UNIVERSITÄT
DUISBURG
ESSEN

Open-Minded

2024

Jahresbericht

Annual Report

IAC Annual Report 2024

Project Reports:
Members of the IAC

Other Articles and Reports:
Gerrit Renner

Torsten C. Schmidt

Ursula Telgheder

Text Editing:
Gerrit Renner

Torsten C. Schmidt

Ursula Telgheder

Lydia Vaaßen

Layout:
Gerrit Renner

Content

Instrumental Analytical Chemistry

Dear friends and colleagues.

As every year, we are pleased to give you an overview of the IAC group activities of the previous year. In research, 2024 at IAC was dominated by a large number of collaborative project proposals. Foremost, our excellence cluster proposal REASONS, "River Ecosystems in the Anthropocene – Sustainable Scientific Solutions," was selected for a full proposal, giving us a chance for the first-ever cluster hosted at UDE. Thus, we have been extremely busy with the full proposal submitted in August and the preparation of the evaluation taking place in January 2025. Likewise, we were involved in the renewal proposal and on-site evaluation of the running CRC RESIST, "Multilevel response to stressor increase and release in stream ecosystems," and the new proposal and on-site evaluation of the research training group AMTEC-PRO, "Advanced Methods and Technologies for Proton Therapy" – both have been positively reviewed and finally endorsed by DFG in their November board meetings. So, we are looking forward to continuing and starting these two collaborative efforts in 2025. In addition, I am very happy that Amir Salemi got his proposal accepted by DFG, which will fund his work on passive sampling for the next two years.

We participated actively in several conferences and meetings in 2024, including the co-organization of the well-established 6th MWAS in Muelheim, together with colleagues from IWW Water Centre. We started the year with the established Hohenroda Ph.D. seminar, where Kjell Kochale achieved second place in the participants' voting for the best oral presentation on his work on comprehensive 2D LC for water monitoring. At the Water Chemistry meeting in May in Limburg, Dr. Lotta Hohrenk-Danzouma received an award for her outstanding Ph.D. thesis. Congratulations to both of them and all other IAC members who did a splendid job presenting our work at national and international conferences throughout the year. This includes the eight Ph.D. students at IAC who successfully defended their theses. Furthermore, twelve Master and four Bachelor students finished their thesis at our department or external partner institutes with a home supervisor at IAC and contributed to our successful work.

Again, we successfully communicated our research results with 31 papers published in international peer-reviewed journals. Many of these stem from collaborative efforts with colleagues, for which I am very grateful. An outstanding example was a critical review on perspectives of compound-specific isotope analysis published in *Nature Water in* early 2024, for which Maik Jochmann was responsible at IAC, but also many original papers involved colleagues from other groups and departments.

4

In 2024, we hosted two international students for internships: Martin David Alexandre Leclerc from the Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques in Toulouse and Merve Cakmakci from the Middle East Technical University (METU) in Ankara. Furthermore, of course, Prof. Sina Dobaradaran revisited us twice, and we look forward to his next stay in Essen.

Finally, in October 2024, I was re-elected unanimously as dean of the faculty of chemistry for another four years. I see this result as a sign of trust that the work in the past five years in that capacity has been perceived as successful.

I thank my fabulous team for their excellent work at IAC and all partners from academia, industry, and funding agencies for their great support and fruitful collaborations.

I hope you are interested in our IAC report and welcome very much feedback or collaboration interests for the future. I wish all of you the best and success in 2025, and I renew my hope for a more peaceful near future.

Group Members

Contact: Instrumental Analytical Chemistry
Faculty of Chemistry
University Duisburg-Essen
Universitätsstr. 5
45141 Essen

Phone: +49 201 183-6772/6774
Fax: +49 201 183-6773
email: torsten.schmidt@uni-due.de

www.uni-due.de/iac

Head of Chair

Prof. Dr. Torsten C. Schmidt

Secretarial Office

Lydia Vaaßen

Regular Staff

Dr. Anam Asghar	Advanced Oxidation Processes
Simone Bettinger	Laboratory engineer, Instrument, and Lab Supervision
Dr. Maik Jochmann	Stable Isotope Analysis, Sample Preparation, and Gas Chromatography
Dr. Klaus Kerpen	Advanced Oxidation Processes, PFAS Analysis, Laser Commissioner, IT Administrator
Dipl.- Ing. Robert Knierim	Laboratory Equipment, Glassware, Support of guest scientists
Dr. Gerrit Renner	Analytical Data Science, Project Administration
Dr. Amir Salemi	Samling & Sample preparation, Gas Chromatography
PD Dr. Ursula Telgheder	Ion Mobility Spectrometry, PFAS analysis, Atomic spectrometry, Expert advice for course of studies, Radiation Protection Commissioner
Claudia Ullrich	Laboratory Assistant, Safety Officer

Apprentices

Rebecca Steger

Research, Teaching, and Technical Assistants

Isabel Halbhuber

Alina Hofrath

Daniel Höhn

Robin Jung

Jan Niklas Oesterschlink

Janina M. Pytlik

Anna Mangels

Isabell Schelhorn

Leonardo Solazzo

Ph.D. Students (Internal)

Felix Drees	Data Processing in Non-Target Screening
Annika Gruhlke	Investigation of Isotopic Fractionation and Transformation Products of Oxidative Degradation of Phosphonates via LC-IRMS and LC-HRMS
Isabel Halbhuber	Methodenentwicklung zur Bestimmung des Fluor-Summenparameters in der PFAS-Analytik unter Einsatz von spektroskopischen und chromatographischen Verfahren
Michelle Hußock	Characterization of Nutrients, Pollutants, and Their Environmental Impacts in a Manure Recycling Process Using an Upflow Anaerobic Sludge Bed Reactor
Katharina Klein	Influence of organic matter on oxidative transformation processes
Shaista Khaliq	Diet-consumer interactions under variable stressor conditions as revealed by stable isotope studies of individual amino acids
Nerea Lorenzo Parodi	Aromatic amines as biomarkers in human urine: Analytical method development and epidemiological studies
Michael Leupold	Investigations of transformation reactions of antibiotics by photocatalysis in aqueous systems
Robert Marks	Coupling techniques in the field of isotope ratio mass spectrometry
Felix Niemann	Isotope fractionation associated with abiotic Imidacloprid degradation
Max Reuschenbach	Automated data processing and data analysis in high-resolution mass spectrometry
Sarah P. Rockel	Development and evaluation of a 2D-LC-IRMS coupling for the use of conventional reversed-phase chromatography in component-specific stable isotope analysis
Lucie K. Tintrop	Automated and miniaturized sample preparation in gas chromatographic analysis

Duaà Tahboub	Studies on electrochemical treatment processes for the decomposition of Persist Organic Pollutants (POPs) in contaminated ground and surface water
Kaliyani Wickneswaran	Development & Optimization of GC-MS/MS and GC-IRMS methods for Fatty Acid Profiling & Food Webs

Ph.D. Students (External)

Reyhaneh Armin	Non-target analysis of organic micropollutants in industrial wastewater
Alexander Augustini	Chemical characterization of the ingredients of electronic cigarettes and the inhaled products.
Indra Bartels	Analysis of suggested SARS-Cov-2 treatment pharmaceuticals in surface waters
Nico Bätz	Effect-directed identification and reduction of diffuse immissions in rivers
Sandro Castronovo	Examination of micropollutant degradation in biological wastewater treatment: a proteomics approach
Joanna Flottmann	Analysis of highly polar trace substances in water with LC-HRMS(/MS)
Matin Funck	Development of a Sampling-Procedure allowing subsequent qualitative and quantitative Pyrolysis-GC/MS analysis for Subµ-Plastics in the Aquatic Environment
Annika Fechner	Kopplung eines miniaturisierten Thermodesorptionschips und einer µ-Plasma-Ionisierungsquelle zur Analyse flüssiger Proben mittels Ionenmobilitätsspektrometrie
Jana Hinz	Development and application of multidimensional GC-IMS methods for the analysis of volatile and semivolatile substances in safety and health research
Susann Holst	Development of procedure tests for hot and cold coils considering the optimization of transport logistics of slabs
Malte Hübschen	Automated sample preparation and gas chromatographic analysis in the field of food and consumer goods
Frank Jacobs	Development of an automated microextraction technique

Michelle Klein	Effect-directed analysis for monitoring and evaluation of surface and wastewater
Kjell Kochale	Automated hyphenation of effect-based and instrumental analysis
Sara Schäfer	Oxidative transformation of organic compounds in ultrapure water by ozonation and UV photolysis
Hannah Schanzmann	Schnelle, nicht-invasive Identifikation nosokomialer Infektionen
Fabian Ude	Non-radioactive, energetically variable ionization unit for pollutant analysis in building materials based on FAIMS technology
Mike Wenzel	Determination of microplastics in soils and mosses
Modestus Wigger	Methoden der digitalen Sensorik von Lebensmitteln basierend auf der Ionenmobilitätsspektrometrie

Guest Scientists

Prof. Sina Dobaradaran

Long-term visiting scientist

Bushehr University of Medical Sciences, Iran

A comprehensive study on environmental emissions of primary aromatic amines by cigarette butts and compare with unsmoked cigarette levels.

Study of the kinetics of aromatic amines releases from cigarette butts into the water environments.

Determining the acute toxicity of CBs leachates for aquatic organisms (my next project)

Prof. Dr. Maryam Vosough

Long-term visiting scientist

Chemistry and Chemical Engineering Research Center of Iran (CCERCI)

Department of Clean Technologies, Chemometrics laboratory

Development of chemometrics-based approaches for Non-Target analysis of micropollutants in water environment using LC-HRMS/MS

One clear challenge with high-resolution mass spectrometric-based instruments is the generation of massive quantities of data ("big analytical data") and their pre-processing and processing steps. So, developing post-acquisition data handling tools is increasingly critical for reliable non-targeted analysis workflows. In particular, this is the case for non-targeted environmental data, as the goal is to track and identify trace quantities of organic micropollutants and their transformation products in the presence of strong matrix effects and generally in a more extensive chemical space than metabolomics study. Chemometrics, a powerful interdisciplinary field that uses mathematical, statistical, and machine learning tools to analyze high-dimensional and complex chemical information, can be appropriately incorporated in different environmental non-targeted analysis workflow stages.

Martin David Alexandre Leclerc

Student Internship (May 8, 2024 to Sep 4, 2024)

Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques, Toulouse, France

Internship Tutor: Anam Asghar, Michael Leupold

Analytical method development for trace component analysis in highly alkaline water and photocatalytic degradation of antibiotics

Merve Çakmakci

Student Internship (Erasmus+)

Middle East Technical University, Ankara, Turkey

Internship Tutor: Amir Salemi

Developing an SPME Arrow GC-MS method for the determination of nicotine biomarkers in raw sewage

IAC News

## IAC organizes upcoming ExTech 2025

We are delighted to welcome ExTech back to Germany! We have made significant strides in preparing for the 27th International Symposium on Advances in Extraction Technologies (ExTech 2025) throughout 2024. We successfully launched the official website at www.extech2025.com and initiated the abstract submission phase supported by our partners from DGM-Inventum. In addition, we have engaged in numerous discussions with potential keynote speakers and exhibitors to ensure a diverse and exciting conference program.

ExTech 2025 is set to take place from September 8 to 11, 2025, in Mülheim an der Ruhr. The symposium will serve as an outstanding platform to showcase the latest developments in sampling and sample preparation, innovative materials and technologies, miniaturization, automation, and robotics—with a particular focus on the analysis of microplastics and PFAS. We look forward to welcoming you all to Mülheim an der Ruhr as we come together to shape the future of analytical chemistry!

Upgrading GC-MS to TED-GC-MS for Advanced Analysis
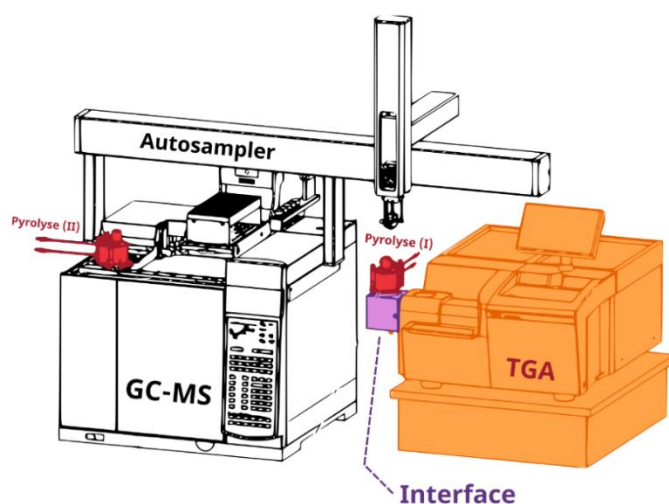
We successfully participated in the MKW funding program, securing support from the Zukunftsvertrag "Studium und Lehre stärken" for facility optimization and technical infrastructure investments. We have enhanced our GC-MS system with these funds by integrating Thermal Extraction-Desorption (TED) and Pyrolysis capabilities.

Scheduled for operation in Spring 2025, this upgraded system will soon be a pivotal resource for master's student research internships. The advanced functionalities of the TED-GC-MS setup are designed to address complex analytical challenges, such as the precise detection and characterization of microplastics and PFAS in environmental samples. We are already in the concrete planning stage for a master's thesis to use this technology to investigate microplastics.

Awards & Honors

Student Award Analytical Chemistry (GDCh)

Alina Hofrath
Awarded for the best performance in the Bachelor's program.

Award of the Faculty of Chemistry

Alina Hofrath
Awarded for the best performance in the Bachelor's program.

Young Scientist Award – Best Poster

Felix Niemann
Awarded for the best poster presentation at the annual symposium of the Benelux Association of Stable Isotope Scientists (BASIS)

1ˢᵗ Feralco Award – Best Master Thesis

Annika Gruhlke

Awarded for the best master's thesis in Water Science. Annika finished her master's thesis in 2024. The title of the work is *Isotope Analysis of Nitrogenous Model Substances – Investigation of Wet Persulfate Oxidation in the Interface of the HPLC-Isotope Ratio Mass Spectrometer*

1ˢᵗ Feralco Award – Best Master Thesis

Kaliyani Wickneswaran

Awarded for the best master's thesis in Water Science. Kaliyani finished her master's thesis in 2024. The title of the work is *Two-dimensional analysis of nitrosamines in aqueous matrices by GC-IMS*

Best Poster Award

Isabel Halbhuber

Awarded for the best poster presentation at the sixth Mülheimer Wasseranalytisches Seminar (MWAS 2024).

Promotionspreis Wasserchemie der Wasserchemischen Gesellschaft
funded by Walter-Kölle-Stiftung

Dr. Lotta Hohrenk-Danzouma

Awarded for the best Ph. D. Thesis. Lotta finished her thesis in 2022. The title of the work is *Data processing strategies for LC-HRMS based non-target analysis of organic micropollutants in aqueous matrices*

https://doi.org/10.17185/duepublico/77351

1st Poster Award

Sasho Joksimoski

Awarded for the best Poster at Jahrestagung der Wasserchemischen Gesellschaft, Limburg 2024. The title of the work is *Advanced remediation in the presence of ferrous iron and carbonate-containing water by oxygen-induced oxidation of organic contaminants*

The Power List 2024, Planet Protectors
by The Analytical Scientist

Prof. Dr. Torsten C. Schmidt

We proudly announce that Professor Torsten C. Schmidt, our Head of Instrumental Analytical Chemistry, has been recognized in The Analytical Scientist's 2024 Powerlist. He is honored among the "Planet Protectors," a category celebrating individuals making significant contributions to environmental sustainability through analytical science.

This recognition underscores Professor Schmidt's commitment to advancing research that safeguards our planet. More information can be found at:

https://theanalyticalscientist.com/power-list/2024.

The addition to the latest Powerlist has been followed by a two-part interview with James Strachan on his work in environmental analysis published in The Analytical Scientist and can be found here:

Part 1: https://theanalyticalscientist.com/fields-applications/charting-the-contaminant-iceberg-part-one

Part 2: https://theanalyticalscientist.com/fields-applications/charting-the-contaminant-iceberg-part-two

Running Projects

Overview

Photocatalysis of the β-lactam antibiotic amoxicillin and clavulanic acid for the prevention of the spread of antibiotic resistances: Kinetics, matrix effects, and transformation processes

Involved staff: Michael Leupold, Isabell Schelhorn, Anam Asghar, Torsten C. Schmidt
Partners: Lukas Fischer
Funding: Zentrum für Wasser- und Umweltforschung, Stiftung Zukunft NRW

The research project aims to remove antibiotics and antibiotic resistance genes in hospital wastewater by photocatalysis to counteract the global contamination of the environment and the associated loss of efficacy of antibiotic agents. In urban areas, antibiotics and resistance genes enter the environment through wastewater. Since wastewater treatment plants are not optimized to remove pharmaceuticals or resistance genes. Resistance genes in the environment threaten human health, as they can travel from there back to the population [1]. If nothing is done, antibiotics will soon become ineffective in combating infectious diseases, which is predicted to lead to 10 million annual deaths worldwide by the middle of this century [2]. One solution strategy is to treat wastewater using photocatalysis [3]. Whether universal antibiotics and antibiotic-resistance genes can be removed in complex matrices is unclear. Nevertheless, photocatalysis is promising because, compared to other treatment methods, it can be expected to produce high yields of reactive oxygen species that can effectively degrade pharmaceuticals.

To test photocatalysis, a photocatalytic reactor was developed that (a) enables selective investigation of photocatalysis without the influence of photolysis using chemical UV filters (e.g., potassium hydrogen phthalate, nitrate, or nitrite). The experimental setup is shown in Figure 1.
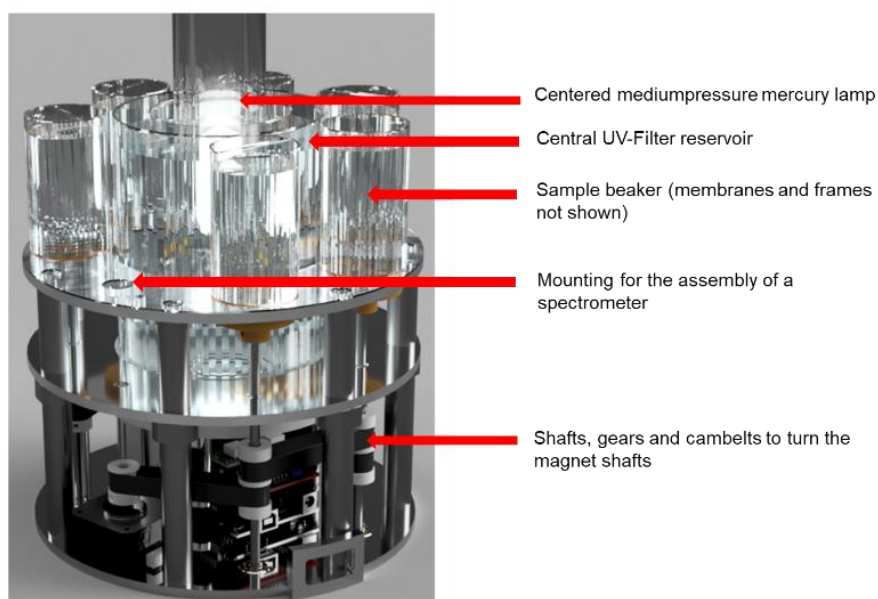
Figure 1: Rendered 3D model of the photocatalysis setup.

This also enables testing excited photocatalysts in the visible wavelength range using powerful mercury vapor discharge lamps. (b) Testing immobilized photocatalysis with simultaneous mixing using membrane mounts. Mixing is achieved using a stepper motor and magnets rotated at the bottom of the sample vessels.

In applying photocatalysis in the environment, the water matrix plays a significant role, as it covers the immobilized photocatalytic material, prevents the formation of reactive oxygen species, and absorbs the wavelength range required for the photocatalytic process. With this in mind, an artificial environmental matrix was simulated using natural organic matter (NOM) from the Suwannee River. It was shown that the application of titanium dioxide bound to a polyethersulfone membrane has a negative effect on the photocatalytic process due to absorbing effects in the relevant excitation ranges of titanium dioxide. Comparative measurements with titanium dioxide in a suspension show that the degradation process is faster and that the NOM matrix positively affects the degradation process.

In the future, different photocatalysts will be compared to predict which are suitable for a wastewater application.

References:

[1] K. Westphal-Settele, S. Konradi, F. Balzer, J. Schönfeld, R. Schmithausen, Die Umwelt als Reservoir für Antibiotikaresistenzen, Bundesgesundheitsblatt - Gesundheitsforschung - Gesundheitsschutz 61(5) (2018) 533-542.

[2] J. O'Neill, Tackling drug-resistant infections globally: final report and recommendations, 2016.

[3] Y. Nosaka, A.Y. Nosaka, Generation and Detection of Reactive Oxygen Species in Photocatalysis, Chemical Reviews 117(17) (2017) 11302-11336.

Development and evaluation of a 2D-LC-IRMS coupling for the utilization of conventional reversed-phase chromatography in component-specific stable isotope analysis

Compound-specific stable isotope analysis (CSIA) is a powerful analytical technique with broad applicability across various fields, including evaluating sources and transformation processes of micropollutants and verifying food authenticity. In particular, coupling liquid chromatography (LC) with an isotope ratio mass spectrometer (IRMS) enables the determination of the stable carbon isotope signature of analytes in water samples. However, implementing LC-IRMS is constrained by several limitations inherent to the method.

One significant challenge arises from the wet chemical oxidation of carbon in the LC-IRMS interface. This process transforms All oxidizable carbon into carbon dioxide (CO_2). Consequently, using organic substances as eluents, buffers, or modifiers leads to inaccuracies in determining the carbon isotope signatures of analytes and must, therefore, be avoided. This requirement restricts established chromatographic methods, as over 90% of applied LC methods rely on organic eluents. To adhere to these limitations, only inorganic buffers and temperature modulation can be employed for method development, rendering the process both challenging and time-consuming—especially for complex sample matrices.

A promising solution to overcome these limitations is the integration of two-dimensional liquid chromatography (2D-LC) with LC-IRMS. Conventional 2D-LC systems employ two chromatographic columns with different separation mechanisms, significantly increasing peak capacity and enabling the separation of coeluting compounds that cannot be resolved in a single dimension. Adapting this system for LC-IRMS allows the utilization of existing LC methods from the literature, including those employing organic additives in the first dimension.

This approach transfers analytes of interest via heart-cut modulation—using a sample loop—onto the second chromatographic dimension (see Figure 1). Here, organic solvents are effectively separated from the analytes before oxidation, preserving the integrity of the isotope signature. This adaptation overcomes the restrictions of organic solvent use and simplifies method development, enhancing the feasibility of analyzing complex samples.
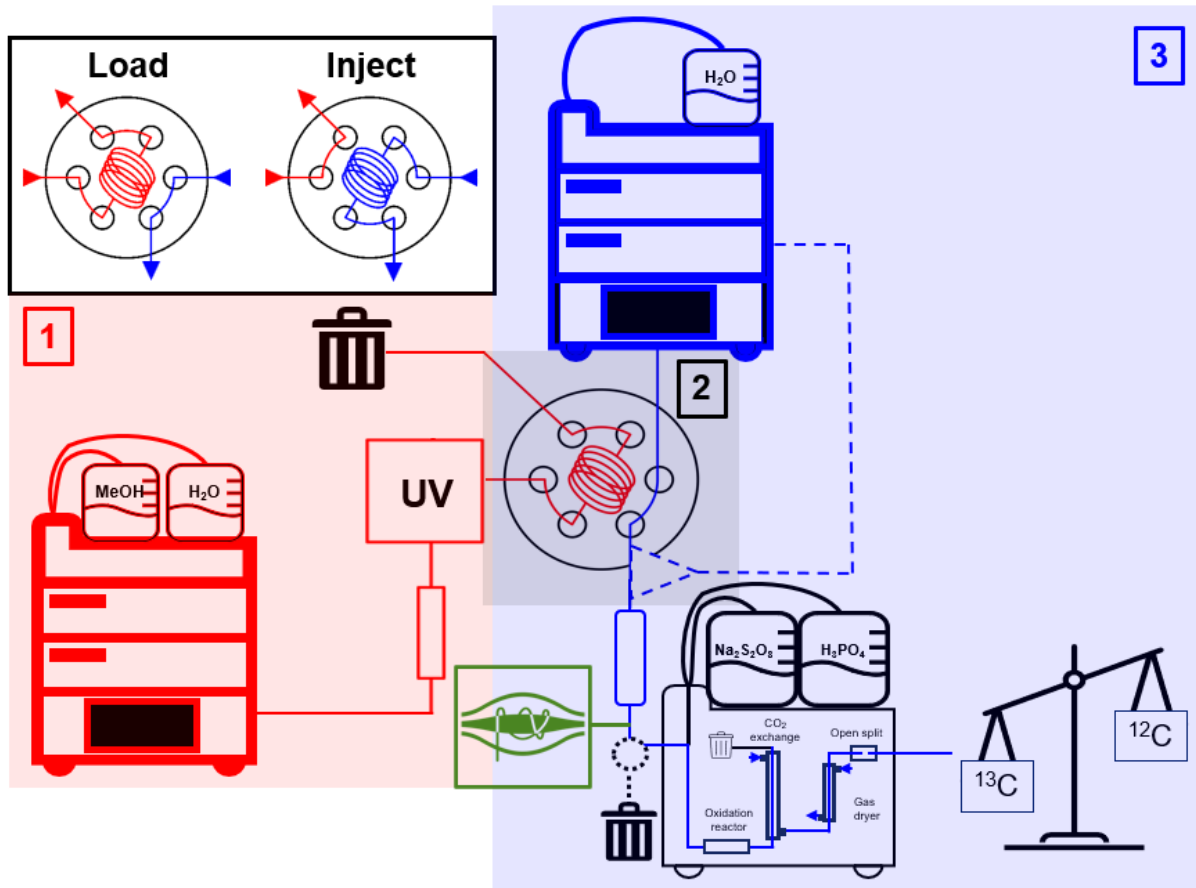
Figure 1: Schematic overview of the experimental setup. (1) 1stD (HPLC System with UV-Detector), (2) Heart cut modulator in a sample loop configuration with optional at-column-dilution (blue dashed lines), the load and inject position are shown in the black box, (3) 2ndD (HPLC system coupled to IRMS-HRMS, with optional additional switching valve after 2ndD column (black dashed line)).

For the first time, this study establishes the coupling of two-dimensional liquid chromatography (2D-LC) with LC-IRMS to address the traditional limitations of aqueous LC-IRMS methods. The development and implementation of the 2D-LC-IRMS system are described, showcasing how this approach expands the analytical capabilities of CSIA. The system's ability to handle complex sample matrices and resolve analyte coelution challenges demonstrates its potential as a transformative tool in stable isotope analysis. Looking forward, the enhanced capabilities of the 2D-LC-IRMS system suggest significant opportunities to broaden the scope of CSIA. By addressing existing analytical challenges, this advancement paves the way for applications in diverse fields requiring precise isotopic measurements, offering a glimpse into the future possibilities of isotope analysis.

Diet-consumer interactions under variable stressor conditions as revealed by stable isotope studies of individual amino acids (A13: CRC RESIST)

Involved staff: Shaista Khaliq, Maik A. Jochmann, Torsten C. Schmidt

Partners: University of Duisburg-Essen, Ruhr-Universität Bochum, Leibniz Institute of Freshwater Ecology and Inland Fisheries, University of Cologne, Kiel University, University of Koblenz-Landau and Helmholtz Centre for Environmental Research

Throughout 2024, the project focused on further developing methods for stable isotope analysis, particularly concerning amino acids in aquatic systems. The review paper "Stable Isotope Analysis of Amino Acids in Aquatic Systems – Problems, Challenges, Solutions: A Review" was accepted by Trends in Analytical Chemistry. A manuscript titled "Trophic Dynamics and Metabolic Pathways in Host-Parasite Interactions: A Nitrogen Isotope Analysis of Amino Acids in Multiple Tissues" was submitted. At the same time, an article entitled "The Asymmetric Response Concept: Solving the Puzzle of Ecosystem Recovery" was co-authored and published in Frontiers for Young Minds. In addition to these publication activities, the project maintained active participation in academic events, including attendance at the monthly RESIST doctoral seminar, the CRC colloquium, and the annual CRC conference, where research findings were presented. A significant highlight was a three-week research stay at the Helmholtz Centre for Environmental Research – UFZ in Leipzig within the Department of Technical Biogeochemistry, which provided more profound insights and enhanced interdisciplinary collaborations. Extensive laboratory work was conducted, with compound-specific isotope analysis (CSIA) of amino acids in both standards and biological samples performed using established GC-IRMS methods. The generated data were integrated into ongoing research projects, contributing to a robust dataset for future publications. Overall, 2024 was characterized by productive advancements in stable isotope analysis, substantial contributions to scholarly publications, and the establishment of valuable interdisciplinary collaborations that lay a solid foundation for future research initiatives.

Inhibitory and stimulatory role of dissolved organic matter in advanced oxidative processes

Involved staff: Anam Asghar, Torsten C. Schmidt
Partners: -
Funding: internal

The degradation of organic micropollutants (OMPs) by advanced oxidation processes (AOPs) poses a significant challenge due to the complexity and diversity of water matrices. Water matrix constituents, mainly dissolved organic matter (DOM), impact their effectiveness. DOM is a complex mixture of heterogeneous compounds with a continuum of functional groups and molecular sizes. The reactivities and concentrations of such functional groups determine the extent of the NOM-oxidant interactions and, thus, simultaneously induce promoting and inhibiting effects. Therefore, during the application of AOPs, DOM can block light penetration, scavenge radicals/oxidants, and enhance the formation and reactivity of valuable reactive oxidative species to eliminate OMPs and alter the transformation pathways. Therefore, the research needs to advance the structural and practical understanding of how DOM can be exploited to enhance the synergistic properties and effects of DOM and improve the performance of oxidative processes.

To develop a comprehensive understanding of DOM's multiple roles in applying AOPs, looking at the underlying mechanisms, probably by choosing appropriate surrogates or model DOM/NOM model compounds of different sizes and functional groups and investigating their role in oxidative processes, is necessary. Therefore, this project aims to pitch the idea of using different NOM/DOM model compounds with different molecular sizes and functional groups to understand the mechanisms governing DOM's synergistic and/or inhibitory properties in AOPs.

Natural Water to Hydrogen- Understanding the dynamics of active sites in electro-catalytic hydrogen production from unpurified water

Involved Staff: Anam Asghar, Torsten C. Schmidt

Partners: Prof. Dr. Corina Andronescu, Prof. Dr. Katrin Domke, Jun.-Prof. Dr. Kai Exner, Jun.-Prof. Dr. Anzhela Galstyan, Prof. Dr. Stephan Schulz, Prof. Dr. Mathias Ulbricht, Prof. Dr. Harry Hoster, Prof. Dr.-Ing. Stefan Panglisch, Prof. Dr. Christof Schulz, Prof. Dr. Ing. Doris Segets, Prof. Dr. Richard Kramer Campen

The "Natural Water to Hydrogen" research profile is an initiative undertaken by the University of Duisburg Essen (UDE). Its primary goal is to enhance the sustainability of hydrogen (H_2) production through water electrolysis. This is achieved by establishing a platform for gaining fundamental insights into the processes occurring at electrodes and membranes within aqueous environments. This understanding will allow us to determine the precise water quality requirements for electrolysis, which can vary depending on the catalyst and membrane used. This will be achieved through comprehensive efforts that draw upon expertise from water research, electrocatalysis, and membrane technology.

The IAC project aims to collaborate with involved groups to understand the impact of water quality parameters on the performance of the electrolysis process and the membrane and catalyst activity. However, analyzing them will be challenging due to the high alkalinity of water samples. Therefore, we will focus on developing analytical techniques to analyze the water quality parameters, which include cations (Na^+, Ca^{2+}, Mg^{2+}), anions (Cl^-, SO_4^{2-}, and NO_3^-, HCO_3^-/CO_3^{2-}), and dissolved organic matter (DOM) in concentration typically present in drinking water samples. Additionally, the project scope will be extended to perform downstream water analysis and evaluate the overall process performance regarding catalyst leaching and inactivation of the membrane.

Unraveling Non-Target Screening Variability: A Deep Dive into Chemical Process Characterization

Involved staff: Felix Drees, Gerrit Renner, Maryam Vosough, Torsten C. Schmidt
Partners: -
Funding: internal

Non-target screening (NTS) aims to identify a wide range of chemical compounds without prior selection, providing a more comprehensive understanding of chemical compositions, including unknown pollutants. However, instrumental limitations, particularly chromatographic separation, restrict the analytical scope. C_{18} columns are commonly used but primarily capture non-polar substances, leaving many polar compounds undetected. This is problematic, as polar compounds are often highly mobile in aquatic environments and increasingly relevant for regulatory monitoring.

Hydrophilic interaction liquid chromatography (HILIC) has been explored as a complementary approach to C_{18} but presents challenges such as stability issues, solubility limitations, and strong dependencies on pH and salinity. Additionally, HILIC favors polar compounds while discriminating against non-polar ones, necessitating dual-column strategies to achieve broad chemical coverage. Although two-dimensional chromatography and column-switching techniques address this issue, they introduce significant instrumental complexity and complicate data interpretation.

As a potential solution, mixed-mode (MM) chromatography offers the simultaneous separation of polar and non-polar substances in a single analytical run, avoiding solubility-related issues. MM chromatography has been successfully applied to surface and wastewater treatment plant effluent samples, demonstrating sufficient matrix robustness. However, industrial wastewater, particularly influent samples, presents a unique challenge due to its highly complex and dynamic composition. Our work aims to further investigate the applicability of MM chromatography in NTS through an extended analysis of industrial wastewater, addressing the current research gap and evaluating its suitability for complex environmental samples.

The industrial wastewater samples were analyzed using C18 and MM chromatography and high-resolution mass spectrometry (Orbitrap). The subsequent non-target screening was performed using MZmine 4.5.0, complemented by our department's proprietary, user-parameter-free approach, qAlgorithm, to assess data quality.

To evaluate the quality of detected features, we compared their Data Quality Scores (DQS) across both chromatographic approaches. Given that data quality can be influenced by chromatographic conditions and coelution—where information-dense regions may lead to a reduction in signal quality—the DQS of each feature is depicted in Figure 1 as a function of its retention time.
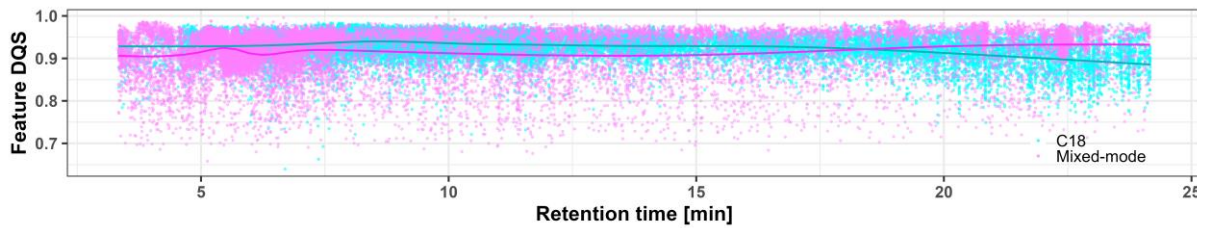
Figure 1: Data Quality Score (DQS) of extracted features as a function of their retention time (dots). Features detected using the C_{18} stationary phase are shown in light blue, while those from the MM phase are displayed in pink. A solid line represents the corresponding weighted mean for each approach.

The figure shows that we obtained sufficiently good and comparable data quality under both chromatographic conditions. Throughout nearly the entire chromatographic range, the feature quality, averaged using the qAlgorithm, remains above 0.9, meeting the quality standards required by the algorithm. Only minor differences in data quality become apparent when examining the distribution of features with a DQS <0.9, primarily found within the first 15 minutes of the C_{18} phase. After this time, this pattern reverses, and features with a DQS <0.9 are predominantly associated with MM chromatography.

In addition to assessing data quality, this study uses statistical and multivariate analyses to evaluate data differences. A portion of the wastewater was treated using an advanced oxidation process (AOP), and the qualitative assessment of this process's efficiency is exemplified in Figure 2.
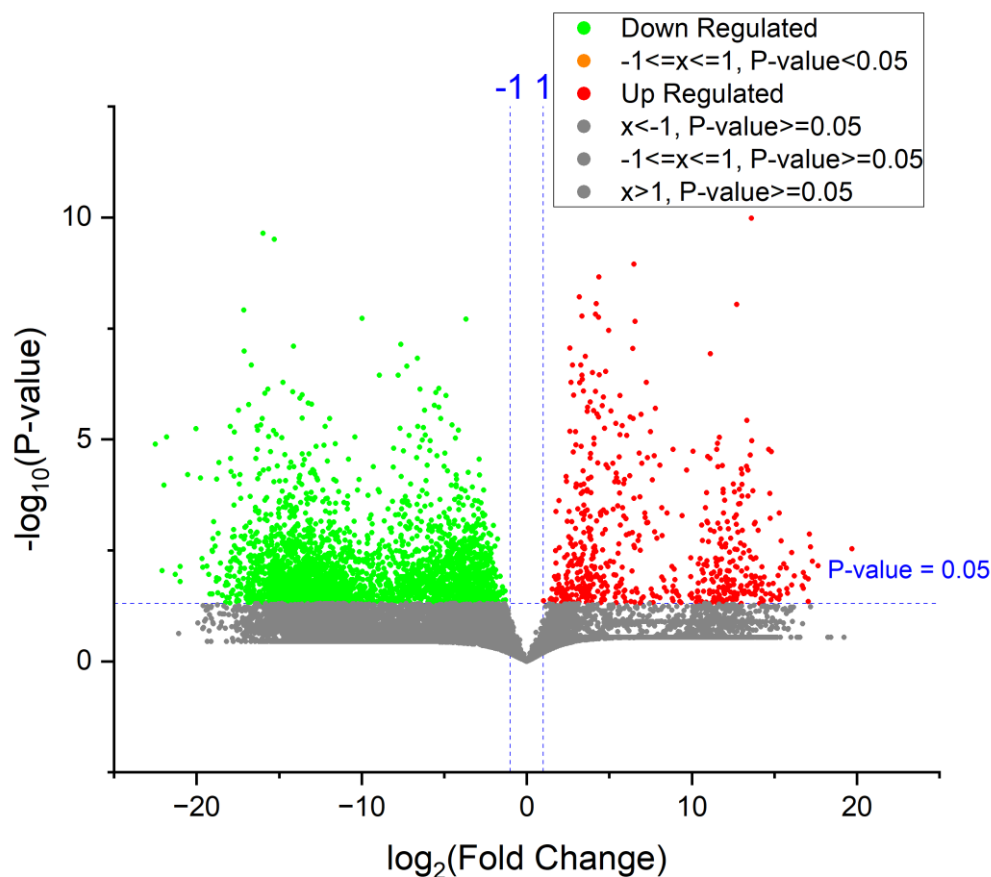
Figure 2: *Volcano plot representing differential feature distribution. The volcano plot illustrates the distribution of detected features based on statistical significance and fold change. The x-axis represents the $\log_2$ fold-change, indicating the magnitude of differences between two conditions, while the y-axis shows the $-\log_{10}(p\text{-value})$, reflecting statistical significance. Features with significantly increased abundance in one condition appear on the* right (red), *while those with decreased abundance are on the left* (green). *The dashed horizontal line denotes the significance threshold. Non-significant features are displayed in gray.*

The analysis reveals that most detected features undergo a significant reduction throughout the process, indicating a high overall efficiency in removing compounds. This suggests that the applied treatment effectively degrades or eliminates most of the original substances present in the sample. However, a small fraction of transformation products emerge, highlighting the occurrence of secondary reactions leading to the formation of new compounds. These transformation products likely result from the partial breakdown of parent substances, reflecting the complex reaction pathways involved. Notably, only a negligible portion of features remains unaffected, indicating that the process is highly effective, with only a minimal subset of compounds exhibiting resistance to degradation.

Development of a pipe reactor system controlled by on-site TOF detection for the remediation of PFAS-containing fire extinguishing water using perfluoroAd precipitation (TOFfloc)

Involved staff: Klaus Kerpen, Simone Bettinger, Ursula Telgheder
Partners: Cornelsen Umwelttechnologie GmbH
Funding: Federal Ministry for Economic Affairs and Climate Protection (BMWK) by the Central Innovation Programme for SMEs (ZIM)

Due to their outstanding properties, such as water, grease, dirt repellency, and chemical and thermal stability, perfluoroalkylated and polyfluoroalkylated substances (PFAS) are particularly interesting to the industry. With single substance analysis such as the LC-MS/MS technique, only a fraction of the existing PFAS can be detected, and many PFAS remain undetected. Determining the sum parameter of organic fluorine is a possible way out. A sum parameter method that reflects the proportion of total organic fluorine compounds (TOF) is desirable. Spectrometric analysis after converting the organic fluorine compounds into hydrogen fluoride represents a promising approach. In the method presented here, the organic fluorine compounds sorbed on solid phase material are converted thermally and quantitatively into HF and then detected spectroscopically. To optimize the thermal conversion of PFAS into HF, the combustion of selected PFAS compounds was investigated at different temperatures and experimental conditions. The results showed that combustion is strongly temperature-dependent, with the optimum temperature range for complete and reliable decomposition being between 900 and 1000 °C.

Before the thermo-module can be coupled with the He plasma, whether a significant emission intensity of known fluorine (I) lines can be observed with the chosen experimental setup must be determined. For this purpose, hexafluoroisopropanol was analyzed and compared with literature data as a model substance. [1].
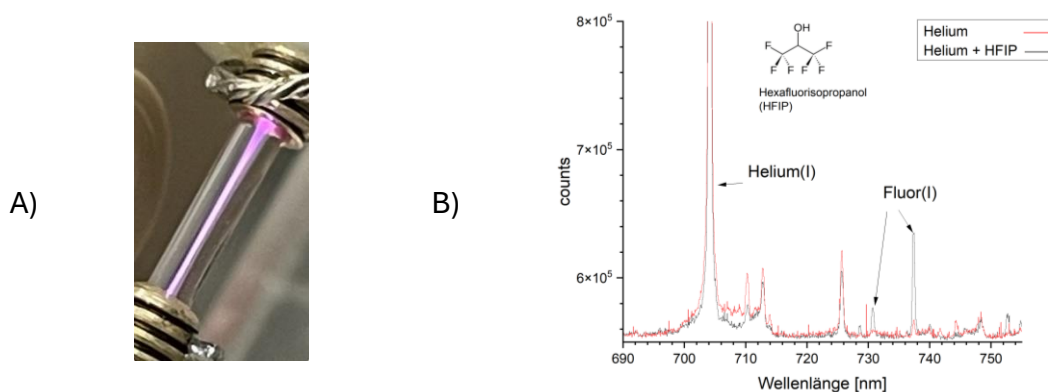

Figure 1: A) Dielectric barrier discharge was ignited in a glass tube with helium. B) Emission spectrum of pure helium (red spectrum) and helium with 1 µL of injected hexafluoroisopropanol (black spectrum) in the spectral range of 690–760 nm.

After injecting approximately 1 µL of hexafluoroisopropanol into the helium plasma via a T-piece (Figure 1A), the spectrum (Figure 1B) shows a decrease in the helium emission line at 704 nm, along with the formation of two new emissions at 733 nm and 739 nm. By comparing these with literature data [2], they can be attributed to fluorine lines. Thus, the intended spectroscopic analysis of HF should also be feasible. By coupling the helium plasma with the thermo-module and enrichment on a suitable solid-phase material, lower detection limits are expected for total fluorine determination. The necessary near-complete decomposition of PFAS into HF is intended to occur in the thermo-module rather than the helium plasma.

[1]   Watanabe, N.; Buscher, W.; Böhm, G., Atmospheric Pressure Barrier Discharge Helium Plasma for Halogen Determination with Optical Emission. *Analytical Sciences/Supplements* **2001**, *17*, i971-i973

[2]   Watanabe, N., Buscher, W., Böhm, G., Determination of Fluorine, Chlorine, Bromine and Iodine by Barrier Discharge Radiofrequency Helium Plasma. *Analytical Sciences* **2002**, *18* (11), 1191-1194.

Development and characterization of a regenerable absorber for the removal of long- and short-chain PFAS in contaminated water (FluorSorb)

Involved staff: Klaus Kerpen, Simone Bettinger, Ursula Telgheder
Partners: InstrAction GmbH
Funding: Federal Ministry for Economic Affairs and Climate Protection (BMWK) by the Central Innovation Programme for SMEs (ZIM)

The project aims to develop a regenerative absorber that removes PFAS from water. In addition to efficiency, the focus is also on sustainable use and, thus, the most frequent possible regeneration of the absorber. The absorber's composition and structure are selected to guarantee the complete removal of PFAS and the substitute substances. In contrast to conventional absorbents, these are designed not to be directly disposed of (incineration) but can be regenerated as often as possible. This means that the absorber can be used several times. An analysis method is being developed to monitor the regeneration cycles of the absorber, and the organic fluorine compounds can be determined as a sum parameter (total fluorine content).

One focus of the analytical work is developing an enrichment method based on solid phase extraction (SPE), with which short-chain PFAS can also be concentrated and detected in the ultra-trace range. The inorganic fluoride is first quantitatively separated from the organic fluorine compounds (PFAS) in this enrichment method. Suitable solid phases are selected for the enrichment of the analytes, and the experimental parameters such as type and volume of the eluent, sample volume, enrichment, and

extraction time are determined. The experimental parameters (suitable separation and delay column, mobile phase, flow rate, parameters for multiple reaction monitoring (MRM)) for the LC-MS/MS method are to be determined using high-resolution mass spectrometry (HR-MS). The influence of typical matrix components (inorganic salts, humic substances, industrial wastewater components) will be investigated using the standard addition method. Analytical performance parameters such as enrichment factor, detection and quantification limit, repeatability, and recovery rate are determined.

In addition to the conventional examination of the individual process steps in absorber production, the structures and inhomogeneities of the regenerable absorbers on the surface and cross-section will be investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX).

Development of a new method for the determination of N-nitrosamines in the air at the workplace in the context of occupational safety - NNOccSafe

Involved staff: Jana Hinz, Ursula Telgheder
Partners: Bonn-Rhein-Sieg University of Applied Sciences
Funding: German Social Accident Insurance (DGUV) Project Grant: FF-FP 0461

The 2024 yearly report, continuing from the previous account, revolves around the newest results obtained within the framework of the NNOccSafe Project, funded by the German Social Accident Insurance (DGUV). The overall aim of the work is to develop a method for the analysis of nitrosamines in matrices relevant to consumer and occupational safety based on the coupling of gas chromatography (GC) and ion mobility spectrometry (IMS), that matches or supersedes the current state of the art regarding sensitivity, selectivity, economy, and ease of operation. The focus in 2024 was the evaluation of thermal desorption (TD) techniques and connected filters for an artifact-free sampling of nitrosamines in air. Furthermore, a method for sensitively analyzing nitrosamines in water matrices using a two-fold enrichment strategy was developed and evaluated.

Calculated breakthrough volumes presented in the previous report could not be confirmed by determining them using sequentially connected TD tubes. Instead, the lead substance NDMA showed a much higher experimentally determined breakthrough volume of 240 L/g Tenax TA 80/100 mesh sorbent. As a result, using regular TD tubes, a sampling volume of 48 L is sustainable. This sampling volume corresponds to limits of quantification of 0.0013 – 0.0084 ng/L for the GC-FAIMS-based analysis method (see *Table 1*).

Table 1 Overview pre-validation results from the TD-GC-FAIMS method for nine N-nitrosamines based on the DIN 32645

Analyte	Regression coefficient	LOD absolute mass (ng)	LOQ absolute mass (ng)	Standard deviation	LOQ normed for sampling volume (ng/L)
NDMA	0,98	0,05	0,14	14%	0,0029
NMEA	0,98	0,06	0,19	11%	0,0040
NDEA	0,98	0,04	0,12	6%	0,0025
NDisoPA	0,99	0,06	0,19	7%	0,0039
NMOR	0,99	0,02	0,06	14%	0,0013
NDnPA	0,98	0,05	0,15	7%	0,0032
NPYR	0,95	0,09	0,27	23%	0,0057
NPIP	0,97	0,11	0,34	18%	0,0070
NDBA	0,99	0,13	0,40	17%	0,0084

This method used TD tubes connected to three different filters (ADS tubes, impingers filled with a 3% acidic solution, and planar filters) to sample the air in mines to check for NDMA signals. Identification was possible using the selective markers' retention time and compensation voltage. Without filters, the tubes for the dusty and non-dusty sampling conditions show results of approximately the same order of magnitude. Distinct NDMA signals can be found on the downstream tube ('back'). It is assumed that these signals do not indicate a breakthrough of the analytes but rather an artifact formation.

With an upstream B70 filter (impinger), NDMA signals can be found on the upstream tube under non-dusting sampling conditions but at a significantly lower intensity than filterless sampling (about 30-fold reduction based on absolute peak areas). When sampling under dusty conditions, NDMA can only be detected on one sample carrier.

The ADS filter hardly lets any analyte pass through; NDMA seems to have been wholly retained. Generally, the associated spectra for these sample carriers show similarity to a sample carrier blank measurement.

The GGP filters behave similarly to the B70 filters under non-dusting sampling conditions. Still, more intense NDMA signals can be detected on the upstream tubes and, in the case of the carrier of the third repeat measurement, either the analyte itself or a precursor substance seems to have penetrated through to the downstream tube, so that an NDMA or artifact signal can be seen there. The finding is consistent with the previous filter tests in that the GGP filters also showed permeation of amines.

Regarding the development of a GC-DT-IMS-based method for nitrosamines in (drinking) water with preliminary twofold enrichment using solid phase extraction and in-tube extraction of the eluent, experiments about its optimization and statistical evaluation regarding the validity and significance of results were carried out and compared to the relevant US EPA method 521 for drinking waters. With two enrichment steps within the sample preparation process, method performance could be achieved in the approximate vicinity of a GC-MS/MS method. As a strategic statistical optimization, a simplex self-directing design was applied to the response signals of the lowest-performing N-nitrosamines so that the calibration range could be reduced tenfold regarding the first concentration level.

While the method's precision and accuracy show definite potential for improvement, detection limits in the low ng/L range (see Table 2) could be obtained. Recovery values fall mostly within the ranges defined by the US EPA method 521, although exceptions (NMEA, ND-iso-PA, and NMOR) show deviations.

Table 2 Overview of detection limits of nine nitrosamines in different drinking waters according to the US EPA method 521. Values given in ng/L including SPE factor.

Matrix	NDMA	NMEA	NDEA	ND-iso-PA	ND-n-PA	NMOR	NPYR	NI
Ultra-pure	12,14	11,78	19,07	12,94	11,68	43,67	24,51	14
Tap	9,38	14,62	9,88	7,50	13,46	31,08	24,64	19
Branded	8,45	12,60	21,19	16,16	15,54	33,75	22,46	16
Fountain	9,12	2,33	15,80	8,62	13,08	33,33	19,25	18

Development of a method for the analysis of the extracellular volatile metabolome of nosocomial pathogens by thermal desorption GC-MS and GC-IMS

Involved staff: Hannah Schanzmann, Ursula Telgheder
Partners: Hamm-Lippstadt University of Applied Sciences, ION-GAS GmbH, Witten/Herdecke University with Helios University Hospital Wuppertal
Funding: Bundesministerium für Bildung und Forschung, Prject Grant: 13GW0428C

Hospital-acquired infections, like nosocomial pneumonia, are one of the most significant challenges in inpatient care. They lead to increased mortality, longer stays, higher treatment costs, and thus a socioeconomic burden. Therefore, a rapid and reliable diagnostic is crucial for starting targeted antibiotic therapy. However, culture-based diagnostic procedures often take up to 48 hours to identify the causal pathogen. Hence, a technology enabling faster detection of specific pathogenic agents must be developed. The project presented here aims to identify pathogens based on their

specific microbiological volatile organic compound (mVOC) profiles in exhaled air. To measure these mVOCs from bacterial reference cultures and human breath, a benchtop system consisting of a thermal desorption (TD) gas chromatograph with a mass spectrometer (MS) is established. In addition, an ion mobility spectrometer (IMS) was coupled as a second detector so that the MS and the IMS shared the same flow line using a flow splitter. Nearly identical retention times can be achieved within the range of up to 30 minutes with slight deviations of 0.06 to 0.24. This enables the identification of unknown compounds in the IMS chromatogram using unambiguous mass spectral identification. The coupling of TD-GC-MS-IMS was built for the first time. To find specific mVOCs as a benchmark of selected known pathogens such as Pseudomonas aeruginosa, Staphylococcus aureus, Streptococcus pneumonia, Legionella pneumophilia, Acinetobacter baumannii complex, and Escherichia coli grown in vitro the volatiles in the culture's headspace were extracted onto TD tubes using a self-made sampling chamber. Then, the TD tubes were subsequently measured with the TD-GC-MS-IMS. The measurements of selected pathogens demonstrate the great advantage of the new coupling: identifying unknowns in the IMS measurements using the mass spectrometric database, as there are still no databases for IMS available. Approximately 600 bacterial measurements were conducted to ensure comprehensive data collection, identifying 25 marker compounds. Among these, 21 were confirmed using MS and validated with reference standards. Mixed cultures of two or more selected pathogens were also prepared, and the identified marker compounds were detected.

To assess the system's efficacy in breath analysis, characteristic VOCs such as ethanol, isoprene, acetone, 2-propanol, and 1-propanol were successfully identified in exhaled air using the dual detector system due to the match of the corresponding IMS and MS spectra.

A proof-of-principle trial has already been conducted in the clinical setting. The breath profiles of 11 patients with nosocomial pneumonia were measured. The data analysis is ongoing, and the volatile fingerprints obtained in these patient measurements will be compared with the results from the in vitro studies.

Non-radioactive ionization for spectrometry and spectroscopy
Involved staff: Annika Fechner, Ursula Telgheder
Partners: Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V.
Funding: -

Ion Mobility Spectrometry (IMS) is a vital analytical technique for detecting volatile organic compounds (VOCs). A critical step in IMS sample analysis is ionization. Since commercially available IMS systems often rely on radioactive ionization sources, developing non-radioactive alternatives is a key priority. The Flexible Microtube Plasma (FµTP), developed by the Miniaturization working group at ISAS e.V., has emerged as a promising candidate. This compact ionization source is ideally suited for integration with the miniaturized design of IMS instruments, offering a novel approach for commercial applications such as food quality analysis in food companies.

The first phase of this project focused on validating and refining the integration of the FµTP with a commercial IMS system. This was achieved by modifying and fabricating components for the IMS using 3D printing technology. These adaptations enabled the effective connection of FµTP to the IMS, demonstrating excellent ionization performance. Current efforts are concentrated on optimizing the negative ion mode of the FµTP-IMS coupling and exploring the ion chemistry of the FµTP. Initial measurements have shown that this coupling offers more profound insights into the ionization processes of IMS devices.

A thermal desorption chip (TDC) has been incorporated to enhance the system's capabilities. This miniaturized device enriches and controllably releases complex sample mixtures, acting as a pre-separation and evaporation step for the IMS through programmable temperature settings. The TDC has proven capable of directly analyzing liquid sample mixtures and pre-concentrating samples. This integrated system is expected to significantly broaden applications, including food safety monitoring.

Foodborne illnesses caused by pathogenic bacteria, such as *Campylobacter* and *Salmonella*, remain a pressing issue in Germany despite strict hygiene standards. Poultry meat is a leading source of *Campylobacter* infections, while poultry and pork are common vectors for salmonellosis. To address this challenge, the project is advancing an automated inline analytical method using the (TDC-) FµTP-GC-IMS system to monitor microbial contamination during slaughtering. The system targets microbial secondary metabolites and bacterial signaling molecules associated with poultry pathogens, specifically *Campylobacter* and *Salmonella*. This approach aims to reduce carcass contamination and enhance food safety in slaughterhouses by providing a rapid, cost-effective means of detecting microbial contamination.

This innovative development underscores the potential of integrating advanced IMS technologies with practical applications in the food industry. This would address critical food safety concerns while paving the way for broader commercial adoption.

Integrative Analysis of Non-Targeted LC-HRMS and High Throughput Metabarcoding Data for Aquatic Environmental Studies Using Combined Multivariate Statistical Approaches

Involved staff: Maryam Vosough, Felix Drees, Guido Sieber, Alexander J. Probst, Jens Boenigk, Torsten C. Schmidt
Partners: -

A significant advancement in environmental analysis has been achieved by non-target screening (NTS) of water resources using LC-HRMS. HRMS-based NTS generates massive datasets, requiring sophisticated chemometrics and machine learning (ML) tools for identifying trends, discriminating, and prioritizing tasks. Further advancement involves integrating NTS data with biological indicators, such as metabarcoding data. The combined analysis of high-throughput chemical and biological data offers a deeper and more holistic understanding of aquatic ecosystems. Through a collaborative study between IAC, Biodiversity, and Environmental Metagenomics departments, a multi-omics approach was developed to process NTS data derived from LC-HRMS, as well as full-length 16S rRNA gene and 18S V9 rRNA gene metabarcoding datasets as part of a DFG-funded project. In this regard, the impact of treated wastewater on an aquatic ecosystem over time has been systematically investigated in a controlled large-scale mesocosm experiment.
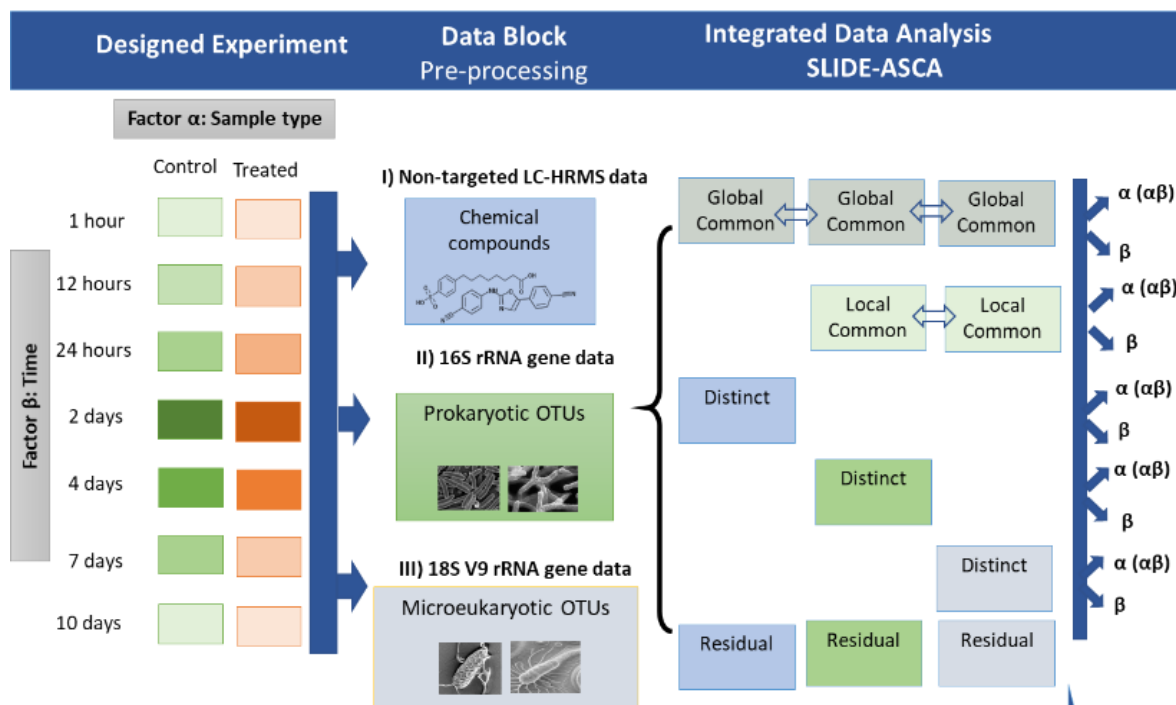
Figure 1: Multi-Omics Workflow

Our novel data fusion method, SLIDE-ASCA, combines ANOVA-simultaneous component analysis with structural learning and integrative decomposition on a

sample-wise concatenated data matrix (Figure 1). This integration allows for the decomposition of global and partial familiar and specific sources of variation associated with each factor, their interactions, and the key influential features. The results of SLIDE-ASCA reveal that treatment and time effects significantly contribute to the variation (41%) in global shared space, and temporal variability explains a much more significant portion of the variance than the treatment effect. Design structure benefits include enhanced interpretability, improved detection of key features, and a more accurate representation of complex interactions between chemical and biological data in aquatic systems (Figure 2).
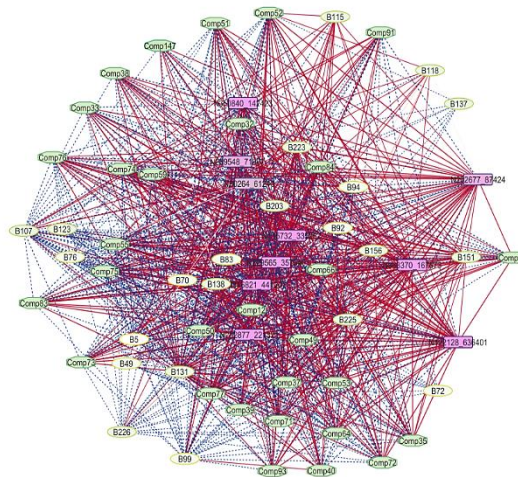
Figure 2: Relevance network for integrated modeling of key features in NTS, microeukaryotic, and prokaryotic data blocks (β effect).

Moreover, we initiated an NTS workflow using LC-HRMS/MS in both data-dependent acquisition (DDA) and data independent-all ion fragmentation (DIA-AIF) modes for different raw wastewater samples to prioritize unknown biomarkers in a complementary manner (Mrs. Sara Khani's MSc thesis). The study's focus in 2025 will be long-term spatiotemporal NTS data processing with ML-based tools and comparative studies funded by DFG.

Studies on electrochemical treatment processes for the decomposition of Persistent Organic Pollutants (POPs) in contaminated ground and surface water

Involved staff: Dua'a M.F. Tahboub, Ursula Telgheder
Partners: -
Funding: The German Academic Exchange Service (DAAD)

The removal of persistent organic pollutants (POPs) from environmental water is a global concern due to the adverse effects on the human and ecological systems. POPs are highly stable, non-biodegradable chemical substances that accumulate in aquatic systems for an extended period. This research project aims to investigate the electrochemical degradation of two groups of water pollutants: (1) organophosphonates compounds, particularly ATMP aminotris(methylenephosphonic acid), and (2) perfluoroalkyl substances (PFAS).

ATMP is a potent chelating agent characterized by a highly stable C-P bond that resists biodegradation. It is widely utilized across various industries and is released into aquatic environments in large quantities. Its degradation primarily produces ortho-phosphate, IDMP, and AMPA. AMPA is a toxic molecule and the primary metabolite of glyphosate, even at trace levels.

The primary purpose is to investigate ATMP's electrochemical oxidation in water using a three-electrode setup using cyclic voltammetry (CV). Graphite and glassy carbon electrodes are used as working electrodes (vs. Ag/AgCl as the reference electrode), and a graphite electrode is the counter electrode. Performing ATMP's oxidation in both the presence and absence of supporting electrolyte salts, aiming to understand the degradation mechanism, reaction reversibility, and kinetics. Analytical techniques such as LC-MS/MS and ^{31}P-NMR are employed for the qualitative and quantitative analysis of ATMP and its transformation products. The study reveals that ATMP undergoes irreversible electrochemical oxidation in acidic perchlorate electrolytes on graphite and glassy carbon electrodes. The graphite electrode also shows a stable and less corroded electrode behavior response.[1]
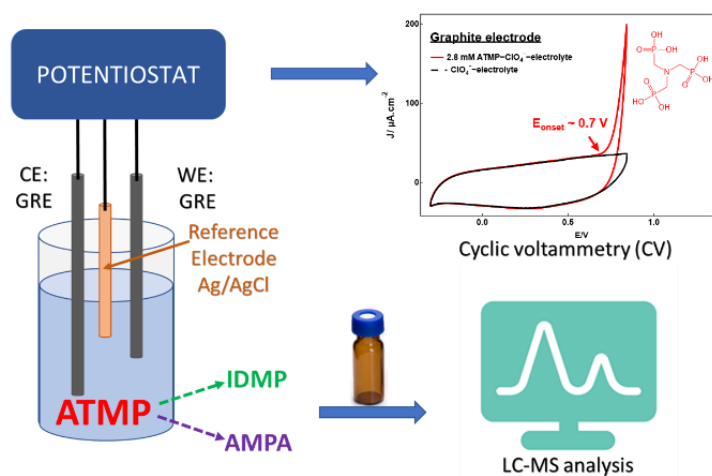
Furthermore, PFAS are synthetic fluorinated surfactants known for their high stability, which is attributed to the strength of the C-F bond. These compounds have been utilized in various industrial applications and firefighting foams. PFAS are extensively released and detected in water sources. This research aims to perform electrochemical degradation of three major PFAS: PFOA, PFOS, and PFBS in different pH media.

A state-of-the-art boron-doped diamond electrode (BDD) flow cell manufactured by (CONDIAS GmbH, Germany) of two-electrode setup of a BDD-electrode as the anode and the stainless-steel surface as the cathode. All are connected to a power supply and employed to degrade three-PFAS solutions. The solution is placed in a glass reservoir and circulated through the cell using a pump. The cell electrodes are connected to a power supply and monitored by applying suitable potential.

All PFAS will be quantitatively and qualitatively measured using LC-MS/MS and, finally, the electrochemical degradation efficiency.
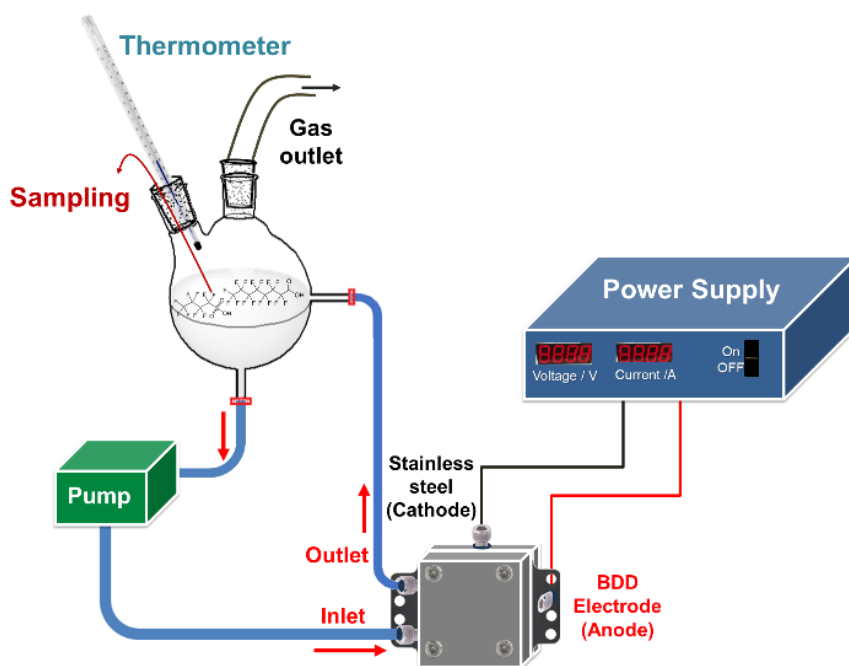
Reference:

Tahboub, D. M.; Telgheder, U.; Rostek, A.; Diesing, D. *Electrochemical oxidation of ATMP (Amino Trimethylene Phosphonic Acid) in low-concentrated acidic electrolyte on graphite and glassy carbon electrodes using cyclic voltammetry*. Journal of Electroanalytical Chemistry **2024**, 967, 118412.

Development of a Data Quality Score for Processing Non-Target-Screening Data generated by HPLC-HRMS

Involved staff: Max Reuschenbach, Daniel Höhn, Gerrit Renner, Torsten C. Schmidt
Partners: -
Funding: Friedrich-Ebert-Stiftung e.V. and internal

In 2024, we made significant strides in enhancing our non-target screening (NTS) data processing platform by transitioning qAlgorithms into a standalone C++ application. Building on last year's work, qAlgorithms offers an integrated, efficient, and user-parameter-free workflow for processing LC-HRMS data. Developed initially as a library, it has been re-engineered into a pre-compiled executable with a low-complexity interface, simplifying the process for users by enabling seamless processing of .mzML files without requiring manual parameter adjustments. Keeping with our philosophy of open data evaluation, the source code is written with minimal encapsulation to communicate every mathematical operation, and we encourage users to review and contribute via our GitHub repository. By integrating the complete NTS processing chain—from centroiding (qCentroids) and binning (qBinning) to peak detection (qPeaks)—into a unified workflow, qAlgorithms leverages data quality metrics to ensure that only statistically significant and high-quality features are reported. Our core design principles, which emphasize eliminating manual thresholds and user-defined parameters, ensure that the inherent properties of the measurement data are intelligently utilized to deliver reproducible and reliable results with every run. Developed in C++ with a focus on computational speed and robustness, qAlgorithms provides fast processing times while maintaining high precision, supporting both profile mode and centroided data (with a recommendation for profile mode to maximize reliability), and outputs detailed CSV files enriched with quality scores (DQSpeak) for every feature.

This year, we proudly participated in the PINTS initiative—a vibrant community of NTS processing developers and users—to propagate our philosophy of transparency, reliability, and automation in analytical data processing. Additionally, qAlgorithms has become a key element in our new collaboration with Ricardo Cunha from IUTA, with whom we have conceptualized CogniFlow, a project focused on advancing automation for analytical data. CogniFlow leverages the strengths of qAlgorithms to streamline complex workflows and enhance data processing efficiency and reliability across diverse applications. In this context, we keep our fingers crossed, as in 2025, the reviewer board will make funding decisions.

We, moreover, continue to invite community feedback, issue reporting, and contributions of benchmark datasets to further refine our tools. Overall, this year's developments mark a significant technical milestone, demonstrating our commitment to community-driven innovation and collaborative research in the field of NTS.

Isotope-labeling in situ derivatization and HS-SPME arrow GC-MS/MS for simultaneous determination of fatty acids and fatty acid methyl esters in water

Involved staff: Lucie K. Tintrop, Maik A. Jochmann, Torsten C. Schmidt
Partners: -
Funding: Internal

The push for sustainable analytical methods is driving the use of eco-friendly microextraction techniques as alternatives to traditional large-scale extraction processes. Solid-phase microextraction (SPME) is particularly popular due to its solvent-free operation, small size, ease of use, and automation capabilities. While SPME has faced challenges such as limited capacity and fragility, the development of SPME-arrow has addressed these issues.

In water analysis using gas chromatography-mass spectrometry (GC-MS), choosing the proper extraction method is crucial for high performance and environmental sustainability. This study examines the performance of SPME and SPME-arrow in GC-MS water analysis, focusing on monitoring industrial processes (via fatty acids and fatty acid methyl esters) and non-targeted wastewater monitoring. Key challenges were addressed, such as integrating microextraction with derivatization, optimizing fiber cleaning, and extracting analytes with varied polarities. Parameters like extraction time, temperature, and pH were optimized using a design of experiments approach, significantly improving results. Detailed discussions of these optimizations offer guidance for future method development.

A novel chemical-thermal fiber cleaning procedure was developed to reduce carryover effects. The method detection limits achieved ranged from low ng L^{-1} to low µg L^{-1}, outperforming many previous studies. Notably, SPME headspace operation eliminated the need for sample pre-treatment, even with complex matrices, and selective tandem mass spectrometry minimized interference in targeted analyses. A non-targeted approach was also tested using GC time-of-flight mass spectrometry with parallel electron ionization (EI) and chemical ionization (CI). Paired with a prototype hydrophilic-lipophilic balanced (HLB) SPME fiber, this method successfully identified a wide range of analytes, suggesting that the HLB fiber could become a versatile material for SPME.

Both SPME and SPME-arrow demonstrated excellent performance, supporting their potential incorporation into future standard analytical methods.

Investigation of Stable Isotope Fractionation during Abiotic Imidacloprid Degradation

Involved staff: Felix Niemann, Annika Gruhlke, Marcel Plonowski, Maik A. Jochmann,
   Torsten C. Schmidt
Partners: -
Funding: Internal

Despite political efforts to ban neonicotinoids like Imidacloprid, it is still found ubiquitously in surface waters around the world. Originally designed as an insecticide for sucking pests, its toxic effects on non-target organisms like pollinators and aquatic organisms are particularly worrying. In the environment, it can undergo physical and (bio-)chemical transformation processes that facilitate mineralization and produce substances with altered toxicological profiles. This raises the importance of characterizing the transformation processes, estimating their contribution, and identifying factors influencing them.

This study focuses on abiotic imidacloprid degradation, such as hydrolysis and photolysis, as they contribute significantly to its natural attenuation in water soil systems. In laboratory experiments, influences like spectral distribution, dissolved oxygen content, and pH value can be investigated.

The novelty of this study is the use of Compound Specific Stable Isotope Analysis (CSIA) as a tool to identify characteristic isotopic effects for individual transformation processes. This technique has proven to provide helpful insight into reaction mechanisms. Polar compounds such as Imidacloprid are challenging analytes for CSIA because they cannot be analyzed directly by gas chromatography. Therefore, liquid chromatography coupled with a conversion interface and an isotope ratio mass spectrometer (LC-IRMS) was used for separation from its transformation products. The developed method uses only aqueous eluents, is robust, and has been successfully tested on samples generated in laboratory batch experiments. Hydrolysis and photolysis showed distinguishable carbon isotope fractionation, allowing mechanistic interpretation. A recently introduced system for simultaneous high-resolution mass spectrometry (HRMS) on an Orbitrap MS allows tentative structures to be assigned to unknown peaks. Data from both instruments complement each other to understand environmental imidacloprid degradation better. A future task is to develop a method for directly analyzing stable isotope ratios by Orbitrap-MS. This could enable the analysis of isotopic ratios of elements inaccessible to traditional LC-IRMS, such as nitrogen and chlorine.
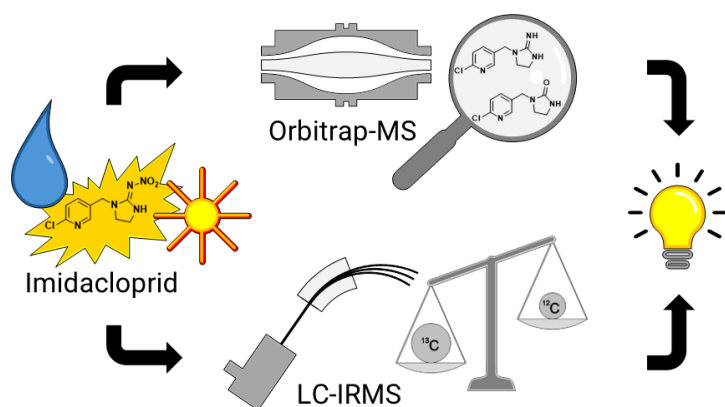
Figure 2: *Investigation of Imidacloprid hydrolysis and photolysis using combined information from LC-IRMS and Orbitrap-MS[1]*

References

(1) Niemann, F.; Gruhlke, A.; Kerpen, K.; Jochmann, M. A.; Schmidt, T. C. Insight into Imidacloprid Degradation through Compound Specific Carbon Isotope Analysis and High-Resolution Mass Spectrometry. *ACS ES&T Water* **2024**. DOI: 10.1021/acsestwater.4c00552.

Determination of atmospherically deposited microplastics in moss: Method development and performance evaluation

Involved staff: Mike Wenzel, Gerrit Renner, Torsten C. Schmidt
Partners: Justus Schoettl, Laura Pruin, Björn Fischer, Carmen Wolf, Christine Kube, Jürgen Schram, Jochen Türk

Microplastics, defined as plastic particles and fibers ranging from 1 μm to 5 mm, have been increasingly detected across various environmental matrices, including water, soil, and air. In this study, we introduced a novel sample preparation method called μPEEL (microplastics extraction through exfoliation), developed to accurately determine atmospherically deposited microplastics on moss. Our study underscores the necessity for accurate qualitative and quantitative analysis methods to comprehensively assess the fate of microplastics in the environment. Traditional analytical approaches, such as Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy, provide qualitative data on microplastics. At the same time, thermoanalytical methods like thermal extraction desorption-gas chromatography-mass spectrometry (TED-GC-MS) offer qualitative and quantitative insights. However, these methods often require extensive sample preparation to mitigate matrix interferences and improve analytical accuracy. The study critically evaluates the μPEEL method against oxidative digestion using Fenton's reagent, a commonly employed sample preparation technique for organic-rich and moss samples.
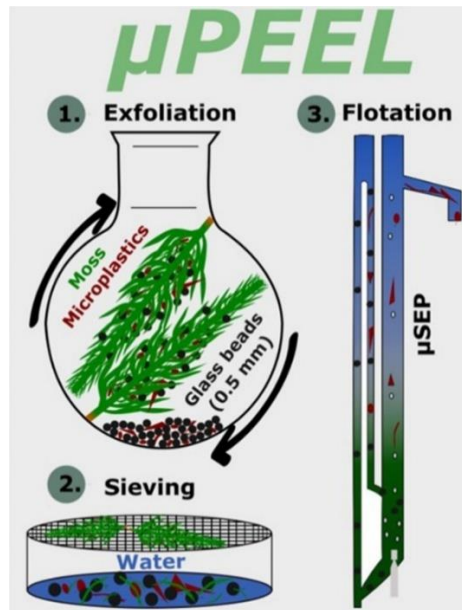
Wenzel, M., et al. (2023). Green Analytical Chemistry, 7, 100078.

The µPEEL method involves three primary steps: (1) exfoliation of microplastics from the moss surface using glass beads, (2) sieving of the exfoliated sample, and (3) separating microplastics from the glass beads and moss abrasion through flotation. The hydrophobicity-water/air-based enrichment cell for microplastics (µSEP) was used for flotation. This innovative approach aims to reduce sample matrix interferences, facilitating more accurate mass- and particle-based analyses. The research meticulously details the experimental procedures, including sample preparation, analytical methodologies (TED-GC-MS and light microscopy), and data evaluation techniques employed to assess the efficiency of the µPEEL method. Results from the study indicate that the µPEEL method achieves high recovery rates for different polymers (PET, PP, PE, and PS), with minimal matrix interferences observed during TED-GC-MS analysis. This contrasts with the oxidative digestion method, which exhibited substantial retention time shifts and signal suppression, potentially leading to inaccurate microplastic quantification. The functionality of the µPEEL method was also demonstrated through light microscopy, showing its capability to facilitate contrast-based particle identification due to the high separation quality achieved. This is particularly advantageous for microplastic analysis utilizing Raman microscopy (µRaman), where the high measurement-time effort and sample throughput are critical concerns.

Furthermore, the green analytical chemistry assessment using the software tool AGREEprep revealed that the µPEEL method outperforms oxidative digestion regarding environmental impact, primarily due to its reduced use of hazardous chemicals, sustainability of materials, and lower waste production. The study concludes that µPEEL offers a robust and environmentally friendly sample preparation method for microplastic analysis and minimizes matrix effects, enabling more accurate and

reproducible results. The study underscores the urgent need for improved analytical workflows and underlines the importance of sample preparation approaches. By developing and evaluating the μPEEL method, the researchers offer a viable and green solution for accurately detecting and quantifying microplastics in complex environmental samples. The findings highlight the potential of the μPEEL method to advance research concerning atmospheric microplastics and demonstrate that the method's greenness can be reconcilable with the method's functionality.

Investigation of Isotopic Fractionation and Transformation Products of Oxidative Degradation of Phosphonates via LC-IRMS and LC-HRMS

Involved staff: Annika Gruhlke, Maik Jochmann, Anam Asghar, Torsten C. Schmidt
Partners: -
Funding: Internal

Aminopolyphosphonates (APPs) are potent chelating ligands and have been used since the 1980s to purify reverse osmosis concentrates in detergents and the paper and textile industries. However, the possible disadvantages of APP use, such as eutrophication of natural waters, remobilization of heavy metals, and the formation of toxic transformation products, are not sufficiently known.

Therefore, the degradation by ozonation, persulfate, and percarbonate oxidation of three APPs, aminotris(methyl phosphonic acid) (ATMP), ethylenediamine tetra (methylenephosphonic acid) (EDTMP), and diethylenetriamine penta(methylenephosphonic acid) (DTPMP), will be investigated. To assess the influence of different reaction conditions, pH, temperature, and oxidizing agent concentration will be varied. In addition, quenchers will be used to investigate the influence of different reactive species on degradation and isotope fractionation. For this purpose, a coupling of liquid chromatography-isotope ratio mass spectrometry (LC-IRMS) and LC high-resolution mass spectrometry (HRMS) with a flow-through splitter after LC separation will be used. This method was successfully developed by *Marks et al*. for ATMP and its photolysis products. LC-IRMS, which measures the isotopic signature of the carbon in the analytes, is used to gain insight into the degradation pathways by isotopic fractionation of the carbon in the APPs during degradation. Since all analytes are mineralized during LC-IRMS measurements to obtain CO_2, an LC-HRMS system is required to identify transformation products.

Of particular interest is (aminomethyl)phosphonic acid (AMPA), considered genotoxic. It is a transformation product of all APPs and glyphosate so that LC-IRMS can determine the origin of AMPA. Furthermore, it has been postulated that glyphosate is a transformation product of EDTMP and DTPMP, so the coupling method can be used to identify glyphosate if it is formed. In addition, it can be used to distinguish between different degradation pathways and industrially produced glyphosate.

Advancing GC-MS/MS methodology for Food Web Analysis in A25, CRC RESIST

Involved staff: Kaliyani Wickneswaran, Torsten C. Schmidt
Partners: University of Duisburg-Essen, Ruhr-Universität Bochum, Kiel University, Leibniz Institute of Freshwater Ecology and Inland Fisheries (IGB), Berlin and Helmholtz Centre for Environmental Research
**Funding:** German Research Foundation (DFG) Project Grant: 426547801

The development of fatty acid (FA) analysis for aquatic food webs in Phase II of CRC RESIST builds upon previous research in Phase I, particularly advances in compound-specific stable isotope analysis (CSIA) of amino acids and method development for isotope fractionation modeling. The work of Hesse et al. (2023, 2025) and Khaliq et al. (2024) refined CSIA applications for trophic biomarker analysis and optimizations of extraction protocols and analytical workflows for isotope studies. These foundational efforts established key methodological insights that Project A25 now extends to fatty acids, integrating them into structural and isotopic food web assessments.

A25 focuses on adapting and automating FA methodologies for biological matrices, transitioning from previous applications in aqueous environments. The methodology builds on the established automatization of FA quantification in water samples by Trintrop et al. (2023), where specifically extraction and derivatization will be developed for biological tissues and environments to meet their distinct analytical requirements. This transition enables high-throughput GC-MS/MS-based FA quantification across diverse sample types, including vertebrates, invertebrates, algae, microorganisms, biofilms, plants, and sediments.

Integrating Quantitative Fatty Acid Signature Analysis (QFASA) with CSIA enhances trophic tracing capabilities, enabling differentiation between autochthonous and allochthonous resources. The method aligns with green chemistry principles, incorporating automated extraction and derivatization strategies to improve reproducibility, sensitivity, and compatibility with future GC-IRMS applications. Field studies in the Boye and Emscher catchments validate FA-based trophic markers, providing insights into ecosystem responses to organic pollution and hydromorphological degradation. Complementary flume experiments utilizing 15N-enriched isotope tracers allow precise tracking of resource flow through trophic networks. This aligns with A25's core objective: understanding how stressors influence the recovery trajectories of aquatic food webs.

By integrating high-resolution FA structural and isotopic analytics, A25 extends the application of mass spectrometry in ecological research. The combination of GC-MS/MS, QFASA, and CSIA establishes a scalable analytical framework for ecosystem assessment. The planned GC-IRMS integration will enhance isotopic resolution, linking FA-based trophic markers to long-term ecosystem recovery processes.

This project refines food web analysis methodologies, highlights the role of FA biomarkers in ecological diagnostics, and contributes to CRC RESIST's overarching mission: quantifying the impacts of anthropogenic stressors on freshwater systems and establishing predictive models for ecosystem stability.
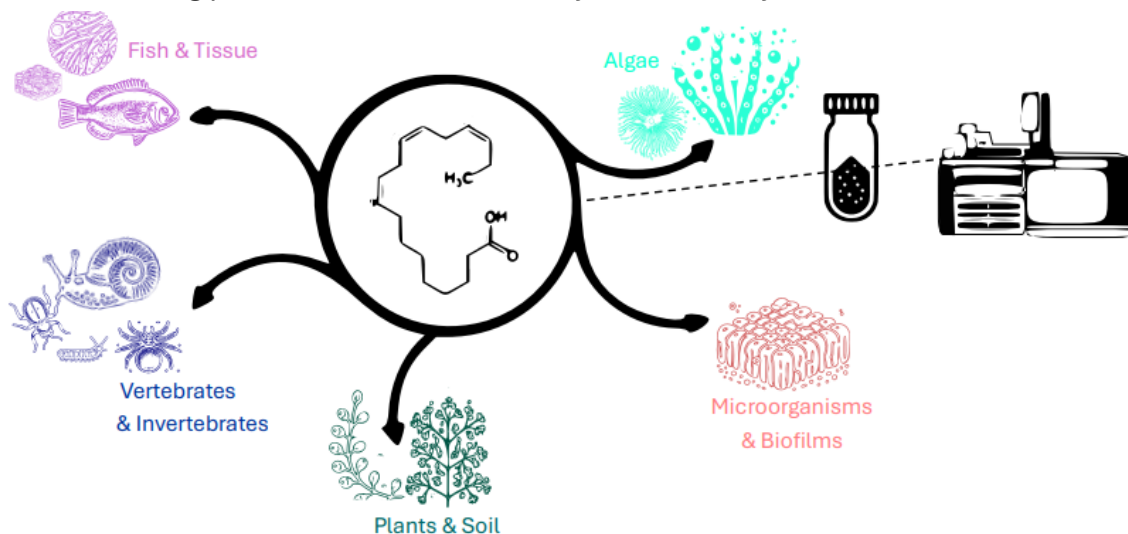
Automatized quantification of functional fatty acids in biological samples with integrated extraction & derivatization via GC-MS/MS.

References:

1. Hesse, Tobias; Nachev, Milen; Khaliq, Shaista; Jochmann, Maik A.; Franke, Frederik; Scharsack, Jörn P.; Kurtz, Joachim; Sures, Bernd; Schmidt, Torsten C. A new technique to study nutrient flow in host-parasite systems by carbon stable isotope analysis of amino acids and glucose. In: Scientific Reports Vol. 13 (2023) Nr. 1, 1054. DOI: https://doi.org/10.1038/s41598-022-24933-9

2. Hesse, Tobias; Niemann, Felix; Khaliq, Shaista; Köster, Daniel; Enss, Julian; Feld, Christian; Nachev, Milen; Kerpen, Klaus; Jochmann, Maik; Schmidt, Torsten Claus. A Proof-of-Principle Study for δ^{15}N Measurements of Aqueous Dissolved Nitrate With a Modified LC-IRMS Interface. In: Rapid Communications in Mass Spectrometry Vol. 39 (2025) Nr. 3, e9950. DOI: https://doi.org/10.1002/rcm.9950

3. Khaliq, Shaista; Jochmann, Maik; Hesse, Tobias; Nachev, Milen; Sures, Bernd; Riekenberg, Philip M.; van der Meer, Marcel T.J.; Schmidt, Torsten Claus. Compound-specific isotope analysis of amino acids for aquatic systems – Problems, challenges, solutions : A review. In: Trends in Analytical Chemistry (TrAC) Vol. 181 (2024) 118038. DOI: https://doi.org/10.1016/j.trac.2024.118038

4. Tintrop, Lucie K.; Lieske-Overgrand, Jana R.; Wickneswaran, Kaliyani; Abis, Rukiyye; Brunstermann, Ruth; Jochmann, Maik; Schmidt, Torsten C. Isotope-labeling in situ derivatization and HS-SPME arrow GC–MS/MS for simultaneous determination of fatty acids and fatty acid methyl esters in aqueous matrices In: Analytical and Bioanalytical Chemistry Vol. 415 (2023) Nr. 26, pp. 6525 – 6536. DOI: https://doi.org/10.1007/s00216-023-04930-1

Optimizing Nitrosamine Analysis: Challenges and Future Directions with GC-MS/MS

Involved staff: Kaliyani Wickneswaran, Amir Salemi, Torsten C. Schmidt, Ursula Telgheder
Partners: -
Funding: Internal

N-nitrosamines (NNOs) are recognized carcinogens that pose significant risks to public health due to their presence in water, industrial emissions, and food products. This study aims to advance detection methodologies by optimizing and comparing various extraction techniques, building upon established EPA standards 521 and 607 for drinking and wastewater. Integrating innovative approaches, such as Headspace-Solid Phase Microextraction (HS-SPME) and Liquid-Liquid Extraction (LLE), addresses analytical challenges posed by complex environmental matrices and trace-level concentrations.

A key focus is the development of advanced and automatized extraction techniques that achieve subnanogram per liter detection limits for volatile and semivolatile nitrosamines, leveraging the enhanced sensitivity and selectivity of GC-MS/MS. SPE, as outlined in EPA 521, serves as a robust foundation. Still, this research extends its applicability to additional nitrosamine derivatives and beyond water matrices, addressing emerging contaminants in industrial and environmental settings. The study aims to reduce solvent use by emphasizing green extraction methods, aligning with sustainable laboratory practices, and contributing to environmental conservation efforts.

This research systematically compares extraction techniques' efficiency, recovery rates, and matrix effects. Statistical evaluation will identify the optimal methods for various nitrosamine compounds, considering their physicochemical diversity. Moreover, the potential for automating these workflows is assessed, enhancing reproducibility and throughput for routine monitoring applications. The outcome of this work is a gap between regulatory standards and innovative analytical techniques regarding rapid NNO trace analysis. The study contributes to actionable solutions for nitrosamine monitoring in water treatment, industrial processes, and environmental remediation by aligning advanced methodologies with real sample applications. Insights gained will serve future water treatment technologies, improve risk assessment frameworks, and support industrial emission controls, ultimately reducing human exposure to these harmful compounds.
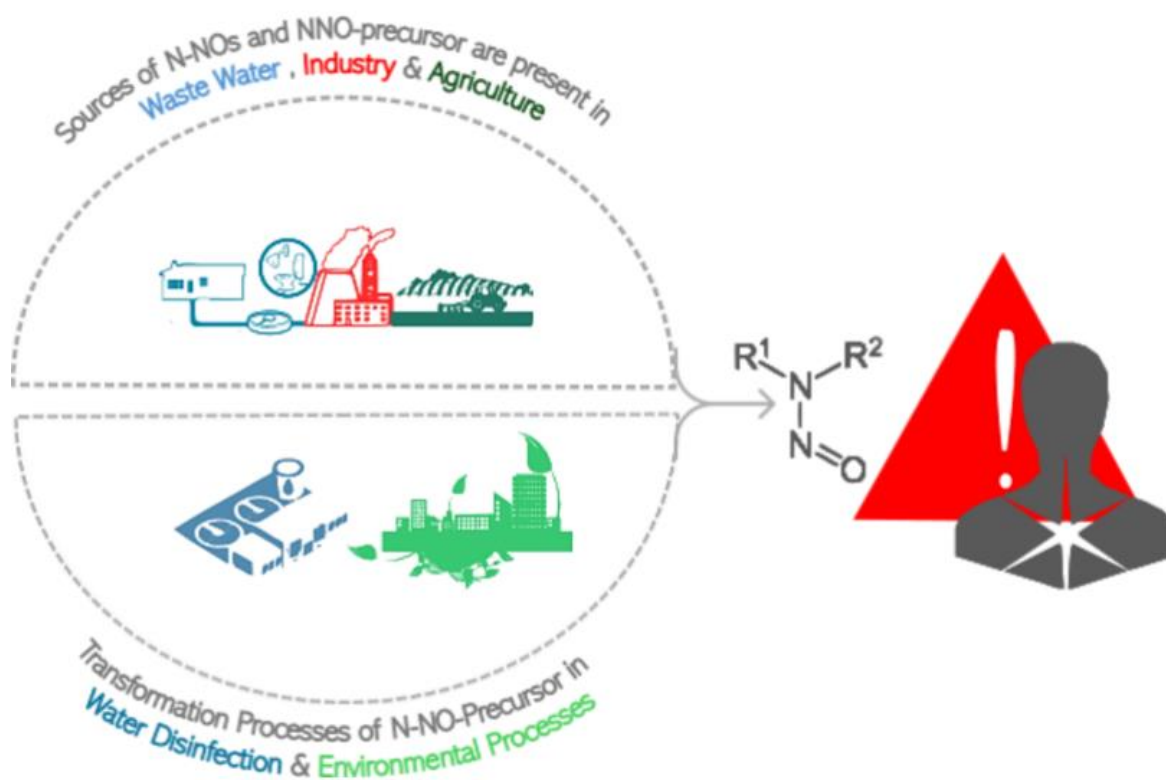
The illustration highlights key sources of NNO precursors in water, industry, and agriculture, along with their transformation into NNOs during disinfection and oxidation processes. NNOs are classified as highly potent carcinogens, posing significant health risks to humans.

Methods of digital food sensing based on ion mobility spectrometry

Involved staff: Modestus Wigger, Stefanie Sielemann, Ursula Telgheder
Partners: Hamm-Lippstadt University of Applied Sciences
Funding: Internal

Food frequently makes the headlines concerning quality defects, contamination, or fraud. These problems are usually uncovered by the control authorities or the industry using analytical methods and sensory test procedures, which focus mainly on the aroma. As this is primarily determined by volatile organic compounds (VOCs), it makes sense to determine these analytically in addition to or instead of the sensory methods. The VOCs give information not only about taste but also additional characteristic information about a product's properties, quality, and origin.

This Ph.D. thesis aims to establish ion mobility spectrometry (IMS) combined with gas chromatography (GC) for quality and product control of selected food products. This involves measuring the VOC profile and using suitable multivariate statistical methods it can be used to classify the food. In addition to multivariate analysis, specific substances, so-called markers, can be used for classification. Due to the lack of comprehensive databases for IMS, it is impossible to identify the markers in non-target analyses using IMS. It is, therefore, necessary to use a mass spectrometer (MS) in parallel to the IMS. The analytical setup shown in Figure 1 is a GC with headspace

sampling and two columns, one connected with the IMS and one with the MS. The different retention times of the signals are correlated via a retention index, and the mass spectra are used in conjunction with the NIST database for chemical identification of the signals.

A: Injector MS
B: Injector IMS

MS

IMS
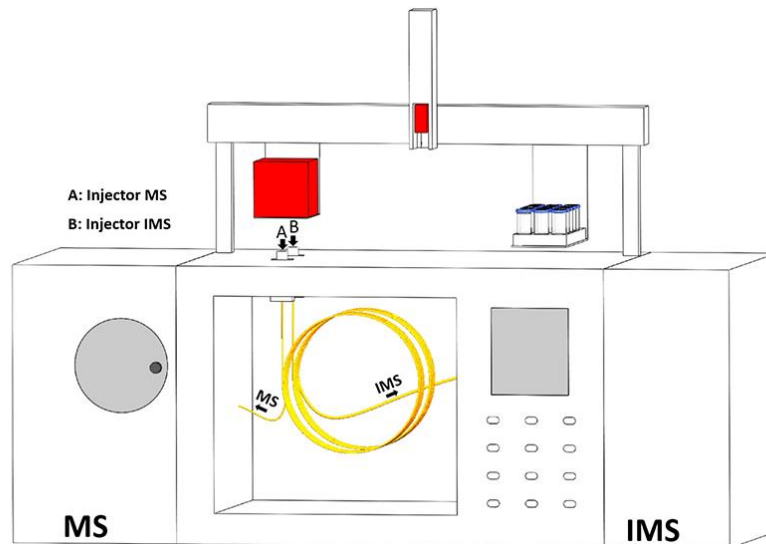
Figure 1 Schematic illustration of the Headspace-GC-MS-/IMS used for VOC analysis of food.

Possible questions include determining the floral origin of honey or detecting adulterations in oregano. Using headspace analysis, no sample preparation is required, making the method fast. Compared to MS, IMS is less expensive and also a very sensitive detector. It is, therefore, a good choice for establishing new methods for quality assessment or detecting food fraud.

Re-thinking Farming and Manure Management (ReFarM)

Involved staff: Michelle Hußock, Gerrit Renner, Ursula Telgheder, Torsten C. Schmidt
Partners: Wetsus, Oosterhof Holman, Agricycling, Humus-Guru, 3N, B.E.S., Mts Broekroelofs, University of Applied Sciences Osnabrück, DLV Advies
Funding: Interreg VI A Deutschland – Nederland; Project Grant: 21128

The ReFarM project—Rethinking Farming and Manure Management—is an innovative initiative designed to transform manure from a costly waste into valuable resources such as alternative fertilizers, soil improvers, and renewable energy through biogas production. This approach supports a circular economy by reducing dependency on imported raw materials and fossil fuels. It enhances soil health and environmental sustainability in regions with high livestock densities.
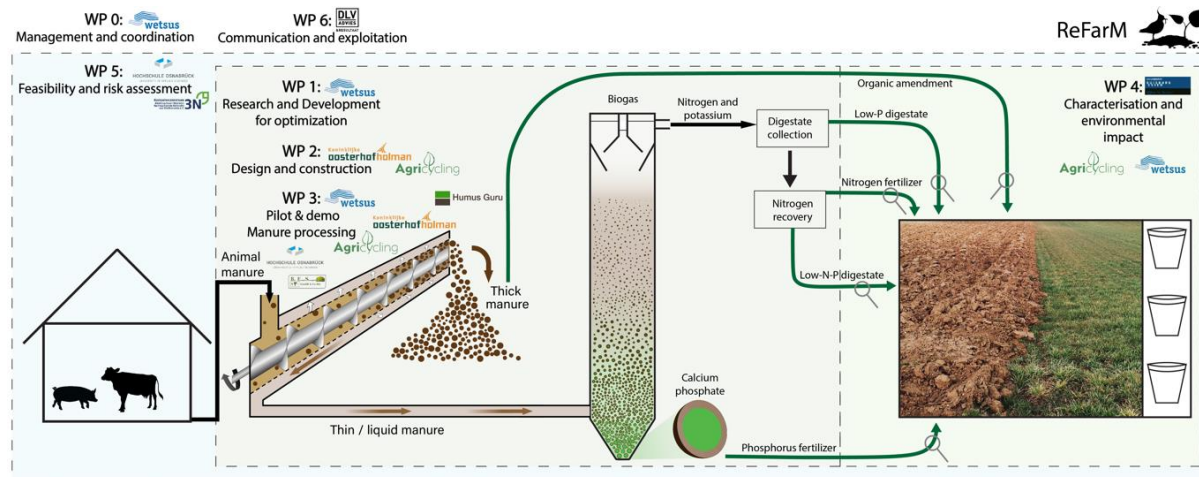
Figure 1: Workplan Overview of ReFarM. IAC is working on the analytical part of the project, which takes place in working package 4.

From the University of Duisburg-Essen (UDE) perspective, our role in this project is central and forward-looking. As the leader of WP4, we are tasked with thoroughly characterizing the recovered products and evaluating their environmental impacts. Our primary focus is developing and refining cutting-edge analytical methods to accurately assess critical parameters such as nutrient content, contaminant levels, and the overall efficacy of recycled materials. IAC aims to pave the way for more resilient and sustainable agricultural practices by ensuring these products meet stringent environmental and quality standards.

During this past year, we initiated the strategic planning phase for our analytical framework, mapping out the necessary steps to implement robust measurement and monitoring techniques. A highlight of our progress was the successful recruitment of our doctoral candidate, Michelle Hußock, following a competitive job posting. Michelle's expertise in environmental analytics and data science is already proving invaluable, bringing fresh insights and innovative approaches to our research endeavors. Michelle's arrival has invigorated our team, and we are confident that her contributions will significantly advance our ability to develop state-of-the-art analytical methods throughout the project's lifecycle. IAC is enthusiastic about further enhancing our research capabilities as we look ahead. We are committed to expanding our analytical toolkit to validate the project's outcomes and set new benchmarks in sustainable manure management.

In summary, this year has marked a pivotal phase for IAC within the ReFarM project. Focusing on detailed analytical planning and strengthening our team with key expertise, we have set the stage for future innovations contributing to a greener, more sustainable agricultural landscape. We eagerly anticipate the coming years when our efforts in developing advanced analytical techniques will drive the project towards achieving its ambitious goals and establishing a new standard in resource recovery and sustainable farming practices.

Design and Development of a Novel 3D-printed Passive Sampler

Involved staff: Dr. Amir Salemi, Merve Çakmakci, Simone Bettinger, Prof. Dr. Torsten C. Schmidt
Partners: Essen University Hospital
Funding: German Research Foundation (DFG) Project Grant: 537712128

Our joint project with Essen University Hospital (and Simone Bettinger from IAC) was completed, and the results were published. Analyzing raw municipal wastewater for the concentration of target biomarkers is a crucial step in wastewater-based epidemiology studies. However, the currently employed SPE and LLE techniques frequently exhibit inadequate selectivity for the target analytes, resulting in chromatograms characterized by elevated background signals and significantly overlapped peaks. An SPME Arrow-GC-MS method was developed and optimized to determine the main nicotine biomarkers in wastewater samples and address these issues. The headspace extraction approach helped remove a central part of the matrix substituents and provided excellent sensitivity after optimization using CCD response surface methodology. Mrs. Merve Çakmakci, a BSc student from Turkey, had a considerable role in this study as her Erasmus+ internship project.
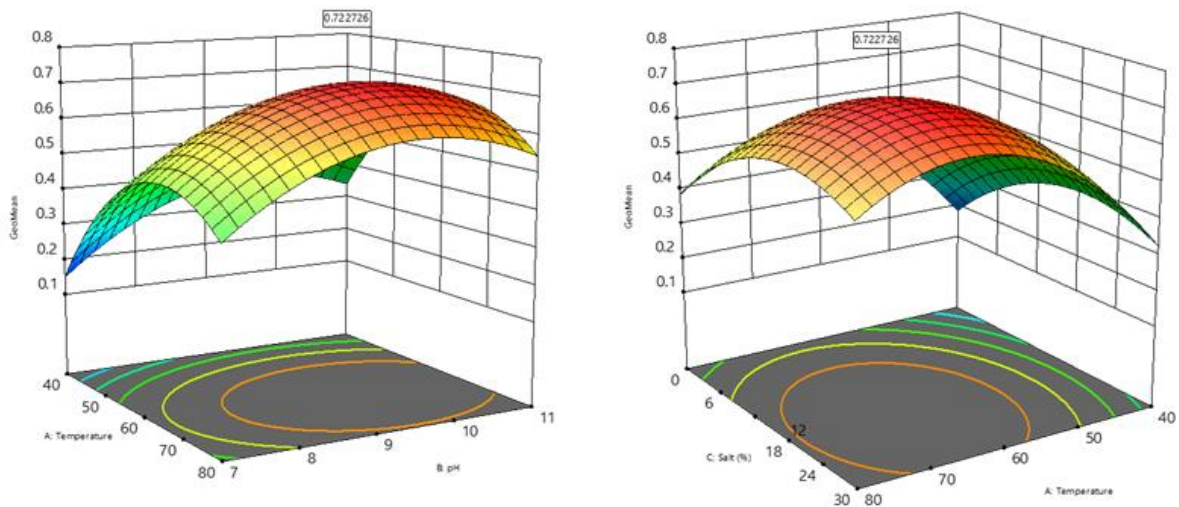
Furthermore, the greenness of four EPA and DIN standard analytical methods was assessed based on the AGREEprep concept and compared with alternative microextraction techniques (as the MSc thesis of Mrs. Albana Luta). The study showed that despite the frequent application of the standard procedures, considerable substitute methods provide more greenness and have better analytical performance characteristics.

The main focus of the studies in 2025 will be on the DFG-funded project: design and development of a novel 3D-printed passive sampler.

Theses Completed in 2024

2024-01-26

Lucie Katharina Tintrop

Automated and miniaturized sample preparation in gas chromatographic analysis

The demand for green analytical methods is increasing. Microextraction methods pose the green alternative to large-scale extractions in research as well as in standard methods. The world's most used and well-accepted microextraction technique, solid-phase microextraction (SPME), is solvent-free, miniaturized, simple to handle, and automatable. The drawbacks of SPME, such as the poor mechanical resilience and small phase volume, were rectified by its further development SPME arrow. For water analysis using gas chromatography mass spectrometry (GC-MS), the choice of the extraction method is a critical step in terms of analytical performance and greenness. Nevertheless, the standardization of microextraction methods is still lacking. Therefore, this thesis investigates the applicability of SPME and SPME arrow for GC-MS water analysis in the fields of industrial process surveillance for the analysis of fatty acids and fatty acid methyl esters and non-targeted wastewater monitoring. Moreover, several challenges such as the combination of microextraction and derivatization, fiber cleaning, and extraction of analytes with different polarities are addressed. The optimization of the critical extraction parameters, such as time, temperature, and pH, by design of experiments significantly increased the gained response in all the applications and is discussed in detail to minimize the effort for future use and development of the methods. A chemical-thermal fiber cleaning procedure was developed, which substantially reduced the carry-over effect. The method detection limits obtained in this study ranged from low ng L-1 to low µg L-1, which is lower than achieved by several research studies. With SPME headspace operation, no pretreatment was necessary, even though the samples possess complex matrices. Additional reduction of sample matrix-based analysis interferences for target analysis was implemented by selective tandem mass spectrometry. A non-target approach using GC time-of-flight mass spectrometry with parallel electron ionization (EI) and chemical ionization (CI) was tested in combination with a prototype hydrophiliclipophilic balanced (HLB) SPME with special focus laid on the identification of substances using the complementary dataset from EI and CI. The approach

extracted and analyzed analytes with very different polarities resulting in the expectation that the HLB could become the new use-one-for-all material in SPME. For the investigated research fields, SPME and SPME arrow performed well, consequently their future implementation in standard methods is supported by the obtained results.

2024-04-19

Robert Georg Heinrich Marks

Liquid chromatography with simultaneous isotope ratio and high-resolution mass spectrometry detection: A powerful new tool for process investigation

Compound-specific stable isotope analysis (CSIA) is a unique analytical technique used to study small variations in isotope ratios within individual compounds in complex mixtures. In liquid chromatography-isotope ratio mass spectrometry (LCIRMS) based CSIA, for instance, all carbon of a compound is quantitatively converted to carbon dioxide for isotopic analysis, thus losing any structural information about the analytes. To overcome this limitation in conventional CSIA, a novel approach combining LC with simultaneous detection by IRMS and high-resolution mass spectrometry (HRMS) has been introduced, enabling the direct identification of unknown or coeluting species. The coupling was optimized using a variable postcolumn flow splitter, ensuring repeatability in peak areas, isotope values, and retention times. The applicability of the method was demonstrated by confirming the presence of pyroglutamic acid in glutamic acid, an international isotopic reference material (USGS41 and USGS41a), highlighting the impurity and urging caution when using it for isotopic calibration.

The strengths of the coupling as a powerful new tool for process investigation were demonstrated by studying the photolytic degradation of the phosphonate aminotrimethylphosphonic acid (ATMP) in aqueous solution. The use of phosphonates, known for their strong metal chelating properties, has increased worldwide and their presence in aquatic systems via industrial and domestic wastewater raises environmental concerns that are compounded by their persistence in traditional water treatment processes. The analysis using LC-IRMS+HRMS coupling provided quantitative data on degradation, carbon CSIA and identification of transformation products (TPs). Combined with ortho-phosphate determination, a complete mass balance of the degradation process could be established. The carbon kinetic isotope effect (KIE) allowed differentiation between direct photolysis and/or

hydroxyl radical oxidation of ATMP during photolysis. Chemical structures for so far unknown TPs were postulated based on the accurate masses obtained by HRMS.

Furthermore, the effects of pH-dependent speciation on the photolysis of ATMP and its TPs, iminodimethylphosphonic acid (IDMP) and aminomethylphosphonic acid (AMPA), were investigated. While the rate constants of ATMP show an influence of pH, IDMP and AMPA show a direct correlation of the rate constants with the pH value. The analysis of the KIE of carbon shows an inverse KIE for ATMP, whereas a normal KIE is observed for IDMP and AMPA. Quantum chemical calculations provide valuable insights for interpreting the degradation pathways and understanding KIEs. Energy barrier calculations differentiated between N-C and C-P bond cleavage, with N-C cleavage being the preferred reaction on average, consistent with the experimentally observed TPs. Additional calculations on possible transition states provide promising approaches to explain the different KIEs. To gain a better understanding of the behavior and fate of phosphonates in the environment, it is crucial to conduct experiments under environmentally relevant conditions. In addition to previously investigated parameters, such as pH, the presence of dissolved divalent metal cations has a significant impact. In general, further experimental studies in combination with theoretical calculations regarding the photolysis of compounds and the associated KIEs are necessary to verify the hypotheses proposed.

Recent instrumental developments utilize Orbitrap systems for stable isotope analysis. Besides liquid direct infusion applications, first studies on direct elution methods using GC-Orbitrap for CSIA are already available. For LC-based CSIA, there are currently no established approaches for direct elution and detection by ESI Orbitrap mass analyzers. This study examines the use of an Orbitrap system for CSIA, with a focus on L-glutamic acid as a model compound. Orientation experiments using direct infusion were used to investigate the effects of resolution settings on isotope separation and the influence of flow rates and methanol content in the sample solutions. Insights into the challenges involved in analyzing eluting peaks were gained through subsequent injection experiments. The obtained results underscore the need for additional examination and integration of a simultaneous detection using classical sector field IRMS for validation purposes. This can be achieved with the LC-IRMS+HRMS coupling presented here. In general, this study offers valuable insights into the utilization of Orbitrap technology for advancing CSIA.

2024-04-22

Nerea Lorenzo Parodi

Aromatic amines in human urine: optimization and automation of the analytical method for their analysis as iodinated derivatives

Several Aromatic amines (AA) have been classified as human carcinogens, and tobacco smoke is one of the most important sources of human exposure. They are metabolized in the body and can ultimately be excreted in urine as metabolites or free AA. They can be analyzed with gas chromatography-mass spectrometry (GC-MS), typically after a complex and labor-intensive sample preparation procedure, involving hydrolysis, extraction, and derivatization steps. The objective of this thesis was therefore to optimize and automate the sample preparation procedure for the analysis of aromatic amines in urine.

As a proof-of-concept, an existing procedure was evaluated and it´s suitability for such analysis studied. Therefore, the relationship between the smoking status of the urine donors and the amount of AA present was studied in 68 samples from 10 smokers (S), 28 past smokers (PS) and 30 never smokers (NS). Furthermore, three different data evaluation approaches were presented: a qualitative analysis, a quantitative analysis, and a quantitative screening. Due to the high variability in concentrations typically observed in biological samples, the quantitative screening was proven a very promising alternative to the quantitative analysis. And a relationship between the smoking status of the donors and the AA present could be established. The method was therefore deemed suitable, and it was further optimized and automated. The Liquid-Liquid Extraction (LLE) step was the first step studied because of the large volumes of sample and toxic organic solvents needed, and the fact that it is a very time-consuming and labor-intensive step. Two alternatives were evaluated, namely Hollow Fiber - Liquid Phase Microextraction (HF-LPME) and Parallel Artificial Liquid Membrane Extraction (PALME) and relevant extraction parameters were optimized. Because significantly higher recoveries could be observed with PALME when comparing the optimized methods, PALME was further validated. PALME was proven a very promising alternative to LLE, with limits of detection (LOD) of 45-75 ng/L, and repeatability and peak area relative standard deviations (RSD) below 20 %. The next step was to evaluate different detectors. To this end, GC-MS in single-ion monitoring (SIM) mode with (1) electron ionization (GC-EI-MS) and (2) negative chemical ionization (GC-NCI-MS), and (3) GC-EI-MS/MS in multiple reaction monitoring (MRM) mode using electron ionization were studied. Most analytes showed excellent LOD (50, 3.0-7.3, and 0.9-3.9 pg/L for (1), (2), and (3) respectively), good precision (intra and inter-day repeatability < 20 %) and excellent recoveries (between 80 and 104 %). From the three techniques studied, the

most promising one was GC-EI-MS/MS. GC-NCI-MS was proven an interesting alternative for qualitative/non-target analysis, since all the derivatized iodinated amines could be easily identified and the significant loss in sensitivity observed over time would not be as detrimental as in quantitative analysis. Finally, in order to minimize the need for human intervention and the opportunities for errors, and improve the overall greenness of the analytical procedure, the sample preparation was automated. Different problems encountered, like volume limitations or needle penetration depth adjustments, are discussed in detail. And thanks to the less labor-intensive and time-consuming sample preparation procedure, several steps, such as reaction/extraction times or some of the reagents which were not optimal for the automated set-up, could be further optimized. The sample preparation procedure for the analysis of aromatic amines in human urine, could therefore be successfully optimized and automated.

Having an automated and optimized sample preparation procedure would enable the analysis of enough real samples so that the relationship between AA, smoking status and smoking-related diseases could be determined. Furthermore, the analytical method could be used to analyze collective samples, for example, from workers at risk of AA exposure and the surrounding population and could enable the real time monitoring of occupational exposure. Moreover, this method could also be used for wastewater-based epidemiology and could help monitor a population´s exposure to tobacco smoke and its health status.

2024-06-03

Susann Holst

Development of an analytical method for the characterization of hot steel samples based on spark spectrometry

This work focuses on the development of an application for the mix-up detection of hot nonprepared steel samples. Based on earlier work on the quantitative analysis of different materials at high temperatures, spark excited optical emission spectrometry was selected for the experiments. Optical emission spectrometry provides an almost non-destructive analysis of samples under consideration of all elements. At the beginning of the investigations, the influence of sample temperature and composition on the course of the raw intensities was analysed. For this purpose, different steel samples were investigated in the temperature range from 20 °C to 500 °C. The development of the application logic for mix-up detection focusses on raw intensities

to keep the temperature influence as low as possible. All intensities of samples investigated decrease with increasing sample temperature. However, pure metal samples behave contrarily. Their intensity increases with raising temperatures. The number and quantity of alloying elements have a strong influence on the course of the intensities. The proposed mix-up check includes a data base comparison of an error quotient to identify the steel grade at different temperatures. The introduced error quotient incorporates the measured intensity as well as the standard deviation of the respective element.

2024-07-25

Nicolai Bätz

Efficient and Sensitive Effect-directed Analysis of Endocrine and Neurotoxic Effects in Aqueous Samples Using High-performance Thin-layer Chromatography in Combination with Effect-based Methods

The constantly increasing production of new synthetic substances, as well as the use and disposal of hundreds of thousands of substances for a wide variety of applications, intensifies the ongoing global release of harmful substances into the environment, with corresponding negative effects on flora, fauna and humans. This require comprehensive monitoring and assessment, which is beyond the current capabilities of chemical and biological analysis as well as ecotoxicology. Effect-directed analysis (EDA) takes this discrepancy into account by focusing on effects, covering a broader range of substances than conventional target analysis, and enabling the targeted analysis of effect-relevant substances with subsequent analytical methods. An EDA that combines effect-based bioanalytical methods with chromatographic techniques makes it possible to focus on the effect-relevant parts of a sample.

In this work, high-performance thin-layer chromatography (HPTLC) was combined with an innovative transgenic yeast assay (yeast multi-endocrine effect screen), which allows the simultaneous determination of estrogenic, androgenic, and gestagenic effects on one HPTLC plate (HPTLC-YMEES). To determine neurotoxic effects an acetylcholinesterase inhibition (AChE-I) assay was also coupled to HPTLC (HPTLC-AChE-I). Sensitivity, precision and efficiency are in the focus of the investigations in order to enable an application-oriented and efficient detection of endocrine and neurotoxic environmental pollution with the optimized methods. Two methods for application of the yeast suspension and AChE solution on HPTLC plates, spraying and

immersion, were compared using dose response relationships for reference substances. A chemical oxidation step was integrated in HPTLC AChE-I to achieve higher sensitivity to organothiophosphates (OTPs). Wastewater, stormwater, and surface water samples were analyzed with the two bioassays after chromatographic separation using HPTLC. In particular, the influence of stormwater-dependent discharges was investigated. Both methods allow reliable detection of environmentally relevant concentrations of the reference hormones and OTPs analyzed. Nevertheless, a further increase in sensitivity is desirable to avoid high enrichment. Compared to the immersion method, a higher sensitivity was achieved by spraying the yeast suspension or AChE solution onto HPTLC plates. An optimized spraying procedure resulted in a more homogeneous distribution of yeast cells on the HPTLC plate and the highest precision. Due to the higher sensitivity and precision, it is recommended to spray yeast cells onto HPTLC plates. In contrast, despite the slightly higher sensitivity of the spray method, it is recommended that the HPTLC plates be immersed in the AChE solution due to a higher efficiency. The ability to simultaneously determine three endocrine effects on one HPTLC plate is very efficient and therefore well suited for a complex EDA, but requires further adjustments. The HPTLC-AChE-I approach was successfully extended by chemical oxidation with n-bromosuccinimide (HPTLC-Ox-AChE-I), which significantly increased the sensitivity to OTPs.

In the study of stormwater-dependent discharges it was found that combined sewer overflows can cause similar or even greater endocrine stress to receiving waters than wastewater treatment plants. In addition, an AChE-I effect in a stormwater basin connected to a highway was detected with the EDA used. However, this effect could not be assigned to a responsible substance by suspect and non-target high resolution mass spectrometry analysis, probably due to interfering substances and matrix effects. HPTLC-YMEES and HPTLC-Ox-AChE-I, are suitable for EDA and allow the detection of multiple endocrine and AChE inhibitory effects in surface water, stormwater and wastewater. HPTLC combined with effect-based methods is a useful method to detect effect-relevant parts of a sample and increase the probability of subsequent identification of the responsible substances by further analytical methods due to reduced sample complexity. EDA is one way to narrow the gap between inputs of substances to the aquatic environment versus the monitoring and assessment of those loads. With EDA, effects and responsible substances, both known and unknown, can be efficiently detected to increase knowledge of environmental contamination and provide the basis for appropriate mitigation strategies.

2024-08-23

Max Reuschenbach

Automated data processing and data analysis in high-resolution mass spectrometry

This thesis focuses on the current challenges and limitations of data processing in non-target screening (NTS) using chromatographic methods coupled to high-resolution mass spectrometry. Due to the complexity and volume of NTS data, the use of automated processing routines is necessary, but established methods often have low transparency and do not provide information on the reliability of results due to variable user parameter inputs and the unclear effect of varying data quality.

This thesis addresses these challenges by developing three innovative algorithms for NTS data processing that are meaningfully combined and integrated into a common toolbox (qAlgorithms). A central role of the algorithms is to investigate the uncertainty with which feature properties (including m/z, retention time, and peak area) are estimated in the mathematical processes of the algorithms. This information is then summarized for the user in the form of a Data Quality Score (DQS) and appended to the generated feature list.

The first algorithm developed in this thesis (qCentroids) is used to centroid high-resolution profile mass spectra. It uses a log-transformed variant of the Gaussian peak function, which can be solved using linear algebra. In contrast to non-linear optimization methods for peak modeling, no initial parameters need to be set and the robustness of the results can be estimated from the standard errors of the regression coefficients.

The generation of extracted ion chromatograms (EICs) from the previously calculated mass centroids was the focus of the second algorithm, called qBinning. In qBinning, m/z values are grouped using a statistical test derived from order statistics so that m/z originating from identical ion populations are assigned to each other. To evaluate the quality of the bins, a performance metric from cluster analysis, the silhouette criterion, has been adapted for this specific processing step.

The last data processing step of the NTS covered in this thesis is the detection and characterization of chromatographic peaks within EICs (qPeaks). For this purpose, a new peakmodel for the description of asymmetric chromatographic peaks was developed which, in contrast to conventional methods, can be calculated using linear

algebra. This means that it is independent of initial parameters and can be used in an algorithm for the combined detection and characterization of chromatographic peaks. The regression is scanned over the chromatogram and the regressions that describe meaningful and statistically significant peaks are stored. A subsequent grouping of non-differentiable peaks completes the algorithm.The qAlgorithms toolbox and all algorithms implemented in this work are available as open source to the scientific community to enable the broad and sustainable application of the concepts developed here. In particular, the concept of the DQS for evaluating the reliability of the collected processing results offers great potential for prioritizing and weighting NTS features in the comparative analysis of samples of different origins in the future.

2024-11-27

Kjell Kochale

Column Switching, Fractionation and subsequent Automation for Trace Analysis in Water Samples: Towards comprehensive Effect-Directed Analysis

The number of chemical pollutants in our waters, for example from industry or agriculture, is continuously increasing and already amounts to thousands of substances, without taking transformation products into account. It is currently not possible to screen for all substances, so the substances that are particularly harmful to the environment should be prioritized first.

Effect-directed analysis (EDA) offers a solution here: the complexity is reduced by fractionating samples and identifying problematic fractions through effect-based methods. Finally, high-resolution mass spectrometric methods can be used to potentially identify the substances that are responsible for a certain effect. The EDA concept is established, but still has potential for improvement, which is addressed in this work.

One approach for improvement is the expansion of the analytical window, for example through online enrichment and the combination of stationary phases with different selectivity. Initially, a column switching was therefore established that enabled improved limits of detection by online enrichment. In addition, online dilution was established as a tool for reducing strong solvent influences. The application was demonstrated on the analysis of polycyclic aromatic hydrocarbons in both aqueous and organic solvents. Polar substances represent a further challenge in water analysis, not only in the field of EDA. Due to the further development of the column switching,

polar and non-polar analytes with a polarity range of logP -5.1 to +13.2 could be enriched and separated.

To optimize the fractionation, the developed column switching had to be miniaturized first, as the flow rates of the conventional LC were too high. By adapting the switching to the miniaturized LC, the flow rate could be reduced from 0.3 mL/min to 25 µL/min. With this flow rate, an autosampler could be converted into a fractionation unit. This setup was not used for fractionation in microtiter plates, as is usually the case, but on thin-layer chromatography plates (TLC). The advantage lies in an additional separation dimension with a freely selectable stationary phase. Applications have shown that this additional separation dimension can separate coeluting substances that are contained in a fraction. However, biochemical assays, especially those based on TLC plates, are very labor-intensive and have a low sample throughput, which makes them particularly suitable for automation. First, however, the theoretical foundation had to be laid, as automation in the laboratory is still hardly widespread. The focus was on an introduction to the available technology and considerations for laboratory automation.

A flexible laboratory automation concept was developed on the basis of the automation principles presented above. The main focus was on simple adaptation to individual requirements, even for complex laboratory processes. Therefore, a concept was developed to flexibly automate complex workflows. Using this concept, the robot-supported automation of the workflow involving seven different stations was achieved without the need for programming knowledge. These stations proved themselves in practical use and the robot was able to carry out the workflow without errors. The next step is to connect the optimized parts of the effect-directed analysis to the overall assay. Once this has been implemented, a significant increase in sample throughput can be expected with a simultaneous increase in information gain.

2024-12-09

Alexander Augustini

The Application of Gas Chromatography Coupled Ion Mobility Spectrometry for the Analysis of E-Cigarette Liquids and their Aerosols

This work presents in three parts the advancement of flavor compound analysis with gas chromatography coupled ion mobility spectrometry (GCxIMS) using the example of

refill solutions and aerosols from electronic cigarettes. The primary focus is establishing and improving GCxIMS systems as analytical tools for routine labs.

Firstly, a novel strategy is introduced to correlate GCxIMS and GC mass spectrometry (GC-MS) results. By validating the applicability of the retention index for GCxIMS measurements and achieving precise correlation (±1%) of both detectors, the method effectively links the sensitivity of GCxIMS with the identification capabilities of GCMS. The use of mass spectra libraries reduces the complexity associated with selecting reference standards, enhancing the efficiency of compound identification when screening.

Secondly, a new calibration method tailored for quantitative GCxIMS-analysis is presented. This method employs linearization based on the relationship between reactant and analyte ions from radioactive atmospheric pressure chemical ionization (R-APCI), contrasting with prevalent non-linear calibration methods. Comparative analysis with established techniques, such as non-linear Boltzmann fitting, validates the effectiveness of the proposed linearization. Moreover, matrix-matched calibrations and internal standards are utilized to account for the influence of matrix compounds on analyte signals, thereby enhancing quantitation accuracy. The determination of detection and quantitation limits through a separate linear calibration further underscores the method's suitability.

Thirdly, a simple and cost-effective setup for sampling aerosols from e-cigarettes is introduced and evaluated. This setup, constructed using standard laboratory equipment, enables the rapid collection of quantitative samples from individual puffs. Aerosol condensates directly into a cooled headspace (HS) vial, which is subsequently analyzed using HS-GCxIMS or HS-GC-MS. This combined approach allows for sensitive identification of unknown ingredients and degradation products in aerosols. Calibration using internal standards ensures precise quantitation within complex mixtures and compensates for differences in the aerosol creation.

Overall, these methods offer a comprehensive framework for analyzing flavor compounds in e-liquids and aerosols using GCxIMS and GC-MS, paving the way for further advancements of lab-based GCxIMS analysis.

Master Theses

Julia Banholzer

"Analysis of selected surface water samples from the Ruhr catchment area for endocrine disruptors"

at Cooperation Laboratory EGLV/RV, Host supervisor: Dr. Christina Meinert-Berning

Arinze Patrick Ekezie

„Evaluation of polycyclic aromatic hydrocarbon and heavy metals in Clarias gariepinus (catfish) cultured in crude oil polluted water and its hepatotoxic impact"

Willi Eßer

"Ozone-based methods for the treatment of isophorone and isophoronediamine contaminated wastewater: influence of hydrogen cyanide on reaction kinetics"

Annika Gruhlke

"Isotope Analysis of Nitrogenous Model Substances – Investigation of Wet Persulfate Oxidation in the Interface of the HPLC-Isotope Ratio Mass Spectrometer"

Isabel Halbhuber

"Development of detection methods for the determination of a sum parameter for organically bound fluorine in PFAS analysis"

David Kniesel

"Investigating the role of natural organic matter and bicarbonate as water matrix components in UV/PAA"

Albana Luta

"Evaluation of Greenness of Selected Analytical Standard Procedures"

Jacqueline Martiny

"Method Development of a two-dimensional reversed-phase liquid chromatography (2D-RP-LC) coupled with an isotope ratio mass spectrometer (IRMS) for the determination of the stable carbon isotope ratios of vitamins"

external from U Wuppertal, Home supervisor: Prof. Nils Helge Schebb

Nic Poppel

"Development of a miniaturized column switching system for the simultaneous analysis of native amino acids and monoclonal antibodies"

at IUTA, Host Supervisor: Dr. Thorsten Teutenberg

Isabell Schelhorn

"Characterization of encapsulated plant protection products by high-performance liquid chromatography"

at BASF, Host supervisor: Dr. Kristina Kösters

Damian Schomers

"Mitigation techniques for bromate formation in oxidative wastewater treatment using ozone strong water treatment"

at IUTA, Host supervisor: Dr. Jochen Türk

Kaliyani Wickneswaran

"Two-dimensional analysis of nitrosamines in aqueous matrices by GC-IMS"

Bachelor Theses

Laura Betzenberger

„Investigating the Inhibitory and/or Stimulatory Effects of Natural Organic Matter on the Ozonation Process"

Alina Hofrath

„LC-MS/MS method development and validation with the SIMPLEX algorithms for the determination of commonly used antibiotics"

Carolin Lohmann

„Validation of a new multi-layer SPE column for broad spectrum sample enrichment in effect-based analytics"

at IUTA, Host supervisor: Martin Klaßen

Louisa Zoubir

„Entwicklung eines Probenahmeverfahrens auf nicht-planaren Oberflächen zur Bestimmung von Zytostatikakontaminationen in der Pharmaindustrie"

at IUTA, Host supervisor: Dr. Mischa Jütte

Publications

An up-to-date list of all our publications can be found on our website via: https://www.uni-due.de/iac/dynamic_publication_list

5. F. Niemann, A. Gruhlke, K. Kerpen, M. A. Jochmann, T. C. Schmidt:
    Insight into Imidacloprid Degradation through Compound Specific Carbon Isotope Analysis and High-Resolution Mass Spectrometry
    ACS ES&T Water **4** (2024), 5437-5446
    DOI: 10.1021/acsestwater.4c00552

6. N. Nahar, I. Sarkar, S. Prati, L. E. Rothe, D. Grabner, S. Zimmermann, A. Asghar, T. C. Schmidt, B. Sures:
    Locomotor activity and physiological responses of parasite-infected Gammarus fossarum exposed to the herbicide metazachlor
    Environ. Pollut. **366** (2024), 125413
    DOI: 10.1016/j.envpol.2024.125413

7. A. Salemi, A. Luta, T. C. Schmidt:
    Greenness assessment of exemplary US EPA and DIN standard analytical methods using the AGREEprep model
    Green Anal. Chem. **11** (2024), 100180
    DOI: 10.1016/j.greeac.2024.100180

8. S. Dobaradaran, A. Salemi, G. E. De-la-Torre, U. Telgheder, T. C. Schmidt:
    The role of different remaining parts of cigarette butts in the transfer of phenolic compounds into aquatic environment
    Sci. Total Environ. **957** (2024), 177584
    DOI: 10.1016/j.scitotenv.2024.177584

9. S. Khaliq, M. A. Jochmann, T. Hesse, M. Nachev, B. Sures, P. M. Riekenberg, M. T. J. van der Meer, T. C. Schmidt:
    Compound-Specific Isotope Analysis of Amino Acids for Aquatic Systems – Problems, Challenges, Solutions: A Review
    Trends Anal. Chem. **181** (2024), 118038
    DOI: 10.1016/j.trac.2024.118038

10. M. Wenzel, G. Renner, L. Pruin, C. Wolf, C. Kube, J. Schram, T. C. Schmidt, J. Tuerk:
    Assessment of sample pre-treatment strategies to mitigate matrix effects for microplastics analysis using thermoanalytical techniques
    Trends Anal. Chem. **181** (2024) 117997
    DOI: 10.1016/j.trac.2024.117997

11. P. A. Figueroa-Gonzalez, T. L. V. Bornemann, T. Hinzke, S. Maaß, A. Trautwein-Schult, J. Starke, C. J. Moore, S. P. Esser, J. Plewka, T. Hesse, T. C. Schmidt, U. Schreiber, B. Bor, D. Becher, A. J. Probst:
Metaproteogenomics resolution of a high-CO_2 aquifer community reveals a complex cellular adaptation of
Microbiome **12** (2024), 194
DOI: 10.1186/s40168-024-01889-8

12. M. Hammad, A. Amina, A. Asghar, O. Anwar, S. Salamon, J. Landers, M.-A. Kräenbring, A. Jain, S. Hardt, H. Wiggers, T. C. Schmidt, H. Wende, C. Schulz, D. Segets:
Polyacrylic acid functionalized superparamagnetic iron-oxide supraparticles for highly efficient adsorption and removal of contaminants from water
J. Water Proc. Eng. **66** (2024), 106025
DOI: 10.1016/j.jwpe.2024.106025

13. K. Kochale; D. Boerakker; T. Teutenberg; T. C. Schmidt:
Concept of flexible no-code automation for complex sample preparation procedures
J. Chromatogr. A **1736** (2024), 465343
DOI: 10.1016/j.chroma.2024.465343

14. N. Baetz, J. R. Cunha, F. Itzel, T. C. Schmidt, J. Tuerk:
Effect-directed Analysis of Endocrine and Neurotoxic Effects in Stormwater Depending Discharges
Water Res. **265** (2024) 122169
DOI: 10.1016/j.watres.2024.122169

15. J. Enss, M. Nachev, M. A. Jochmann, T. C. Schmidt, C. K. Feld:
Stable isotopes (^{15}N) facilitate non-invasive labelling of large quantities of macroinvertebrates across different species and feeding types
Ecol. Evol. **14** (2024), e11539
DOI: 10.1002/ece3.11539

16. M. Reuschenbach, F. Drees, M. S. Leupold, L. K. Tintrop, T. C. Schmidt, G. Renner:
qPeaks: A Linear Regression-Based Asymmetric Peak Model for Parameter-Free Automated Detection and Characterization of Chromatographic Peaks in Non-Target Screening Data
Anal. Chem. **96** (2024), 7120–7129
DOI: 10.1021/acs.analchem.4c00494

17. L. K. Tintrop, S. Bräkling, M. Vetter, W. Eßer, F. Drees, A. Salemi, M. A. Jochmann, S. Klee, T. C. Schmidt:
Evaluation of GC-EI&CI-TOFMS for non-target analysis of wastewater using hydrophilic-lipophilic balanced SPME
Anal. Chem. **96** (2024), (16), 6122-6130
DOI: 10.1021/acs.analchem.3c04114

18. F. Abbasi, S. Dobaradaran, G. E. De-la-Torre, M. Reza KalantarHormozi, T. C. Schmidt:
A review of endocrine disrupting chemicals migration from food contact materials into beverages
Chemosphere **355** (2024), 141760
DOI: 10.1016/j.chemosphere.2024.141760

19. X. A. M. Mutke, P. Swiderski, F. Drees, O. Akin, H. V. Lutze, T. C. Schmidt:
Efficiency of ozonation and sulfate radical - AOP for removal of pharmaceuticals, corrosion inhibitors, x-ray contrast media and perfluorinated compounds from reverse osmosis concentrates
Water Res. **255** (2024), 121346
DOI: 10.1016/j.watres.2024.121346

20. M. Vosough, T. C. Schmidt, G. Renner:
Non-target screening in water analysis: recent trends of data evaluation, quality assurance, and their future perspectives
Anal. Bioanal. Chem. **416** (2024), 2125-2136
DOI: 10.1007/s00216-024-05153-8

21. N. Lorenzo-Parodi, S. Moebus, T. C. Schmidt*:
Analysis of aromatic amines in human urine using comprehensive multidimensional gas chromatography-mass spectrometry (GCxGC-MS)
Intern. J. Hygiene Environ. Health **257** (2024), 114343
DOI: 10.1016/j.ijheh.2024.114343

22. M. Vosough, A. Salemi, S. Rockel, T. C. Schmidt:
Enhanced efficiency of MS/MS all ion fragmentation for non-targeted analysis of trace contaminants in surface waters using multivariate curve resolution and data fusion
Anal. Bioanal. Chem. **416** (2024), 1165–1177
DOI: 10.1007/s00216-023-05102-x

23. A. Asghar, D. Lipfert, K. Kerpen, T. C. Schmidt:
Elucidating the Inhibitory Effects of Natural Organic Matter on the Photodegradation of Organic Micropollutants: Atrazine as a Probe Compound
Chemosphere **352** (2024) 141390
DOI: 10.1016/j.chemosphere.2024.141390

24. T. B. Hofstetter, R. Bakkour, D. Buchner, H. Eisenmann, A. Fischer, M. Gehre, S. B. Haderlein, P. Höhener, D. Hunkeler, G. Imfeld, M. A. Jochmann, S. Kümmel, P. Martin, S. G. Pati, T. C. Schmidt, C. Vogt, M. Elsner:
Perspectives of compound-specific isotope analysis of organic contaminants for assessing environmental fate and managing chemical pollution
Nature Water **2** (2024), 14-30
DOI: 10.1038/s44221-023-00176-4

25. K. Kochale, B. Lang, R. Cunha, T. Teutenberg, T. C. Schmidt:
Online coupling of miniaturized HPLC and high performance thin layer
chromatography by a fractionation unit for effect directed analysis
Adv. Sample Prep. **9** (2024), 100102
DOI: 10.1016//j.sampre.2024.100102

26. V. I. Merkus, M. S. Leupold, S. P. Rockel, T. C. Schmidt*:
Ozonation products of purine derivatives, the basic structures of antiviral
micropollutants
Sci. Total Environ. **912** (2024), 169073
DOI: 10.1016/j.scitotenv.2023.169073

27. K. Kochale, R. Cunha, T. Teutenberg, T. C. Schmidt:
Development of a column switching for direct online enrichment and separation of
polar and nonpolar analytes from aqueous matrices
J. Chromatogr. A. **1714** (2024) 464554
DOI: 10.1016/j.chroma.2023.464554

28. S. Dobaradaran, T. C. Schmidt, G. De-la-Torre, S. P. Rockel, X. A. M. Mutke, U.
Telgheder:
Elucidating nicotine transfer into water environments via cigarette butt remaining
parts
Environ. Pollut. **341** (2024), 122943
DOI: 10.1016/j.envpol.2023.122943

29. R. G. H. Marks, S. Rockel, K. Kerpen, H. Somnitz, P. R. Martin, M. A. Jochmann, T. C.
Schmidt:
Effects of pH-dependent speciation on the photolytic degradation mechanism of
phosphonates
J. Photochem. Photobiol. A: Chem. **448** (2024), 115327
DOI: 10.1016/j.jphotochem.2023.115327

30. D. M. F. Tahboub, U. Telgheder, A. Rostek, D. Diesing:
Electrochemical oxidation of ATMP (Amino Trimethylene Phosphonic Acid) in low-
concentrated acidic electrolyte on graphite and glassy carbon electrodes using
cyclic voltammetry
J. Electroanal. Chem. **967** (2024), 118412
Doi: 10.1016/j.jelechem.2024.118412

31. S. M. Seyed Khademi, V. Ilbeigi, Y. Valadbeigi, M. Tabrizchi, U. Telgheder:
Solid phase microextraction arrow-ion mobility spectrometry for determination of
selected pesticides in water
International Journal of Environmental Science and Technology **21(10)** (2024), 6925
DOI: 10.1007/s13762-024-05469-z

32. S. Joksimoski, K. Kerpen, U.Telgheder:
Advanced remediation in the presence of ferrous iron and carbonate-containing water by oxygen-induced oxidation of organic contaminants
Chemosphere **356** (2024), 141856
DOI: 10.1016/j.chemosphere.2024.141856

33. F. Ude, A. Schumann, U. Telgheder:
Non-destructive, solvent-free quantification of wood preservatives in wood flour and wooden objects using GC-DTIMS
Talanta **268(Part_1)** (2024), 125331
DOI: 10.1016/j.talanta.2023.125331

34. H. Schanzmann, V. Ruzsanyi, P. Ahmad-Nejad, U. Telgheder, S. Sielemann:
A novel coupling technique based on thermal desorption gas chromatography with mass spectrometry and ion mobility spectrometry for breath analysis
Journal of Breath Research **18(1)** (2024), 016009
DOI: 10.1088/1752-7163/ad1615

35. V. Nachtigall, M. Krug, F. Kracht, C. Mainka, F. Özcan, S. Reichenberger, G. Renner, D. Siegmund:
Examining the impact of video production quality and presenter identity in science communication on knowledge acquisition and attitude change
International Journal of Science Education: Part B: Communication and Public Engagement (2024), 1-17
DOI: 10.1080/21548455.2024.2414358

Invited Lectures

1. T. C. Schmidt, N. Lorenzo-Parodi, W. Kaziur-Cegla, A. Gjelsta, E. Leitner:
   Advances in sample preparation for the analysis of aromatic amines as biomarkers in urine
   Chania, 3rd European Sample Preparation Conference (EuSP2024), September 18, 2024

2. T. C. Schmidt, R. Armin, F. Drees, L.K. Tintrop, G. Renner, M. Reuschenbach, A. Salemi, M. Vosough:
   Comprehensive Analysis of Organic Micropollutants in Industrial Wastewater: a Tool Towards Net Zero Emissions
   Leuven, 18th Symposium on Hyphenated Techniques in Chromatography and Separation Technology, May 30, 2024

3. T. C. Schmidt, R. G. H. Marks, S. P. Rockel, F. Niemann, T. Hesse, M. A. Jochmann:
   LC with simultaneous IRMS and HRMS detection: A powerful new tool for process investigations
   Garching, Orbitrap Isotope Workshop, April 12, 2024

4. T. C. Schmidt, R. G. H. Marks, S. P. Rockel, F. Niemann, T. Hesse, M. A. Jochmann:
   New prospects in LC hyphenation of isotope ratio mass spectrometry to trace origin and fate of anthropogenic compounds
   Munich, Analytica Conference 2024, April 10, 2024

5. T. C. Schmidt:
   Liquid Lies: Aquatic Fringe and Pseudoscience
   ZWU Water Day 2024, Essen, March 22, 2024

6. T. C. Schmidt, R. Armin, F. Drees, L.K. Tintrop, G. Renner, M. Reuschenbach, A. Salemi, M. Vosough: Emerging Contaminants in Water: Occurrence and Analysis
   virtual@7th International Conference on Environmental Health, Hormozgan University of Medical Sciences, Kish, February 22, 2024

7. G. Renner, M. Reuschenbach:
   Development of a high-performance peak model for fast, robust, automated, and input parameter-free peak detection for spectroscopy & -metry applications
   Munich, Analytica Conference 2024, April 11, 2024

8. G. Renner, M. Reuschenbach:
   Datenqualitätsbasierte Auswertung im Non-Target Screening: Wie uns Datenqualität hilft, Ergebnisse besser zu bewerten
   Mülheim a.d.R., MWAS 2024, September 11, 2024

Conferences and Meetings

Ruhr-Rhine-Main Meeting

The 2024 Ruhr-Rhine-Main Meeting occurred at the University of Duisburg-Essen on September 26th and 27th. Our IAC group successfully organized it under the dedicated planning of Ursula Telgheder and Gerrit Renner. Continuing the tradition of fostering scientific exchange in water and environmental analytical chemistry, the event brought together experts from UDE, IUTA, BfG, TU Darmstadt, and beyond.

On Thursday, September 26th, the meeting kicked off at 12:30 with a welcoming session and a light vegan buffet, setting a relaxed tone for the day. The technical program commenced after the greeting and a brief announcement about the next meeting in Koblenz. Kevin Guerrero (IUTA) opened the scientific session by discussing strategies to reduce bromate formation in ozone-based wastewater treatment, setting the stage for innovative thinking. Shortly after, Jeremy (Ji Jie) from TU Darmstadt presented his investigation on the reactive species of O_3/PMS compared to O_3/H_2O_2, highlighting novel approaches in oxidative treatment. Damian Schomers (IUTA) then introduced the INNO-KOM_MF project, showcasing an automated method for determining ozone consumption (µAutOzon).

After a well-timed break, Duaa Tahboub (UDE) took the floor to address challenges and workarounds in handling free chlorine and insights into electrochemical treatment processes to decompose persistent organic pollutants in contaminated waters. The scientific discussions culminated with Nils Keltsch (BfG) presenting an effect-directed analysis for identifying genotoxic compounds. The day concluded with a memorable dinner in Rüttenscheid at a popular Spanish restaurant, where participants enjoyed delicious tapas and engaging conversations in a convivial atmosphere.

Friday, September 27th, began with Daniela Krüger (BfG) outlining innovative strategies for the data evaluation of GC-based non-target screening (GC-NTS) data. Felix Niemann (UDE) then shared his work on imidacloprid degradation, employing compound-specific carbon isotope analysis coupled with high-resolution mass spectrometry—a testament to the advanced analytical approaches embraced by our community. Following a short break, Rebecca Süßmuth (BfG) discussed the challenges in analyzing 4HDPA. Amir Asadi (TU Darmstadt) presented a pilot study on the emissions of MCPA and metals from bituminous roof sheets. The meeting ended with a comprehensive group discussion, paving the way for future collaborations and research endeavors.

The 2024 meeting was a resounding success, characterized by rigorous scientific exchange, lively discussions, and a strong sense of community. We look forward to building on this momentum at future gatherings, further advancing our expertise in environmental analytical chemistry.

MWAS 2024

The 6th Mülheimer Water Analytical Seminar (MWAS 2024) was a truly outstanding event that once again brought together professionals from across the field of water analysis, fostering interdisciplinary exchange and collaboration. Organized by IWW with long-standing support from the IAC, the seminar attracted over 200 participants, including academic researchers, industry experts, water suppliers, and manufacturers of analytical instruments.

As in previous editions, MWAS 2024 provided an ideal platform for sharing innovative ideas and advances in water analysis. The program featured excellent presentations and engaging poster sessions, which sparked lively discussions and created ample networking opportunities. This time, Gerrit Renner delivered an insightful presentation on data quality in non-target screening during his invited lecture. In addition to the presentations, the poster sessions were a significant success, showcasing the latest research and developments in the field. This year, Isabel Halbhuber was honored with the poster prize for her exceptional contribution, recognizing her achievement and the innovative spirit of the entire water analysis community.

Beyond the formal program, MWAS 2024 provided an excellent opportunity for informal discussions and networking, further strengthening the bonds between researchers, industry professionals, and other stakeholders. The seminar once again demonstrated how regular exchange and collaboration are essential for addressing current challenges and advancing innovative solutions in water analysis. Overall, MWAS 2024 was an inspiring and highly successful seminar that reaffirmed the critical role of such events in driving progress in water analysis.

Teaching

At IAC, we are involved in teaching mainly in the Bachelor and Master program "Water Science," which is a unique science-based curriculum with a focus on chemistry, analytics, and microbiology (see details at https://www.uni-due.de/water-science/). All courses are also optional for students in the Bachelor and Master program "Chemistry." Some are also offered as elective courses for chemistry students studying towards a teacher's degree and for students of the related Master programs "Environmental Toxicology" (offered in the faculty of biology) and "Management and Technology of Water and Wastewater – MTW3" (offered in the faculty of engineering).

Summer term

Lecture and Tutorial "Water Chemistry" *(B.Sc. Water Science, in German)*

Lecture "Water – The Lecture" *(B.Sc. Water Science, in German)*

Lecture and Tutorial "Oxidative Processes" *(M.Sc. Water Science, in English)*

Lecture and Tutorial "Stable Isotope Analysis" *(M.Sc. Water Science, in English)*

Laboratory Practical "Stable Isotope Analysis*" (M.Sc. Water Science, in English)*

Lecture and Tutorial "Quality Management*" (M.Sc. Water Science, in English)*

Laboratory Practical "Environmental Analytics*" (M.Sc. Environmental Toxicology, in English)*

Winter term

Lecture and Tutorial "Water Analysis" *(B.Sc. Water Science, in German)*

Laboratory Practical "Analytical Chemistry" *(B.Sc. Water Science and Chemistry, in German)*

Laboratory Practical "Water Chemistry and Analysis" *(B.Sc. Water Science, in German)*

Lecture and Tutorial "Water Chemistry" *(M.Sc. Water Science and Environmental Toxicology, in English)*

Lecture, Tutorial, and Seminar "Chemometrics and Statistics" *(M.Sc. Water Science and Environmental Toxicology, in English)*

Individual Practical Projects "Analytical Chemistry" *(M.Sc. Water Science, in English)*

Outreach

S.U.N.I SommerUni in Natur- & Ingenieurwissenschaften

„Der Blick ins Wasser" – August 15, 2024

S.U.N.I. is a unique platform for young people to support their study choice orientation in the natural and engineering sciences. By attending impressive experiments and presentations, the participants can experience the university's everyday life in special events and get to know the fields of work in science and technology to receive support for their study and career development process. The event "A glance at the water" includes a sampling procedure at a small lake with subsequent analysis and water treatment of the samples in the lab. The participants learned fundamental strategies for chemical analysis and treatment techniques.

Sampling Session in front of our fantastic building.

Trial Course of Studies (Probestudium Chemie)

"Water Science – Zur Struktur des Wassermoleküls und den Folgen" – December 17, 2024

In addition to the early studies, pupils from the upper classes have the opportunity to gain in-depth insights into the study areas of natural sciences, engineering, and (economic) computer science, to speak with teachers, and to explore the facilities of the University of Duisburg-Essen. Within the faculty of chemistry program, Claudia Ullrich, Dr. Klaus Kerpen, and Dr. Ursula Telgheder presented an experimental lecture about the unique properties of water. At first glance, the water molecule has a straightforward structure. And yet, it is something very special. Physicochemical: water is different from all structurally related compounds.

That's why life, as we know it, makes it possible. Meaning: Water is involved in all biological and very many non-biological processes in our environment. It is an ideal solvent for many components; therefore, the chemistry of and in aqueous systems is remarkably diverse.

The lecture went on from the unique properties of water to water purification, illustrated with simple experiments.