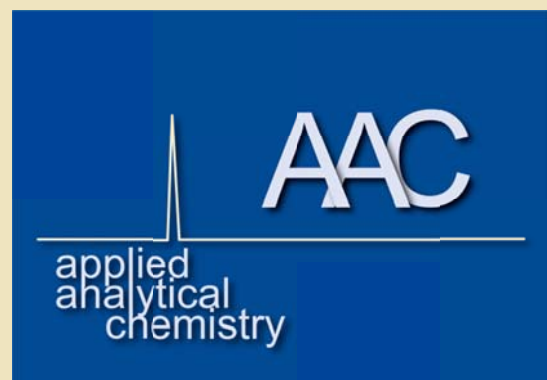


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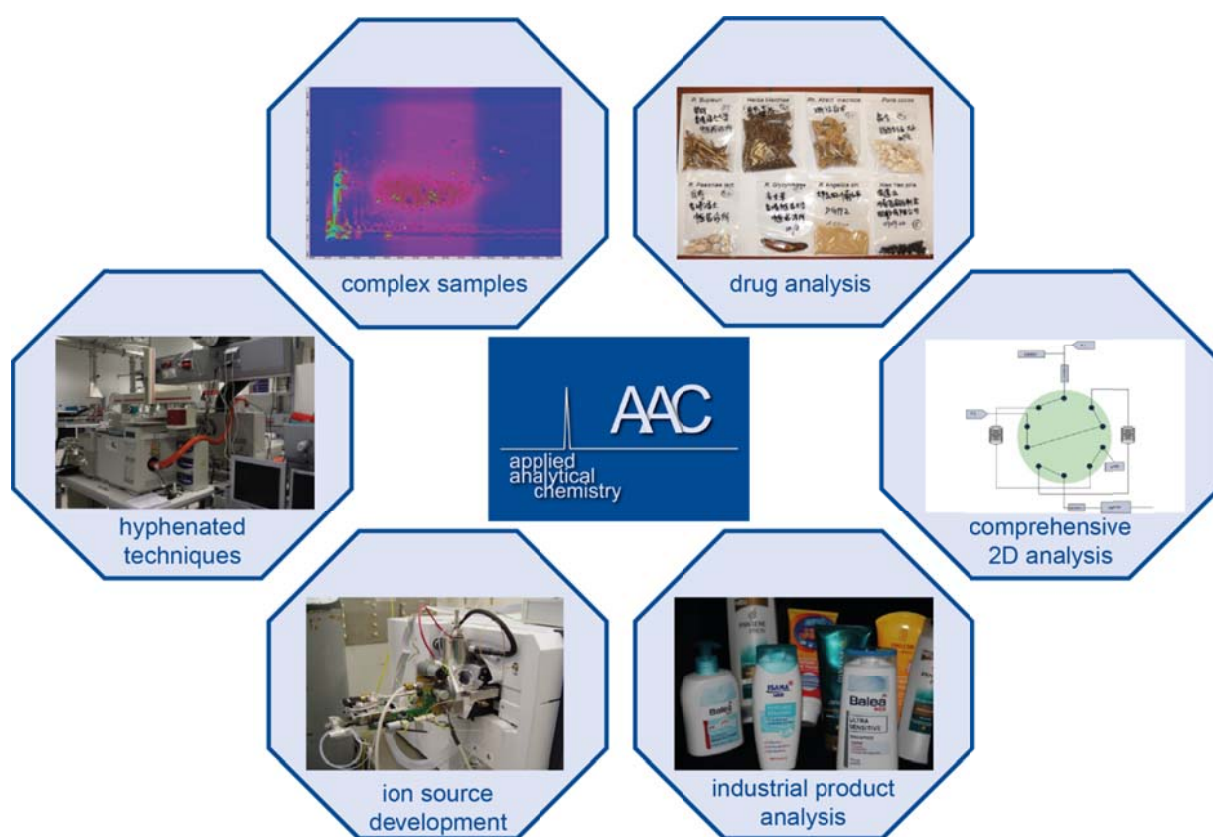
Applied Analytical Chemistry (AAC)

Annual Report 2014



Applied Analytical Chemistry

Annual Report 2014



University of Duisburg-Essen
Faculty of Chemistry
Applied Analytical Chemistry
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45141 Essen
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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 analysis of complex samples (e.g. chinese herbal medicine) by multi-dimensional separation techniques (GCxGC or LCxLC) and the metal(oid) species analysis by ICP-MS in combination with gas chromatography (GC) or liquid chromatography (LC).

2014 was the second year of the Applied Analytical Chemistry research group at the University of Duisburg-Essen and now the construction phase is finished. 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 Maria Mandani and Dr. Jörg Hippler, who were indispensable in organizing the new research group.

During 2014 several new projects are approved, e.g. two projects founded by the AIF (Federation of Industrial Research Associations) regarding the development of a new direct inlet probe photoionization system and the stability analysis of pharmaceuticals. In addition, several cooperations with Agilent, Phenomenex, Shimadzu and SIM were continued to further increase industrial related research.

Together with Prof. Torsten Schmidt and PD Dr. Thorsten Teutenberg (all members of the Faculty of Chemistry at the University of Duisburg-Essen) a special issue about "Multidimensional Chromatography" was organized and will be published in January 2015 by Analytical and Bioanalytical Chemistry. Furthermore several book projects started in 2014 (Multidimensional Chromatography, together with Prof. Margit Geißler and Prof. Luigi Mondello; Analytische Chemie, together with Prof. Georg Schwedt and Prof. Torsten Schmidt; HPLC for Experts (chapter: State of the art in the LC / MS), together with Stavros Kromidas.



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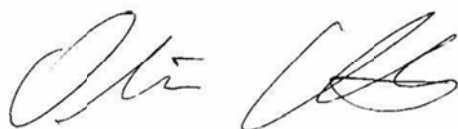
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I want to take this opportunity to thank all co-workers for their excellent work in 2014 as well as the many collaborators in and outside the University of Duisburg-Essen for pleasant and efficient collaborations.

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

I wish you an interesting reading of this annual report and all the best in health and happiness for the year 2015.

A handwritten signature in black ink, consisting of two distinct parts. The first part is a cursive 'A' followed by a horizontal line, and the second part is a more complex cursive signature.

Essen, 21.12.2014

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
Robin Meya	Apprentice
Jennifer Schang	Apprentice

Ph.D. Students:

University Duisburg-Essen

Amela Bronja
Eduard Deibel
Maxim Diel
Lin Gan
Simeon Horst
Susanne Stephan
Mei Omar
Claudia Lenzen
Pia Rosendahl

University Wuppertal

Sonja Krieger
Alexandra von Trotha
Nils Wienand

External

Susanne Brüggem
Jackelyn Aragón Gómez

M.Sc. Students:

Amela Bronja, Satrugna Vinjarapu, Sweeja Vasireddy, Cornelia Jakob, Oliver Knoop, Surina Surina, Anne Ackmann, Ti Hau Bui

B.Sc. Students:

Tobias Bormann, Christian Lipok, Simon Schade

Post-Docs:

Dr. Duxin Li

Guest Scientists:

Prof. Dr. A. Elbashir (Visiting Professor / Georg-Forster-Scholar), Prof. Dr. A. V. Hirner (Prof. em.)

Major News 2014

First LC/GC/CE-IMS-qTOF-MS in Germany!

As one of the first instruments worldwide an Agilent Ion Mobility-Quadrupol-Time of Flight Mass Spectrometer System (Agilent 6560) was installed at the Applied Analytical Chemistry in June 2014. The System was successful coupled to an HPLC and CE system and will be also coupled to GC and ambient desorption ion sources to analyse very complex samples in the field of metabolomics, lipidomics etc. In the near future we will build a data base of collision cross sections for many analytes to generate a helpful tool for identification of unknown substances.



Hero of the Year 2014



In 2014 the scientific output of Dr. Duxin Li was very successful. He published three papers (one review, one paper in forefront and another very interesting work about LCxLC and mixed-mode phases) and is preparing a second review article.

List of Projects 2014

(Abstracts of these projects within the next pages)

Imaging of Zinc in breast cancer tissue after development of a new LA cell by ICP-MS

M. Diel, A. Ackmann

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

J. Hippler, S. Vinjarapu, S. Surina

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

A. von Trotha

Comprehensive two-dimensional Liquid Chromatography (LCxLC)

D. Li

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

C. Jakob

Silicons in human breast tissue

P. Rosendahl, R. Meya

Developments in DIP-APCI/APPI/ESI-MS

S. Horst, C. Lenzen

CZE- and HPLC-IMS-QTOF-MS

S. Stephan

GC-APPI-Orbitrap-mass spectrometer ion source

O. Knoop

Origin of Life – Analysis of liquid inclusions in Australian quartz samples

P. Rosendahl

Applications with a GC-APCI-MS and a Dean Switch

A. Bronja

LDI-MS with Gold Nanoparticles

S. Stephan, D. Li

Determination of acrylamide in Sudanese food by QuEChERS pretreatment method and high performance liquid chromatography coupled with LTQ Orbitrap mass spectrometry

M. M. A. Omar, A. A. Elbashir

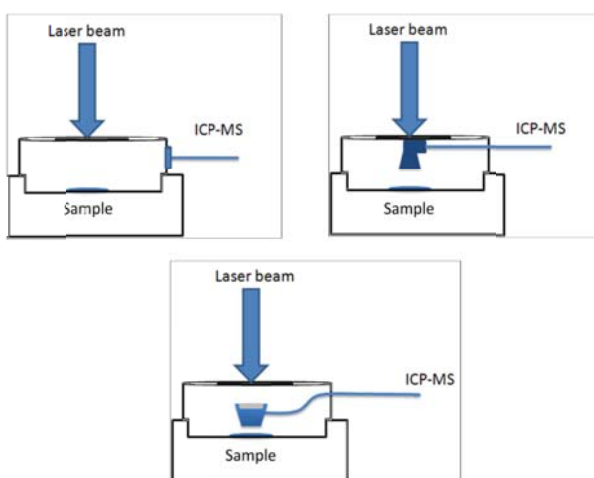
Imaging of Zinc in breast cancer tissue after development of a new LA cell by ICP-MS

Maxim Diel, Anne Ackmann

The correlation between the zinc concentration and the pathological grading in malignant breast cancer tissue was investigated with the use of a LA-ICP-MS. In this attempt a commercial available laser ablation (LA) chamber was used.

For the analysis, the University Medical Centre Essen provided 28 breast cancer tissue samples, which are divided into six different groups regarding their pathological grading as well as HR and HER2 status. The results indicate an increase of zinc concentrations with higher pathological grading and higher tumour percentage in the sample. Additionally, a difference between HR positive and HR negative was pointed out.

To improve the laser ablation processes of a LA-ICP-MS three new laser ablation cells were tested, based on the analysis of copper in cyan printed samples. For the three different cells, which consist of a capillary and cone at the end, a new designed laser ablation chamber was developed and tested. The developed cells were compared to the original commercially available laser ablation chamber. The measurements with a 213 nm Nd:YAG laser ablation system indicated that a design, in which the cone with a quartz glass is inserted at the top with an bended capillary performed best in terms of signal intensities and wash-out rates from the laser to the ICP-MS.



▲ Fig.1: Three different cell designs for laser ablation.

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

Jörg Hippler, Surina Surina, Satrugna Vinjarapu

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 µg/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).

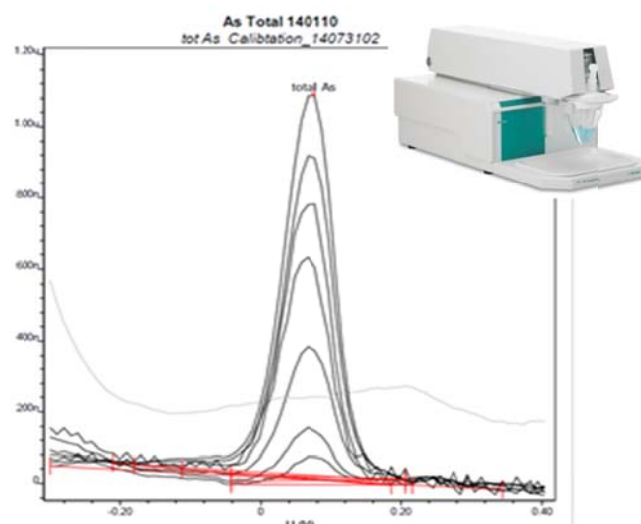
High-performance liquid chromatography (HPLC) and Ion chromatography coupled to an ICP/MS have become invaluable analytical tools for the determinations of trace levels of individual arsenic compounds (speciation). But using an ICP/MS is quite expensive and chromatography time consuming! Anodic stripping voltammetry (ASV) can be a fast and cost-saving alternative to distinguish between As(III) and As(V). Out of these reasons we compared the chromatographic methods for As speciation in Indian water samples with the ASV.

Four Indian water samples (Ind S1-S4) were analysed by HPLC-ICP/MS, IC-ICP/MS and ASV using ascTRACE gold sensor in a 797 VA Computrace (Metrohm AG, Herisau, Switzerland). Differentiation between As(III) and total arsenic concentration was made by appropriate selection of the deposition potential (Fig.1).

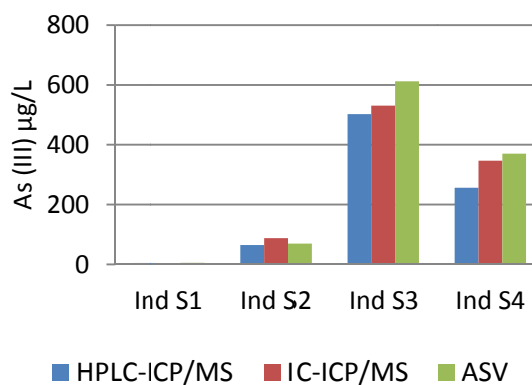
Total As concentrations measured by ASV are in good agreement with the sum of the species measured by HPLC and IC. For speciation with ASV, As(III) was tested directly, while As(V) was calculated as the difference between total As and As(III). The results for As(III) are also comparable to the concentrations determined by IC-ICP/MS and HPLC-ICP/MS (Fig 2).

Fig.2: ►

As(III) concentration in Indian Water Samples measured by three different techniques (HPLC, IC, ASV).



▲ Fig.1: Voltamogram for total As determination by Anodic stripping voltammetry



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

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

Quality control in Traditional Chinese Medicine (TCM) by GCxGC-MS

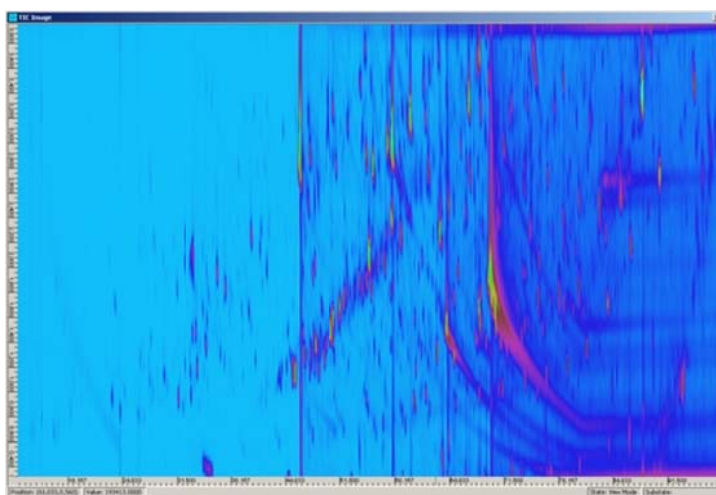
Alexandra von Trotha

Recently, traditional Chinese medicine (TCM) has become an alternative to western medicine, also in Europe and USA. Furthermore, herbs of the TCM could be a source for a lot of chemical components. Therefore scientists are interested in the pharmacological activities of these constituents which could be probably used for new medical applications. A lot of written notes of the medicinal experiences during the last 2000 years can support this research. However, there are problems with the TCM drugs when they are adulterated or confounded, at the worst this can induce poisoning because of toxic ingredients in a single drug. 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. The detection of specific chemical markers and fingerprints of the herbs can ensure this. Till now chemical markers for a lot of medicinal drugs are not determined. Because plant samples present very complex compositions, it is necessary to analyse them with the use of high-performance analytical methods, e. g. GCxGC-MS.

The root of *Angelica sinensis* is one of the most important traditional Chinese herbal remedies. Sometimes it is substituted by other species of *Angelica* roots without any change of declaration. In our work we could demonstrate that GCxGC-MS is a very

powerful method to distinguish different *Angelica* species and to differentiate between high and low

qualities of Chinese mint herb (*Herba Menthae haplocalycis*). But it is also possible to control the composition of a herbal formula (Xiao Yao pill) which consists of several herbs by the use of specific chemical markers. Moreover, we could show that ionic liquid columns could be an interesting tool for quality control of complex samples like herbs.

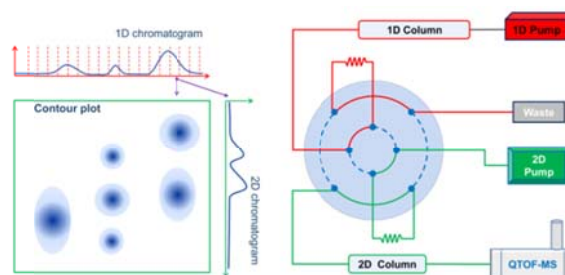


▲ Fig. 1: GCxGC-MS analysis of a traditional Chinese medicine (TCM) extract.

Comprehensive two-dimensional Liquid Chromatography (LCxLC)

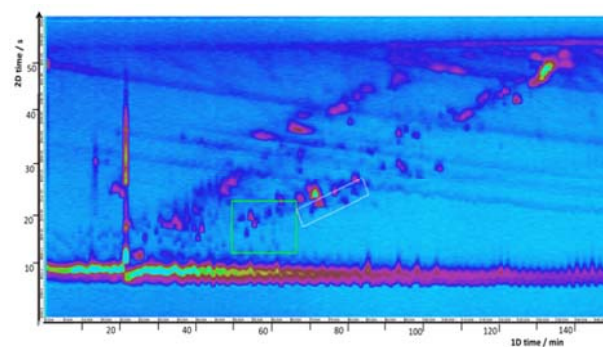
Duxin Li

Traditional high-performance liquid chromatography (HPLC) uses a single column, which is not sufficient for analysis of complex samples. If the number of components exceeds 37% of the peak capacity, peak resolution is statistically reduced. And if several ingredients of a sample are eluted and ionized at the same time in the ion source, this can lead to ion suppression and/or formation of artefacts. Therefore, a high-performance chromatographic platform in front of the MS is always the gold standard. Comprehensive two-dimensional liquid chromatography (LCxLC) is characterized by greatly increased resolving power and selectivity as compared with one-dimensional separation. The general setup of an LCxLC system comprises of two separation dimensions, which are coupled online via an interface, as shown in Fig. 1. The interface is usually a ten or eight-port switching valve with two equivalent sampling loops or trapping columns, operating in alternating cycles. The eluents from first dimensional elution were collected in the loop and subsequently transferred into the second dimensional separation column.



▲ Fig. 1: Schematic of a LCxLC instrument).

The great advantage of increased peak capacity of LCxLC enables the characterization of very complex samples, in present case, *Hedyotis diffusa* (Rubiaceae). Therefore, an LCxLC-QTOF-MS system was used to analyse flavonoids glycosides (FGs) and iridoid glycosides (IGs) in aqueous extraction of *H. diffusa*, as shown in Fig. 2. Tentative identification of compounds was done by accurate mass interpretation and validation by UV spectrum. A clear classification of FGs (Green solid line), acylated FGs (White dot line) and iridoid glycosides (IGs) was shown in different regions of the LCxLC contour plot. Totally, five FGs, four acylated FGs and three IGs were tentative identified. In addition, several novel flavonoids were found, which demonstrate that LCxLC-QTOF-MS detection has also a great potential in herbal medicine analysis.



▲ Fig. 2: LCxLC analysis of *H. diffusa* with accurate mass QTOF-MS detection

Funded by: CSC & DAAD (China Scholarship Council and German Academic Exchange Service) and Phenomenex

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

Claudia Jakob

The coupling of a LCxLC system to an Ion-mobility spectrometer (IMS) with a high resolution MS is expected to further increase resolving power and selectivity. Ion mobility spectrometry allows to separate isobaric substances such as constitutional isomers, which in many cases are not separated satisfactory with chromatographic methods and show the same mass-to-charge ratio (m/z) in the MS. Therefore, an LCxLC-IMS-MS system would be a most powerful method for non-target analysis of analytes up to 2000 Da.

In comprehensive LCxLC each peak that is eluted from the first dimension is fractionated several times. The fractions are then introduced into the second dimension column. In an LCxLC-IMS-MS instrument the analytes eluting from the second dimension column would be ionized and subjected into the drifttube of IMS by a discontinuously way in so called ion-packets. This would add an additional dimension to the two dimensions of LCxLC. After IMS the ions are subjected to high resolution qTOF-MS.

On the one hand each separation dimension, as well as the MS, increase the potential to identify single compounds in highly complex samples. On the other hand results become more complex with each separation and detection dimension. IMS-qTOF-MS itself offers separation and identification possibilities. To reduce the complexity of the data evaluation it was decided to simplify the LCxLC data set. By increasing the modulation time to several minutes it is aimed to collect each peak coming from the first dimension in only one or maximal two modulation periods. Thus each analyte will only appear once or at maximum twice in the LCxLC data set. To differentiate this procedure from traditional LCxLC it is referred to as LC+LC.



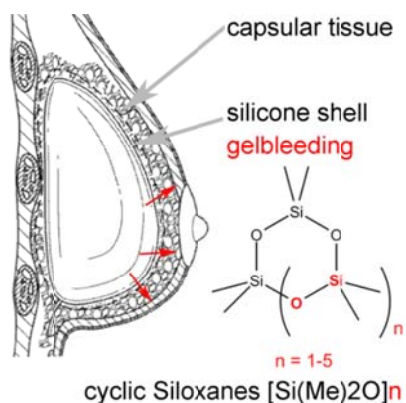
Funded by: Phenomenex

Silicons in human breast tissue

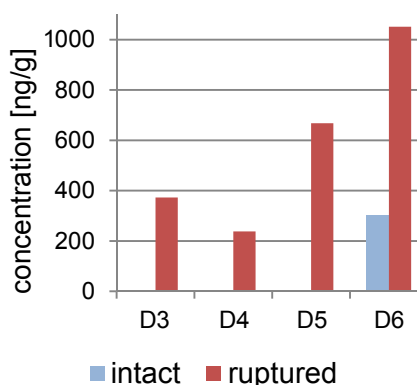
Pia Rosendahl

Since the silicone crisis in the 1990s the topic "safety of silicone breast implants" is from time to time in the public eye. After the implantation of low quality silicone in silicone gel-filled breast implants (short SBI) of the manufacturer Poly Implant Prothèse (short PIP) and the distributor company Rofil Medical Nederland B.V reported in 2010, it became apparent that the need for non-invasive and sensitive monitoring and screening methods exists. Especially with the fact that PIP/Rofil-implants have an increased rupture tendency compared to high class implants and the standard diagnostic, such as breast ultrasound and magnetic resonance imaging, are of limited significance, a fast, cost-effective analysis method would be advantageous.

The aim of this project is to confirm the indication for SBI exchange on the basis of an increased concentration of a biomarker in the blood of a patient via GC- or comprehensive GCxGC-MS-analysis. Based on the fact that volatile silicone ingredients (e.g. cyclic siloxanes) diffuse from the silicone gel through the silicone shell into the surrounding tissue (called gel-bleeding), we developed a GC-MS method to quantify this class of compounds in the capsular tissue and in the blood samples of the patients. Due to the high volatility of the analytes, the focus of the sample preparation step lies upon a nearly closed cold chain, the prevention of cross-contamination and the reduction of siloxanes-background based on the GC-column.



After homogenization of the tissue and extraction with organic solvents, first GC-MS-results show significant higher cyclic siloxanes multitude and siloxanes concentration in the capsular tissue of women with ruptured SBI than with intact SBI. Based on these early results, further investigations will focus on increasing sensitivity of the developed method to quantify cyclic siloxanes in blood samples (e.g. GC-column, injection technique) and searching for biomarker and possible metabolites of siloxanes via non-target analysis.



Collaborative Project - Project Partner: Prof. em. Dr. Alfred V. Hirner (University Duisburg-Essen) and Dr. Peter Rusch (University Hospital Essen)

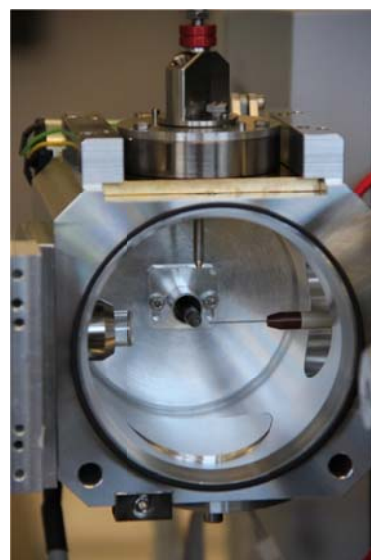
Funded by: Sigma-Aldrich

Developments in DIP-APCI/APPI/ESI-MS

Simeon Horst, Claudia Lenzen

Since the invention of ambient ionization technologies in 2004 this field of analytical chemistry is rapidly grown. The great advantage of ambient mass spectrometry over other analytical procedures is that no or less sample pretreatment is necessary. 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 overcome this disadvantage a temperature controlled desorption is achieved by the DIP-APCI interface developed in our group.

In the work of C. Lenzen several pharmaceuticals were analysed by DIP-APCI-MS. The interest of this research is to look for differences between the halved, repacked drugs (blistered), such as those be made for elderly homes and the original packaging drugs in the mass spectrum. It was of special interest if decomposition or oxidations products of the pharmaceuticals and impurities can be detected. Although most of these impurities are well known, we found some that are not described in the literature. Nevertheless for the most drugs there are no differences detectable between the halved, repacked and the original drugs. However more polar pharmaceuticals such as hydrochlorothiazide were difficult to ionized by DIP-APCI. Therefore, a DIP-ESI source is developed and optimized and in near future the drugs will be analyzed and the results of DIP-APCI-MS, DIP-ESI-MS and LC-MS will be compared. In the project of S. Horst a DIP-APPI coupling has been developed. An optimization of the position of the VUV Lamp and of the corresponding gas flows has been successfully finished. The analysis of different compounds with DIP-APCI-MS and DIP-APPI-MS show for some analytes an increase in sensitivity with the DIP-APPI system.



Collaborative Project - Project Partner: SIM Scientific GmbH, Bruker Daltonics, iGenTraX UG

Funded by: AIF

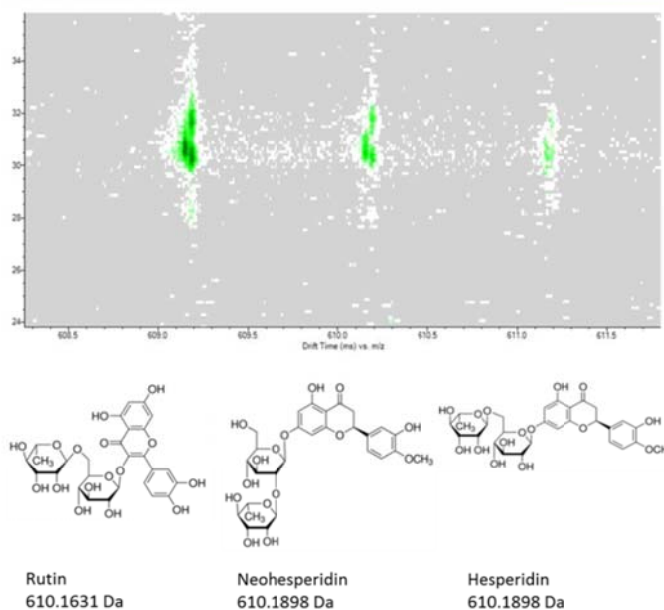
CZE- und HPLC-IMS-QTOF-MS

Susanne Stephan, Sweeja Vasireddy

The coupling of classical separation methods like capillary zone electrophoresis (CZE) or high performance liquid chromatography (HPLC) to ion mobility mass spectrometry provides an interesting technique for the analysis of complex samples due to an additional separation dimension compared to normal CZE-MS or HPLC-MS systems.

In capillary zone electrophoresis, charged compounds are separated due to their electrophoretic mobility while it is not possible to separate uncharged analytes. In IMS, ions drift through a low electric field in a drift tube filled with a neutral buffer gas and are separated by their size-to-charge ratio. After the drift tube, ions are pulsed into the time-of-flight mass spectrometer to be separated by their mass-to-charge ratio.

The coupling of CZE to the new ion mobility (IM) Q-TOF mass spectrometer system (Agilent 6560) with electrospray ionization was realized. Different samples of citric fruit juices were analyzed with this technique. It was possible to show that several neutral compounds like sugars, which elute with the electroosmotic flow (EOF), are separated in the IM dimension by their size. Additionally, it could be shown that some Flavanone-Glycosides, which have the same molecular mass and therefore have the same electrophoretic mobility in CZE and the same m/z , can be separated in IMS because of their different collision cross sections resulting from the different position of the glycosidic binding (see figure). A series of substances in juice and tea samples could be identified using this CZE-IMS-QTOF-MS system.



▲ Fig.1: Plot of drift time vs. m/z of three coeluting substances (CZE-ESI (neg)-IM-Q-TOF-MS) in lemon juice.

Coupling of HPLC to the IM-Q-TOF-MS was used for first measurements of juice samples. The results show that the IMS can be used as an additional separation dimension for the complex samples and that the drift time provides another parameter to characterize single compounds.

GC-APPI-Orbitrap-mass spectrometer ion source

Oliver Knoop

Atmospheric pressure photoionization (APPI) shows high sensitivity for non-polar, and chlorinated environmental pollutants as well as for drugs and steroids when applied in liquid chromatography/mass spectrometry. Recent developments show the high affinity to introduce APPI in gas chromatography/mass spectrometry (GC/MS).



A new gas chromatography-APPI-Orbitrap-mass spectrometry interface with an outstanding sensitivity, that was recently developed at the University of Wuppertal, was further investigated in this study to determine the features of this new analytical platform. The adaptability for the analysis of environmental pollutants was shown with the EPA-8270 Mix, and 63 out of 78 compounds were successfully determined. Furthermore the ionization efficiency for 95 compounds were specified showing a dependency of the ionization energy. Additionally the adaptability of the new platform for compound-specific stable isotope analysis of chlorinated compounds was examined and for the analysis of complex biological samples in the field of metabolomics. In both fields it was possible to show a first fitness for purpose. The results of the optimization procedure indicated that in the current setup the very old Orbitrap MS (without S-lense) is the limiting factor. It is expected that the full capacities of the analytical platform could be evaluated using an Orbitrap instrument with higher scan rates and higher resolution power.

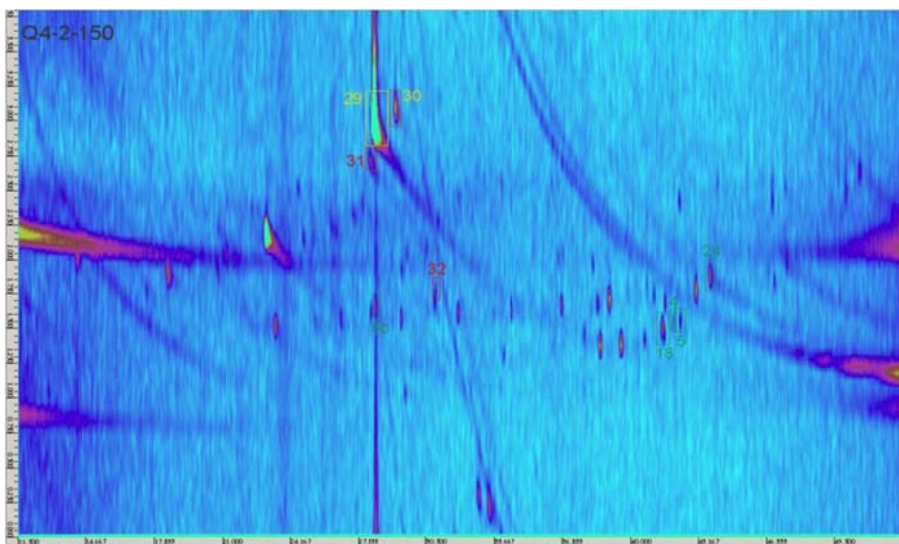
Collaborative Project - Project Partner: Prof. Thorsten Benter, Physical Chemistry, University of Wuppertal
Funded by: iGenTraX, ThermoFisher

Origin of Life – Analysis of liquid inclusions in Australian quartz samples

Pia Rosendahl

The question about the origin of life is found in all cultures and was differently answered in each era. In this age of science we try to explain the origin of life on a purely chemical way.

A new and very promising theory was developed by Prof. Schreiber and Prof. Mayer, both from the University of Duisburg-Essen: Deep-reaching gas permeable tectonic faults of the early crust may provide possible reaction habitats for the formation of prebiotic molecules. Their fillings consist of supercritical and subcritical waters and supercritical and subcritical gases. Here, all necessary raw materials for the development of prebiotic molecules exist in variable concentrations and in sufficient quantities. Inside faults with high gas contents in a mixture of CO_2 , CO , NH_3 , H_2 reactions similar to the Fischer-Tropsch synthesis occur which yields hydrocarbons and a plurality of components of organic chemistry. Faults are often documented by quartz mineralization. Quartz minerals conserve the chemical composition of the given fluid medium in fluid inclusions. The



special feature of this theory is that in the case of accuracy, it should be possible to prove this theory with the help of modern analytical methods. Therefore we are analyzing liquid inclusions in various - more than three billion years - old quartz samples.

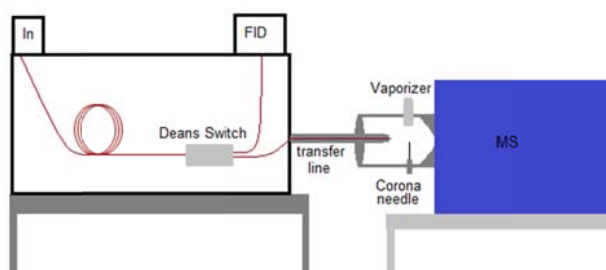
Collaborative Project - Project Partner: Prof. Ulrich Schreiber , Geology, and Prof. Christian Mayer, Physical Chemistry, University of Duisburg-Essen

Applications with GC-APCI-MS and Deans Switch

Amela Bronja

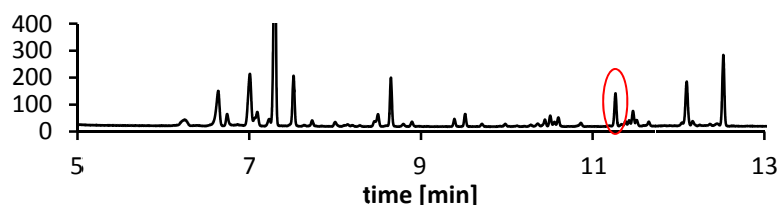
The coupling of a gas chromatograph – flame ionization detector (GC-FID) with an integrated Deans Switching system and one in our laboratory developed atmospheric pressure chemical ionization (APCI) ion source with an Ion Trap mass spectrometer (MS), leads to application possibilities which will be demonstrated. The obtained GC-FID-APCI-MS system contains two detectors and with the

Deans Switch it is possible to perform in oven heart cut and to divert specific signals depending on interest to FID or through a transfer-line to MS (Fig. 1). The analytes are ionized by atmospheric pressure chemical ionization and lead to the ion trap mass analyzer. If required MS^n can be performed to identify the analytes of real samples. Figure 2 shows the resulting FID chromatogram of a

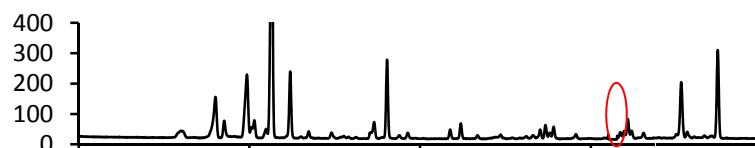


▲ Fig.1: GC-FID-APCI-MS system juice.

perfume sample after gas chromatographic separation. The cycled signal was proposed to be the fragrance Methyl (3-oxo-2-pentylcyclopentyl) acetate with a molecular weight of 226 g/mol.



The signal was diverted to MS and an $[M+H]^+$ ion peak with m/z 227 appears. To ensure that this peak in fact is belonging to the target molecule MS^n spectra were generated with the ion trap



▲ Fig.2: FID chromatogram of a perfume sample after gas chromatographic separation.

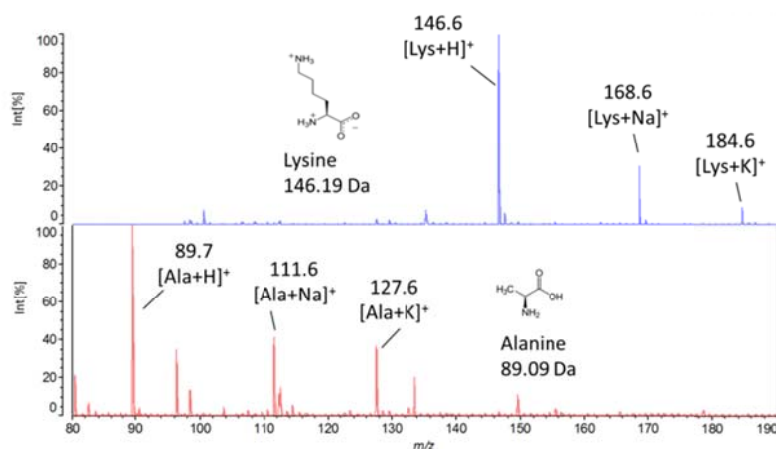
MS. Based on the cleavage reactions more information about the molecule structure could be received to verify the signal as the proposed fragrance.

LDI-MS with Gold Nanoparticles

Susanne Stephan, Duxin Li

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 tested.

A simple sample preparation technique spotting a layer of sample solution onto a dried layer of gold nanoparticles emerged to produce the best results. The ligand-free gold nanoparticles agglomerate faster than the ones stabilized with ligands like lipoic acid, but show the lowest background and result in the best mass spectra for most of the compounds.



▲ Fig. 1: AuNPs-LDI mass spectrum of the amino acids lysine and alanine.

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 the mycotoxins Aflatoxin B1 and Ochratoxin A and steroid structure 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.

Collaborative Project - Project Partner: Lehrstuhl für Technische Chemie I, Universität Duisburg-Essen, Prof.

Dr.-Ing. Stephan Barcikowski

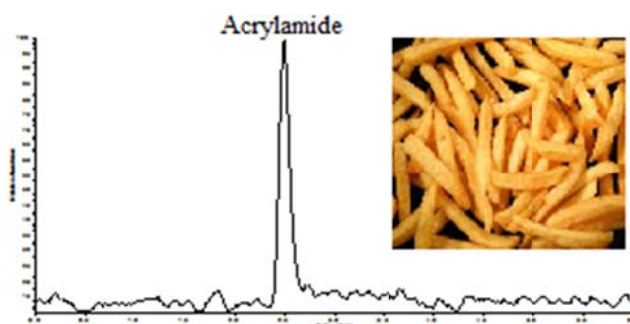
Funded by: Shimadzu/Kratos

Determination of acrylamide in Sudanese food by QuEChERS pretreatment method and high performance liquid chromatography coupled with LTQ Orbitrap mass spectrometry

Mei M. A. Omar, Abdalla A. Elbashir

Acrylamide is a heat-induced food contaminants naturally forms as a by-product of cooking process in carbohydrate-rich foods at high temperatures and low moist conditions. Maillard reaction of reducing sugars with asparagine at temperature higher than 120 °C is the most probable route to acrylamide formation during the browning process. Acrylamide is a neurotoxic compound identified as a probable human carcinogen (group 2A) and genotoxic.

In this work, a method based on modified Quick, Easy, Cheap Effective, Rugged and Safe (QuEChERS) sample preparation with aluminum oxide (Al_2O_3) as dispersive solid phase extraction (dSPE) material and high performance liquid chromatography-orbitrap-mass spectrometry (HPLC LTQ-Orbitrap MS) was established for determination of acrylamide contents in Sudanese food samples. The method involves two simple steps. First, the homogenized samples are extracted and partitioned using an organic solvent and salt solution. Then, the supernatant is further cleaned using a dSPE technique. Parameters affecting dSPE efficiency such as Al_2O_3 amount and contact time were optimized. The performance of two analytical columns namely Kinetex C18 and Rezex ROA-organic acid was compared for acrylamide separation. The performance of the method was validated in term of matrix effect, linear range (standard addition method), limit of detection (LOD), limit of quantification (LOQ), precision (repeatability) (RSD%) and accuracy (recovery). Good linearity ($r^2 > 0.9979$) was achieved using standard addition method in the concentration range 0 - 200 $\mu\text{g}/\text{kg}$. The LOD is in the range from 2.91 to 4.04 $\mu\text{g}/\text{kg}$ and 1.50 to 3.94 $\mu\text{g}/\text{kg}$ for C18 and ROA columns, respectively. The precision of the method was 7.3 and 5.6% for C18 and ROA columns, respectively. Recoveries of acrylamide ranging from 90 to 97%, ($n = 3$) were obtained when all target food samples were spiked at two concentration levels. The proposed Al_2O_3 -dSPE method was successfully applied to the analysis of acrylamide in real food samples and compared with a traditional primary secondary amine (PSA)-dSPE method. In conclusion, the modified QuEChERS method with Al_2O_3 cleanup step showed reliable method validation performances and good cleanup effects in this work.



▲ Fig.1: Chromatogram of acrylamide in fried potato.

Bachelor Theses accomplished 2014

Christian Lipok

Aufbau einer Plattform zur Herstellung von analytischen HPLC-Säulen, University of Duisburg-Essen

Simon Schade

Einsatz der DIP-APCI-IonTrap-MS zur Analyse von Nebenprodukten im Arzneimittel, University of Duisburg-Essen

Master Theses accomplished 2014

Surina Surina

Determination of Arsenic in water by Anodic Stripping Voltammetry using the scTRACE Gold Sensor

Amela Bronja

Entwicklung und Einsatz eines GC-APCI-Ionenfallen-MS, University of Duisburg-Essen

Satrugna Vinjarapu

Determination of arsenic species – A comparative study by voltammetry and high performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS), University of Duisburg-Essen

Cornelia Jakob

Development of a LC+LC-System for coupling to an IMS-qTOF-MS with an APCI- and ESI-Ion Source, University of Duisburg-Essen

Oliver Knoop

Establishment of a new gas chromatography-atmospheric pressure photoionization-orbitrap-mass spectrometer ion source, University of Duisburg-Essen

Anne Ackmann

Laser ablation inductively coupled plasma mass spectrometry for zinc analysis in breast cancer tissue and optimization of ablation process, University of Duisburg-Essen

Ph. D. Theses accomplished in 2014

Dr. Sonja Krieger

Entwicklung und Applikationen einer DIP-APCI Ionenquelle zur direkten Analyse mittels Q-TOF- und Ion Trap-Massenspektrometrie, Dissertation University of Wuppertal, 26th December 2014.

Dr. Jackelyn Aragon Gomez

Experimental Investigations on the Dissolved Gas Analysis Method (DGA) through Simulation of Electrical and Thermal Faults in Transformer Oil, Dissertation University of Duisburg-Essen, 27th June 2014

Dr. Eduard Deibel

Synthese und Anwendung neuer Ionisationsmarker für die APLI-(TOF)MS, Dissertation University of Duisburg-Essen, 6th June 2014

Dr. Dennis Klink

Optimierung der Laserionisation bei Atmosphärendruck und Aufbau einer SFC-APLI-Kopplung, Dissertation University of Wuppertal, 7th March 2014

Dr. Nils Wienand

Untersuchungen zum Abbau des nicht-fluorierten Netzmittels Oelylaminoethoxylat in Glanzchromelektrolyten, Dissertation University of Wuppertal, 6th March 2014

Accepted and/or published scientific publications 2014

Original Paper / Peer-reviewed

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**, accepted in Food Chemistry.

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 (DOI 10.1007/s00216-014-8179-8).

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 (DOI 10.1007/s00216-014-8090-3).

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 (DOI 10.1007/s00216-014-8057-4).

D. Li, R. Dück, O. J. Schmitz, **The Advantage of Mixed-Mode Separation in the First Dimension of Comprehensive Two-Dimensional Liquid-Chromatography**, J. Chromatogr. A (2014) 1358: 128-135.

S. Krieger, O.J. Schmitz **Non-destructive mass spectrometric plasticiser screening using a direct inlet probe-atmospheric pressure chemical ionization source and ion trap MS**. Rapid Commun. Mass Spectrom. (2014) 28: 1862-1870.

I. Hinderstmann, J. Hippler, Hirner AV, Mansfeldt T, **Mercury volatilization from a floodplain soil during a simulated flooding event**. Journal of Soils and Sediments (2014) 14: 1549-1558.

A. Abdalla. Elbashir, Mei M Ali Omar, Wan Aini Wan Ibrahim, Oliver J. Schmitz, and Hassan Y. Aboul-Enein **Acrylamide Analysis in Food by Liquid Chromatographic and Gas Chromatographic Methods**. Critical Reviews in Analytical Chemistry (2014) 44: 107-141.

Abdalla A. Elbashir, Sonja Krieger, Oliver J. Schmitz **Simultaneous Determination of Polyamines and Acetylpolyamines in human urine by Capillary Electrophoresis with Fluorescence Detection**. Electrophoresis (2014) 35: 570-576.

Book chapters

Stavros Kromidas Hrsg. **Der HPLC-Experte - Möglichkeiten und Grenzen der modernen HPLC**, (Chapter 1.1), Wiley-VCH (2014)

Non-peer reviewed

O. J. Schmitz, D. Li, **Exploring Chinese Medicine with 2D-LC**, The Analytical Scientist, April (2014) 42-43

Poster presentations

S. Horst, O. J. Schmitz, **Development of a DIP-APPI ion source**, analytica conference Munich, April 2014

C. Lenzen, O. J. Schmitz, **Comparison of original and repacked pharmaceuticals with DIP-APCI-MS**, analytica conference Munich, April 2014

Invited Lectures / Oral Presentations

Prof. O. Schmitz

Product control of Chinese herbal medicine by comprehensive two-dimensional chromatography and novel ion sources

Fesenius Lecture of the GDCh, University of Bremen, January 2014

Comprehensive two-dimensional Chromatography (GCxGC and LCxLC) for metabolom analysis

8th International Conference on Breath Research & Cancer Diagnosis, July 2014, Torun, Poland (invited speaker)

Tutorial: Photo- and chemical ionization in atmospheric pressure mass spectrometry

30th International Symposium on Chromatography, September 2014, Salzburg, Austria (invited speaker)

A novel ultra-sensitive GC-ion source for an Orbitrap-MS

7th Shanghai International Symposium on Analytical Chemistry in Shanghai, China, September 2014

Possible Quality control of modern and folk medicine

8th Analytical Anacon Conference in Hyderabad, India, November 2014

Dr. J. Hippler

Change of Zinc Homeostasis in Human Breast Carcinomas by Laser Ablation ICP-MS

analytica conference Munich, Munich, April 2014 (invited speaker)

Metall(oid) speciation in environmental matrices

Landesamt für Natur, Umwelt und Verbraucherschutz NRW (LANUV), October 2014

Toxicity of As and Hg and its determination and speciation (in german)

Lecture at Heinrich-Heine-University, Duesseldorf, November 2014

S. Krieger

DIP-APCI: Eine neue Ionenquelle zur direkten massenspektrometrischen Analyse

24th Doktorandenseminar, Hohenroda, January 2014

Miscellaneous

Conference organization

Oliver J. Schmitz, Chair of the session *Hyphenated Techniques in Modern Analytical Chemistry* of the analytica conference Munich in Munich, April 2nd 2014

Oliver J. Schmitz, Chairman (together with Prof. Jin-Ming Lin (Chinese Chemical Society and Tsinghua University) of the 7th Shanghai International Symposium on Analytical Chemistry in Shanghai, China, September 24-25th 2014

Oliver J. Schmitz, Chairman (together with Gautam Rajan (Indian Analytical Instruments Association) of the 8th analytica Anacon Conference in Hyderabad, India, November 6-7th 2014

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 commission for the Ernst Bayer price

Member of the scientific committee of HPLC 2015 in Beijing

Institute Colloquium

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

Prof. Dr. Pham Hung Viet, Director of the Research Centre for Environmental Technology and Sustainable Development (CETASD) Hanoi University of Science, Vietnam National University 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. Philip Marriott, Monash University, Australia, Multidimensional methods based on MDGC, GCxGC, MS, and olfactometry for assessing aromas and flavours, 3.02.2014

Prof. Dr. Bernd Spengler, University of Gießen, Hochauflösende bildgebende Massenspektrometrie von biologischem Gewebe, 20.01.2014

Prof. Dr. Ralf Zimmermann, University of Rostock, Abgase aus Schiffdieseln, Holzverbrennung und Co: Chemische Zusammensetzung und Gesundheitseffekte, 13.01.2014

Prof. Dr. Pham Hung Viet, VNU University of Science, Hanoi, Vietnam, Study on Mobilization of Arsenic during Deep Aquifer Exploitation at Nam Du – Hoang Mai – Hanoi, 7.04.2014

Prof. Dr. Pascal Boeckx, University of Gent, Application of isotopic analyses of aminosugar and fatty acid biomarkers: microbial residue turnover and sediment source apportionment, 29.04.2014

Prof. Dr. Eckhard Worch, TU Dresden, Geosorptionsprozesse im Wasserkreislauf: Mechanismen und Modellierungsansätze, 12.05.2014

Prof. Dr. Hartmut Herrmann, Leibniz-Institut für Troposphärenforschung Leipzig, Troposphärische Multiphasenchemie: Von physikochemischen Laboruntersuchungen zu Modellierung und Feldmessung, 2.06.2014

Dr. Andreas Peter, Kantonales Labor Zürich, Schweiz, Mikroverunreinigungen im Trinkwasser - der (unabhängige) Weg der Schweiz, 16.06.2014

Prof. Dr. Günter Gauglitz, U Tübingen, Optische Sensoren für Umwelt und Diagnostik, 30.06.2014

Dr. Dwight Stoll, Gustavus Adolphus College, USA, Mobile phase mismatch in two-dimensional liquid chromatography – Effects and practical solutions, 20.10.2014

Dr. Matthias Pursch, Dow Chemical, Qualitative and quantitative target analysis in complex matrices by multiple heart-cut 2D LC, 3.11.2014

Prof. Dr. Petra Dittrich, ETH Zürich, Mikrokammern und Mikrotropfen: Lab-on-Chip-Technologie in der Bioanalytik, 1.12.2014

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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