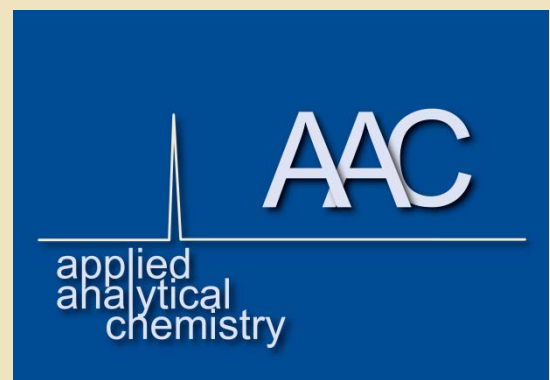


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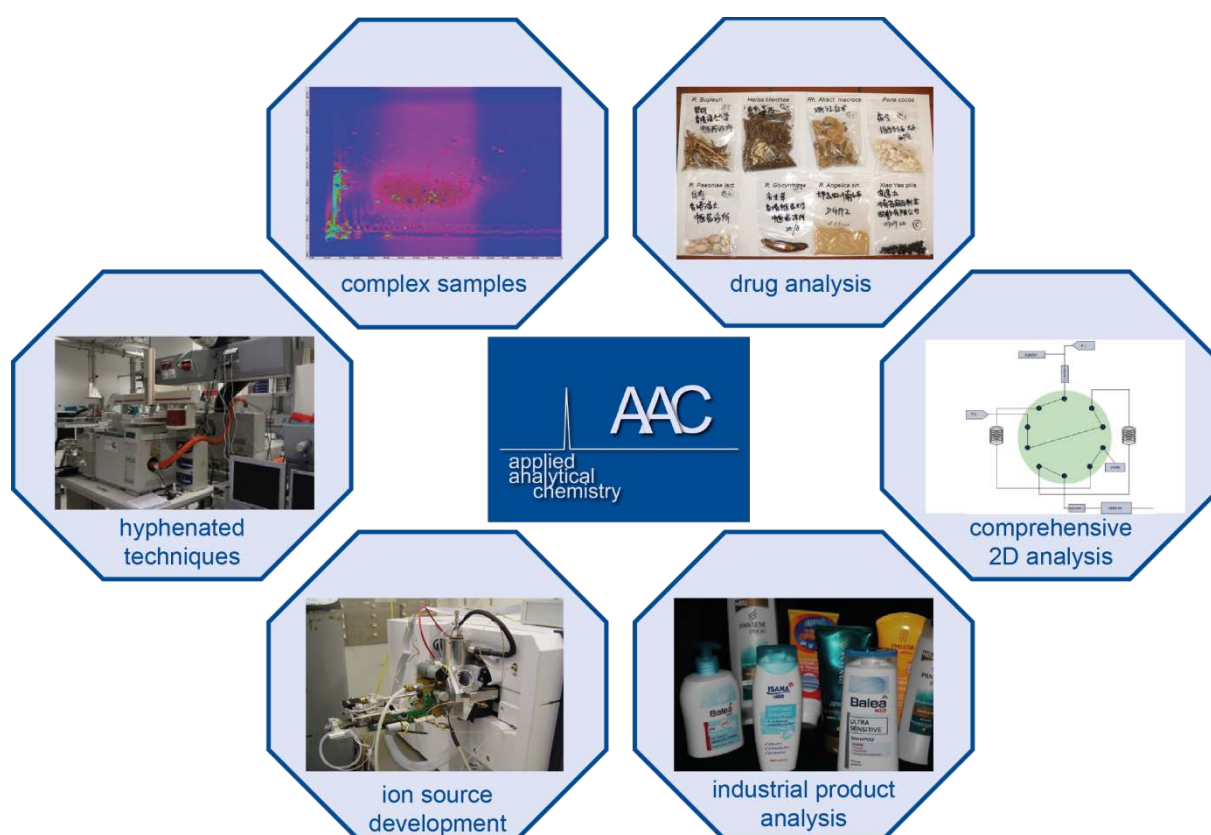
**Applied Analytical Chemistry
(AAC)**

Annual Report 2015



Applied Analytical Chemistry

Annual Report 2015



University of Duisburg-Essen
Faculty of Chemistry
Applied Analytical Chemistry
Universitaetsstr. 5
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Germany

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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.

2015 was the third year of the Applied Analytical Chemistry research group at the University of Duisburg-Essen and up to now the most successful one. Many colleagues have contributed to an exciting year of research, teaching and last not least to shouldering many other tasks.

This time I would like to thank especially Dr. Jörg Hippler, who was indispensable in organizing the research group, to manage all smaller and bigger problems in the labs and to write a successful proposal.

During 2015 several new projects are approved, e.g. one project founded by the AIF (Federation of Industrial Research Associations) regarding the development of an atmospheric pressure photoionization ion source to an ion mobility spectrometer, or an IGF-ZIM project to compare the separation power of various 1D- and 2D-LC systems in combination with MS and IM-MS. In addition, several cooperations with Phenomenex, Shimadzu and SIM were continued to further increase industrial related research. Especially the cooperation with Agilent Technologies was further expanded.

For the first time, Prof. Georg Schwedt, Prof. Torsten Schmidt and me have together written the third edition of the successful textbook "Analytische Chemie", which will be published in 2016.

I want to take this opportunity to thank all co-workers for their excellent work in 2015 as well as the many collaborators in and outside the University of Duisburg-Essen for pleasant and efficient collaborations.



Prof. Dr. Oliver J. Schmitz
(Head of the research Group)

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

I wish you an interesting reading of this annual report and all the best in health and happiness for the year 2016.

Two handwritten signatures in black ink, one on the left and one on the right, both appearing to be cursive and somewhat stylized.

Essen, December 21, 2015

Applied Analytical Chemistry – Staff**Regular Staff**

Prof. Dr. Oliver J. Schmitz	Head
Dr. M. Sulkowski	Senior Researcher
Dr. J. Hippler	Senior Researcher
M. Madani	Technician / Lab Assistant
B. Wöstefeld	Secretary

Ph.D. Students

University Duisburg-Essen

Ahmad Abu awwad

Amela Bronja

Maxim Diel

Lin Gan

Simeon Horst

Claudia Kowalczyk

Junjie Li

Susanne Stephan

Mei Omar

Claudia Lenzen

Pia Rosendahl

University Wuppertal

Alexandra von Trotha

External

Susanne Brüggem

Niklas Danne-Rasche

Dinh Lien Chi Nguyen

Bing Peng

M.Sc. Students

Ti Hau Bui, Patricia Julia Kahl, Ineet Kaur, Andreas Mohren

B.Sc. Students

Dominik Brecht, Timo Köhler, Martin Meyer, Kristina Rentmeister

Guest Scientists

Prof. Abdalla A. Elbashir (Karthoum University, Sudan), Prof. Dr. A. V. Hirner (Prof. em.), Dr. Adela Jing Li (Hong Kong Baptist University, China), Jessica Pandohee (RMIT University, Melbourne, Australia)

Major News 2015

Sino-German Symposium in Essen

Between June, 17th and 20th the 9th Sino-German-Symposium of Chinese and German analytical chemists since 1981 was held at the University of Duisburg-Essen in Germany.

In these days we have heard 34 lectures (each 20 min) and used also one day for a visiting tour to Shimadzu Europe in Duisburg and the City of Düsseldorf. After all lectures we organized a speed dating, where always two professors – one from China and one from Germany – could discuss further bilateral cooperation.



Medicine Price in 2015



For the development of a diagnostic method for the determination of faulty breast implants from blood by GC-MS, Pia Rosendahl (PhD student in our group) received, together with Dr. Cornelia Jonkmanns-Nowacki (Institute of Diagnostic and Interventional Radiology and Neuroradiology, University Hospital Essen), Dr. Peter Rusch (working group of Prof. Rainer Kimmig, Obstetrics and Gynecology, University Hospital Essen) and Dr. Oliver Hoffmann (Obstetrics and Gynecology, University Hospital Essen) the Medicine prize 2015 in the category of research.

This prize was endowed with EUR 20,000 and awarded by the Foundation University Medical Center Essen.

Hero of the Year 2015



In 2015 Dr. Jörg Hippler was very successful. He submitted one paper about a new two-dimensional chromatography method in combination with ion mobility and high-resolution mass spectrometry, another one about biomarker analysis of blood from women with defect breast implants (both still in review process).

He also submitted a successful proposal about Hg species analysis in sediments and water and developed a CCS data base, which allows to identify substances in a non-targeted approach with IM-MS. In addition he repaired and installed many of our systems in the labs.

List of Projects 2015

(Abstracts of these projects within the next pages)

Ultra fast 2nd dimension in LCxLC

Lin Gan

Arsenic Speciation by Anodic Stripping Voltammetry (ASV) and its application on (Indian) water samples compared to other speciation techniques

J. Hippler, Martin Meyer

Quality control of Chinese herbal medicine with chemical marker analysis by GCxGC-MS

A. von Trotha

Analysis of urine, blood and other excrets from a person who was poisoned by unknown Hg-haloaromatics

Ineet Kaur

Development of a LC+LC-System for coupling to an IM-qTOF-MS

S. Stephan, J. Hippler

Cyclic volatile methylsiloxanes in human blood as markers for ruptured silicone gel-filled breast implants

P. Rosendahl

Development of a DIP-APPI-MS and the analysis of various coffee samples

S. Horst

Development of a DIP-ESI-MS and analysis of Piracetam and its impurities

C. Lenzen

GC-APPI-Orbitrap-mass spectrometer ion source

A. Bronja

Origin of Life – Analysis of reactions in a scCO₂/Water phase at higher temperature

S. Stephan

LDI-MS with Gold Nanoparticles

Ti Hau Bui, D. Li

Investigations to GC+GC

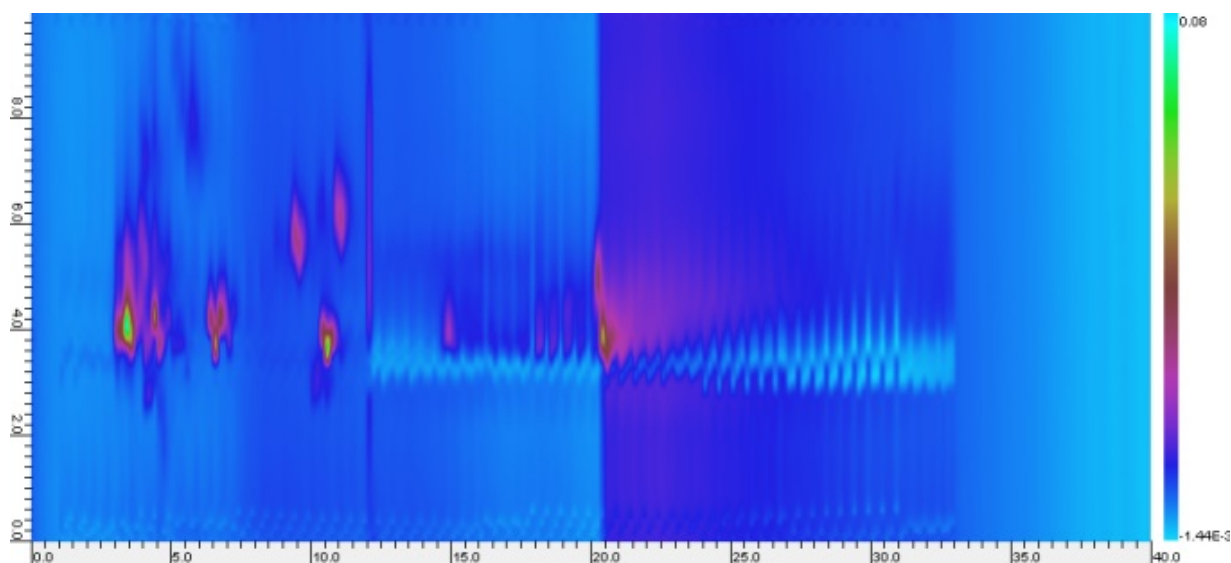
Junjie Li

Ultra fast 2nd dimension in LCxLC

Lin Gan

Multidimensional chromatography has been treated as a robust technique for complex sample analysis, because of its outstanding resolving power. Comprehensive two-dimensional liquid chromatography (LCxLC) is a novel approach with 25 years research history based on the coupling of two more or less independent separation mechanisms with orthogonal selectivities. One of the greatest impediment for the widespread use of LCxLC is the long analysis time of often more than 1 h. Large numbers of improvements for decreasing the elution period in HPLC appeared in the past years, including small particles, core-shell phases, monolithic columns, higher pressure and higher temperature operation.

The great advantage of LCxLC is the increased peak capacity, which enables the analysis of complex samples. In this project, aqueous extraction of *Hedyotis diffusa* is used as a complex sample. The combination of a PFP column (Kinetex, 2.6 μ , 30x3 mm) coupled with a specially designed C18 one (Nucleodur, 5 μ , 10x4.6 mm) from Macherey-Nagel is used with a 10 s modulation (Fig. 1).



LCxLC-DAD analysis of *Hedyotis diffusa*

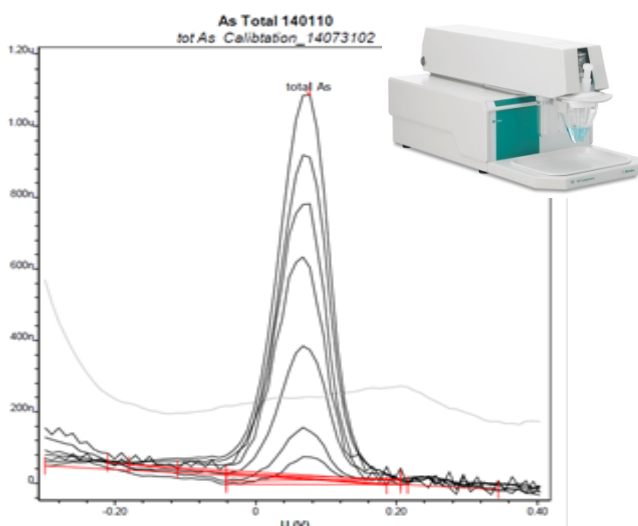
Collaborative Project - Project Partner: Dr. Sascha Giegold, Shimadzu Deutschland GmbH, Duisburg
Funded by: Shimadzu Deutschland GmbH, Phenomenex and Macherey-Nagel

Arsenic Speciation by Anodic Stripping Voltammetry (ASV) and its application on (Indian) water samples compared to other speciation techniques

Jörg Hippler and Martin Meyer

Arsenic can be found in nearly every part of the geosphere and is one of the most harmful toxin in drinking water worldwide. It is recognized as carcinogenic and causes cancers of the skin, lungs and bladder. At many places (e.g. India/Bangladesh, Vietnam, and Latin America) arsenic concentration in drinking water is above 10 $\mu\text{g/L}$, which significantly exceed the tolerable value recommended by the WHO (World health organization). In water, arsenic is predominantly present in inorganic form, as As(III) and As(V).

High-performance liquid chromatography (HPLC) and Ion chromatography coupled to an ICP/MS have become invaluable analytical tools for the determinations of trace levels of individual arsenic compounds (speciation). But using an ICP/MS is quite expensive and chromatography time consuming. Anodic stripping voltammetry (ASV) can be a fast and cost-saving alternative to distinguish between As(III) and As(V). The influence of matrix effects for the determination of total As and As(III) and the intraday- and interday calibration were determined. To analyse also higher concentrations, which is necessary for many places in e.g. India, the use of a non-linear calibration was investigated. With this kind of calibration total As and As(III) could be determined between 1 and 75 $\mu\text{g/L}$.



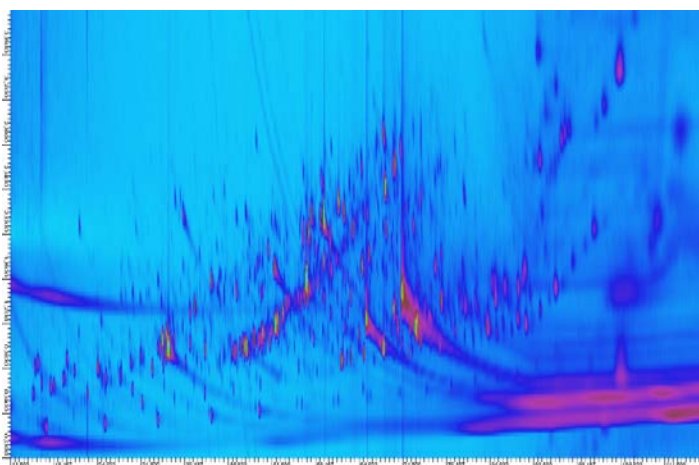
Collaborative Project - Project Partner: Metrohm AG (Herisau, Switzerland)

Funded by: Metrohm AG (Herisau, Switzerland) and Phenomenex

Quality control of Chinese herbal medicine with chemical marker analysis by GCxGC-MS

Alexandra von Trotha

Worldwide, traditional Chinese medicine (TCM) has become more and more popular as an alternative to western medicine in the last decades, especially in Europe and USA. Drug therapy with nearly 90% of medicinal Chinese plants is the heart of TCM and has the most influence on health of all therapeutic TCM methods. These plants can also be a good source for new pharmaceutical substances and for the treatment of chronic illnesses like cardiovascular disease or pain. Lots of written notes of the medicinal experiences during the last 2000 years can support this research and development. However, the prevalent problems with TCM drugs are adulteration and confusion of the herbs. At the worst this can cause adverse effects for human health because of toxic or carcinogenic ingredients in a single drug.



GCxGC-MS analysis of a TCM formulation extract

Hence, for the safety of the patients it is very important to develop a quality control which guarantees the correct composition and the potency of herbal formulas. Because these samples present very complex compositions, it is necessary to analyse them with the use of high-performance analytical methods, e.g. GCxGC-MS, which can be combined with the detection of specific chemical markers and fingerprints of the herbs as useful tools. Chemical

markers for a lot of medicinal drugs do not even exist today or have not yet been sufficiently determined for the differentiation of unequal herbs and for a successful quality control.

In our work we could demonstrate that GCxGC-MS is a very powerful method e.g. to distinguish powders of different *Angelica* species, to differentiate between high and low qualities of Chinese mint herb (*Herba Menthae haplocalycis*) and to discover potential new chemotypes of herbal species. But it is also possible to control the composition of a herbal formula which consists of several herbs by the use of specific chemical markers.

Collaborative Project - Project Partner: Dr. Kelvin Leung (Hongkong Baptist University, China)

Funded by: Sigma-Aldrich / Supelco (Taufkirchen, Germany; Bellefonte, PA, USA)

Analysis of urine, blood and other excreta from a person who was poisoned by unknown Hg-haloaromatics

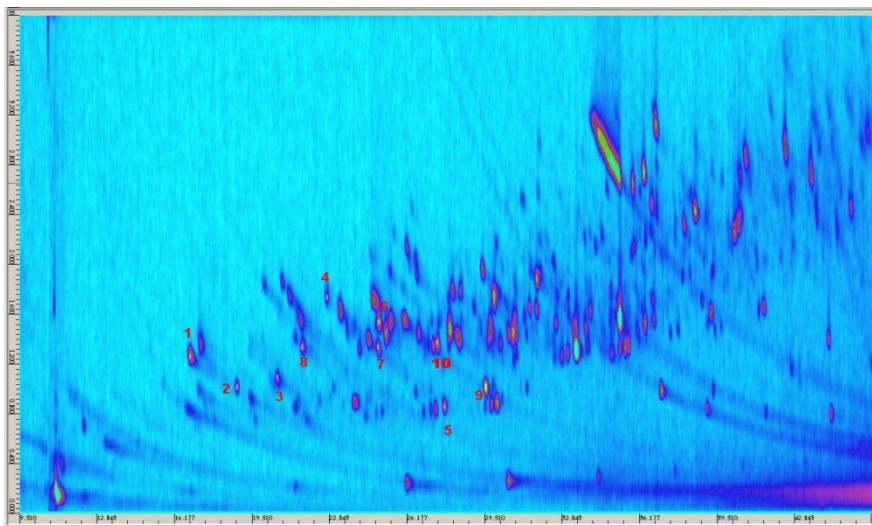
Ineet Kaur

Non-targeted metabolomics is a holistic approach in order to improve disease diagnosis and to understand its pathological mechanisms. It is the global unbiased analysis of all the small-molecule metabolites present within a biological system, under a given set of conditions.

In this work, body fluidic samples of a person, which was exposed to mercuric halogenated polyaromatic compounds while working in a lab, were measured via GCxGC-MS and LC-APCI-QTOF MS. The results were compared with healthy control samples. The collected samples from the contaminated person and other control samples were extracted by SPE or organic solvents and only compounds which were found in the targeted samples were reported.

Unfortunately, no Mercuric halogenated compounds were detected in any of the measurement, but some identified compounds (suggested from library database of the instruments) are reported as toxic to human health.

An interesting compound $C_{10}H_{15}BrNO_6$ was found and should be investigated with ion trap-MS for structure identification.



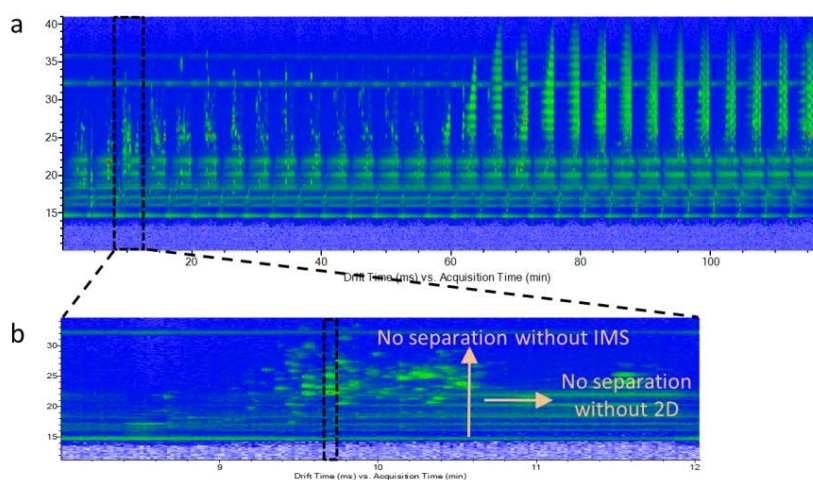
Development of a LC+LC-System for coupling to an IM-qTOF-MS

Susanne Stephan and Jörg Hippler

The request to qualify and quantify as many compounds as possible in very complex samples leads to more extensive and powerful analytical platforms. For this purpose, comprehensive two-dimensional chromatographic techniques (GCxGC or LCxLC) are coupled to modern high resolution mass spectrometers. The introduction of ion mobility spectrometry (IMS), separating compounds according to their shape-to-charge ratio, obtains the possibility to add a further separation dimension resulting in a four dimensional analytical system.

A two-dimensional LC method, based on a work from Erni and Frei in 1978, was developed and coupled to an ion mobility-high resolution mass spectrometer (IM-qTOF-MS). This approach called LC+LC works as a continuous multiheart-cutting LC-system, using a long modulation time of four minutes, which allows the complete transfer of most of the first

dimension peaks to the second dimension column without fractionation. Hence, it is possible to look at the data from a 2D analysis in a simple 1D chromatogram, which enables the data handling even when IMS as a third and MS as a fourth dimension are introduced. The analysis of a plant extract from *Ginkgo biloba* shows the separation power of this four dimensional separation method with a calculated total peak capacity of more than 8700. Furthermore, the advantage of ion mobility for characterizing unknown compounds by their collision cross section (CCS) in a non-target approach was shown. At the moment CCS values of more than 300 standards have been measured to establish a database, which is still to be extended.



Heat map of a LC+LC-IM-qTOF measurement of a *Ginkgo biloba* extract (a). The separation on the second dimension column of one fraction collected between 4 and 8 minutes (eluting from the second dimension between 8 and 12 min) from the sample is zoomed in (b).

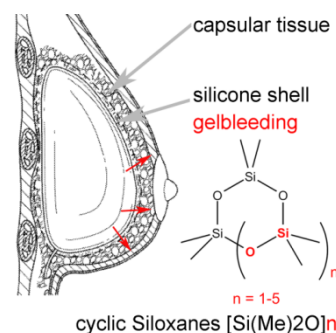
Cyclic volatile methylsiloxanes in human blood as markers for ruptured silicone gel-filled breast implants

Pia Rosendahl

The use of low quality silicone material in silicone gel-filled breast implants (SBI) of the manufacturers Poly Implant Prothèse and Rofil Medical Nederland B.V., as reported in 2010, demonstrates the need for non-invasive, sensitive monitoring and screening methods. Up to this date imaging methods, like mamma sonography (SONO) and magnetic resonance imaging (MRI), are used as diagnostic tool for detection of defect SBI. Under the financial point of view in health system SONO – which is much cheaper, but less precious than the "gold standard" MRI – is the commonly used clinical method. The aim of this work was the development of an analytical, non-invasive method based on blood analysis for the identification of ruptured SBI, which is more accurate than SONO.

We developed a novel, sensitive method based on large volume injection-gas chromatography coupled to mass spectrometry to determine octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) in blood samples of women with intact and ruptured silicone breast implants. A reduction of the siloxanes fluctuation in the instrumental blank could be reached by surrounding the injection system with an "argon-cage". Extraction efficiencies up to 100% and limits of quantification between 0.10-0.18 ng D4-D6/g in human blood were achieved.

In contrast to women with intact SBI ($n = 13$) in blood of women with ruptured SBI ($n = 11$) higher D4- and D6-concentrations up to 0.57 ng D4/g and 0.16 ng D6/g blood could be analyzed. In this study, it was the first time that a correlation between siloxane-blood-concentration and the operative evidence of SBI could be observed. With the definition of D4- and D6-blood-concentrations over 0.18 ng D4/g and 0.10 ng D6/g blood as significant criteria for ruptured SBI, eight of in total eleven ruptured implants could be verified. Compared to the SONO diagnostic results a higher precision with an error rate of 17% with the developed analytical diagnostic method instead of 46% was achieved.



Bleeding process from silicone gel through the silicone elastomer shell into surrounding the tissue

Collaborative Project - Project Partner: Dr. Peter Rusch (University Hospital Essen)

Funded by: Axel Semrau (Sprockhövel, Germany), Gerstel (Muelheim an der Ruhr, Germany), Macherey-Nagel (Düren, Germany), Sigma-Aldrich (St. Louis, USA)

Development of a DIP-APPI-MS and the analysis of various coffee samples

Simeon Horst

Ambient ionization methods are a rapid growing type of ion sources in mass spectrometry. The direct inlet probe-atmospheric pressure photo ionization (DIP-APPI) ion source belongs to this field of ion sources. All these ion sources have in common, that they do not need – more or less – sample preparation and that all contain a desorption and an ionization step.

For desorption the DIP-APPI ion source contains a heatable push rod with a probe tip at the top. The push rod can be heated with temperature gradients up to 2°/s to temperatures of 400°C. Hence the analytes in the probe tip are evaporated subsequently according to their vapour pressure and afterwards ionized. Therefore, a VUV lamp, that emits light with a wavelength of 116 nm and 124 nm (10.6 and 10 eV) is used. The great advantage of this ion source – over classical HPLC-APPI-ion sources – is its nearly solvent-free ionization chamber.

The ionization mechanism of the source can be easily switched between APCI, APPI and ESI by replacement of only the vaporizer (APCI and APPI) with an ESI sprayer. It is not necessary to remove the APCI needle and the APPI lamp in ESI mode, which makes an ionization switch very simple. With this ion source three different types of Nespresso coffees have been investigated.

The aim was to identify differences between the single coffees. As expected, all three coffees show a more or less similar mass spectrum. But beside the main components it was possible to identify some components that differ between all three coffees. By the help of the exact mass these compounds could be related to sum formulars.



Photo of the DIP-APCI-IMS-qTOF

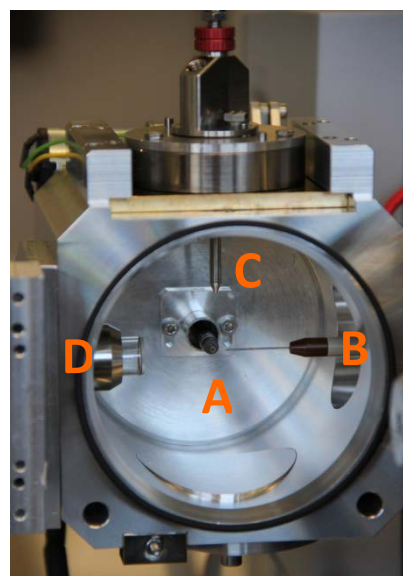
Development of a DIP-ESI-MS and analysis of Piracetam and its impurities

Claudia Lenzen

The great advantage of ambient mass spectrometry in comparison with e.g. LC-MS is that no or less sample pretreatment is necessary. The samples are introduced into the instrument without any modification. Therefore, it simplifies and shortens the analytical procedure. The great disadvantage of ambient ionization methods is that there might be problems by matrix components which would not occur if the sample is cleaned in front of the measurement. To reduce this disadvantage, a temperature controlled desorption by the direct inlet probe-atmospheric-pressure chemical ionization (DIP-APCI) interface, developed in our group, can be used.

Based on this ion source a direct inlet probe-electrospray ionization (DIP-ESI) was developed. It was coupled to an ion trap mass spectrometer (MS) for the detection of more polar compounds such as degradation products from pharmaceuticals. At first, the position of the ESI-tip, the gas and solvent flow rates as well as the gas temperature were optimized by the use of the statistic program Minitab® 17 and a caffeine standard. The ability to perform quantitative analyses was also tested with different concentrations of caffeine und camphor. Calibration curves with a quadratic calibration regression with $R^2 = 0.9997$ and 0.9998 for caffeine and camphor, respectively, were obtained.

Furthermore, a solution of Piracetam was used to compare established analytical methods for this drug such as HPLC-DAD and HPLC-ESI-MS with the DIP-APCI and the developed DIP-ESI. With HPLC-DAD and 10 µg piracetam on column, no impurity could be detected. With HPLC-ESI-MS two impurities (A and B) were identified with only 4.6 µg Piracetam while with DIP-ESI an amount of 1.6 µg Piracetam was sufficient. In case of the DIP measurements all detected impurities could be identified by MS/MS-studies.



DIP-ESI setup (view into the ion source from the mass spectrometer) A: DIP B: Corona-needle C: ESI-sprayer D: UV-Lamp

Collaborative Project - Project Partner: Dr. Andreas Winterfeld, Adler-Apotheke, Burscheid, SIM Scientific GmbH, iGenTraX UG

Funded by: AIF

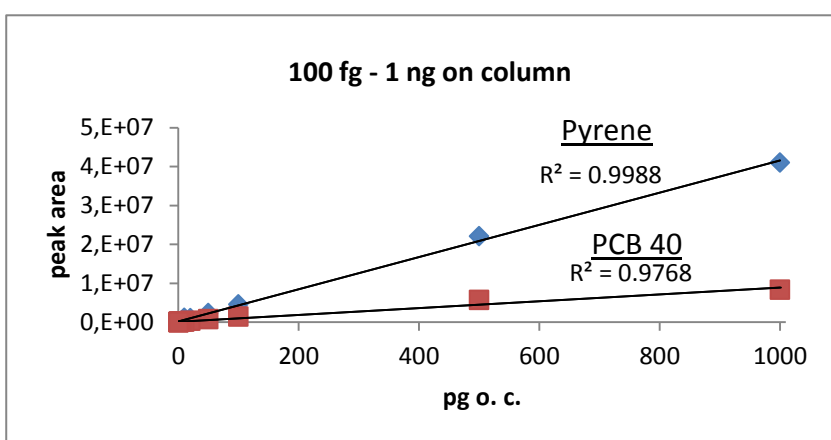
GC-APPI-Orbitrap-mass spectrometer ion source

Amela Bronja

A new gas chromatography-APPI-Orbitrap-mass-spectrometer interface with an outstanding sensitivity, recently developed at the University of Wuppertal (Germany), was used to determine the analytical features of this analytical platform. The atmospheric pressure photoionization (APPI) ion source allows the coupling of a GC to an Orbitrap high resolution mass spectrometer. The special design of the APPI-source enables an outstanding sensitivity without peak broadening. Only the ionization energy (IE) of some analytes (IE>10eV) and heat induced fragmentation are limiting factors.

The full potential of the analytical platform can be evaluated by using Orbitrap instruments with high scan rates and high resolution power.

After coupling the ion source to modern Orbitrap-systems the sensitivity was improved by a factor of approximately 10-20 in comparison with old systems without S-lenses.



GC-APPI-Orbitrap (Q Exactive Plus) linear range of Pyrene and PCB 40

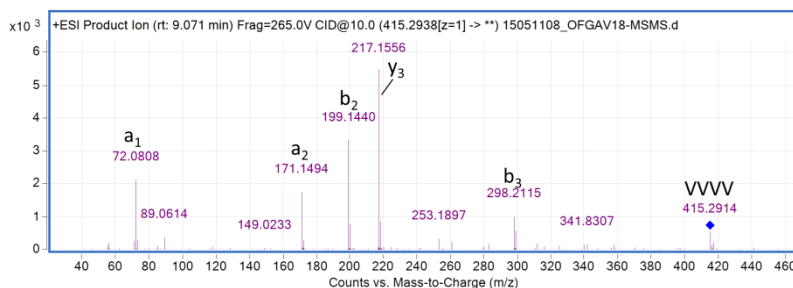
In combination with these mass spectrometers APPI allows a high sensitivity – especially for chlorinated compounds. It is therefore ideally suited for the analysis of environmental contaminants. The figure shows the linear range provided by the system. For the aromatic compound pyrene and also for the chlorinated compound PCB 40 linearities up to five orders of magnitude are determined.

Origin of Life – Analysis of reactions in a scCO₂/water phase at higher temperature

Susanne Stephan

The origin of life on Earth has been discussed over a long time. In the theory of Schreiber et al. [1], the Earth crust is supposed to depict a plausible environment for the development of the first complex organic molecules. Deep-reaching open, interconnected tectonic fault systems provide pressure and temperature conditions under which supercritical CO₂ could play an important role as a nonpolar solvent. The formation of molecules from small educts under these reaction conditions was examined in this work. Therefore, experiments were performed with different amino acids and nucleobases in a special reaction cell under high pressure, high temperature and supercritical CO₂ in the working group of Prof. Schreiber. HPLC-qTOF-MS analysis of these samples was carried out in our working group.

The results show that under the given conditions, small peptides can be generated from single amino acids. In a mixture of different amino acids, after the reaction several dipeptides and also diketopiperazines could be detected according to their exact mass. Here, amino acids with unpolar side chains seem to react preferred compared to more polar ones. This supports the idea that reaction takes place in the unpolar scCO₂ phase. In a more simple experiment valin was the only educt, which formed not only a



MS/MS spectrum of a tetrapeptide generated from valin (VWWW) in the reaction cell under supercritical CO₂ – typical peptide fragments are labeled.

dipeptide and a diketopiperazine, but also a tri- and a tetrapeptide. Those products were further confirmed by MS/MS-experiments (see figure). In subsequent experiments, possible reaction products between amino acids and nucleobases (mainly cytosine and adenine) were found. Additional measurements are going on to examine their structures and the further pathway to putative DNA precursor molecules.

LDI-MS with Gold Nanoparticles

Duxin Li and Ti Hau Bui

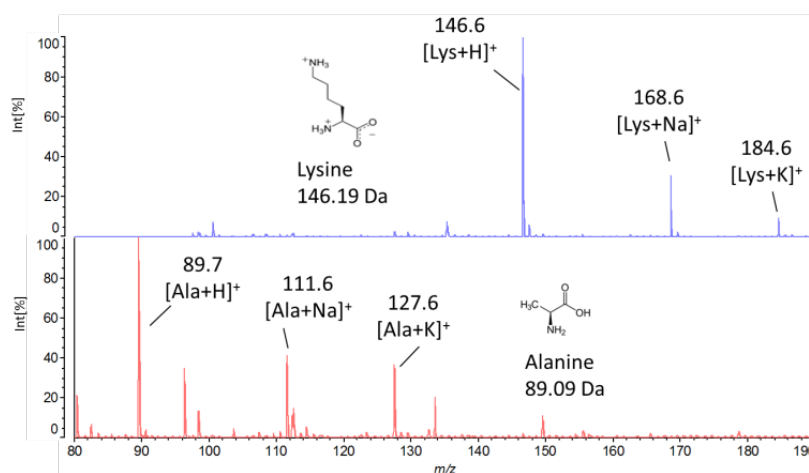
Laser desorption ionization mass spectrometry (LDI) is a powerful technique for the analysis of a variety of substances like organic polymers, proteins or carbohydrates. The use of organic matrices in matrix assisted laser desorption ionization (MALDI) allows the ionization of molecules up to 1,000,000 Da. Problems may occur in a mass range below 500 m/z because common MALDI matrices form fragment ions which result in intensive background signals in this lower mass range. A lower background and therefore better results for analytes below 500 m/z can be received using gold nanoparticles (AuNPs) instead of a conventional organic matrix. In this project the applicability of laser generated gold nanoparticles, ligand-free or stabilized with different ligands, for the AuNPs-LDI analysis of a variety of compounds like carbohydrates, amino acids and mycotoxins was investigated.

The ligand-free gold nanoparticles showed the lowest background and best mass spectra for most of the compounds.

Different monosaccharides with a molar mass of 180.16 Da like glucose and

mannose could be detected as $[M+Na]^+$ and $[M+K]^+$. Amino acids like lysine and alanine even showed peaks for $[M+H]^+$, $[M+Na]^+$ and $[M+K]^+$.

Furthermore it was possible to detect e.g. the mycotoxins Aflatoxin B1, Ochratoxin A and the steroid cortisol, which are all in the mass range of 300 to 400 Da. Further steps will be to produce complete salt free laser generated gold nanoparticles to determine the applicability of this technique for peptides and proteins.



AuNPs-LDI mass spectrum of the amino acids lysine and alanine.

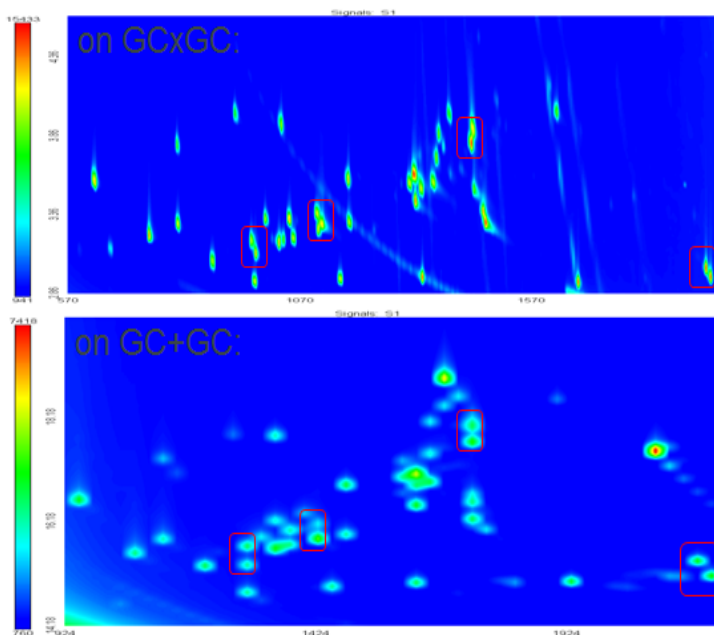
Investigations to GC+GC

Junjie Li

Multi-dimensional gas chromatography (MDGC) was firstly demonstrated by Simmons and Snyder in 1958, which now leads to current two typical MDGC techniques – conventional "Heart-cutting" MDGC and "comprehensive" GCxGC. However, these two methods have limitations on the balancing of the comprehensiveness and second dimension separation power during the measurements, which leads to the drawbacks in either qualitative or quantitative analysis. In order to solve these problems, it will be preferable to find a new technique, here called "GC+GC", where the separation runs at continuous conditions but high second dimension resolution for more precise integrations.

Different from the current GCxGC, the GC+GC is applied with middle-polar but longer column (~7 m) compared to 1.5 m column (GCxGC) for its second dimension and an increase of modulation time to 28 s instead of 5 s. As a result, larger amount of samples from the first column will be collected by the modulator within each single modulation period.

A GC-MS standard mixture, containing about 40 compounds, was analyzed with both GC+GC and GCxGC coupling to flame ionization detector (Figure). As shown in the red-circled regions, there is a better separation in second dimension on GC+GC and, of course, a slightly lower separation in the first dimension. But the major advantage is the much easier quantification, because only one peak for one compound is produced by GC+GC instead of normally 3 to 8 in GCxGC.



Comparison of GC-MS standard mix measurements on GCxGC (top) and GC+GC (bottom)

Bachelor Theses accomplished 2015

Dominik Brecht

Hg-species analysis with HPLC-ICP-MS

Timo Köhler

Development and use of a CCS database for non-target analysis

Martin Meyer

Determination of Arsenic with ASV in a non-linear calibration range

Kristina Rentmeister

Fundamental studies for component-specific chlorine isotope analysis by GC-MS and Orbitrap APPI-In-Tube extraction GC- quadrupole-MS

Master Theses accomplished 2015

Ti Hau Bui

Laser desorption ionization mass spectrometry with gold nanoparticles for the analysis of biomolecules

Andreas Mohren

Development of an online-SPE coupled to an LC-MS/MS for determination of trace compounds in water (accomplished externally at IUTA Duisburg)

Patricia Julia Kahl

Evaluation of thermal and UV-photografting approaches for the synthesis of monolithic ion exchangers for protein separations (accomplished externally at the University of Amsterdam)

Inet Kaur

Metabolomic study of body fluids of contaminated person and comparison with control samples using GCxGC-MS and LC-APCI-qTOF-MS

Accepted and/or published scientific publications 2015

Original Paper / Peer-reviewed

D. Klink, O. J. Schmitz, **SFC-APLI-(TOF)MS – a novel hyphenation of Supercritical Fluid Chromatography to Atmospheric Pressure Laser Ionization Mass Spectrometry**, Analytical Chemistry DOI 10.1021/acs.analchem.5b04402

A. Li, O. J. Schmitz, S. Stephan, C. Lenzen, P. Y.-K. Yue, K. Li, H. Li, K. S.-Y. Leung, **Photocatalytic transformation of acesulfame: transformation products identification and embryotoxicity study**. Water Research DOI 10.1016/j.watres.2015.11.035

D. Li, L. Gan, A. Bronja, O. J. Schmitz, **Gas chromatography coupled to atmospheric pressure ionization mass spectrometer (GC-API-MS): Review**, Analytica Chimica Acta (2015) 891:43-61.

F. O. Suliman, A. A. Elbashir, O. J. Schmitz, **Study on the separation of ofloxacin enantiomers by hydroxyl-propyl- β -cyclodextrin as a chiral selector in capillary electrophoresis: a computational approach**, Journal of Inclusion Phenomena and Macrocyclic Chemistry (2015) 83:119-129.

E. Deibel, Dennis Klink, O. J. Schmitz, **New derivatization strategies for the ultrasensitive analysis of non-aromatic analytes with APLI-TOF-MS**, Analytical and Bioanalytical Chemistry (2015) 407:7425-7434.

M. M. A. Omar, A. A. Elbashir, O. J. Schmitz, **Determination of acrylamide in Sudanese food by high performance liquid chromatography coupled with LTQ Orbitrap mass spectrometry**, Food Chemistry (2015) 176:342-349.

D. Li, C. Jakob, O. J. Schmitz, **Review: Practical considerations in comprehensive two-dimensional liquid chromatography systems (LC x LC) with Reversed- phases in both dimensions**, Analytical and Bioanalytical Chemistry (2015) 407:153-167.

V. Elsner, V. Wulf, M. Wirtz, O. J. Schmitz, **Reproducibility of retention time and peak area in comprehensive two-dimensional liquid chromatography**, Analytical and Bioanalytical Chemistry (2015) 407:279-284.

D. Li, O. J. Schmitz, **Comprehensive two-dimensional liquid chromatography tandem DAD and accurate mass QTOF-MS for the analysis of flavonoids and iridoid glycosides in *Hediotys diffusa***, Analytical and Bioanalytical Chemistry (2015) 407:231-240.

Book chapters

Stavros Kromidas Hrsg. **The HPLC-Expert – Possibilities and Limitations of Modern High Performance Liquid Chromatography**, (Chapter 1.1), Wiley-VCH (2016)

Poster presentations

P. Rosendahl, J. Hippler, P. Rusch, O. J. Schmitz, **Analysis of cyclic siloxanes in capsular tissue and blood samples of women with silicone breast implants**, Anakon, Graz (Austria), March 2015

C. Lentzen, O. J. Schmitz, **Comparison of original and blisted pharmaceuticals with DIP-APCI-MS**, Anakon, Graz (Austria), March 2015

S. Stephan, S. Vasireddy, O. J. Schmitz, **Analysis of fruit juice samples with HPLC and CE coupled to IMS-qTOF-MS**, Anakon, Graz (Austria), March 2015

O. Knoop, A. Bronja, O. J. Schmitz, **Establishment of a new gas chromatographic-atmospheric pressure photoionization ion source for Orbitrap-mass spectrometry**, Anakon, Graz (Austria), March 2015

D. Li, T. H. Bui, C. Streich, S. Stephan, S. Barcikowski, O. J. Schmitz, **Laser Desportion Ionization - Mass Spectrometry (LDI-MS) with Gold Nanoparticles**, CENIDE Nanobiophotonics Symposium, Essen (Germany), March 2015

P. Rosendahl, J. Hippler, P. Rusch, O. J. Schmitz, **Analysis of cyclic siloxanes in capsular tissue and blood samples of women with silicone breast implants**, analytica conference Vietnam, Ho Chi Minh City (Vietnam), April 2015 (**1st International Poster Prize sponsored by Agilent Technologies**)

C. Lentzen, O. J. Schmitz, **Comparison of original and blisted pharmaceuticals with DIP-APCI-MS**, analytica conference Vietnam, Ho Chi Minh City (Vietnam), April 2015

S. Stephan, S. Vasireddy, O. J. Schmitz, **Analysis of fruit juice samples with HPLC and CE coupled to IMS-qTOF-MS**, analytica conference Vietnam, Ho Chi Minh City (Vietnam), April 2015

O. Knoop, A. Bronja, O. J. Schmitz, **Establishment of a new gas chromatographic-atmospheric pressure photoionization ion source for Orbitrap-mass spectrometry**, analytica conference Vietnam, Ho Chi Minh City (Vietnam), April 2015

D. Li, T. H. Bui, C. Streich, S. Stephan, S. Barcikowski, O. J. Schmitz, **Laser Desportion Ionization – Mass Spectrometry (LDI-MS) with Gold Nanoparticles**, analytica conference Vietnam, Ho Chi Minh City (Vietnam), April 2015

P. Rosendahl, A. M. Steinhäuser, J. Li, O. J. Schmitz, **Development of a multi-dimensional GC-technique (GC+GC) – Preliminary studies for coupling to IM-qTOFMS**, 39th International Symposium on Capillary Chromatography (ISCC) and the 12th GCxGC Symposium, Fort Worth (USA), May 2015

S. Stephan, O. J. Schmitz, **Analysis of fruit juice samples with HPLC and CE coupled to IMS-qTOF-MS**, 63rd ASMS Conference on Mass Spectrometry and Allied Topics, St. Louis (USA), June 2015

J. Hippler, O. Knopp, A. Bronja, D. Li, R. Ahrends, O. J. Schmitz, **GC coupled to an Orbitrap-MS with a novel atmospheric pressure photoionization (APPI) ion source**, 63rd ASMS Conference on Mass Spectrometry and Allied Topics, St. Louis (USA), June 2015

Invited Lectures / Oral Presentations

Prof. O. Schmitz

Combination of the best of two worlds: LCxLC and IMS-QTOF-MS

Agilent Infinity II Tour, Frankfurt, January 2015 (invited speaker)

Combination of the best of two worlds: LCxLC and IMS-QTOF-MSAgilent Lunchseminar at 48th Annual Conference of the German Mass Spectrometry Society (DGMS) 2015, Wuppertal, March 2015 (invited speaker)**Combination of the best of two worlds: LCxLC and IMS-QTOF-MS**

Pittcon 2015, New Orleans, March 2015 (invited speaker)

Comprehensive two-dimensional liquid chromatography: Theory and applications

2D-LC Symposium from Phenomenex, Frankfurt, March 2015 (invited speaker)

Atmospheric-pressure laser ionization (APLI) in trace analysis: scientific findings, latest developments and outlook (part 1)**Comprehensive two-dimensional liquid chromatography: Potential and Limitation (part 2)**

Hanoi University of Science, Vietnam, April 2015

Combination of the best of two worlds: LCxLC and IMS-QTOF-MS4th analytica Anacon Conference in Ho Chi Minh City, Vietnam, April 2015**Combination of the best of two worlds: LCxLC and IMS-QTOF-MS**

Agilent Ion Mobility Workshop at Swedish Metabolomics Center, Umea, Sweden, May 2015

Combination of the best of two worlds: LCxLC and IMS-QTOF-MSAgilent Lunchseminar at 42nd HPLC, Geneva, Switzerland, June 2015 (invited speaker)**2D-LC in combination with IMS and qTOF-MS for next generation metabolome analysis**

Peking University, Beijing, China, September 2015

2D-LC in combination with IMS and qTOF-MS for next generation metabolome analysis

Institute of Chemistry – Chinese Academy of Science (ICCAS), Beijing, China, September 2015

New atmospheric pressure ion sources for mass spectrometry

Tsinghua University, Beijing, China, September 2015

Personalized Medicine – or Metabolomics 2.0

Beijing-Humboldt Forum, Beijing, China, September 2015 (invited speaker)

Ion mobility spectroscopy as a new separation dimension in LC-MS (Tutorial)9th analytica Anacon Conference in Hyderabad, India, October 2015**Ion mobility spectroscopy as a new separation dimension in LC-MS**

Metabolomics IMS-QTOF Meeting, Duesseldorf, Germany, October 2015 (invited speaker)

A forgotten two-dimensional liquid chromatography approach coupled to an ion mobility-mass spectrometer

DICP Symposium (XXXIX) on Functional metabolomics, Dalian, China, November 2015
(invited speaker)

S. Stephan

Analyse von Fruchtsäften mittels HPLC/CZE-IMS-qTOF-MS

48th Annual Conference of the German Mass Spectrometry Society (DGMS), Wuppertal, March 2015

Miscellaneous

Conference organization

Oliver J. Schmitz, Chairman (together with Prof. Dr. Pham Hung Viet, Hanoi University of Science) of the 4th analytica Anacon Conference in Ho Chi Minh City, Vietnam, April 15-16th 2015

Oliver J. Schmitz, Chairman (together with Prof. Dr. Lihua Zhang, Dalian Institute for Chemical Physics) of the Sino-German Seminar about "Frontiers of Chromatography and Mass Spectrometry in –Omics Time" in Essen, Germany, June 17th – 21st

Oliver J. Schmitz, Chairman (together with Gautam Rajan, Indian Analytical Instruments Association) of the 9th analytica Anacon Conference in Hyderabad, India, November 15-16th 2015

Editorial Tasks by Prof. O. Schmitz

Advisory Board member of Chromatographia

Editorial Board member of Journal of Pharmaceutical Analysis

Guest-Editor of Analytical and Bioanalytical Chemistry (Special issue: Multidimensional Chromatography)

Member of the "Fachbeirat" der analytica Munich

Member of the scientific committee of HPLC 2015 in Beijing

Institute Colloquium

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

Dr. Alexander Makarov from Thermo Fisher Scientific, inventor of the Orbitrap mass analyzer, 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:



PD Dr. Frank Steiner, ThermoFisher Scientific, Das Konzept der Peakkapazität in der 2D-LC und 1D-UHPLC und die Sinnhaftigkeit dieses Wertes beim Methodenvergleich für die Analyse hochkomplexer Proben, 19.01.2015

Prof. Dr. Dr. Philippe Schmitt-Kopplin, German Research Center for Environmental Health (GSF), Unraveling the chemical space of terrestrial and meteoritic organic matter, 27.04.2015

Prof. Dr. David McCalley, University of the West of England, Bristol, Hydrophilic interaction chromatography – a complimentary technique to reversed phase for the separation of polar and ionised compounds, 01.06.2015

Prof. Dr. Jacel Namiesnik, TU Gdansk, Poland, Application of green sample preparation techniques for the isolation, preconcentration and gas chromatographic determination of organic environmental pollutants, 15.06.2015

Dr. Alexander Makarov, ThermoFisher Scientific, Orbitrap Mass Spectrometry: Past, Present and Future, 22.06.2015

Dr. Andreas Peter, Wasserversorgung Zürich, Switzerland, Mikroverunreinigungen im Trinkwasser – der (unabhängige) Weg der Schweiz, 06.07.2015

Dr. Alexander Ruderisch, agrolab, Chromatographie als Dienstleistung – Kann ich Analytikergebnisse in der gleichen Weise wie Autos produzieren?, 19.10.2015

Prof. Dr. Dietrich Volmer, University of Saarbrücken, Determining metabolic signatures in patients samples using advanced mass spectrometry techniques, 02.11.2015

Dr. Detlef Schulz-Bull, IOW Warnemünde, TBA, 30.11.2015

Dr. Elisabeth Janssen, ETH Zürich, Phototransformation of biomolecules and the dual role of natural organic matter, 14.12.2015

Teaching

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

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

Tutorial Analytical Chemistry I (in German, Dr. J. Hippler)

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

Tutorial Analytical Chemistry II (in German, Dr. J. Hippler)

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

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

Tutorial Analytical Chemistry I (in German, Dr. J. Hippler)

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

Tutorial Analytical Chemistry II (in German, Dr. J. Hippler)

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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