the University of Tübingen and Prof. Oliver J. Schmitz from the University of Duisburg-Essen are the chairmen of this conference.

The HPLC symposium series is known as the world leading conference on liquid phase separations and related technologies. Its program covers all aspects of separation sciences in liquid and supercritical fluid phases as well as hyphenation with advanced detection technologies in particular mass spectrometry. The program will span from fundamentals and theory of chromatographic separations and detection principles, over methodological and technological advances including separation materials, column technologies and instruments, to applications in various fields and quality assurance aspects. The symposium will feature workshops and tutorials, plenary and keynote lectures from the leading scientists in the field. Yet, the majority of lectures will be selected from submitted abstracts to make sure that participants can share and discuss their newest results with the audience. Besides, HPLC 2021 will

have a big exhibition and vendor seminars in which attendees can see the latest innovations from the leading vendors in the field.

Mark your calendar! We look forward to your participation.

Hero of the Year 2017

In 2017 Dr. Florian Uteschil was very successful. He finished his PhD thesis with summa cum laude and due to a cooperation with Hitachi High-Tec in Japan, he has been responsible for two research projects.

For these projects, in addition to a great theoretical knowledge and an extraordinary practical skill, intercultural work is also necessary. Florian Uteschil has mastered these tasks with great success.

List of Projects 2017

(Abstracts of these projects within the next pages)

Archean fluid inclusion of hydrothermal quartz minerals – archives of prebiotic chemistry on early earth?
A. Bronja

Peptide-vesicle systems as an early stage of life
A. Bronja

Metabolome studies of *Hedyotis diffusa* and *Scutellaria barbata* by LC-IM-MS
L. Gan, P. Shrestha, L. Morguet

Comparison of CCS values determined with DTIMS and TWIMS
J. Klein

Characterization of the plasma lipidome using LC-IM-qTOF-MS
S. W. Meckelmann, T. Köhler

Development of a LC+LC-IM-qTOF-MS application for Lipidomics
S. W. Meckelmann

Comprehensive Analysis of Cannabis by GCxGC-MS
J. Li, H. Simpson

GC+GC-IM-qTOF-MS
C. Lipok

Development of a new GC-APCI ion source
C. Lipok

Speciation of mercury (II) and methylmercury in sediments by HPLC-ICPMS
C. Kowalczyk, K. Rentmeister, R. D Costa

Study the influence of licorice and pomegranate drinks on nicotine metabolism in human urine by LC-orbitrap-MS
A. Abu-awwad

Coupling of a thermoanalyzer with a quadrupole mass spectrometer
F. Uteschil, D. Brecht

Archean fluid inclusion of hydrothermal quartz minerals – archives of prebiotic chemistry on early earth?

Amela Bronja

The hydrothermal environment like those of geyser systems (Fig.1) may provide an ideal habitat for prebiotic chemistry and the formation of protocells. The composition of fluid inclusions in minerals such as quartz which have grown during the Archean period might provide important information about the first organic molecules formed by hydrothermal processes.

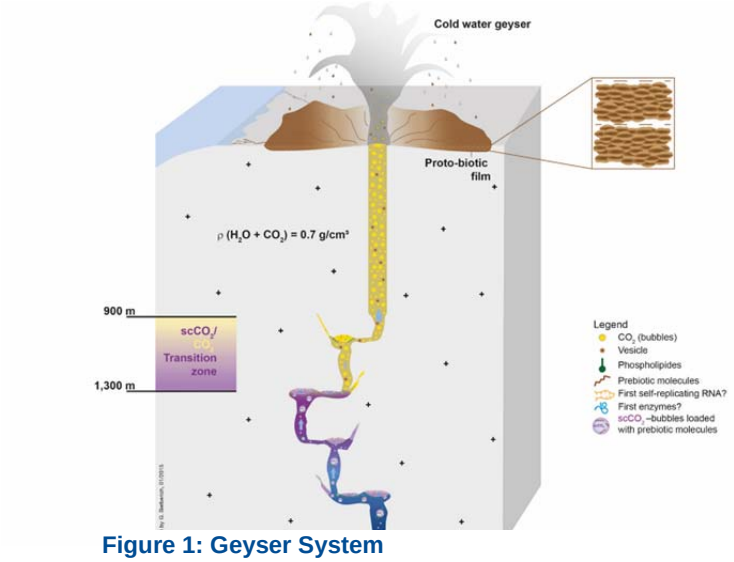

Figure 1: Geyser System

We have analyzed via GCxGC-MS the organic compounds, which were preserved in fluid inclusions of more than 3 billion years old Archean quartz minerals from Western Australia. Many different organic substances (aldehydes, alcohols, halocarbons) (Tab. 1) were found in the fluid inclusions. The findings indicate that chemical components have been conserved in the fluid phase within the earth`s crust from early beginning until the present day. The conclusion might be, that these organic substances, occurring in the hydrothermal environment of tectonic fault zones in the upper continental crust, could have made an important contribution to prebiotic chemistry which eventually has led to the formation of the first living cell.

	Spot Nr	Library NIST/W9N08	Match [%]
Halocarbons	1	2,2-Dichloroethanol	85
	20	1,1,2,3-Tetrachloropropane	89
	5	3-Chloro-1-propanol	93
	3	1,1-Dimethyl-3-chloropropanol	82
	14	3,3-Dichloropropan-1-ol	84
	10	1,3-Dichloro-2-propanone	85
	15	2,2,3-Trichloropropionaldehyde	82
		2,2,3-Trichloropropane-1,1-diol	81
	22	1,2,3-Trichloro-1-propene	90
	19	2,2-Dichlorobutane	63
	21	1,4-Dichlorobutene	71
	6	2,3-Dichloro-1-propanol	75
	11	1,3-Dichloro-2-propanol	77
		Chloro-2-hydroxy-propanoic acid	76
	13	Chloroacetyl chloride	73
	12	Ethane, 1,1,2,2-tetrachloro-	95
Alcohols	4	4-Methyl-2-pentanol	90
	7	3-Methyl-4-penten-1-ol	90
		4-Hexen-1-ol	88
	8	cis-3-Hexen-1-ol	89
		3-Methyl-3-penten-1-ol	88

	Spot Nr	Library NIST/W9N08	Match [%]
Aldehydes	16	3-Methoxybutyraldehyde	81
		2-Methyl-3-pentanol	81
	23	Heptanal*	87
	24	Octanal *	91
	25	Nonanal*	91
	26	Decanal *	92
	27	Undecanal*	91
	28	Dodecanal*	91
	29	Tridecanal *	92
	30	Tetradecanal*	92
	31	Pentadecanal*	93
	32	Hexadecanal*	90
		Pentadecanal	92
	33	Heptadecanal	-
		Hexadecanal	91

*confirmed with standards

Table 1 Substances found in the quartz fluid inclusions with NIST/Wiley database match factor > 70

Collaborative Project – Project Partner: Prof. Ulrich Schreiber (UDE), Prof. Christian Mayer (UDE), Prof. Heinz F. Schöler (Ruprecht Karls University Heidelberg)

Peptide-vesicle systems as an early stage of life

Amela Bronja

There is no doubt that compartmentalization is a key issue in the early evolution of life. In addition, it may have played a role even at a very early stage because many of the presumed steps of molecular evolution can develop much more efficiently in a confined state. Therefore, it is necessary to look at a scenario where, under natural conditions, small cell-like compartments can be formed in large numbers over an extended period of time.

Figure 1: High pressure cell

Tectonic fault systems in the continental crust offer huge networks of interconnected channels and cavities. Filled mainly with water and carbon dioxide (CO_2) and containing a wide variety of hydrothermal chemistry. In these systems, an accumulation zone for organic compounds can develop. Periodic pressure changes caused for example by geyser activity may generate a cyclic process involving a periodic formation and destruction of vesicles, that could offer a perfect environment for molecular evolution in small compartments.

In recent experiments our collaborating partners reproduced these conditions in a high pressure cell (Fig. 1) using lipid vesicles and 11 amino acids. Fig. 2 shows the LC-ESI-qTOF-MS analysis of the aqueous phase of the reaction products in the two phase system H_2O/CO_2 after 160 h. The experiment was performed at 90 °C and a pressure of 100 bar. Fig. 2a shows the EIC (m/z 328.223) of the $[M+H]^+$ adduct of a tripeptide consisting of valine, isleucine/leucine and proline. It was formed in the presence of vesicles. In contrast Fig. 2b shows the EIC of the same mass, using the same experimental setup, just without the presence of vesicles in the cell. In this case no tripeptide was formed, which indicates the special function of the vesicle membrane for the condensation reactions of the amino acids.

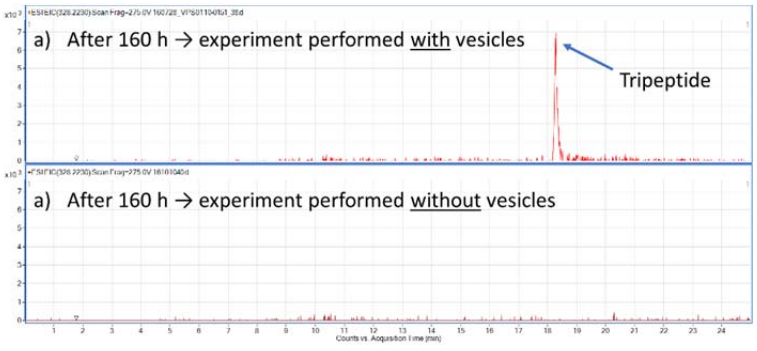

Figure 2: LC-qTOF Analysis of products from high pressure experiment with (a) and without (b) vesicles

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Collaborative Project – Project Partner: Prof. Ulrich Schreiber (UDE), Prof. Christian Mayer (UDE)

Metabolome studies of *Hedyotis diffusa* and *Scutellaria barbata* by LC-IM-MS

Lin Gan, Pratima Shrestha and Lisa Morguet

The medical plants, *Hedyotis diffusa* and *Scutellaria barbata*, are popular herbs used in traditional Chinese medical prescription. Different cooking approaches may lead to mutual assistance, restraint, suppression or antagonism leading to improved medical effect or a reduction of negative side effects for the medical effect. There are two modes employed in this project, one is cooking the two herbs together and the other is cooking them separately and combined later. In each approach, amount of both herbs and used water are equal. It is no doubt that all parameters, for further measurements by LC-IM-MS (1290 HPLC and 6560 IM-Q-TOF, Agilent Technologies) to compare the metabolites of both aqueous, are also exactly same.

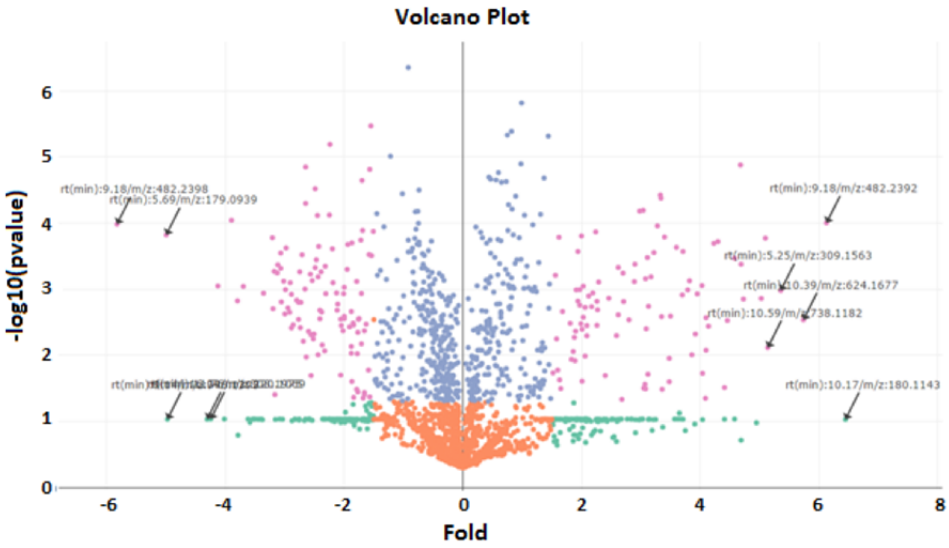


Figure: Differences in a fold change range (green); without significant volume differences (orange); with significant volume differences (blue); with significant volume differences in a fold change range (pink)

The achieved volcano plot depicts the average volume of all detected features for comparing the two different cooking approaches. Several very interesting differences in the two cooking procedures of *Scutellaria barbata* and *Hedyotis diffusa* are observed. At moment we try to identify the compounds, which are only detectable in one of these cooking procedures by MS^n.

Comparison of CCS values determined with DTIMS and TWIMS

Julia Klein

One task of analytical chemistry is to determine as many compounds as possible in very complex samples. Therefore, more complex and powerful analytical methods are required. For this purpose, multidimensional chromatographic techniques (e.g. GCxGC or LCxLC) are coupled to modern high resolution mass spectrometers. The introduction of ion mobility spectrometry (IMS) offers the possibility of a further separation dimension by separating compounds according to their shape-to-charge ratio. Beside this, IMS allows the separation of isobaric compounds according to their different collision cross sections (CCS). The collision cross section describes the effective area for the interaction between an ion and the neutral gas and is a characteristic physicochemical property of an ion. In consequence, the CCS can be used for the identification of substances in complex samples. Therefore, a CCS database containing several hundred compounds was build up in our working group.

As different kind of ion mobility spectrometers are available on the market (e.g. drift time and travelling wave ion mobility spectrometer, DTIMS and TWIMS respectively), a comparison of CCS values determined with different IM techniques is necessary in view of building up an instrument independent CCS database. For this purpose, we determined the CCS of 121 substances of different substance classes with the Agilent *6560 Ion Mobility qTOF-MS* (DTIMS) and compared them to the CCS determined with the Waters *Vion IMS QTof* (TWIMS). As seen in the Figure below, the deviation between both systems is mostly higher than 1%. Considering the tolerance range of ±0.5% for the identification of compounds with the databank the CCS determined with DTIMS and TWIMS are assumed as not comparable. Regarding the inter-day reproducibility of both instruments, the deviation of the Agilent DTIMS system was <1% for most compounds whereas the deviation of the Waters TWIMS system was >1% for most compounds. In conclusion, an instrument independent CCS database for DTIMS and TWIMS systems is not possible, so far.

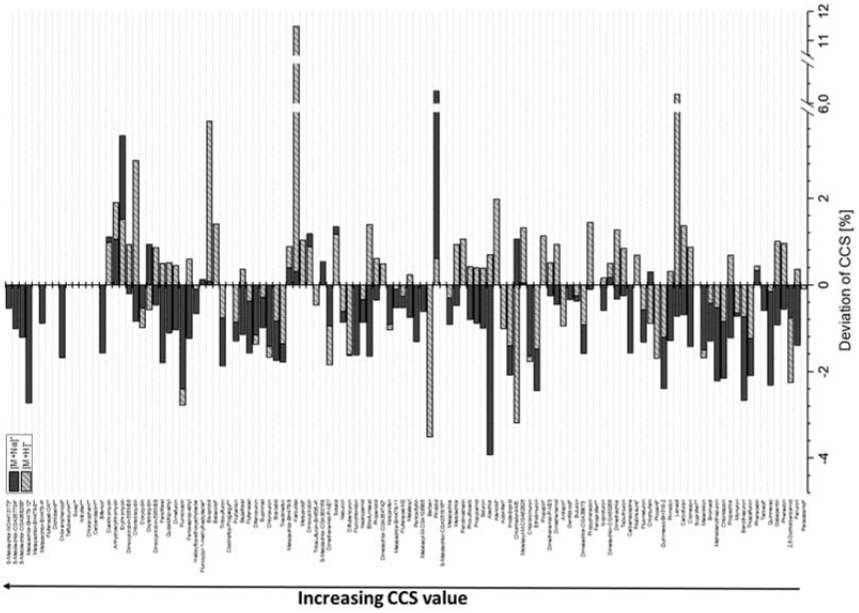


Figure: Deviation of CCS determined with DTIMS (Agilent 6560 Ion Mobility qTOF-MS) and TWIMS (Waters Vion IMS QTof)

Collaborative Project – Project Partner: Prof. Torsten Schmidt (UDE)

Funded by: Agilent Technologies, Santa Clare, USA

Characterization of the plasma lipidome using LC-IM-qTOF-MS

Sven W. Meckelmann and Timo Köhler

Lipids play essential structural roles, control a variety of physiological and pathophysiological events and act as nutrients. To develop a more personalized medicine and to understand import pathophysiological processes it is important to identify and quantify large numbers of lipids simultaneously. To date, it is estimated that over 100,000 lipids exist in nature, however, the biggest database only holds about 40,000 lipids, which are known. To analyse a large number of lipids, we established an analytical method using a long 60 minutes liquid chromatography run, to maximize peak capacity, coupled with the Agilent 6560 IM-qTOF-MS. This methods enables us to perform a three dimensional lipidomics analysis (Figure left) by using LC in the first dimension, ion mobility in the second and high resolution MS in the third dimension.

Especially the separation by ion mobility helps to maximize the analytical coverage by separating coeluting isobaric lipid species (Figure right). Moreover, due to the easy calculation of CCS values this method provide a more accurate identification of lipids in complex mixture. Using this LC-IM-qTOF-MS method, we were able to detect about 3,000 potential lipids in pooled human plasma of which roughly 1,000 could be identified by our in-house m/z and retention time database. In addition, the established three dimensional lipidomics method showed low limits of detection below 100 nM for most lipid classes (~2 pM on column). At the moment, we are building a CCS, retention time and m/z database to accurately identify lipid species in biological samples and are using the method for functional lipidomics in protein-lipid interaction.

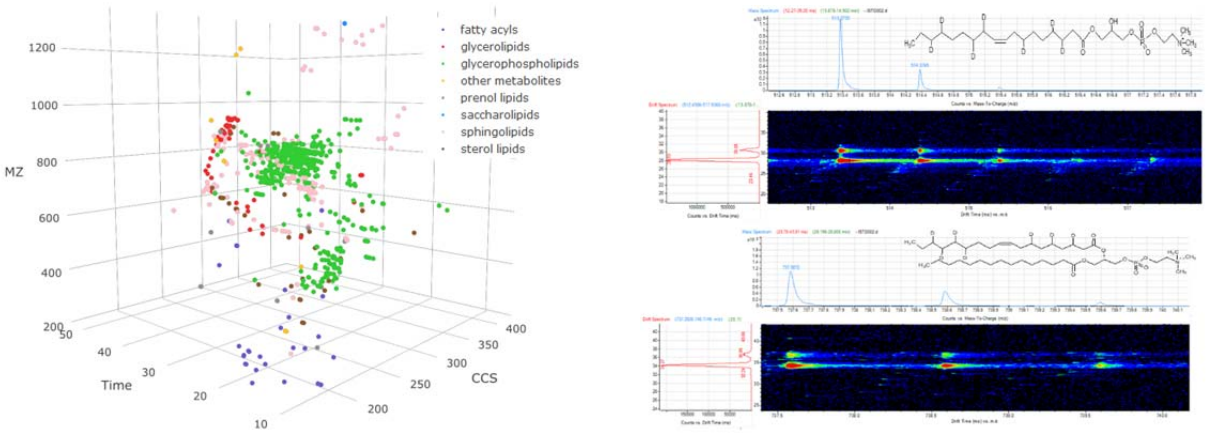


Figure: Left: 3D-Scatter plot of identified lipids from a pooled plasma sample. Lipids are categorized according to their major lipid classes. Right: IMS-qTOF separation of two coeluting LPC isomers and PC isomers

Collaborative Project – Project Partner: Dr. Stephan Buckenmaier, Agilent Technologies

Funded by: Agilent Technologies, Inc. Research Project Grant

Development of a µLC+LC-IM-qTOF-MS application for Lipidomics

Sven W. Meckelmann

Characterizing the lipidome of biological samples is often challenging because of the complexity of the samples. Biological samples such as human plasma can contain hundreds or thousands of different lipids in various concentration, which is leading to a series of problems such as ion suppression or difficulties in the separate detection of isobaric lipids species. One possible approach to solve this problem is to increase the separation power of the analytical platform prior to high resolution mass spectrometric detection. Based on the four dimensional separation and detection system, published 2016 by our group, we started to develop an analytical platform to separate and analyse lipids in four dimensions. First µLC dimension is a micro-zicHilic column (0.3 x 150 mm; 3.5 µm) which is suitable to separate the injected lipid mixture according to their lipid class. Second LC dimension is a Kinetex C18 column (2.1 x 50 mm; 1.7 µm) to separate the lipids according to the length of the carbon chains. Due to the long modulation time of four minutes between the first and second LC dimensions, it is possible to run a "slower" gradient when compared to comprehensive LCxLC. This, however, reduces the separation power of the first dimension but strongly increases the separation power of the second dimension. In addition, peaks are only modulated once or twice, which makes data analysis much easier and simultaneously increases the sensitivity. Finally, lipids are detected using the Agilent 6560 IM-qTOF-MS, which adds ion mobility as a third and high-resolution qTOF-MS as a fourth dimension. As can be seen, even after two LC dimensions there are still lipid species that were separated by ion mobility only. Currently, we are optimizing the method with regard to the separation power of the second dimension and the sensitivity of the method.

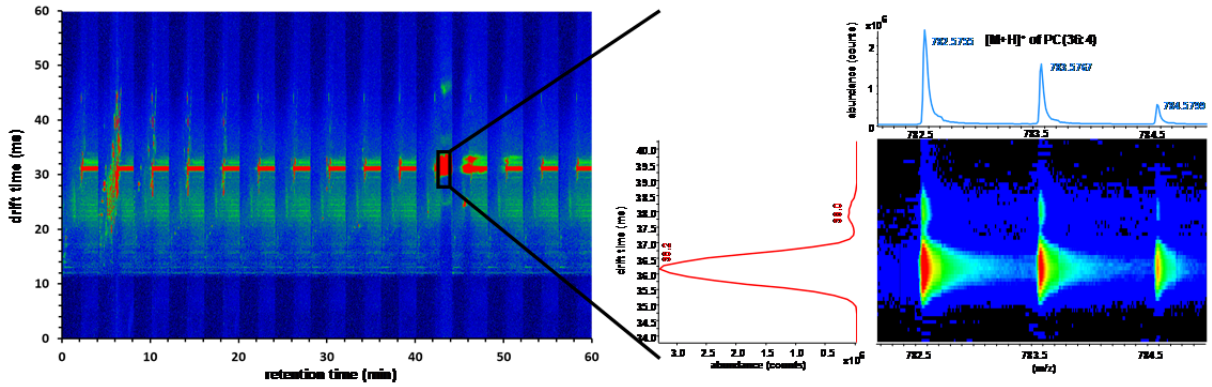


Figure: Left: Heat map of a µLC+LC-IMS-qTOF lipid analysis of a human plasma; Right: extracted drift and mass spectrum for the [M+H]+ ion of phosphatidylcholine 36:4 showing two distinct drift time peaks indicating the separation of two isobaric PC(36:4) species.

Collaborative Project – Project Partner: Dr. Stephan Buckenmaier, Agilent Technologies

Funded by: Agilent Technologies, Inc. Research Project Grant

Comprehensive Analysis of Cannabis by GCxGC-MS

Junjie Li and Hayley Simpson

Cannabis, also popularly known as marijuana, is an herbaceous plant used across different cultures to cure ills and in textile manufacture. Cannabinoids, with their well-known pharmaceutical and psychotic potencies, are the major constituents of cannabis. Their medicinal properties have been linked to treating symptoms of cancer, HIV/AIDS, neurological disorders and autoimmune diseases. Consequently, considerable researches have been done worldwide to characterize and pinpoint the medicinal mechanisms of cannabis. There are numerous publications released outlining several validated methods, developed for the analysis of cannabinoids. Notably, TLC, GC, HPLC, SFC, and CE.

In this study, a comprehensive method, utilizing comprehensive two-dimensional gas chromatography (GCxGC) coupled to MS, has been developed to qualitatively analyze the components of cannabis. The separation was carried out on the column combination of Rxi-5sil MS and Rxi-17sil with 3.8 s modulation time. Liquid-liquid extraction was employed in sample preparation considering that cannabinoids are most abundant in the leaves and flowers of the plant. After the evaporation of extraction solvent, BSTFA, as a derivatization reagent, was added to the samples, which were then silylated in an oven at 70 °C for 15 min.

As a result, over 50 compounds from the cannabis extract were separated and identified, including esters, carboxylic acids and cannabinoid. It provided a general metabolic profile of cannabis and indicated the feasibility of the method to investigate further derivatization reactions with other reagents such as MSTFA and catalysts like pyridine in the future.

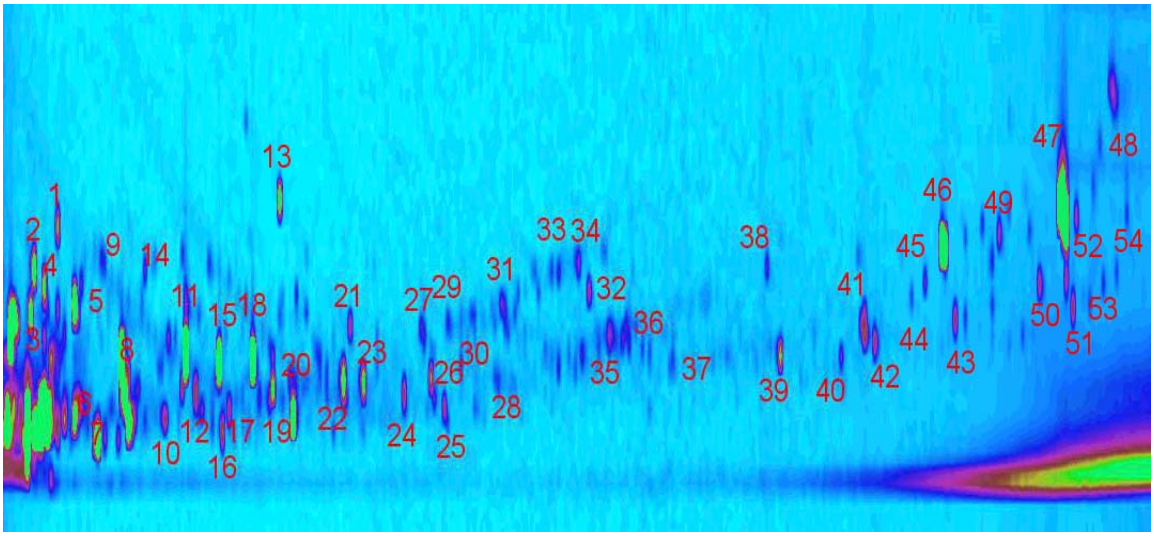


Figure: The 2D contour plot with metabolites from Cannabis separated on GCxGC-MS after derivatization by BSTFA

Funded by: International Restek Academic Support Program

GC+GC-IM-qTOF-MS

Christian Lipok

The analysis of complex samples as the metabolome of plants or humans needs very powerful separation methods to get the highest possible separation of all compounds. For this purpose a four-dimensional separation method based on continuous heart-cutting gas chromatography (GC+GC) coupled with ion mobility (IMS) and a high resolution mass spectrometer (MS) was developed. The GC+GC-IMS method can be used – more or less – as a generic separation method for different samples without any method optimization. The Figure shows the four-dimensional analysis of a real sample, *Calendula officinalis,* and demonstrates the good resolution of this method. For example, spot 32 shows the separation of two compounds with sum formula $C_{11}H_{16}O_3$ resulting in two separated spots in the contour-plot of the Figure. The peak at higher retention time has also a higher retention time in the second dimension. This indicates that the signals are two isobars and not a fraction of the same compound. The heat map (IM-MS separation) of one modulation (37.71 – 38.03 min, yellow rectangle) demonstrates that various compounds with different drift times and m/z values elute from the column. Furthermore, one of the signals (red arrow) in this modulation is separated in the drift tube in two compounds with m/z 257.2476 and 257.2497. The GC+GC-IMS approach shows an outstanding separation power and can be used as a generic method for a wide range of different samples.

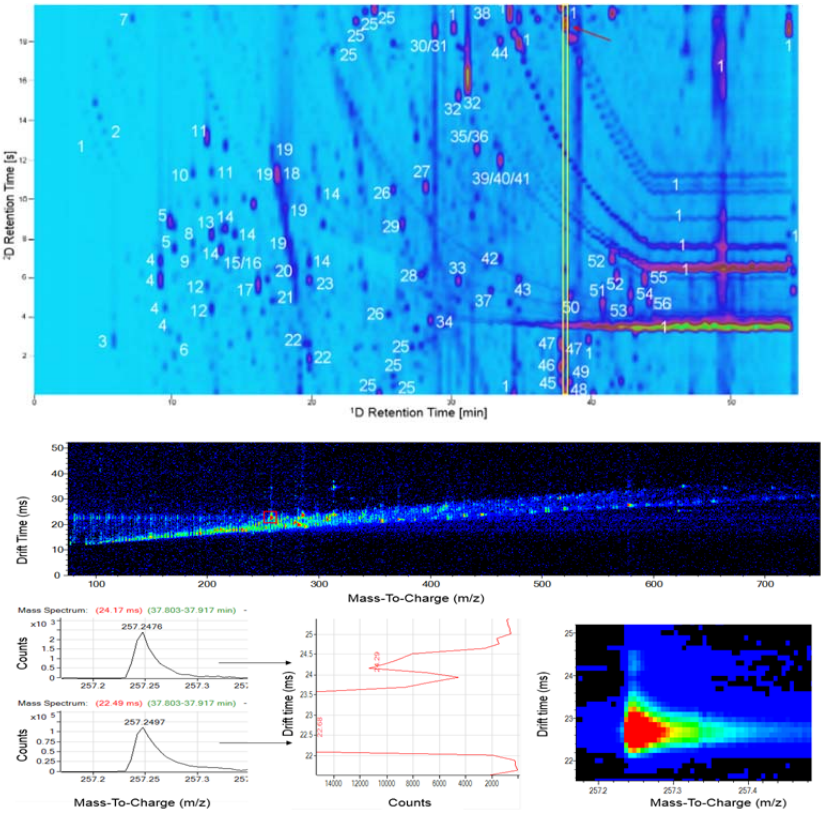


Figure: Analysis of *Calendula officinalis* with GC+GC-IM-qTOF-MS. Top: GC+GC contour-plot, bottom: heat map (IM-MS separation) of one 20-s-fraction (between 37.71 and 38.03 min, yellow rectangle in the contour-plot)

Development of a new GC-APCI ion source

Christian Lipok

Although the coupling of GC/MS with atmospheric pressure ionization (API) has been reported in 1970s, the interest in coupling GC with atmospheric pressure ion source was expanded in the last decade. The demand of a "soft" ion source for preserving highly diagnostic molecular ion is desirable, as compared to the "hard" ionization technique such as electron ionization (EI) in traditional GC/MS, which fragments the molecule in an extensive way. These API sources include atmospheric pressure chemical ionization (APCI), atmospheric pressure photoionization (APPI), atmospheric pressure laser ionization (APLI), electrospray ionization (ESI) and low temperature plasma (LTP).

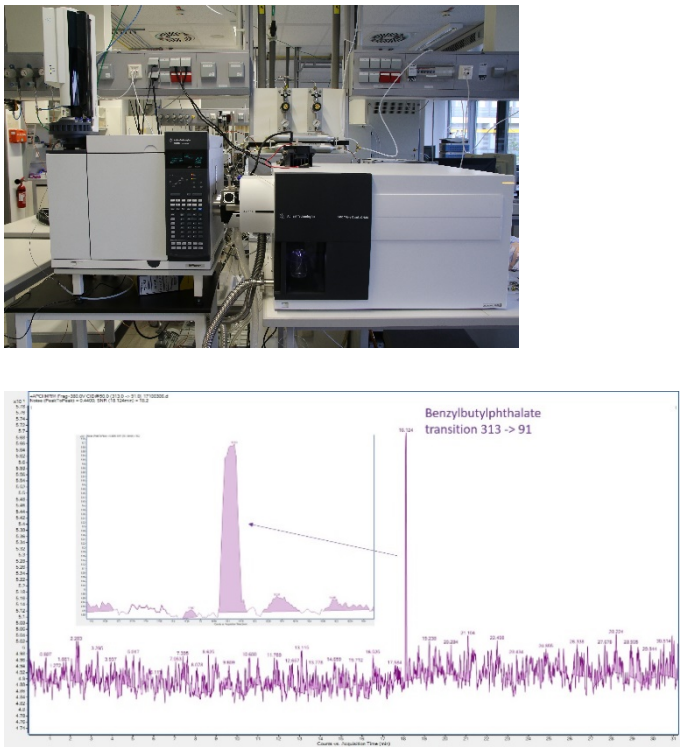


Figure: GC-APCI-Triplequad-MS (left) and 0.1 pg Benzylbutylphthalate (on column) (right)

In this project we combine a GC via an APCI source to an atmospheric pressure triplequad-MS. We want to increase the sensitivity of this hyphenated system by optimization of i) the ion transportation by the dynamic flow and the source geometry and ii) the ionization process by active water and temperature control in the ion source.

Collaborative Project – Project Partner: Dr. Terry Sheehan, Agilent Technologies
Funded by: Agilent Technologies, Santa Clara, USA

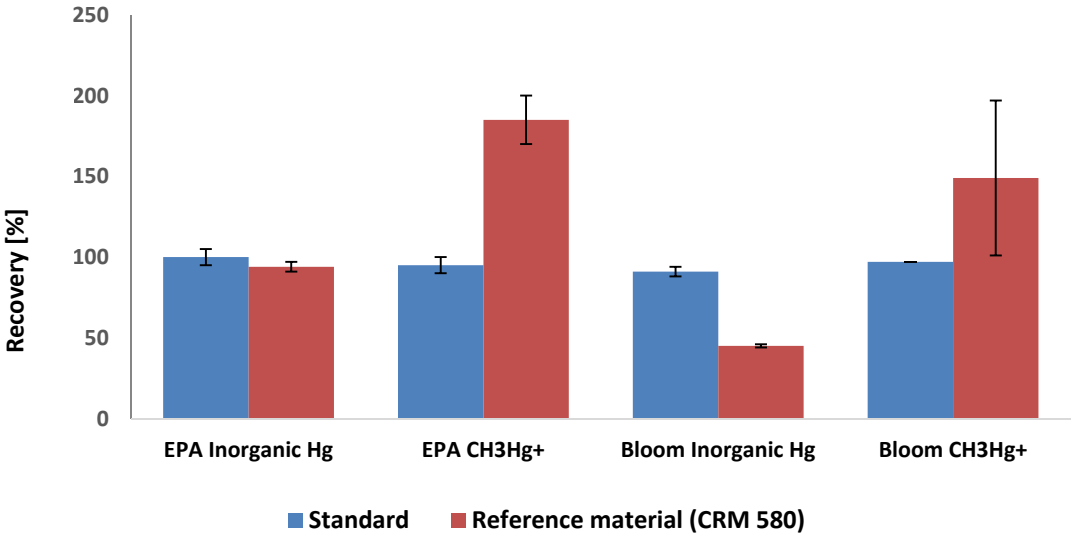
Speciation of mercury (II) and methylmercury in sediments by HPLC-ICPMS

Claudia Kowalczyk, Kristina Rentmeister and Richel D Costa

The speciation of mercury in sediments is still being discussed and continues to pose a great challenge for analytical chemists. This is due to the fact that the concentration of methylmercury in sediments is less than 1% of the total mercury content. Therefore the use of an adequate extraction, separation and detection method is indispensable.

Despite an enormous number of publications in this area, there is no gold-standard about the speciation of mercury in sediments. The literature includes a large number of different extraction procedures, which can be categorized in acid leaching, alkaline extraction and distillation. Due to the occurrence of a low artifact formation and good recovery the acidic extraction is used very frequently in many modifications.

The very low content of methylmercury and the high amount of inorganic mercury in sediments often require a prior separation of the species, since problems with the determination of both species may arise. To realize this separation a thiol-linked modified SPE is frequently used. The recovery rates of various methods for inorganic and organic mercury are shown below. It should be noted, however, that the SPE was used only for the recovery of methylmercury, whereas inorganic mercury was analyzed directly.



Based on the results, it becomes clear that due to the complex matrix of sediments, there are very high fluctuations of the recoveries. This illustrates the difficulties that arise in the analysis of mercury species in sediments, why further investigations are needed for the speciation of mercury in sediments.

Funded by: Federal Institute of Hydrology, Koblenz, Germany

Study the Influence of Licorice and Pomegranate Drinks on Nicotine Metabolism in Human Urine by LC-Orbitrap MS

Ahmad Abu-awwad

Nicotine (Nic)-diet interactions have a particular impact on human health. Some food substances are subject to influence nicotine metabolism rate in terms of hepatic enzymes interactions in smokers consequently. This study intends to investigate the influence of pomegranate and licorice drinks on Nic metabolism, using a new developed and validated method for simultaneous determination of Nic with its major metabolites cotinine (Cot) and nicotine N-oxide (Nox) in human urine by LC ESI-orbitrap-MS. The extracted urine samples by 10% w/v of trichloroacetic acid solution, containing deuterated internal standard, were injected into a Kinetex-C18 column (150 × 2.1 mm, 5 µm) and eluted by mobile phase of methanol:water:formic acid (10:90:0.001, v/v/v). Nic, Cot, Nox and IS were detected accurately by ESI-Orbitrap-MS at positive m/z of 163.1235, 177.1028, 179.11881 and 166.1423, respectively. The validated method according to European and American guidelines for bioanalytical method validation was successfully applied to measure urinary Nic/Cot ratio in a twenty four Jordanian healthy and smoker volunteers, in addition to measure Nic/Nox ratio, as a new introduced metabolic marker in this study. A consistent trend of increased metabolism rate for Nic was observed from urine analysis under pomegranate or licorice drink conditions compared to control conditions.

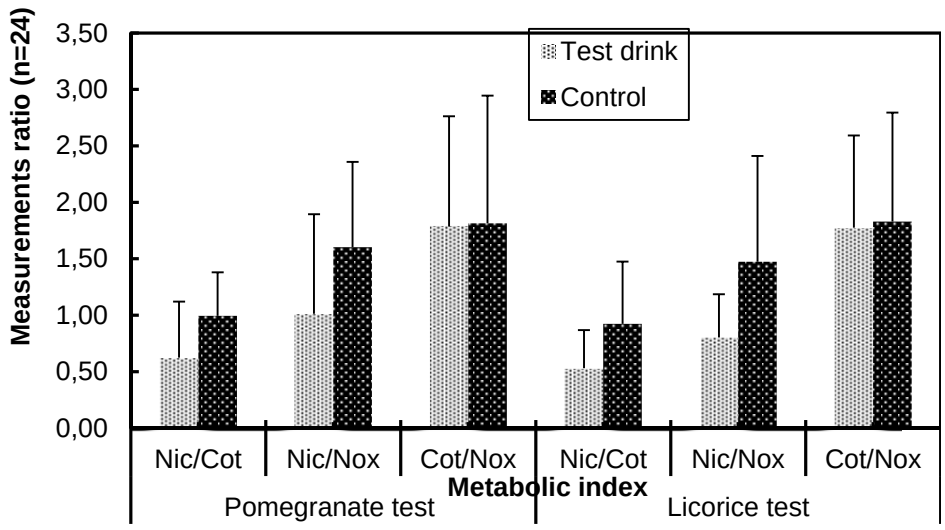


Figure: Metabolic index under pomegranate and licorice drinks with their corresponding control conditions in human urine for 24 volunteers.

Collaborative Project – Project Partner: Prof. Tawfiq Arafat (University of Petra, Amman, Jordan)
Funded by: Phenomenex

Coupling of a thermo analyzer with a quadrupole mass spectrometer

Florian Uteschil and Dominik Brecht

In 2003 the European Union introduced the RoHS (restriction of hazardous substances), that regulates the use of compounds which endanger the environment and hazardous the health in the production of electronic devices. Therefore, the EU issued thresholds especially for the use of plasticizers and brominated flame retardants in polymers. The threshold is 0.1 weight percent of the determined sample. The most common plasticizers, which are utilized to produce polymers, are derivates of the orthophthalic acid. Also, the most used brominated flame retardants are the derivates of the diphenylether or the bisphenol A which has an annual production of 196000 t/a.

For the fast identification of the plasticizers and the brominated flame retardants in polymers a thermo analyzer is coupled to a quadrupole mass spectrometer and atmospheric pressure photoionization (APPI) is applied to the coupling. The evaporated substances of the thermo analyzer are transported through an APPI-interface into a quadrupole mass spectrometer, which allows detection and quantification of the substances by comparison with standards. Although the thermo analyzer is built to analyze solid samples, we developed a method to determine solutions of the plasticizers and brominated flame retardants in hexane and dichloromethane. The figure presents the testing of the reproducibility performed by a six-fold injection of a 1 g/L DBP solution in hexane. The analysis of the peak area results in a relative standard deviation of 3.6%. Therefore, the developed device received with the coupling of the thermo analyzer and the mass spectrometer with APPI-ionization is stable and a promising device for the identification of plasticizers in polymers.

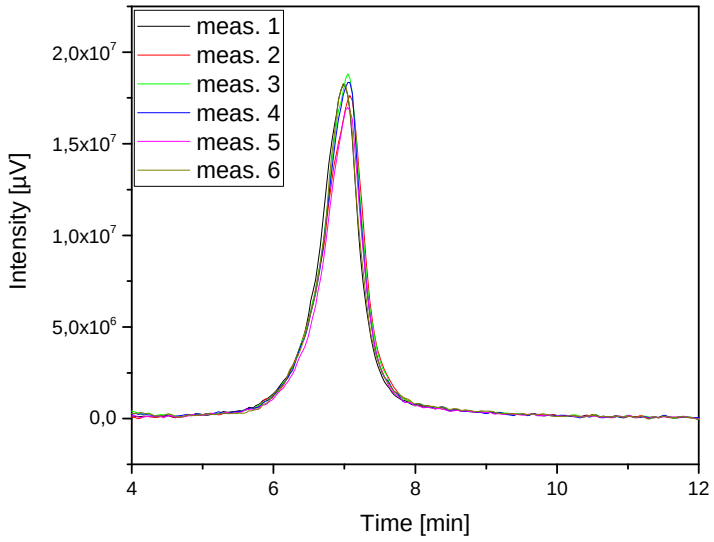


Figure: Testing the reproducibility with a solution of 1 g/L dibutylphthalate (DBP) in hexane, performed by a six-fold injection of the sample.

Funded by: Hitachi High-Technologies Corporation, Tokyo, Japan

Doctoral Theses accomplished 2017

Ahmad Abu-awwad
Determination of nicotine, cotinine and nicotine N-oxide in human blood, plasma, urine, semen and sperm by LC-Orbitrap MS: Application to clinical study

Master Theses accomplished 2017

Dominik Brecht
Coupling of a thermo analyzer with a quadrupole mass spectrometer

Richel D Costa
Evaluation of different extraction procedures for the determination of mercury species in sediments

Timo Köhler
Use of 2D-LC-IM-qTOF-MS in lipidomics and metabolomics

Lukas Benedikt Maskow
Development of a method for the determination of phosphonic acid in various foods with LC-MS/MS

Kristina Rentmeister
Method development for the analysis of organic and inorganic mercury species in sediments by HPLC-ICP-MS

Pratima Shrestha
Non-Target Analysis of Aqueous Extract from *Scutellaria barbata* and *Hedyotis diffusa* used in Traditional Chinese Medicine by LC-IM-QTOF-MS

Bachelor Theses accomplished 2017

Nikolai Adler
LC-IM-q-TOF-MS Analysis of *Hedyotis diffusa* and *Scutellaria barbata*

Yuliya Dietle
Development of an enrichment and measurement strategy for the analysis of organotin compounds by GC-MS (external)

Accepted and/or Published Scientific Publications 2017

Original Paper / Peer-reviewed

S. Horst, O. J. Schmitz **Quantitative analysis of bisphenol A in recycled paper with a novel Direct Inlet Probe – Atmospheric Pressure Photoionization-IonTrap-MS**, Journal of Analysis and Testing 1 (2017) 255-263 (open access)

C. Lipok, J. Hippler, O. J. Schmitz **A four dimensional separation method based on continuous heart-cutting gas chromatography with ion mobility and high resolution mass spectrometry**, Journal of Chromatography A (2017) dx.doi.org/10.1016/j.chroma2017.07.013

A. A. Deeb, S. Stephan, O. J. Schmitz, T. C. Schmidt **Suspect screening of micropollutants and their transformation products in advanced wastewater treatment**, Science of the Total Environment 601-602 (2017) 1247-1253

P. Weyrauch, A. V. Zaytsev, S. Stephan, L. Kocks, O. J. Schmitz, B. T. Golding, R. U. Meckenstock **Conversion of *cis*-2-carboxycyclohexylacetyl-CoA in the downstream pathway of anaerobic naphthalene degradation**, Environmental Microbiology 19 (2017) 2819-2830

U. Schreiber, C. Mayer, O. J. Schmitz, P. Rosendahl, A. Bronja, M. Greule, F. Keppler, I. Mulder, T. Sattler, H. F. Schöler **Organic compounds in fluid inclusions of Archean quartz – archives of prebiotic chemistry on early Earth**, PLoS ONE 12(6): e0177570 (open access)

H. Y. Aboul-Enein, A. A. Elbashir, O. J. Schmitz **Application of capillary electrophoresis with capacitively coupled contactless conductivity detection (CE-C4D): an update**, Biomedical Chromatography (2017) e3945 (DOI 10.1002/bmc.3945)

S. Stephan, J. Hippler, T. Köhler, D. Brecht, O. J. Schmitz **A powerful four-dimensional separation method for complex samples**, Journal of Analysis and Testing DOI 1 (2017) 1-9 (open access)

A. Abu awwad, T. Arafat, O. J. Schmitz **Study the Influence of Licorice and Pomegranate Drinks on Nicotine Metabolism in Human Urine**, Journal of Pharmaceutical and Biomedical Analysis 132 (2017) 60-65

M. M. A. Omar, A. A. Elbashir , O. J. Schmitz **Capillary Electrophoresis Method with UV-detection for Analysis of Free Amino Acids concentrations in Food**, Food Chemistry (2017) 214:300-307

Books / Book Chapters / Misc. Publications

Stavros Kromidas Hrsg. **The HPLC-MS Handbook for Practitioners**, (Chapter 1.1), Wiley-VCH (2017)

Stavros Kromidas Hrsg. **Das HPLC-MS-Buch für Anwender**, (Chapter 1.1), Wiley-VCH (2017)

Poster Presentations

C. Mayer, U. Schreiber, M. J. Dávila, A. Bronja, O. J. Schmitz, **Evolution of Prebiotic Peptides in Amphiphilic Environments**, ISSOL (San Diego, USA) July 2017 **Excellent poster award**

U. Schreiber, C. Mayer, A. Bronja, O. J. Schmitz, **Archean fluid inclusion of hydrothermal quartz minerals – archives of prebiotic chemistry on early Earth?**, ISSOL (San Diego, USA) July 2017

C. Kowalczyj, L. Duester, O. J. Schmitz, **Investigation of an extraction and separation method for the analysis of mercury species in sediments**, HPLC (Prague, Czech Republic) June 2017

J. Klein, P. Shrestna, L. Morguet, O. J. Schmitz, **Analysis of a Chinese herb formulation with HPLC and high resolution IM-qTOF-MS**, HPLC (Prague, Czech Republic) June 2017

A. Doell, M. Hollmann, C. Jahn, O. J. Schmitz, **Development of a sensitive nano LC-MS approach for the in-vivo analysis of antibodies on peptide level**, HPLC (Prague, Czech Republic) June 2017

C. Lipok, J. Hippler, O. J. Schmitz, **GC+GC-APCI-IM-qTOF-MS for the analysis of complex samples**, ANAKON (Tübingen, Germany) April 2017

J. Klein, S. Stephan, J. Hippler, O. J. Schmitz, **Analysis of complex samples with a four-dimensional separation technique using 2D-LC-IM-qTOF-MS**, ANAKON (Tübingen, Germany) April 2017

C. Kowalczyk, O. J. Schmitz, **Influence of the extraction medium on the recovery and HPLC performance: A pre-study for the speciation of mercury(II) and methylmercury in sediments by HPLC-ICPMS**, ANAKON (Tübingen, Germany) April 2017

J. Klein, S. Stephan, J. Hippler, O. J. Schmitz, **Analysis of complex samples with a four-dimensional separation technique using 2D-LC-IM-qTOF-MS**, 5th analytica Vietnam conference (Hanoi, Vietnam) March 2017

C. Kowalczyk, O. J. Schmitz, **Influence of the extraction medium on the recovery and HPLC performance: A pre-study for the speciation of mercury(II) and methylmercury in sediments by HPLC-ICPMS**, 5th analytica Vietnam conference (Hanoi, Vietnam) March 2017

A. Bronja, C. Mayer, U. Schreiber, O. J. Schmitz, **Origin of life in deep-reaching tectonic faults: Analysis of fluid inclusions with GCxGC-MS**, 5th analytica Vietnam conference (Hanoi, Vietnam) March 2017

C. Lipok, O. J. Schmitz, **GC+GC-APCI-IM-qTOF-MS for the analysis of complex samples**, 5th analytica Vietnam conference (Hanoi, Vietnam) March 2017 **1st International Poster Prize sponsored by Agilent Technologies**

S. Meckelmann et al., **Global Plasma Lipidomic Profiling of Genetic Risk Variants for Cardiovascular Disease**, Keystone Symposia: Lipidomics and Bioactive Lipids in Metabolism and Disease (Tahoe City, USA) February 2017

Invited Lectures / Oral Presentations

Prof. Oliver J. Schmitz

Multidimensional Chromatography coupled with Ion Mobility - Mass Spectrometry: Hype or Ripe?
BCEIA, Beijing, China, October 2017

LC+LC- and GC+GC-IM-qTOF-MS as a potential tool in non-target analysis
HPLC, Prague, Czech Republic, June 2017

Novel trends in mass spectrometry
Hitachi, Ibaraki, Japan, May 2017

2D-LC and 2D-GC coupled with IMS-qTOF-MS as a potential tool for the analysis of Traditional Chinese Herbs
International Congress on Analytical Sciences (ICAS), Hainan, China, May 2017

A four-dimensional separation method for the comprehensive analysis of natural products
ANAKON, Tübingen, Germany, April 2017

2D-Chromatography coupled to IM-qTOF-MS for the analysis of complex samples such as medicinal plants
5th analytica conference, Hanoi, Vietnam, March 2017

New and unusual ionization methods for mass spectrometric analysis of nonpolar substances
Merck KGaA, Darmstadt, Germany, March 2017

Dr. Sven Meckelmann

Global Plasma Lipidomic Profiling of the Rare Genetic Risk Variant LDLR (rs6511720) for Cardiovascular Disease
ANAKON 2017, Tübingen, Germany, April 2017

Plasma Lipidomic Profiling of Genetic Risk Variants for Cardiovascular Disease by Means of Liquid Chromatography Coupled with High Resolution Orbitrap Mass Spectrometry
Analytica Vietnam 2017, Hanoi, Vietnam, March 2017 (invited speaker)

Miscellaneous

Conference organization

Prof. Oliver J. Schmitz, Chairman (together with Prof. Dr. Pham Hung Viet, Hanoi University of Science) of the 5th analytica Vietnam conference in Hanoi, Vietnam, March 29-30th 2017

Prof. Oliver J. Schmitz (together with Claudia Kowalczyk and Lin Gan), Organization of the 27th PhD seminar of the Working Group "Separation Science" of the Section for Analytical Chemistry of the GDCh in Hohenroda

Editorial Tasks by Prof. Oliver J. Schmitz

Advisory Board member of Chromatographia

Editorial Board member of Journal of Pharmaceutical Analysis

Associate Editor-in-Chief of Journal of Analysis and Testing

Member of the "Fachbeirat" der analytica Munich

Member of the DAAD selection committee (Foreigners from Asia and Oceania)

Member of the DAAD selection committee (Project-related people exchange with India)

Member of the committee for the Eberhard-Gerstel-Price

Member of the committee for the Ernst-Bayer-Price

Deputy Chairman of the Working Group Separation Science of the Section for Analytical Chemistry of the GDCh

Institute Colloquium

(in cooperation with the research group of Prof. Torsten Schmidt)

Prof. Dr. Alejandro Cifuentes from the National Research Council of Spain visited the Applied Analytical Chemistry (AAC) at University of Duisburg-Essen. He was one of the speakers at the Analytical Chemistry-Colloquium held in cooperation with the research group of Prof. Torsten Schmidt (IAC).

We would also like to thank all our other guests who participated in our colloquium:

Prof. Dr. Alejandro Cifuentes, National Research Council of Spain (CSIC), Madrid, Spain Omics Technologies, Food and Health: Foodomics, 23.01.2017

Dr. Flock, ThyssenKrupp Steel, Analytische Chemie für den Werkstoff Stahl – Dienstleistungen für Entwicklung und Produktion, 24.04.2017

Prof. Dr. Erich Leitner, TU Graz, Geruch und Fehlgruch in Lebensmittel und Bedarfsgegenständen, 15.05.2017

Prof. Dr. Jens Brockmeyer, University of Stuttgart, Germany, What makes an allergen? Characterization of heterogeneity and gastrointestinal metabolism of food allergens using mass spectrometry, 29.05.2017

Prof. Dr. Nils Schebb, University of Wuppertal, Quantifizierung von Eicosanoiden und anderen Oxylipinen in biologischen Proben mittels LC-MS: Analytische Herausforderungen und Lösungsstrategien, 03.07.2017

Dr. Tobias Licha, University of Goettingen, New perspectives arising from the application of organic molecules as indicators in the aquatic environment: How to teach an old dog a new trick, 23.10.2017

Prof. Dr. Michael Rychlik, Technical University of Munich, Quantifizierung und Tracing von bioaktiven Lebensmittelinhaltsstoffen durch stabile Isotope, 20.11.2017

Dr. Axel Boddenberg, Saltigo GmbH, Analytischer Rundum-Service unter den Herausforderungen des Custom Manufacturing, 04.12.2017

Teaching

Chemistry (B.Sc. / M.Sc.)

Lecture Analytical Chemistry I (in German, Prof. Dr. O. J. Schmitz)

Tutorial Analytical Chemistry I (in German, Dr. S. Meckelmann)

Lecture Anaytical Chemistry II (in German, Prof. Dr. O. J. Schmitz)

Tutorial Analytical Chemistry II (in German, Dr. S. Meckelmann)

Water Science (B.Sc. / M.Sc)

Lecture Analytical Chemistry I (in German, Prof. Dr. O. J. Schmitz)

Tutorial Analytical Chemistry I (in German, Dr. S. Meckelmann)

Lecture Anaytical Chemistry II (in German, Prof. Dr. O. J. Schmitz)

Tutorial Analytical Chemistry II (in German, Dr. S. Meckelmann)

Lecture Applied Analytical Chemistry (in English, Prof. Dr. O. J. Schmitz)

Tutorial Applied Analytical Chemistry (in English, Prof. Dr. O. J. Schmitz)

Lecture Environmental Chemistry: Pollutants (in English, Prof. Dr. O. J. Schmitz)

Tutorial Environmental Chemistry: Pollutants (in English, Prof. Dr. O. J. Schmitz)

Exercise Environmental Chemistry: Soil and Waste (in English, Dr. M. Sulkowski)

Environmental Toxicology (M.Sc.)

Lecture Applied Analytical Chemistry (in English, Prof. Dr. O. J. Schmitz)

Tutorial Applied Analytical Chemistry (in English, Prof. Dr. O. J. Schmitz)

Lecture Environmental Chemistry: Pollutants (in English, Prof. Dr. O. J. Schmitz)

Tutorial Environmental Chemistry: Pollutants (in English, Prof. Dr. O. J. Schmitz)

Magisterium

Lecture Environmental Chemistry: Soil (in German, Dr. M. Sulkowski)

Seminar

Analytical-chemical seminar
(in German/English, Prof. Dr. O. J. Schmitz in cooperation with Prof. Dr. T. Schmidt)

Practical courses

Practical course analytical chemistry

Research practical courses

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Faculty of Chemistry
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