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JOINT MASS SPECTROMETRY CENTRE

HICE › Aerosols and Health
Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health

Progress Report
Joint Mass Spectrometry Centre (JMSC)
Helmholtz Zentrum München and University of Rostock

Progress Report Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE)

Summer Term 2012 – Winter Term 2013/2014

DES Department of Environmental Sciences

HELMHOLTZ ASSOCIATION

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→ The JMSC reports from 2008-2014 can be downloaded here:
www.helmholtz-muenchen.de/cma/publikation

Foreword

In the following pages you find the fifth progress report of the Joint Mass Spectrometry Centre (JMSC), which works since 2008 as a cooperative, joint research facility of the University of Rostock (Institute of Chemistry, Chair of Analytical Chemistry) and the Helmholtz Zentrum München (Comprehensive Molecular Analytics, CMA). The JMSC conducts research in the field of environmental health and in the area of development and application of analytical techniques for the characterization of complex molecular mixtures. Furthermore you'll find also the first progress report of the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health - Aerosols and Health (HICE).

In the first part of this report the concept and structure of the JMSC are summarized, selected highlights as well as new JMSC PhD-students and projects are briefly introduced. In the following scientific reports on some of the highlights achieved in the last two years are presented. Finally, the members of the JMSC are briefly personally introduced and the JMSC's performance parameters, such as cooperations, publications, lectures and acquired third-party funded projects are listed. The second part reports about research and activities performed under the umbrella of "Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health - Aerosols and Health (HICE)". The successful implementation of HICE is particular important for the JMSC, also in the view of the intended extension and consolidation of the cooperation of Rostock University and Helmholtz Zentrum München in the current research topics. I believe that the progress report at hand gives a good overview on the achievements and capabilities of the current cooperation between the Helmholtz Zentrum München and the University of Rostock. Last but not least I have to thank many persons for helping to bridge the gap between Munich in Rostock. I'm indebted to the rector of the University of Rostock, Prof. Dr. Schareck, and the scientific CEO of the Helmholtz Zentrum München, Prof. Dr. Wess, for the ongoing support of JMSC and HICE. I have to acknowledge the excellent work and support of all the co-workers and co-operational partners of JMSC and HICE. Finally I like to thank our HICE-project manager, Ms. Sorana Scholtes, for compiling the current progress report and setting up a new design. I close with expressing my hope that the following two years will be as successful and interesting as the preceding reporting period.

Prof. Dr. Ralf Zimmermann

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Concept

Since April 2008, the University of Rostock (Chair of Analytical Chemistry) and the Helmholtz Zentrum München (Comprehensive Molecular Analytics) are cooperating in the general fields of environmental health research (e.g. human-health related ambient and emission aerosols research) as well as in the area of development and application of mass spectrometric and chromatographic analytical techniques for the characterization of complex molecular mixtures. A joint research unit of University of Rostock and the Helmholtz Zentrum München, the "Joint Mass Spectrometry Centre" (JMSC), was founded for this purpose. The JMSC is headed by Prof. Dr. Ralf Zimmermann, who concurrently holds the Chair of Analytical Chemistry (CAC) at the University of Rostock (UR) and directs the independent cooperation unit "Comprehensive Molecular Analytics" (CMA) at the Helmholtz Zentrum München (HMGU). The JMSC thus consists of CMA at HMGU and the CAC at UR. Since 2012 the cooperation is further intensified by the successful application, funding and successful implementation of the "Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health - Aerosols and Health (HICE)". HICE is an international research consortium with 8 partner institutions, funded for 5 years by the Helmholtz Impulse and Networking Funds of the Helmholtz Association (INF), and supported financially by HMGU and UR. Prof. Dr. Ralf Zimmermann holds the position of speaker of HICE. In this progress report the first two years of the activities of HICE are also covered.

In the next years the main tasks for JMSC are to consolidate and further increase the cooperation between the University of Rostock and the Helmholtz Zentrum München and to further sharpen the research strategy using the momentum of the successful implementation of the Helmholtz Virtual Institute HICE. This includes the perpetuation of the HICE initiative beyond the five year seed funding period. In this context, in addition to various applications for EU and US-FDA consortium funding, curently different possibilities, including an initiative for a Helmholtz Institute, an extension of the HMGU activities in Rostock and a proposal for a Helmholtz Research Alliance of the topic "Aerosol and Health" are under consideration or preparation.

JMSC Research Areas

The scientific activities of the JMSC are currently structured in two general research fields. The objective of the first general research field of the JMSC is to study environmental aspects and their impact on human health (i.e. environmental health research). Environmental factors which are directly or indirectly relevant for human health and wellbeing are studied. This includes the analysis of the effects of environmental factors of biological systems, animals and humans. A pronounced activity in this research field is the investigation of health effects of ambient and emission aerosols.

The second general research field comprehends the area of development and application of mass spectrometric and chromatographic analytical techniques for the characterization of complex molecular mixtures.

The work in the two general research fields is organized in three corresponding and interlinked research areas at UR and HMGU, respectively (Figure 1).

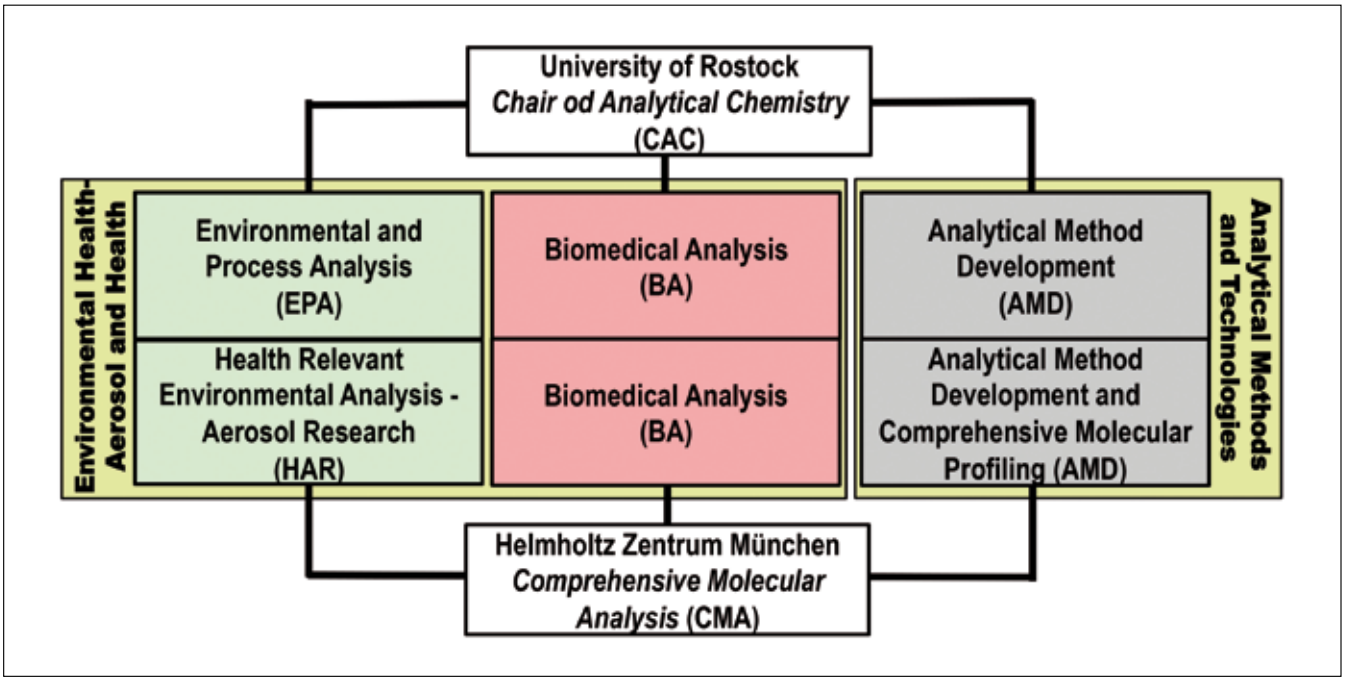


Figure 1: The JMSC is divided into three corresponding research areas at the University of Rostock and the Helmholtz Zentrum München, respectively. They intensely cooperate with each other. The activities can be comprehend in two major themes, the Environmental Health topic (with "Aerosol and Health" being most intensely studied) and the topic Analytical Method and Technology Development. The cooperation partner bifa Environmental Institute GmbH and Photonion GmbH (not shown here) are closely related to the research areas HAR/EPA and AMD, respectively.

The main objective of the research area "Environmental and Process Analysis" (EPA) in Rostock is the analysis of chemical signatures of technical processes and environmental samples. The corresponding area at the HMGU is "Health Relevant Environmental Analysis - Aerosol Research" (HAR), which is embedded in the framework of the HMGU "Environmental Health" program-oriented funding (POF) as well as in the Department of Environmental Sciences (DES). In HAR ambient aerosols and emission aerosols and their health effects are of interest.

The second research area of the JMSC is concerned with biomedical and health related applications. Focus points of the area "Biomedical Analysis" (BA) in Munich is the comprehensive analysis of biological effects of aerosols and the detection of biomarkers of exposure or disease in human samples and is embedded in the framework of the HMGU "Environmental Health" POF program. This includes human lung cell-based toxicological studies on the effect of inhaled aerosols and non-targeted metabolic characterization, for instance in diabetes research. The corresponding (smaller) research area in Rostock is named BA as well. For example metabolic or proteomic samples (latter: cooperation with Proteome Centre of the Medical Faculty of UR) are investigated by FT-ICRMS.

The work on the first general research field of the JMSC, the environmental health research, is mainly performed in HAR, EPA and the two BA research areas in Rostock and Munich.

The JMSC activities the second general research field, the analytical method and technology development, are done in the "Analytical Method Development" (AMD) research areas in Rostock and Munich. One particular motivation for the work in the AMD research areas is that without new analytical approaches and tools many of the questions arising from the Environmental Health research cannot be solved.

In Rostock, the AMD area is particularly strong and focuses on the advancement and implementation of single and multiphoton ionization-mass spectrometry technologies (PIMS) and on ultra-high resolution mass spectrometry. The photon sources for PIMS consist of laser or lamp-based light sources, such as electron-beam pumped rare gas excimer light sources (EBEL). At the HMGU the corresponding research area is called "Analytical Method Development and Comprehensive Molecular Profiling". Examples for the activities include comprehensive two-dimensional gas chromatography, GC- and LC-high-resolution TOFMS application and thermal analysis (TA) coupled to single-photon ionization time-of-flight mass spectrometry. Furthermore the development and application of analysis techniques for petrochemical samples (e.g. fuels relevant for anthropogenic aerosol generation) is conducted in Rostock and Munich in AMD.

Facilities and Equipment

At the University of Rostock the JMSC is represented by the Chair of Analytical Chemistry. It is located in the buildings of the University of Rostock in the Dr.-Lorenz-Weg. Currently 18 scientists and students (senior scientists, postdocs, PhD-students and MSc- or BSc-students) are working at the Chair of Analytical Chemistry. Three scientists occupy permanent academic positions, while eleven scientific members of CAC have temporary third-party funded employment contracts or are scholarship holders. Furthermore there are 3.5 technical staff positions located at CAC (2 technicians, one secretary and 0.5 engineer position). Facilities in Rostock comprise 515 m2 of laboratory space (200 m2 for teaching) and 125 m2 of office space, including an office container. In 2015 JMSC will move with some instruments and personnel into the Mass Spectrometry Facility at the new research building of the Department "Life, Light &Matter" (LLM) of the interdisciplinary faculty (INF), which is currently under construction. Finally also replacement of the old buildings at Dr.-Lorenz-Weg by a new building at the natural science campus was granted by the steering council of the University and the Ministry of Education of the state of Mecklenburg-Vorpommern. Thus the still very problematic room-situation in the premises of Dr.-Lorenz-Weg will be improved by 2015 and hopefully finally solved in 2019.

The research equipment and instrumentation in Rostock include six photoionisation time-of-flight-mass spectrometers and one proton transfer mass spectrometer for online analyses (breath gas analysis, combustion and pyrolysis analysis, process analysis). For the ultra-high mass resolution application and developments a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICR-MS) system is available. The system is based on a 7T superconducting cryomagnet and has two FTICR-MS carts (Solarix and APEX III, Bruker GmbH, Germany). The system can be used with MALDI, ESI and GC-APCI ion sources and interfaces and reaches mass resolutions of up to 500.000. Furthermore CAC has an Orbitrap high resolution mass spectrometer with ESI ion source. A laser laboratory is available for the application and development of photoionisation techniques (Nd:YAG laser, tunable OPO and dye laser, CO2 laser, excimer laser, electron-beam pumped rare-gas excimer light sources), two LCMS systems and several GC-MS used for method development. For applications of analytical pyrolysis, combustion research and pyrolysis research, a pyrolysis furnace with two chambers and a pyrolyzer that is inter-connectable with a GC/MS are available. For development and application in thermal analysis, a thermo balance system, coupled by a skimmer-molecular beam-interface to a quadrupole mass spectrometer system is available. Thermal desorption equipment is available to study carbon content in solid samples. It is coupled to a photo ionization mass spectrometer. Finally, a laboratory reactor used to study Fischer-Tropsch synthesis (heterogeneous catalysis) is implemented.

The cooperation unit "Comprehensive Molecular Analytics" (CMA) at Helmholtz Zentrum München in Neuherberg consists of 13 scientists. Nine scientists are permanently employed at Helmholtz Zentrum München. Two scientists are exempt employees, working as Helmholtz employee representatives for half a day. 18 PhD students are employed on a temporary basis with contracts through third-party funding or are stipend-holders. The cooperation unit also has six technical staff members and two retired scientists serving as associated scientific consultants. The CMA laboratory rooms are currently dispersed in several buildings on the campus of the Helmholtz Zentrum München (Buildings 24, 25, 35 and 57). However, it was currently announced by the CEO of the

HMGU that in the near future all members of CMA will move together in one building. The cooperation unit in Neuherberg operates a HPLC-MS/MS system, an unique LC-ultra high resolution TOFMS (cooperation with LECO GmbH, Germany), two HPLC systems equipped with a diode array and fluorescence detector, one system for multi-dimensional gas chromatography time- of-flight mass spectrometry (GCxGC-TOF-MS), one system for multi-dimensional gas chromatography fast quadrupol mass spectrometry (GCxGC-QMS), a prototype of a multi-dimensional gas chromatography high resolution multi reflection time- of-flight mass spectrometer GCxGC-HR-TOFMS (cooperation with LECO GmbH, Germany), four GC-MS systems (partially equipped for thermal desorption) and several instruments coupled for thermal analysis (TG, DSC, etc.) with EI - quadrupole mass spectrometry and FTIR. Physico-chemical characterization of particulate matter and aerosol particles is performed using a high resolution aerosol mass spectrometer (AMS, WTOF), two scanning mobility particle size spectrometers (SMPS), two electric low pressure impactors (ELPI), an aerodynamic particle size spectrometer (APS), a white light optical particle size spectrometer (WELAS) and diverse particle sampling equipment (several Berner impactors, a rotating-drum impactor, a MOUDI impactor and several low volume samplers). In the framework of the current activities in the field of analytical method development we use and are currently implementing the following, rather experimental instruments:

- A laser desorption/thermal desorption-resonance enhanced multiphoton ionization-single particle-time-of-flight mass spectrometer (LD-TD-REMPI-SP-TOFMS) for the online characterization of aerosol particles.
- A laser-desorption ionization/laser-desorption resonance enhanced - multiphoton ionization/single photon ionization - time of flight mass spectrometer (LDI/LD-REMPI/SPI-TOF-MS) for the analysis of solid samples, sampled aerosol particles and biological samples.
- A thermal analysis - single photon ionization - quadrupole mass spectrometer (TA-SPIxMS).
- A thermal analysis - single photon ionization - time of flight mass spectrometer (TA-SPI-TOFMS) for the determination of organic signatures in thermal processes.

Four instruments for the multidimensional analysis of highly complex samples in bioscience and environmental science are currently available in CMA:

A) Thermal analysis - single-photon ionization comprehensively coupled with gas chromatography time of flight mass spectrometry (TA-GCxSPI-TOFMS).
B) Gas chromatography - EBEL-single photon ionization - time of flight mass spectrometry (GCxSPI-TOFMS),
C) Comprehensive two-dimensional gas chromatography - EBEL-single photon ionization - time of flight mass spectrometry (GCxGC-SPI-TOFMS) including two thermal-desorption - photo ionization - ion trap - mass spectrometers (TD-SPI-ITMS) for the determination of security relevant compounds (drugs, explosive substances and etc.)
D) A multidimensional comprehensive HPLCxGC System coupled to quadrupole MS (cooperation with Shimadzu GmbH, Germany).

The Joint Mass Spectrometry Centre cooperates with the bifa Environmental Institute through a contractual partnership with the CMA. The bifa is a non-profit limited liability company (GmbH) with the State of Bavaria, the Chamber of Industry and Commerce of Swabia and the City of Augsburg as shareholders. It is an application-oriented scientific institute located in Augsburg and provides a supply of services in development, engineering and consulting focused on technical environmental protection for its customers. One employee of the bifa currently works as senior scientist in a third-party funded project of the JMSC at the HMGU on the fundamentals of work place aerosol characterization.

Technology Transfer: Photonion GmbH

Ongoing developments in online single photon ionisation mass spectrometry (SPI-MS) in our cooperation unit have led to a number of patents and third party projects, often carried out with direct industrial support. To satisfy the upcoming demand, a spin-off company was founded: Photonion GmbH. It is closely connected to scientific research and aims at the further development of innovative trace gas analysis instruments based on the JMSC photo ionization-mass spectrometry (PI-MS) techniques and expertise. The SPI-MS technique involves either an electron-beam pumped excimer light source (EBEL) or an laser induce frequency tripling gas cell for generation of VUV light, which allows the efficient and soft ionization of organic compounds. Furthermore system base in the REMPI PI-MS techniques are developed and marketed. SPI-MS is applicable for on-line analysis of complex mixtures of organic compounds. Various applications, for instance in process and product surveillance for food, drugs, and mineral oil, chemical and medical products have been performed. The technique is also used in fundamental and applied research, for example for the analysis of synthetic material, the quality assurance of petrochemical feedstock and natural products and also for the analysis of thermal processes, such as the puff-resolved analysis of pollutants in tobacco smoke. Partners of Photonion GmbH are Ascenion GmbH (patent realization association of the Helmholtz Zentrum München), Tofwerk AG (custom time-of-flight mass spectrometers in Thun, Switzerland) and Airsense Analytics (innovative sensor technologies and safety equipment in Schwerin, Germany). Seed capital came from these partners and from a presidential grant (HEF) of the Helmholtz Community (HGF). Research-related parts of Photonion are located at Helmholtz Zentrum München. The head office is based at Airsense Analytics, Schwerin. Interrelations exist with companies (Borgwaldt KC GmbH, Hamburg; Netzsch Gerätebau GmbH, Selb) that use the EBEL photoionisation mass spectrometry technique for the characterisation of tobacco smoke and thermo analysis, respectively. The EBEL-SPI-MS technique has a high potential for further development. The coupling of EBEL-SPI-MS systems with chromatographic separation (GC, HPLC, CE and etc.) may be a key technique for further fields of application.

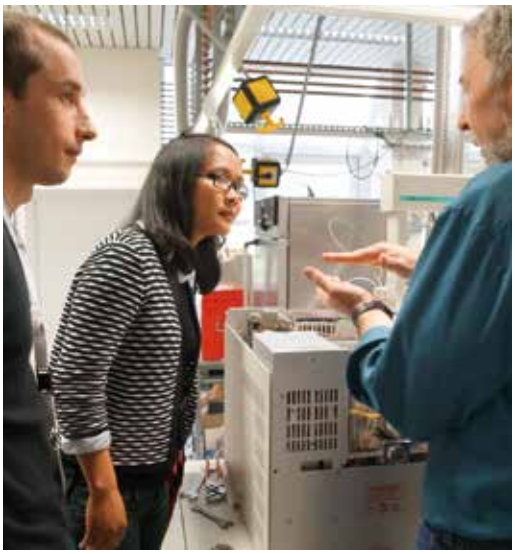
The cooperation unit Complex Molecular Analysis (CMA) is located on the campus of Helmholtz Zentrum München

PhD student working on the photo ionization-mass spectrometer at the Chair of Analytical Chemistry in Rostock

The JMSC inauguration took place in the historical main building of the University of Rostock in 2008

The spin-off company Photonion GmbH also uses photo ionization-mass spectrometry techniques and expertise

A JMSC PhD Student is analyzing the sizes of particles with a white light optical spectrometer



PhD Students at an internal Spring School

Selected News & Highlights

CMA starts cooperation with Shimadzu

In 2012 a cooperation between Shimadzu and CMA was launched with the goal to evaluate Shimadzu's LCxGC-MS System for petrochemical applications. Shimadzu provided a LC-GC-QMS System, which was built-up at CMA. Since the installation the system was further upgrades by CMA to LCxGCxGC-qMS and is mainly used for characterization of Fischer-Tropsch products and crude oil cuts.

Shimadzu LC-GC-qMS after installation in 2012

CMA starts cooperation with LECO

In 2012 a cooperation between LECO and CMA was launched. The bases of the cooperation are two high resolution time-of-flight systems, which were built up in 2012 at the CMA facilities. The Pegasus GC-HRT System was installed in summer 2012 and was recently upgraded to GCxGC.

LECO Pegasus GC-HRT System after Installation in 2012

Sino-German Workshop and Analytica Shanghai

In 2012 CMA attended the Sino-German Workshop on "Analysis of Biomarkers in Complex Samples" in Dalian as well as the corresponding satellite Symposium "Advances in High Performance Separation and MS-Detection of Complex Samples" at the Analytica China in Shanghai.

2012 Sino-German Workshop in Dalian, China

Alois Fendt, Jürgen Orasche, Michael Elsasser, Romy Hertz-Schünemann, Marion Schäffer

Dissertations

In the JMSC five PhD Students completed their dissertation thesis at the University of Rostock:

- June 2013: Alois Fendt, Jürgen Orasche
- November 2013: Michael Elsasser, Romy Hertz-Schünemann
- January 2014: Marion Schäffer

Installation of Leco Citius LC-HRTOF-MS

In October 2012 a Leco Citius High resolution time of flight mass spectrometer coupled to an ultrahigh performance liquid chromatography system was installed at the Helmholtz Zentrum München. The instrument was obtained within a co-operation with Leco Corporation. The unique prototype is used for the investigation of complex, mainly biological samples. Its high resolution combined with very fast scan rates renders it also attractive for targeted and non-targeted analysis.

Foundation of VAO

Inspired by the Umweltforschungsstation Schneefernerhaus (UFS) and encouraged by the Bavarian State Ministry of the Environment and Consumer Protection the cross-border network „Virtual Alpine Observatory“ (VAO) was established. The Virtual Alpine Observatory is currently a co-operation between the UFS, the High Altitude Research Station Jungfraujoch (Switzerland), the Height Observatory Sonnblick (Austria) and other international partners. It offers an excellent platform for environmental research relevant to health and climate.

Umweltforschungsstation Schneefernerhaus (UFS) below the mountain top Zugspitze

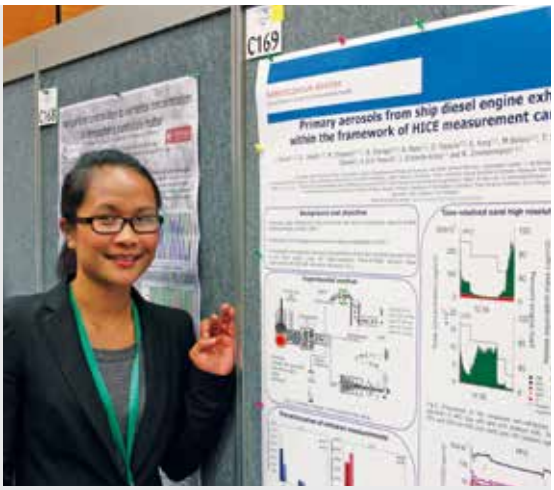
Within the framework of VAO the JMSC plans future investigations to determine source-specific tracer compounds, like levoglucosan, by highly sensitive In-situ-Derivatization-Thermal-Desorption-Gas Chromatography-Time of Flight-Mass Spectrometry (IDTD-GC-TOF-MS). The idea is to distinguish the origin from aerosols (e.g. short-term-transported wood smoke products or long-term-transported coal combustion products) by trajectory-controlled sampling, detailed chemical characterization with IDTD-GC-TOF-MS and highly time resolved measurements of black carbon and brown carbon via an Aethalometer.

European Aerosol Conferences 2012 and 2013

The annual European Aerosol Conferences (EAC) are an important scientific stage for the JMSC members. They present their current results there and meet experts in aerosol science from all over the world. At the EAC 2012 in Granada, Spain, George Dragan, Markus Oster, Jürgen Orasche and Ralf Zimmermann presented their results on the topics combustion aerosols and new analytical techniques for investigating particles. The JMSC group also showed several posters. The social program included a visit of the Alhambra by night and an evening at the representative place of the councilor of Granada.

In 2013 the EAC took place in Prague, Czech Republic. Raeed Qadir, George Dragan, Jürgen Orasche and Ralf Zimmermann gave talks about ambient aerosols, secondary organic aerosols, ship emission aerosols and novel analytical techniques for investigating aerosols. The first results from the Helmholtz Virtual Institute HICE were also presented at the EAC 2013.

The JMSC PhD students, Laarnie Müller and Michael Elsasser, won an EAC Best Poster Award.



Laarnie Müller won an EAC Best Poster Award for her research on primary aerosols from ship diesel engine exhaust

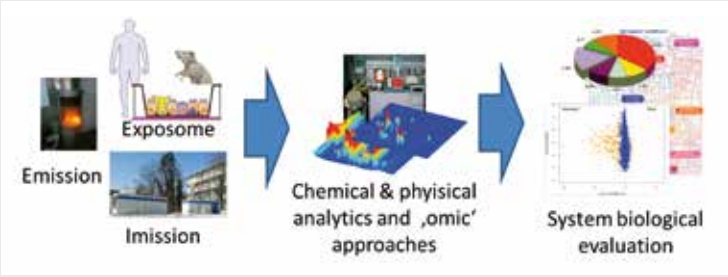
JMSC and HICE members attended the EAC 2012 in Granada, Spain

61st ASMS Conference on Mass Spectrometry and Allied Topics

In 2013 a delegation of the JMSC and Photonion attended the 61st ASMS Conference on Mass Spectrometry and Allied Topics in Minneapolis (USA). Beside several oral and poster presentations also a session about photoionization and a workshop were headed by Ralf Zimmermann and Jack Syage.

61st ASMS Conference on Mass Spectrometry and Allied Topics, Minneapolis, USA

Third funding period of the Helmholtz Association



Workflow and capabilities for the investigation of aerosols and its interaction with biological systems

In 2014 the 3rd funding period of the Program-oriented funding (POF III) of the Helmholtz Association started. CMA participates in the strategic research "Genes and Environment in Common Diseases" (GEnCoDe) program of the Helmholtz Zentrum München. The scientific focus of the programme is the systematic analysis of the interactions between the genome, environmental factors and ageing. Within this research area CMA focusses on new approaches to quantify internal markers of exposure resulting from environmental exposure such as measuring chemicals and their transformation products in body fluids, oxidative stress markers (Topic 1) and aims to establish the interaction between exposure and exposome studying pathways and dynamics of cell-culture responses to aerosol exposure (Topic 5). Furthermore in Topic 5 new analytical methods and technologies are developed to improve the exposure characterization as well as the detection of biological- or health-effects in lung-cell based test systems and human or animal samples.

Helmholtz Virtual Institute HICE

The Helmholtz Virtual Institute in Aerosols & Health HICE was officially opened in May 2012. All HICE Partners, the Chancellor of the University of Rostock, Prof. Dr. Wolfgang Schareck, and the scientific manager of the Helmholtz Zentrum München, Prof. Dr. Günther Wess, participated in the opening event at the Leibniz Institute for Baltic Sea Research (IOW) in Warnemünde. The opening was covered by the local media. HICE is led by the Helmholtz Zentrum München and the University of Rostock and it combines 13 partners from research, education and industry. The aim of the project is to find out about the causes of the adverse health effects of anthropogenic aerosols.

HICE hold its first joint measurement campaign at the University of Rostock in November 2012. During the three weeks campaign engineers, chemists, physicians and biologists worked together to investigate on the impact of aerosols from ship diesel emissions. First results are available. Other sources of aerosols that HICE is intensively analyzing are wood and pellet burner in households. The experiments with different types of wood took place at the University of Eastern Finland in Kuopio in October 2013. The analyses are proceeding.

Young scientists analyzing aerosols from wood combustion at the University of Eastern Finland

The HICE members in front of the HICE mobile lab at the University of Rostock

Opening of the Department of Environmental Sciences: Environmental research to improve health

The Department of Environmental Sciences (DES) at the Helmholtz Zentrum München was opened on Wednesday, 18 July 2012. Seven environmental research units have been amalgamated at the Helmholtz Zentrum München with the aim of improving the link between environmental and health research at the center in the future. Shortage of resources, the impact of climate change on terrestrial ecosystems, pollution or air, water and soil as well as the spread of species to new habitats have consequences for human health. With its integrated concepts and new technologies, the Helmholtz Zentrum München contributes to the sustainable use of resources and environmental health research. From now on, the seven institutes and departments that are networked under the roof of the DES will be largely responsible for their own organization under one joint management and will pursue common scientific goals. The broader aim of the research is to examine the effects of global changes on eco-systems, to record the consequences for human health and, on that basis, to develop strategies to sustainably protect people and the environment. In this regard, the Helmholtz Zentrum München offers unique opportunities through the close collaboration of researchers from different disciplines. The Department of Environmental Sciences combines the following three institutes, three departments and the cooperation group with the University of Rostock (CMA) under one roof: the Institute of Biochemical Plant Pathology headed by Professor Jörg Durner (currently spokesman for the DES), the Institute of Soil Ecology headed by Professor Jean Charles Munch, the Institute of Groundwater Ecology headed by Professor Rainer Meckenstock, the Research Unit Analytical BioGeoChemistry headed by PD Dr. Philippe Schmitt-Kopplin, the Research Unit Environmental Genomics headed by Professor Michael Schloter, the Research Unit Microbe-Plant Interactions headed by Professor Anton Hartmann, and the Comprehensive Molecular Analytics cooperation group (CMA) headed by Professor Ralf Zimmermann. While the DES partners concentrate their research on the environmental compartments soil, plant and water, CMA focusses on the elucidation of environmental and health effects of anthropogenic aerosols (environmental compartment air). It is noteworthy, that CMA is associated in the framework of the program-oriented funding structure (POF III) not in program “Terrestrial Environment (TE)“ but in the program “Genes and Environment in Common Diseases“ (GEnCoDe, topic 1: “Systemic analysis of genetic and environmental factors that impact health” and topic 5:”New technologies for biomedical discoveries”). CMA thus is taking a bridging position between health and environmental activities at the HMGU.

DES
Department of
Environmental Sciences

JMSC Meeting in Munich 2012

The 2012 meeting of the JMSC members took place in Munich from 27th till 29th of June. The Munich hosts and the Rostock guests started the event with a barbecue evening. In the following seminars the JMSC researchers and students presented their work during 15 minutes talks each. The group hiked to Klosterbräu Andechs in the south of Munich, visited the abbey, which is famous for its brewery, and spent an afternoon in the beer garden. The next day the group followed a guided tour through the Munich City Centre and finished the joint event in the English Garden.

JMSC Meeting in Rostock 2013

The annual meeting of the JMSC group 2013 took place at Rostock from June 25th to June 28th. It started with the PhD defenses of Alois Fendt and Jürgen Orasche, which were celebrated together with the whole group. The scientific topics and further plans of the JMSC were discussed during a group seminar at the Leibniz Institute for Baltic Sea Research (IOW) in Warnemünde. The JMSC group visited the old town of Stralsund and experienced an underwater journey at the Ozeaneum.

The JMSC group at the Leibniz Institute for Baltic Sea Research in Warnemünde (IOW)

New PhD Students

Laarnie Müller

Laarnie Müller (formerly Tumolva) earned her Master of Science degree in Environmental Science and Engineering at Gwangju Institute of Science and Technology (GIST) in South Korea in 2010 and her Bachelor of Science in Chemistry degree at the University of the Philippines (UP) Diliman Campus in 2004. She obtained her professional chemist license in 2004 and worked for 2 years at the UP Natural Sciences Research Institute Research and Analytical Services Laboratory. In 2007, she participated in the Joint Program of the United Nations University-GIST Internship in South Korea. From 2010 till end of 2011, she attended courses at the Department of Nanobiomaterials and Electronics at GIST, joined international exchange program, and at the Laboratory of Applied Macromolecular Chemistry. Since July 2012 she is a JMSC and HICE PhD student and working on the topic chemical and physical characterization of combustion aerosols from different sources investigation of their dynamics and transformation using aerosol instrumentation techniques.

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Yvonne Giesen

Yvonne Giesen studied chemistry and received her diploma at the University of Cologne in September 2006. Afterwards, she worked for the Max Planck Institute for Neurological Research in the section of radiochemistry for three years. Main task was the production and development of PET-radiopharmaceuticals for preclinical and clinical research. In 2011 she started her current position at the Institute for Occupational Safety and Health of the German Social Accident Insurance. She works in the division "Chemical and Biological Hazards" which provides its analytical capabilities to the Social Accident Insurance Institutions for determining the degree of exposure to hazardous substances. In November 2013 she started her PhD thesis "Individual Production of Reference Materials for Volatile Compounds". Due to their complex production and limited stability, reference materials for VOCs are extremely rare. The aim of her work is to develop a system that provides reference materials for VOCs on demand. She focuses on reference materials that are suitable for use flexibly and under practical conditions with regard to specific working areas. In order to assure flexibility and low working place concentrations microdosing methods capable of dosing extremely small substance quantities reproducibly are required. Various MS-systems should be used for quality management.

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Christopher Rüger

Christopher Rüger studied Chemistry at the University of Rostock and received his Master of Science degree in September 2013. His research is focused on the characterization of complex mixtures using high resolution mass spectrometry. Therefore, different types of ionization techniques as well as mass analyzer technologies are applied. High resolution and ultra-high resolution are achieved with Orbitrap and Ion-cyclotron-resonance mass analyzer. The main aim of his thesis is the deeper investigation of the chemical composition of different fuel types as well as combustion aerosol samples. Due to the different selectivity of various ionization sources, several ionization techniques such as electro-spray-ionization (ESI) and laser-desorption-ionization (LDI) are used. Laser-based ionization techniques and their development and implementation is one target of his research. The highly complex spectra with several thousand of mass-to-charge signals require different levels of data exploration, hence, the development of appropriate multivariate data analysis and programming of specialized algorithms are further objectives of his work.

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Sabrina Erdmann

Sabrina Erdmann studied Biology and Chemistry at the University of Rostock and received her diploma degree in July 2007 and September 2012. Her research is concerned with the analysis of natural water samples of the Baltic Sea and its catchment area draining rivers with the help of gas chromatography x mass spectrometry. It is embedded in the joined AT-KiM-Project, under the chair of the Institute for Baltic research (IOW), Warnemünde, Germany. The main focus lies on monomeric phenolic compounds, originating from the terrigenous lignin to fulfill the aim to understand the availability and distribution pathways as well as to examine the photochemical and microbial degradation timescales of the macromolecular geochemical tracer respectively. Therefore the within the scope of the diploma dissertation developed complex preparation manual for aqueous samples has to be refined and optimized for the new stated measuring system of GC x double focusing sector field MS, to achieve the highest possible sensitivity in combination with the most suitable resolution.

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José Antonio Sánchez López

José Antonio Sánchez López studied Biotechnology at Athlone Institute of Technology and Chemistry at the University Jaume I (Spain). He received his Master's degree in 2008. Since then, he has worked in research both in public (University Jaume I, Albacete's Hospital) and private institutions (CICbiomaGUNE, Unilever). In April 2013 he joined the Marie Curie ITN project PIMMS (Proton Ionization Molecular Mass Spectrometry). He is an external PhD student based at ZHAW under the supervision of Prof. Dr. Chahan Yeretzian. His research is focussed on: "Process monitoring with soft ionization mass spectrometry techniques". The main aim of his research is the development and application of soft ionization mass spectrometry tools (mainly proton transfer reaction and photoionization) allowing to follow chemical changes happening in foodstuff in real time. Processes in scope are those which can impact the final consumer experience and can be found along the whole food production chain: industrial processing, food preparation or food consumption. The knowledge and tools developed during this project will help companies to optimize their processes and/or improve their final product from a sensory point of view.

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Maximilian Jennerwein

In July 2012, Maximilian Jennerwein successfully completed his state examination in Food Chemistry at the Institute for Molecular Sensory and Food Chemistry in Freising, Weihenstephan. After a half year practical work placement at the meyer.science GmbH, he joined the CMA and started his PhD in January 2013 at the co-operation partner ASG Analytik-Service GmbH. His work focuses on the development of comprehensive GCxGC-TOFMS methods for the analysis of middle distillates. The studies combine the creation Visual Basic Scripts (VBS) for an automated identification and classification of middle distillates like jet fuel, diesel fuel and heating oil and the development of a group-type quantification using different internal standards for an interpolation of response factors. Furthermore, his research focuses on the analysis of heterorganic compounds comprising sulfur, nitrogen and oxygen compounds as minor components. Max collaborates with Benedikt Weggler, who uses GCxGC-TOF-MS and VBS for the analysis of particulate matter. The work is carried out at co-operation partner ASG in Augsburg.

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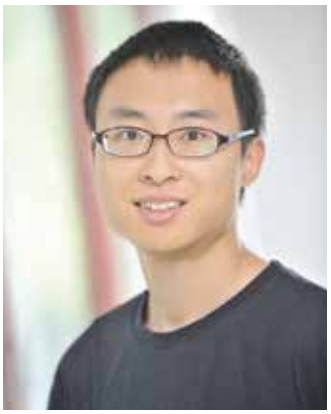
Xiao Wu



Xiao Wu studied Environmental & Occupational Health at the Public Health School of Shandong University and received his Master degree in 2012. He joined the CMA and started his PhD in October 2012. He successfully applied the scholarship from the Chinese Scholarship Council (CSC). His doctorate can be divided into three parts. The first step is the development, optimization and validation of an LC-MS method for the determination of markers of oxidative stress in biological samples. The target compounds include markers like 8-hydroxy-deoxyguanosine and malondialdehyde. Due to the low concentrations in complex samples the sample processing plays an important role. In a second step the method shall be applied for the investigation of biological samples generated during two projects: Urine samples originating from a joint project with the Institute of Epidemiology (ULTRA III) and cell extracts derived from measuring campaigns within the HICE project. Evaluation and interpretation of the data shall be the final step of his work.

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Hendryk Czech

Hendryk Czech studied chemistry at University of Rostock and received his Master's degree in 2013. The project of research he is involved is called "WOOd combustion and SHIpping – primary aerosol emissions and secondary aerosol formation potential (WOOSHI)". In 2014, Hendryk Czech successfully applied for a PhD scholarship from European Social Fund (ESF). The WOOSHI-Project includes studies about primary emissions from wood combustion and ship engines together with their secondary products from conversion processes in the atmosphere. On-line gas phase analysis is carried out by photo ionisation time-of-flight mass spectrometry (TOFMS), which provides high temporal resolution to monitor even fast events during combustion. Moreover, particulate emissions are examined by thermal/optical carbon analyzer (ECOC) which has been coupled to a time-of-flight mass spectrometry instrument. This setup gives the opportunity to obtain information about the molecular composition of single carbon fractions from EC/OC analysis.

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Theo Schwemer

Theo Schwemer studied Chemistry and received the diploma degree at the University of Rostock in September 2012. His work contributes to the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health: Aerosols and Health. The topic of his research is "High Resolution Mass Spectrometry coupled to Atmospheric Pressure Chemical Ionization Gas Chromatography". His doctorate is focused on the development and application of a GC-APCI FTICR system for the characterization of volatile and semi-volatile compounds in emission aerosols. Therefore he is using the high resolution and accurate mass spectrometry to get compositions and retention times of compounds.

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Tamara Kanashova

Tamara Kanashova studied Biosystems Engineering at Otto von Guericke University Magdeburg and received her Diploma in 2011. She started her PhD in February 2012 in the laboratory of Dr. Gunnar Dittmar in Max-Delbrück-Centrum for Molecular Medicine in Berlin. Her research focuses on „Applying quantitative mass-spectrometry based proteomics on relevant questions of combustion gas-induced health effects". To ad-

dress these questions Tamaras work is embedded in the HICE consortia. Here the lung cells are exposed to combustion gases using a sophisticated air-liquid interface, while all parameters of the gas, the aerosol and the cellular responses are determined using different techniques. For the measurement of the cellular response she applies latest isotope-based labeling techiques (SILAC) and combines her data with data obtained by transcriptomics, metabolomics and FLUX analysis, performed by other members of the HICE consortia.

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Benedikt Weggler

Benedikt Weggler completed his Diploma in Chemistry with main emphasis on analytical Chemistry in December 2012 at Ulm University. In January 2013 he joined the CMA group in Munich in order to contribute scientifically in the field of comprehensive multidimensional gas chromatography. His doctorate is strongly linked to the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE), The main objective of HICE is a comprehensive biological, chemical and physical characterization of anthropogenic aerosols. Therefore, the main objective of his doctorate is setting up and improve existing non-targeted, two dimensional, gas chromatographic methods for the analysis of the particulate phase of such aerosols as well as the development of data analysis routines to cope with the vast amount of data produced by such techniques. Finally, those results should be correlated to the chemical and biological findings produced by other techniques applied in the HICE project.

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Matthias Fuchs

After finishing secondary school, Matthias Fuchs did an apprenticeship as chemical worker in dental industry after which he got his qualification for university entrance on continuation education. He studied Engineering Physics at the University of Applied Science in Munich and finished his diploma

: of an optical pH-Sensor. He worked for WTW as an application engineer for physical and chemical measuring sensors in water analysis und also did R&D work in this field. After his diploma he went on studying Photonic for his M. SC. and finished with a thesis about the simulation of lightscattering from aerosol particles in order to improve their recognition during particle sizing. Currently he is working on his doctoral thesis at the CMA at Helmholtz-zentrum Muenchen about the analytics of particle bound PAHs.

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Janos Varga

Janos Varga studied chemical engineering at the Budapest University of Technology and Economics. After working one year as a research chemist in the pharmaceutical industry, he joined the CMA and started his PhD in June 2013. His work is embedded in a joint research project between Netzsch-Gerätebau GmbH, Photonion GmbH and the CMA group, and is funded by the Bavarian Science Foundation (BFS, Bayerische Forschungsstiftung). The PhD project runs in cooperation with Prof. Dr. Armin Reller from the Chair of Resource Strategy of the Augsburg University. The major objective of his research is the optimization of skimmer coupling between thermal analysis and single photon ionization mass spectrometry. Next to this issue, new applications of the developed instrument are being investigated in the field of inorganic chemistry, monitoring of chemical reactions and industrial process simulation.

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New research projects

WOOd combustion and SHIpping – primary aerosol emissions and secondary aerosol formation potential (WOOSHI)

Wood burning and ship emissions represent two poorly understood sources of primary and secondary organic aerosol (POA and SOA) that have potentially serious health and environmental effects. Emissions from deep sea transport vessels are a serious environmental problem due to high heavy metal and condensed aromatic hydrocarbon content. Neither the detailed POA composition nor the SOA-forming potential have been investigated in detail. This is an aim now of a cooperation of the Paul-Scherrer-Institute, Laboratory of Atmospheric Chemistry, Switzerland, and the JMSC. The WOOSHI-project is funded by the Swiss National Science Foundation (SNF) and the German Research Foundation (DFG).

The aim of the ship emissions component of the study is the consideration of the total aerosol produced by ship diesel including both directly emitted aerosol and aerosol produced via plume ageing in a controlled smog chamber. For the wood burning experiments, the purpose is the characterization of the total aerosol produced under conditions relevant for wintertime domestic heating (e.g. temperatures of ~0°C). While much effort has been devoted to studying wood burning POA, related SOA is not well understood. For both systems, the gas/particle interactions are studied using a comprehensive set of on-line and off-line analytical techniques. Important aims include the quantification and chemical characterization of POA and SOA and estimation of health effects via measurement of reactive oxygen species (ROS).

Gaseous species are measured by a resonance-enhanced-multi-photon-ionisation time-of-flight mass-spectrometry (REMPI-TOF-MS) and/or a single-photon-ionisation (SPI-) TOF-MS. Additionally a real time detection of volatile organic compounds (VOC) is performed by proton-transfer-reaction mass-spectrometry (PTR-MS). Moreover an indirect determination of OH-radicals, the most common ageing reactant in the atmosphere, is possible. The size-resolved chemical composition of submicron particles is measured on-line by a high-resolution aerosol mass spectrometer (HR-AMS). The on-line measurements will be supported by offline analysis of samples from gas and particle phase by In-situ-Derivatization-Thermal-Desorption-Gas Chromatography-Time of Flight Mass Spectrometry (IDTD-GC-ToF-MS). Additionally, samples from the emissions and the end status of the experiments will be characterised with state of the art ultra-high resolution mass spectrometry and two-dimensional GC. This allows studying and describing of highly functional organic molecules with similar masses which are formed during the ageing processes.

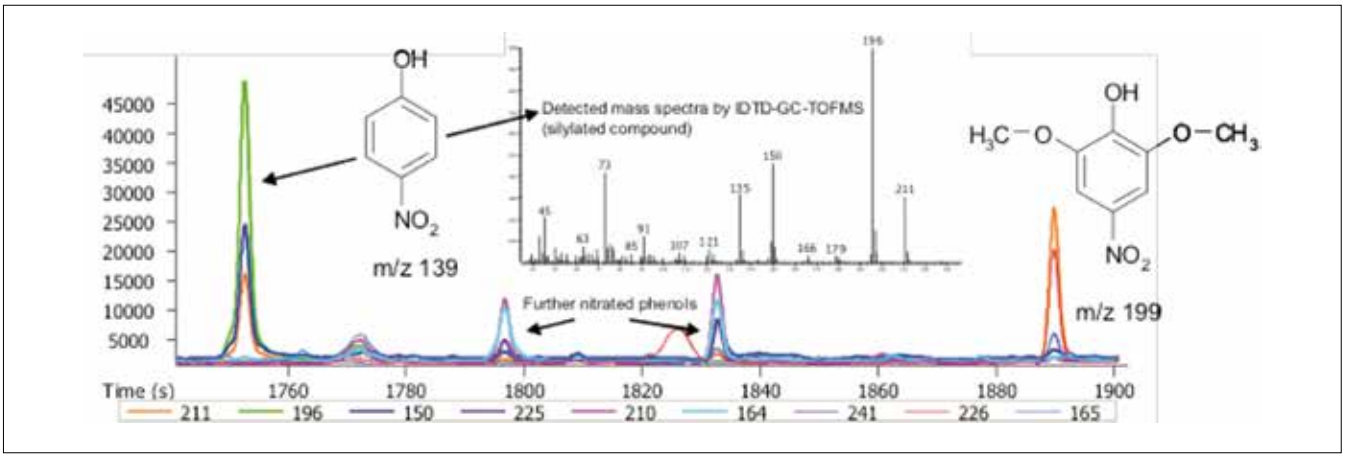


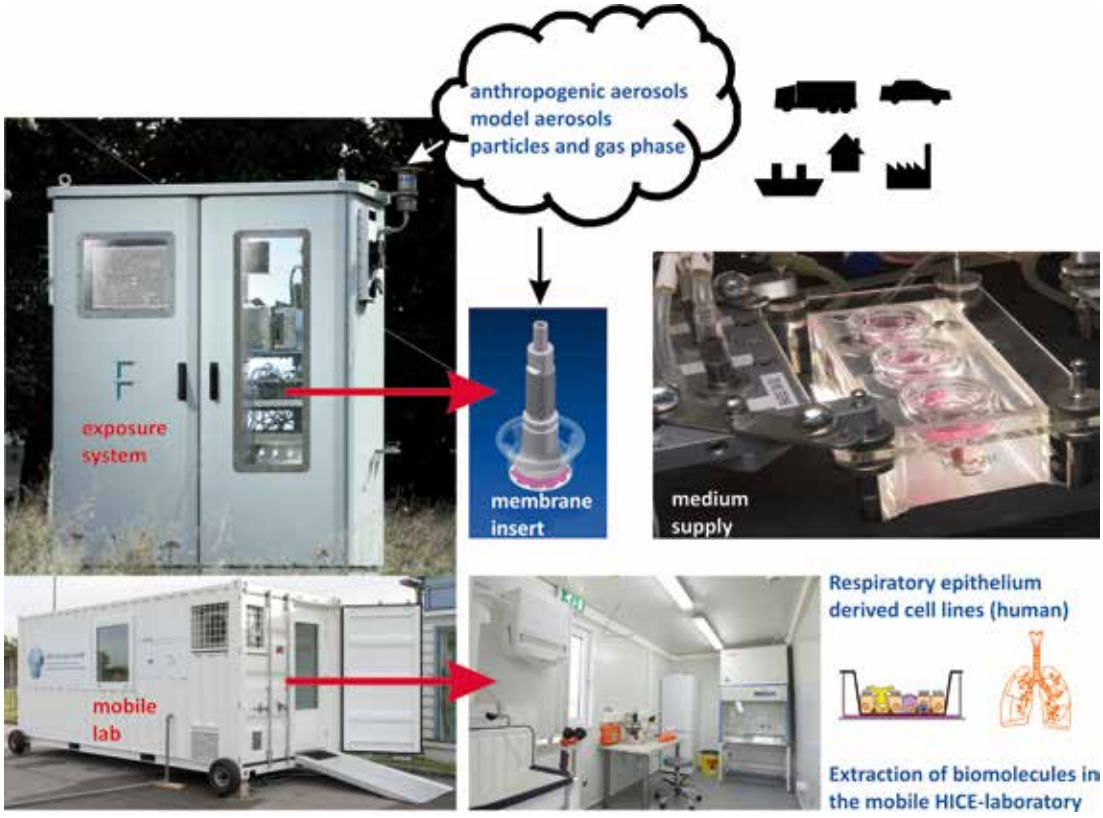
Fig. 1: Identification of nitrated SOA products with IDTD-GC-TOFMS (4-Nitrophenol and 2,6-Dimethoxynitrophenol and two further nitrated phenols with typical mass spectra).

As wood combustion and ship emissions are the major sources of organosulfates and organonitrates, one aim of this study is to investigate on determination of these hitherto hardly known substances, their concentrations and their formation potential under atmospheric conditions in the smog chamber. Some of these compounds were already observed in ambient air with IDTD (Fig. 1).

Air-Liquid Interface and Metabolomics

The first measurement campaigns of the HICE project took place in 2012 (Rostock) and 2013 (Kuopio). Many experiments have been performed and a lot of data has been generated. Questions which could be answered after the campaigns naturally gave birth to new questions that have to be addressed. It is of course not possible to completely do this by means of week-long measurement campaigns with high expenditures and personnel expenses. Fortunately the JMSC has the opportunity to perform small scale measurement campaigns at the Helmholtz Centre in Munich either on its own or with the involvement of some of the HICE partners. A state of the art biological laboratory (safety level S1) as well as a mobile container laboratory (safety level S2) allow for the cultivation of well-established human lung cell lines. The cells can be exposed to environmental or synthetic air as well as to environmental or freshly emitted combustion aerosols at the air liquid interface inside the Karlsruhe Exposure System ("ALI system") [Paur et al. 2011]. The ALI system can be operated inside our facilities for model experiments and also inside the container laboratory for (anthropogenic combustion aerosol-) source specific exposure experiments or environmental monitoring. The ALI exposure system has innately been designed as a toxicological measurement method for airborne particles and gases. It is for this reason necessary to use biological standard cell viability assays (e. g. lactate dehydrogenase assay, Resazurin based assays) to assess the toxic effects on the exposed cells. Since most of these assays long for microplate readers with common detection modes (absorbance, fluorescence, luminescence) we are happy to have access to the assay development and screening platform of the HMGU. For the expansion of the very general results of the bioassays by more specific and deeper information, LC/MS/MS Metabolomics is ideally suited. We developed a LC/MS/MS multi method which allows us to analyse up to 100 polar metabolites from human lung cells in one LC run. The cell pellets are extracted with methanol/chloroform/water. The cells itself can directly be scraped off the disposable culture membrane inserts that are used inside the three VITROCELL® 6/6 exposure modules (three modules with six membrane inserts in 6-well size each) within the exposure chamber of the ALI system. Our future goal is to transfer the targeted LC/MS/MS method to a LC-HRT system to develop a more comprehensive, non targeted method which allows for also detecting some of the unknown metabolites inside the cell extracts.

H.-R. Paur, R. R. Cassee, J. Teeguarden, H. Fissan, S. Diabate, M. Aufderheide, W. G. Kreyling, O. Hänninen, G. Kasper, M. Riediker, B. Rothen-Rutishauser, O. Schmid, O. J AEROSOL SCI 2011, 42, 668–692



Application of Multidimensional Thermal and Chemical Analysis for the Characterization of Materials and Chemical Processes

within the framework of the project „Multidimensional Chemical Analysis of Thermal Processes“

In June 2013, a joint project, associated with the project “Multidimensional Chemical Analysis of Thermal Processes” funded by the Bavarian Research Foundation (Bayerische Forschungsstiftung, BFS) was launched. In its initiative, the Bavarian Research Foundation promotes young scientist to write their doctoral thesis in Bavaria. The PhD project runs in cooperation with Prof. Dr. Armin Reller from the Chair of Resource Strategy of the Augsburg University.

The basis of this add-on project is the investigation of the skimmer technology for thermal analysis –mass spectrometry coupling systems. Main goals are the optimization of the system and the cooling effect of the skimmer, investigated by photo ionization as a fragment-free soft ionization technique. Next to the optimization of the system, new applications of the developed instrument are being investigated in the field of inorganic chemistry, monitoring of chemical reactions and industrial process simulation.

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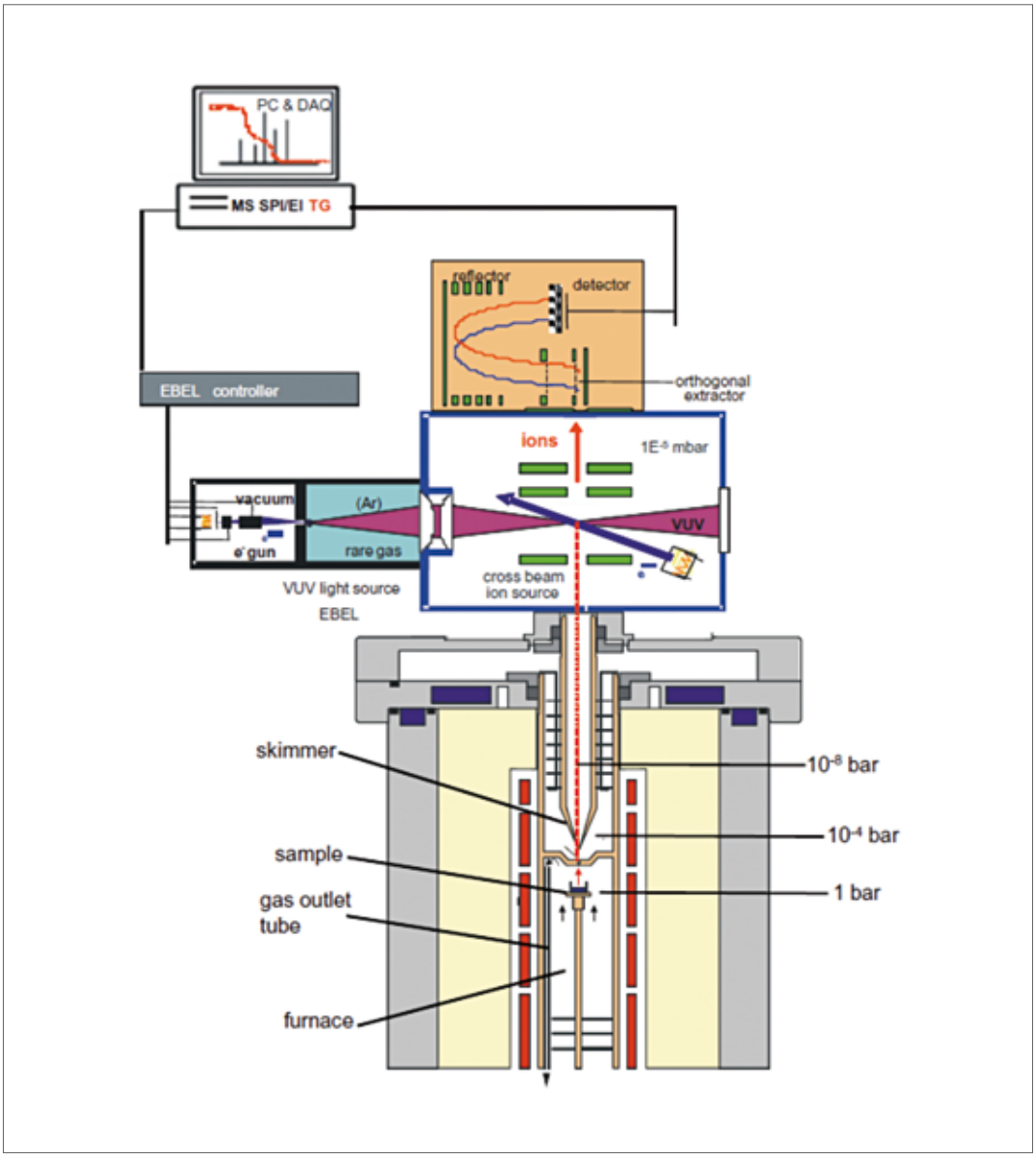
Funding: This project is being funded by the Bavarian Research Foundation.

Schematic setup of the TA-Skimmer-SPI/EI-MS



Environmental nanoparticles and Health: Exposure, Modeling and Epidemiology of Nanoparticles and their Composition within KORA

In August 2013 a joint project between our cooperation group "comprehensive molecular analytics" (CMA) and the Institute of Epidemiology II started.

Ultrafine particles (UFP) contribute little to mass concentration, but are the dominating contributors to number concentration. They can penetrate deeply into the respiratory system, translocate to other important organs of human body via the circulation system and therefore cause systemic health effects [1]. Studies on health effects of long-term nanoparticle exposure are urgently needed for European Union decision makers to consider regulations for environmental nanoparticles. Moreover, knowledge is missing regarding nanoparticle chemical composition profiles and their specific health effect relevance. A long

term study with thorough nanoparticles monitoring, sampling and analysis as well as health effect outcome measurement and assessment is granted. A one year sampling campaign cycling among 20 monitoring sites in the Augsburg area has started in February 2014 to characterize temporal and spatial variation of UFP. Chemical composition of nanoparticles sampled at 5 master sites will be analyzed by CMA. Urine samples collected from the KORA FF4 cohort are analyzed to obtain information on representative biomarkers. A dataset of nanoparticle exposure and human health outcome will be generated and serve as one important backbone for exposure model development of the epidemiologists.

The CMA group samples nanoparticles using a Rotating Drum Impactor (RDI) in series with an automatic filter sampler thus providing ultrafine particles only on the filters and, additionally, PM10-2.5, PM2.5-1, PM1-0.1 particle fractions on the drums. It benefits the analysis of chemical compounds by avoiding sampling under too low pressure conditions. Lab experiments were carried out using ambient and lab-generated ammonium sulfate particles to check the cut-off size and sampling setup of the RDIs. Both experimental tests, in the lab as well as pilot parallel sampling on the HMGU campus and on the reference site in Augsburg, confirmed the comparability and applicability of both samplers for parallel reference site and master site sampling.

CMA is responsible for the determination of biomarkers of oxidative stress in selected urine samples collected from participants of the KORA FF4 cohort. For this purpose LC-MS based methods are actually optimized and validated.

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Funding: This project is funded by the Helmholtz Zentrum München – Health and Environment Funding.

Selected research projects

Pyrolysis-gas chromatography with electron-ionization and selective photo-ionization mass spectrometry for characterization of complex crude oils

Stefan Otto (UR), Thorsten Streibel (UR/HMGU), Martin Sklorz (UR), Ralf Zimmermann (UR/HMGU)

Introduction

Aromatic compounds, especially PAH play an important role in fossil fuels and their byproducts. Referred to MULLINS et. al. [1] in the crude oil feedstock the content of high molecular species as well as the aromaticity increases. The fractions of polar compounds containing sulfur are increasing as well. All this cause problems with the refinery process, desulfurization and storage [6], which is the reason that these procedures are getting more and more complicated.

In complex samples such as crude oil, several thousands of different chemical species are present and the identification and quantification of individual compounds is difficult. ESCHNER [2] developed a quasi-simultaneous acquisition of hard EI- and soft single photon ionization mass spectrometry (SPI-MS) for GC/MS analysis by rapid switching between both ionization methods. The system has been successfully applied to diesel fuel. In this study an analytical system has been developed, that is able to break high molecular weight structures efficiently, has a high separating capacity and provides both universal and selective and sensitive substance spectra.

Experimental

A conventional gas chromatograph (HP 5890 Series II) was coupled with a pyrolyzer system (Frontier Laboratories, Double-Shot-Pyrolyzer, model: PY-2020iD). The samples first undergo a desorption process at 300 °C. After the thermal desorption process, the same sample is introduced for a second time after the pyrolyzer oven is heated up to 600 °C.

After both steps, the evolved substances are injected in the gas chromatograph. It is equipped with a non-polar column (SGE-BPX-5; 30 m x 0,25 mm x 0,25 µm). After passing the chromatographic column the gas flow was split by a Y-Splitter (deactivated PressFit 3-way Y-Splitter for FS Tubing with 0,20 to 0,75 mm OD) and transferred simultaneously to an electron ionization quadrupole MS (EI-QMS) and a Resonance-Enhanced-Multiphoton-Ionization Time-of-Flight MS (REMPI-ToFMS). For REMPI, a Nd:YAG laser (BIG SKY ULTRA, Quantel, Les UliCedex, France) with two frequency doubling units at 266 nm was employed. The laser is operated with 10 ns pulse width and a 20 Hz repetition rate with a power density of approximately 7 x 10^6 W / cm^2. A reflectron time-of-flight mass spectrometer (Reflectron CTF10, Kaesdorf Geräte für Forschung und Industrie, Munich, Germany) was utilized for the detection of the molecular ions. A scheme of the coupled system is given in figure 1.

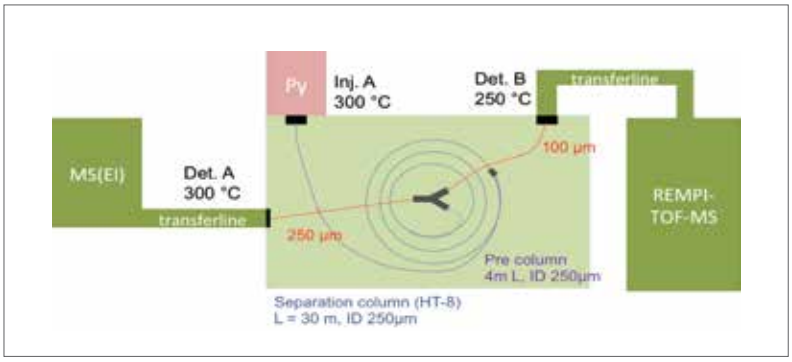

Figure 1: Scheme of the experimental setup depicting the pyrolyzer unit (Py), the GC and both mass spectrometric detection systems (EI-QMS and REMPI-TOFMS)

Results and Discussion:

Figure 2 shows two 2D-chromatograms of the Turkish crude oil under thermo-desorption and pyrolysis conditions. Under thermo-desorption conditions a broad substance spectrum is revealed and aromatic compounds are registered in a mass range between 100 and 450 m/z. The separation process along the column and the different retention times allow an insight into the different species contributing to one mass-to-charge ratio. In the pyrolysis step also a broad substance spectrum is visible, but the signal intensities are lower. The aromatic substance spectrum starts with benzene [m/z = 78] and toluene [m/z = 92]. Those are pyrolysis products of larger low volatile structures, which have not been evaporated in the thermo-desorption step.

Figure 3 shows specific ion traces for dibenzothiophene and the first up to the fourth degree of alkylation for REMPI-TOFMS and EI-QMS detection, respectively. The isotope ratio of sulfur can be used for identification. Interesting are the

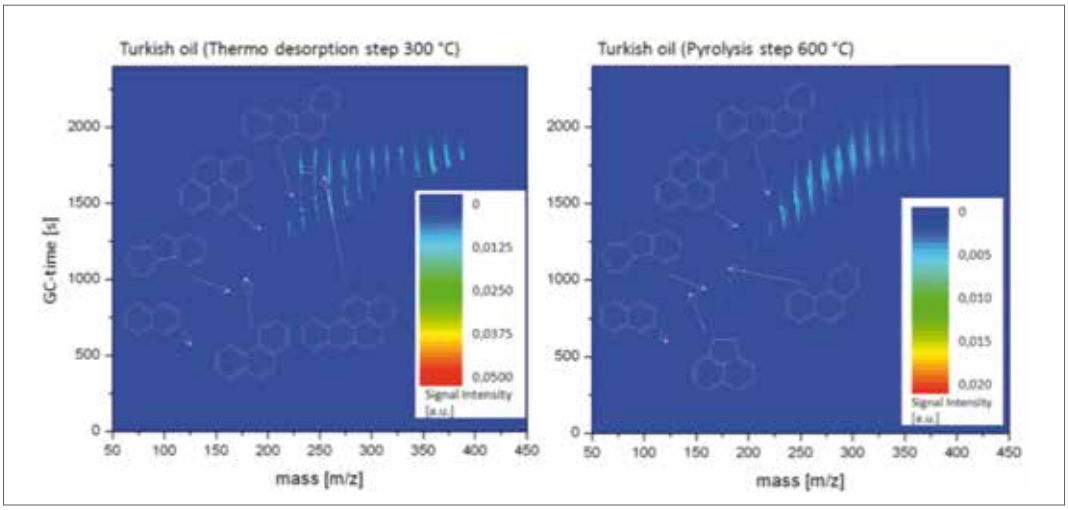

Figure 2: Two-dimensional GCxREMPI-TOF-MS analysis of Turkish crude oil. On the y-axis the GC- retention time is plotted. On the x-axis the mass-to-charge ratio is shown. Intensities are graduated in color. Left: chromatogram of a sample injection temperature of 300 ° C. Right: chromatogram of a sample injection temperature of 600 ° C.

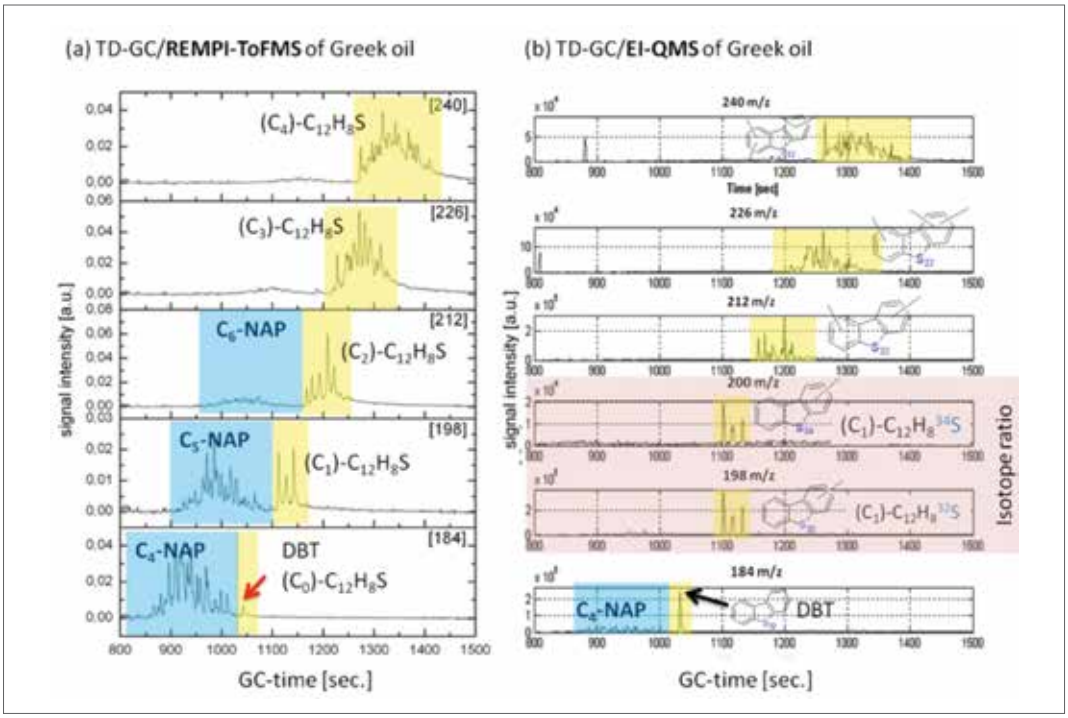

Figure 3: Dibenzothiophene and its alkylated derivatives (CX) in Greek crude oil. Direct comparison of the ion traces which resulting from REMPI-ToFMS (left) and EI-QMS (right). On the x-axis GC-time is plotted and on the y-axis the peak intensity is shown.

isotopes 32-S and 34-S, which occur in a ratio from 95% to 4%, respectively. The figure shows the occurrence of methyldibenzothiophene with 32-S [m/z = 198] in comparison to 34-S [m/z = 200]. If the retention times of the two peaks are coinciding, then with high probability it is a sulfur compound. By doing so, one may distinguish between PAH and PASH, which have the same nominal mass.

Comparing EI and REMPI data, the high selectivity with REMPI at a wavelength of 266nm is obvious. REMPI-ToFMS is able to separate between dibenzothiophene and C4-alkylated naphthalenes. In the EI chromatogram fourfold alkylated naphthalene exhibit significantly lower signals than dibenzothiophene. In the REMPI chromatogram the conditions are the other way round. It is even possible to see five and six times alkylated naphthalenes, which are no longer detectable with the EI setup. Hence, both ionization methods complement each other.

The obtained information such as distribution of alkylated PAH, size of aromatic structures or the fraction of heteroatomic substances may be important in increasing the efficiency of petroleum processing. Furthermore, the developed system can also be used for other applications such as environmental studies (e.g. characterization of dissolved organic matter in sea water etc.).

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On-line coffee roast monitoring of a single coffee bean with resonance enhanced multiphoton ionization

Romy Hertz-Schünemann (UR), Thorsten Streibel (UR/HMGU), Ralf Zimmermann (UR/HMGU)

Resonance-enhanced multiphoton ionisation time-of-flight mass spectrometry (REMPI-TOF-MS) has been proven as powerful tool for fast and sensitive on-line monitoring of volatile- and semi-volatile organic compounds (VOC/SVOC) formed during coffee roasting (1-3). Whereas green coffee beans only contain small concentrations of VOC/SVOC; roasted coffee is very rich in flavour compounds. So far, more than 850 VOC/SVOC compounds have been identified and they represent up to 0.1 % VOC/SVOC per dry weight of roasted coffee (4). Up to now, the knowledge about these processes remains fragmentary in face of extensive research on coffee flavour formation.

In this context a new sampling method for PI-MS was developed to analyze the formation of coffee roast aroma inside a single coffee bean. The application of the so called "µ-probe" technology to coffee beans allows the on-line monitoring of dynamic processes.

Gas sampling and REMPI-technique

For the single bean experiments, a µ-probe sampling setup was used, which has been described elsewhere (5). The µ-probe (Figure 1a) consists of an aluminium base body which is coupled to the transfer line. The essential part of the µ-probe is a small stainless steel capillary (ID 0.2 mm / OD 0.4 mm), which is connected to the transfer capillary using a capillary union. The µ-probe capillary sticks out of the base body by approximately 4 mm and is thereby indirectly heated up to 120 °C at the cone of the capillary by the full heated sampling system. For sampling of the roast gases at the surface of a single coffee bean, the bean was placed in a 2 ml glass flask, which was attached to the µ-probe (Figure 1a-left). For measurements of roast gases inside a single coffee bean a Ø 1 mm hole was drilled approximately 5 mm deep into the beans (Figure 1a-right). For the simulation of the roast process a hot air gun was used and the temperature was controlled by a mantle thermocouple. In this study green Coffea arabica beans from Bolivia and green Coffea canephora beans from India (both in organic quality) were used. Four replicates were measured for each experiment.

For the detection of VOC/SVOC a REMPI-TOFMS was taken (Figure 1b). A frequency-tripled (355 nm) Nd-YAG laser (Continuum, Santa Clara, CA, USA, repetition rate 10 Hz, pulse width 5 ns) 89 % of the 355 nm output is guided by a beam splitter

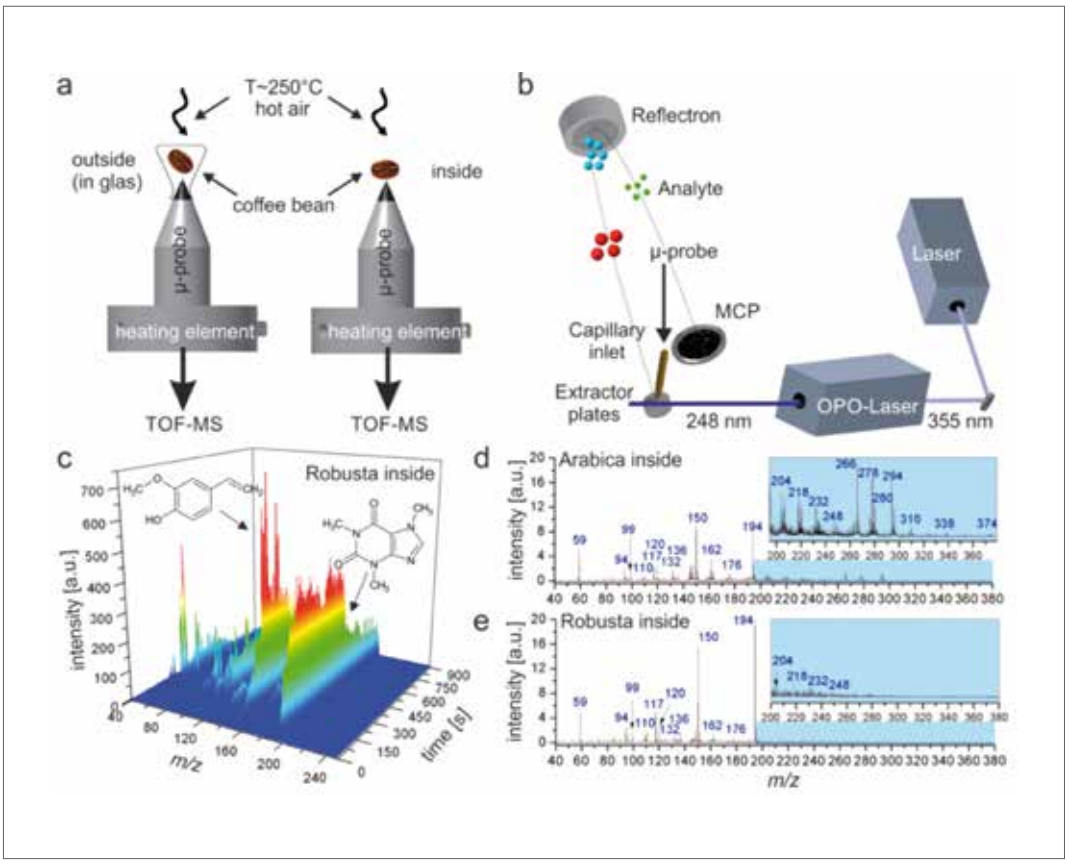

Figure 1: a) Overview of the roast gas sampling setup for µ-probe measurements inside or in the vicinity (outside) of a single coffee bean. b) Scheme of the REMPI-TOFMS. c) 3D representation of VOC/SVOC time intensity profiles sampled inside a single Robusta coffee bean and REMPI-TOF mass spectrum measured inside of single Arabica bean (d) or inside a single Robusta bean (e).

to an optical parametric oscillator (OPO, VISIR 2 + SHG, GWU-Lasertechnik GmbH, Erftstadt, Germany). By doubling the OPO output UV pulses are generated for REMPI. Here, the wavelength of 248 nm is chosen, because it is well-suited for detection of aromatic compounds. The laser beam is focused underneath the inlet needle in the ion source of the mass spectrometer, where it crosses the effusive molecular beam of the evolved roast gases. The generated molecular ions are extracted into the flight tube of a reflectron TOFMS (Kaesdorf Instrumente für Forschung und Industrie, Munich, Germany). The resulting mass spectra (10 Hz) are recorded by two PC cards (Acquiris, Agilent Technologies, Basel, Switzerland, 250 MHz, 1 GS/s, 128 kb). Data recording and processing is performed by a purpose-written LabView (National Instruments, Austin, Texas, USA) based software programme.

Results

In Figure 1c/d/e REMPI-TOFMS data for Arabica and Robusta sampled via the µ-probe from inside the bean are shown. The three-dimensional plot (Figure 1c) depicts an overview on exemplary single bean roasting results for a Robusta bean. In general the time-intensity profiles are dominated by the masses m/z 150 and m/z 194, which can be predominately assigned to 4-vinylguaiacol and caffeine, respectively. Regarding the mass spectra of Arabica (Figure 1d) and Robusta (Figure 1e), the latter exhibits a higher content of these components, which is corresponding to the literature (4). Furthermore, a striking and consistent difference between measurements on Robusta and Arabica is the occurrence of masses above m/z 200 for Arabica beans. In Robusta masses above m/z 200 are nearly absent.

With the new sampling method in combination with REMPI-TOFMS we could show that the postulated degradation pathway of caffeoyl quinic acid (6) (Figure 2a) can be confirmed by monitoring its time-formation profiles (Figure 2b). Corresponding to the degradation steps (I, II, III, IV) out of the reaction pathway the time-formation profiles show their formation maxima at different roasting times. Vinylcatechol (II) shows the earliest maximum and methlycatechol has the latest maximum (IV), whereas the components catechol (III) and ethylcatechol (III) exhibit a formation maxima in between.

Time-formation profiles of selected compounds inside and outside the coffee bean provide unique insights into the permeability of the beans' structure. Averaged time-intensity profiles for each compound from inside and outside the bean have been superimposed and normalised to the same maximum intensity. In Figure 2c the results for the components m/z 110 (dihydroxybenzenes, methylfurfural) and m/z 124 (guaiacol) are presented. Whereas for m/z 110 the maxima in the time-intensity profiles from inside the bean shows an earlier formation than outside the bean, the time-intensity profiles of m/z 124 do not show a time-shift between their formation maxima. Obviously the generated volatiles in the interiors' structure of the coffee bean require some finite time for the diffusion to the surface of the coffee bean.

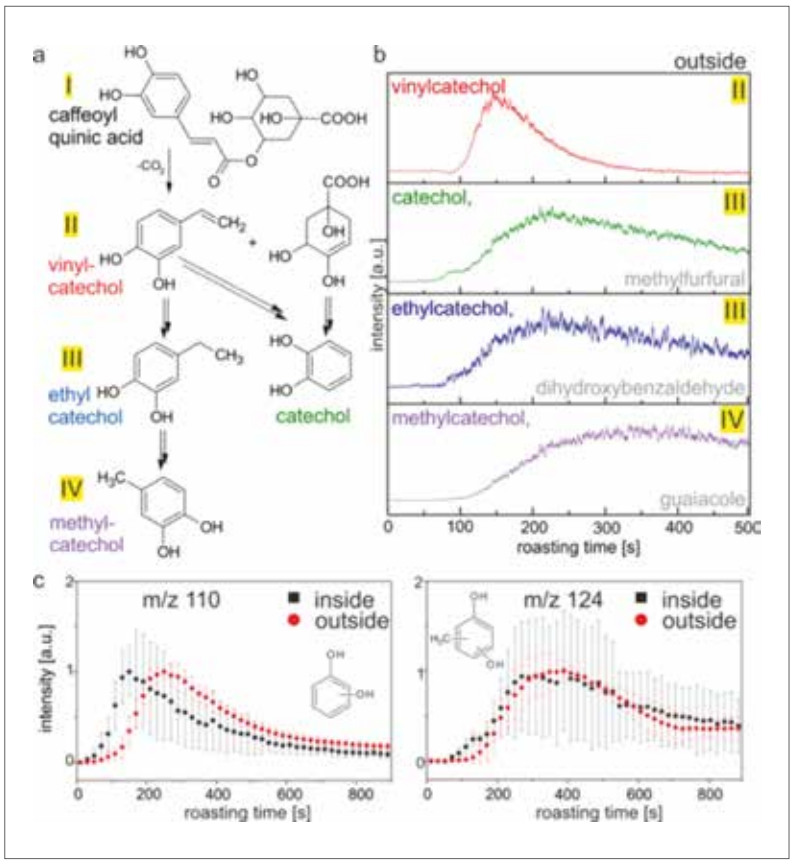

Figure 2: a) Chemical reaction/degradation pathways of caffeoyl quinic acid(6) during coffee roasting. b) Corresponding time–intensity profiles (base line corrected) of selected VOCs monitored from a single Robusta bean sampled in the vicinity of a bean with the µ- probe REMPI-TOFMS. c) Roasting profiles of two VOCs (including the standard derivation) with are either rather similar (right) or show different (left) release characteristics from inside and outside of a Robusta beans.

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Integration of two-dimensional gas chromatography and high-resolution mass spectrometry for the characterization of the heroin manufacturing process: a combined complementary approach.

Marion Schäffer (HMGU), Theo Schwemer (UR), Michael Pütz (BKA), Thomas Gröger (HMGU), Martin Sklorz (UR), Ralf Zimmermann (UR/HMGU)

The Joint mass spectrometry Centre (JMSC) has further extended their core capacities in mass spectrometry (MS). After the successful implementation of a fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) in 2011 at the JMSC facilities at the University of Rostock (UR) also the JMSC facilities at the Helmholtz Zentrum in Munich (HMGU) were upgraded in 2012 with high resolution and high accuracy MS instrumentation. Unlike FTICRMS the new high resolution time-of-flight systems (HRT) are designed for the hyphenation of fast chromatography systems and were operated in close cooperation with LECO. A first application driven pilot study combines the benefits from both techniques and integrates already well-established two-dimensional gas chromatography with the merits of high resolution and accurate mass spectrometry. The forensic study was focused on identification of impurities to characterize the illicit manufacturing process of heroin.

Introduction:

The illicit manufacturing processes for heroin are only vaguely described in the literature. During the isolation of morphine also other main and minor alkaloids present in opium poppy are extracted, and the subsequent chemical conversion of morphine to the corresponding diacetylmorphine (heroin) leads to the formation of various by-products. These minor and trace compounds present in illicit heroin generate a specific impurity profile of each batch and manufacturing process. In a proof of concept study we already demonstrated the applicability of two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOFMS) for the analysis of illicit heroin samples. GC×GC-TOFMS benefits from its very high chromatographic resolution combined with the high sensitivity and the selectivity of the mass spectrometric detection. However, common GCxGC-MS instrumentation is based provided only unit mass resolution. Identification of compounds is mainly done by comparison of the fragmentation pattern generated by electron ionization, to mass spectral libraries. An independent interpretation of the spectra's is very elaborate and time consuming. A major step forward is the implementation of high resolution spectrometry to allow the elucidation of the elemental composition based on the accurate mass and the isotopic pattern. Two gain high and accurate mass information about the spectra as well as the molecular ion two complementary HR Techniques were further applied and hyphenated to gas chromatography. For the acquisition of HR fragmentation pattern the samples were also analyzed by recently introduced gas chromatography coupled to high resolution time-of-flight mass spectrometer system (GC-HRT) which provided a mass resolution up to 50.000 and a mass accuracy bet-

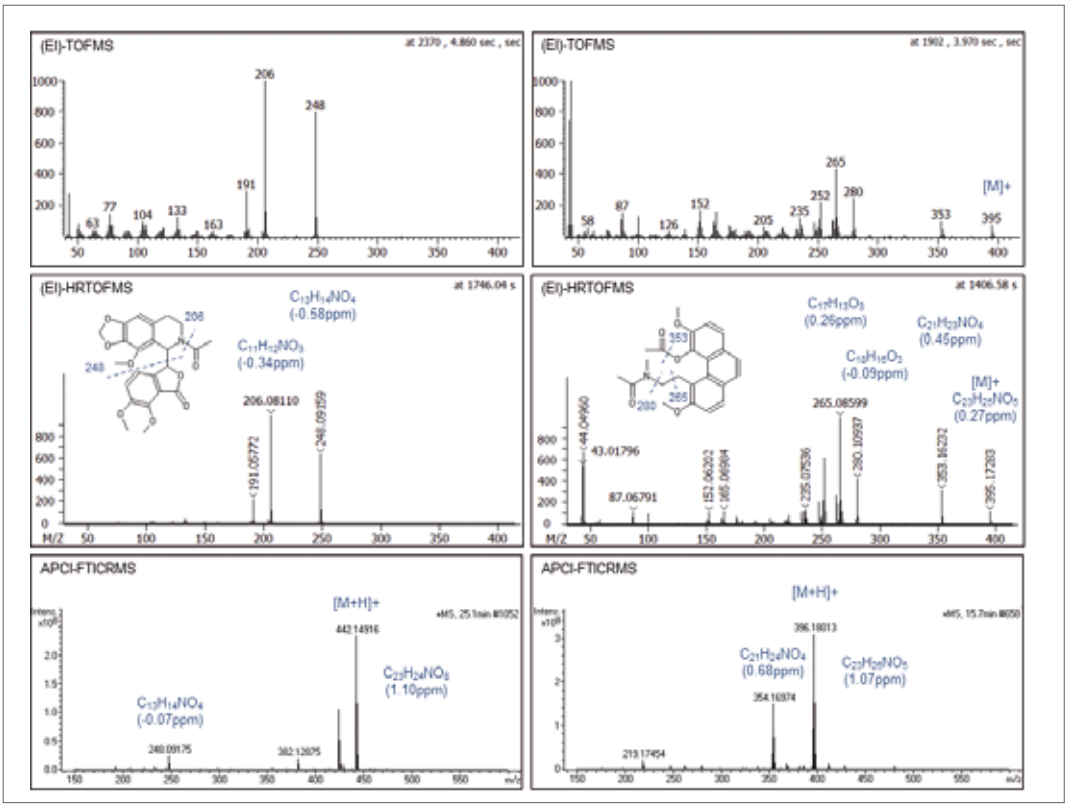

Figure 1: Acquired mass spectra of N-Acetylnornarcotine (left) and 3,6-Dimethoxy-4-acetoxy-5-(2-(N-methylacetamido)) ethylphenanthrene (right) acquired with (EI)-TOFMS (upper part), (EI)-HRTOFMS (middle part) and APCI-FTICRMS (lower part)

ter than 1 ppm with an acquisition rate of up to 200 Hz. The absence of an observable molecular ion for some compounds is the major drawback of electron impact ionization (EI). Therefore, the second approach was focused on the generation of molecular ions. For the presented work, a gas chromatograph was coupled to a Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS) using APCI as interface. The ultrahigh mass resolution provided by FTICRMS systems combined with the chromatographic separation (GC) and the soft ionization (APCI) is an efficient tool for the characterization of a sample and the elucidation of the elemental composition based on the observed molecular ion. The combination of GC×GC and GC hyphenated to high-resolution mass spectrometry was used in this study to characterize the acidic and neutral impurities in samples taken from the different steps during an authentic heroin manufacturing process to obtain basic information about the composition and origin of the impurities resulting from such a controlled synthesis.

Experimental & Results:

Samples from a documented authentic heroin manufacturing in Afghanistan were kindly provided by the Bundeskriminalamt. Samples were collected at all stages of the manufacturing process, starting from raw opium. As intermediates and final products the morphine base, the heroin base (brown), the heroin base (white) and the heroin hydrochloride were collected. Extraction was done according to the guidelines of the heroin analysis program. The extracts of raw opium were additionally treated with trimethylsilyldiazomethane (TMSD) prior to analysis for methylation of the fatty acids. The samples were subsequently analyzed by GCxGC-(EI)TOFMS, GC-(EI)-HRTOFMS and GC-(APCI)FTICRMS. In the first step known compounds were identified based on their EI mass spectra which were compared to mass spectral libraries. Mass spectral hits were furthermore verified using the accurate molecular mass information from the FTICRMS measurement, the relative retention time and manual comparison of the EI fragmentation pattern. Chromatographic comparison of the impurities of the heroin extract and the acetylated alkaloid standards were used to determine the origin of unknown impurities and to reveal the basic molecular structure of the unknowns. In a next step, the elemental composition was obtained based on the accurate molecular weight measured by FTICRMS. The potential elements used for formula generation were restricted to CHNO. Calculated sum formulas were verified manually by comparison of the theoretical and the observed isotopic pattern caused by natural occurring 13C, 15N and 18O isotopes. Major EI fragments were studied using GC-EI-HRT to distinguish isomers and detected compounds were also compared to compounds described in the literature.

No significant qualitative differences between the different batches of raw opium could be observed with respect to the entire impurity profile. With respect to the opium alkaloids only papaverine, papaveraldine, narcotine and narceine were still detectable in the morphine base and the brown heroin base. Impurities of the brown heroin result mainly from the acetylation step during manufacturing. Amongst them the 18 target compounds were present. Other compounds that could be of potential interest with respect to profiling of heroin were investigated in more detail within this study by application of high resolution mass spectrometry. As expected only very few compounds could be detected in the purified white heroin base and the heroin hydrochloride. The white heroin base is commonly not available on the illicit market; therefore in the following the focus was set on the brown heroin base. Twelve compounds, amongst them four opium alkaloids, were found to be directly derived from the used raw opium; they were preserved unaltered through the manufacturing process. For 21 acetylated derivatives, the original alkaloid was known or could be determined during this study providing basic information on the impurities' origin. Some of the reported unknown compounds were found to be present in moderate or high abundance (e.g. UNK254(3)) in the brown heroin base. These compounds can be useful for an enhanced characterization of seized illicit heroin samples. Provided that they can be frequently found in illicit heroin seizures, these compounds may then be considered for profiling of heroin. For elucidation of the elemental composition of unknown compounds, GC hyphenated to high resolution mass spectrometry was used. GC-(EI)HRTOFMS provided accurate masses that enabled the generation of sum formulas of major peaks in the mass spectra. Due to the frequent absence of an observable molecular ion using EI ionization the elucidation of the elemental composition of the molecule was often prevented. FTICRMS provided ultrahigh mass resolution and in combination with APCI it provided the accurate molecular mass for elucidation of the elemental composition of most of the unknown compounds investigated during this study.

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Comprehensive breath gas analysis using needle trap micro extraction and two-dimensional gas chromatography for simultaneous proton-transfer reaction – mass spectrometry

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The objective of this study was to establish and evaluate an off-line method based on needle trap micro extraction and comprehensive two-dimensional gas chromatography – time of-flight mass spectrometry that is applicable to an on-line proton-transfer reaction - quadrupole mass spectrometry approach for the monitoring of rapid changes in breath profiles. Once approved and evaluated, it holds great promise for the screening of volatile organic compounds originated from metabolic stress. In combination with proton-transfer reaction - mass spectrometry it has diagnostic potential for the monitoring of early breath biomarkers.

Introduction

Analysis of metabolites in body fluids is of great interest for monitoring the human metabolism and health state. Breath analysis offers potential advantages for the medical diagnosis of diseases over urine or blood analysis including that breath testing is non-invasive and painless [1]. Many studies are focused on screening human breath samples to identify unique biomarkers and to classify volatile organic compounds (VOCs) into endogenous/ exogenous substances [2]. However, in most cases diagnostic applications require the detection of a large pattern of breath gas biomarkers rather than unique biomarker compounds. This renders analytical techniques with a powerful molecular profiling capability such as comprehensive two-dimensional gas chromatography – time-of-flight mass spectrometry (GCxGC-TOFMS) to be in particular useful [3]. Another diagnostic approach is to follow the change in the concentration of target VOCs in breath as in pharmacokinetic studies [4] or metabolic tracer tests. Here, on-line real-time analysis based on direct inlet and soft ionization mass spectrometric approaches including proton-transfer reaction - mass spectrometry (PTR-MS, [4]) are of interest. Identical results determined by breath gas analysis and blood measurements in studies of volatile biomarkers in diabetes research demonstrated the feasibility of the analysis of exhaled breath to separate Type 2 diabetics from healthy individuals. Halbritter et al. [5] applied successfully on-line breath gas analysis by proton-transfer reaction - quadrupole mass spectrometry (PTR-Quad-MS) for the screening of gestational diabetes mellitus (GDM). The breath gas data correlated with GDM diagnosis, but the compounds could not be identified.

The off-line analysis of exhaled breath is, due to the high relative humidity (RH), quite challenging and requires a sophisticated adaption of the method to the particular sampling situation. Off-line GCxGC-TOFMS analysis of human breath gas has been applied in combination with pre-concentration techniques such as needle trap micro extraction (NTME) [3]. The implementation of NTME with gas chromatography - mass spectrometry (GC-MS) has been proven to be a powerful tool for the identification and quantification of VOCs in breath gas by direct sampling [3]. To benefit from highly sensitive and highly selective off-line analytical methods and highly time-resolved on-line methodology the simultaneous application and the comparison of the results is a promising step.

Therefore, an analytical method for the off-line time-resolved analysis of breath gas which complies with the restrictions during a parallel on-line PTR-Quad-MS sampling was developed and evaluated. The combined off- and on-line analysis of breath gas was utilized during an oral glucose tolerance test (OGTT) as a metabolic stress situation for the future identification of a metabolic pattern that can be linked to an early state of a metabolic disorder caused by diseases such as diabetes.

Results and discussion

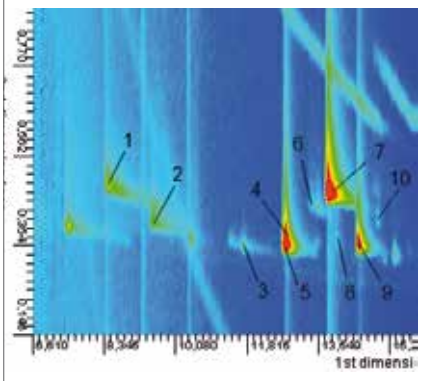
For chromatographic separation a polar thick film capillary column (BPX-Volatiles) was used in the first dimension to have a slight separation of the analytes by polarity and boiling point. On the second dimension capillary column (Rtx-200) the intermediate polar analytes that display lone pair electrons such as acetone are separated. Using this column combination a good separation of water and CO2, column bleed and the analytes was obtained.

Figure 1 shows a part of a total ion chromatogram of a GCxGC-TOFMS run of a breath sample taken in the fasting status prior to the glucose-intake as first demonstration results. The indicated predominantly detected highly volatile organic compounds are listed in Table 1. For comparative reasons, relative values related to the fasting value have been considered for further investigations.

During simultaneous measurements by PTR-

Quad-MS and NTME-GCxGC-TOFMS representative end-tidal concentration profiles over time of ethanol were obtained by NTME-GCxGC-TOFMS (a) and m/z signal 47 (protonated molecule mass of ethanol or isobaric compounds) by PTR-MS (b) (shown in Figure 2). Similar time profiles were obtained for ethanol by both methods. Directly after administration of the glucose solution ethanol concentration increased dramatically due to the alcohol content of the OGTT solution (0.01-0.06 Vol.-%), turned around and plunged during the first 10 minutes. Afterwards, exhaled ethanol levels rose considerably, peaking between 20 and 30 minutes and dropped rapidly. Similar gradient were also observed in other studies due to alcoholic fermentation of glucose by gut bacteria and yeast and following diffusiveness into the respiratory system. NTME-GCxGC-TOFMS results for ethanol were comparable to PTR-Quad-MS results for m/z signal 47. Higher relative changes in ethanol concentrations were observed by NTME-GCxGC-TOFMS than for m/z signal 47 by PTR-Quad-MS potentially resulting from interferences by means of PTR-Quad-MS.

Figure 1: Part of a GCxGC-TOFMS total ion chromatogram of a breath sample taken in the fasting status. For peak assignment refer to Table 1



no.	compound name
1	acetaldehyde
2	methyl alcohol
3	pentane
4	ethanol
5	isoprene
6	2-propenal
7	acetone
8	dimethyl sulfide
9	isopropyl alcohol
10	acetic acid, methyl ester

Table 1 Compound list of the GCxGC-TOFMS total ion chromatogram of a breath sample in the fasting status

This could include fragmentation processes of ethanol and the formation of ethanol clusters resulting in more than one signal for ethanol and therefore in a reduced signal for m/z=47. Furthermore, the discrimination of isobaric compounds due to unit mass resolution by PTR-Quad-MS may have an influence on the results. Therefore, time-resolved NTME-GCxGC-TOFMS is a potential tool for the evaluation of targets with dynamic profile changes detected by PTR-Quad-MS.

In conclusion, time-resolved off-line NTME-GCxGC-TOFMS and clinically approved on-line PTR-MS is a powerful combination for the monitoring of potential target compounds. In follow-up studies combined off- and on-line breath gas analysis is applied for the future identification of early biomarkers.

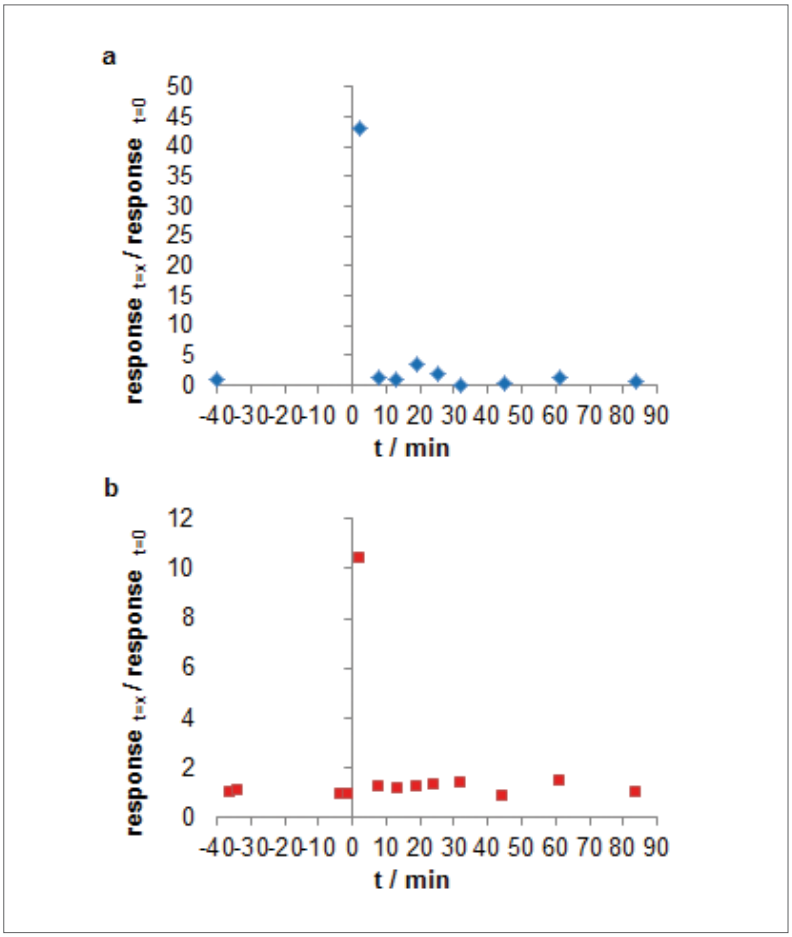


Figure 2: Breath ethanol profile by NTME-GCxGC-TOFMS (a) and the profile of m/z signal 47 by PTR-Quad-MS (b) during an OGTT by simultaneously measurements

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Diesel Exhaust Particles (DEP) are Involved in the Formation and Strengthening of Allergic Diseases

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It is assumed that polycyclic aromatic hydrocarbons (PAHs) are responsible for the effects caused by DEP, regardless of the nature of the particles, due to the production of reactive organic species (ROS) induced by PAHs

In January 2012, a project based on two bachelor theses for the development of a new method for the determination of PAHs and their metabolites in human blood was started. The method will be based on the thermal extraction of the PAHs from a 1 µl blood sample, using a lancing device for capillary blood sampling and a 1 µl disposal capillary pipette.

Introduction

Airborne particulates and gases related to human activities, or ambient air pollution, are important environmental issues that affect human health. In recent years, epidemiological studies have demonstrated an association between exposure to roadside emissions and increased symptoms of asthma and allergic rhinoconjunctivitis [1]. Major components of inhaled particles less than 2.5 µm in size are diesel exhaust particles (DEPs) and their associated organic compounds, such as polycyclic aromatic hydrocarbons (PAHs). Experimental and clinical evidences indicate that DEPs can exacerbate allergic immune responses [2] and increase total immunoglobulin IgE in the human upper airway in vivo following intranasal challenge [3]. Less attention has been attributed so far to the involvement of organic compounds of diesel emissions in IgE-mediated allergic inflammation at the level of mediator cells. Devouassoux and coworkers demonstrated spontaneous histamine release from and enhanced IL-4 production in basophils of allergic and nonallergic subjects exposed to DEP extracts [4]. Recent data provide evidence that DEP-associated PAHs may account for basophil activation and enhanced IL-4 production in response to crosslinking the high-affinity IgE receptor [5]. Phenanthrene (Phe) is a main component of environmental polycyclic aromatic hydrocarbons (PAHs) and occurs in various ambient sources, like particulate matter formed from diesel emissions and tobacco smoke, as well as in foodstuffs. Since its metabolites are excreted in large quantities in the urine, Phe is of high diagnostic value in the biomonitoring of occupational and epidemiological PAH exposure situations. Furher, Phe is a known substrate for cytochromes P450 (CYPs). However, the multiple and overlapping species of CYPs cover the role of individual isoforms in PAH metabolism. Whole blood elimination studies may help to elucidate the role of individual CYPs. Unfortunately, up to now, the quantification of Phe in (human) blood is a time consuming complex and costly issue and due to the required volume (> 1 ml) needs the help of a physician.

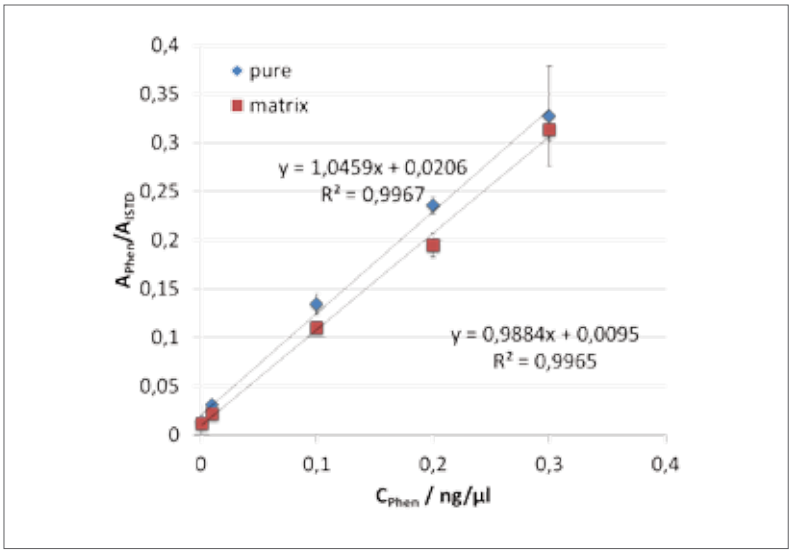


Figure 1: Calibration curves of pure Phenanthrene and spiked human blood samples (matrix).

The new developed method is based on the direct thermal extraction of Phen from human blood samples (1µl) using a lancing device for capillary blood sampling and a 1 µl disposal capillary pipette. This enables an easy, fast and low invasive sampling without the help of a physician and opens the way for animal studies where sample amounts of > 1 ml may be lethal. As further sample preparation, the blood sample is transferred onto a stripe of a quartz fiber filter and placed in a thermal desorption tube. Before sealing of the tube, an additional 1 µl disposal pipette, containing an internal standard solution of Phenanthrene D10 (1 ng/µl) is added to the tube. For the quantification, the ion intensities of m/z 178 (Phenanthrene) and 188 (Phenanthrene D10) were measured by GC-MS (PolarisQ, Thermo Scientific). Fig. 1 exhibits the calibration curves of pure Phenanthrene as well as spiked matrix (human blood) samples. The recovery of the phenanthrene in human blood can be calculated by the two slopes of the calibration curves and results to about 95 %.

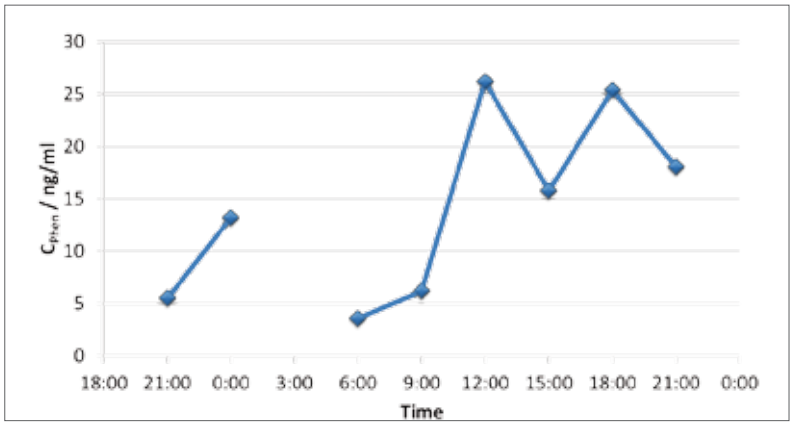
The precision of the method was determined by two series with n=10 samples at the lower (0.05 ng/µl) and upper (0.2 ng/µl) end of the calibration curve as well as a human blood sample. The

calculated standard deviations are based on the respective area ratios (APhen/AISTD) and result to 10 and 11 % respectively for the calibration standards and to 10 % for the human blood sample. For the day to day variability, 12 samples at a concentration of 0.01 ng/µl were prepared ant measured on three consecutive days. The standard deviations from the day to day analyses did not differ significantly from those of the individual days series (n=4) and were below 10 %.

For a human monitoring study, the phenanthrene blood concentrations of a 22 years old male volunteer were measured over 24 and 48 hours.

The first series (24 h) started at 9 pm. Blood samples (duplicates) were taken every 3 h. As expected, the morning value at 6 am is quite low (compared to the night concentration) since Phen was depleted overnight. After the first coffee at around 8:30 the Phen concentration rises and reaches its maximum after lunch at 11:30. The second peak can be observed at 6 pm, directly after dinner (see Fig. 2).

Figure 2: Phen blood concentrations of a male volunteer over 24 h.



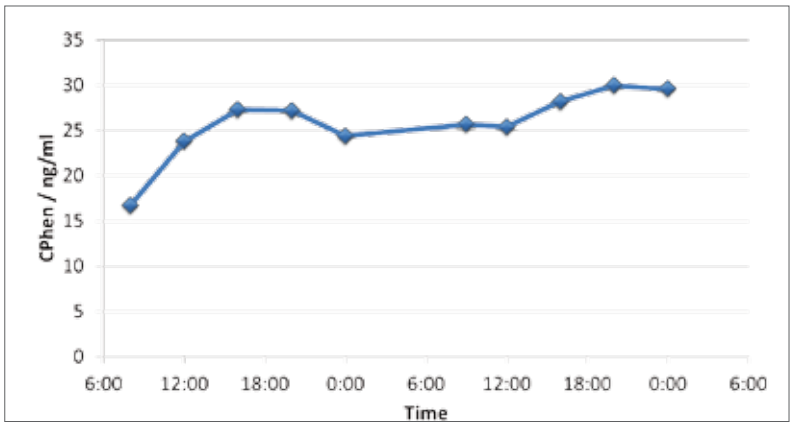


Figure 3: Phen blood concentrations of a male volunteer over 48 h.

In the second series over 48 h (duplicate samples every 4 h), the course of the Phen concentration is not varying significantly over the time. This is mainly due to the different eating behavior during this test period. During the first test-period, two distinct meals were taken by the volunteer. In different, during the second test-period, besides lunch and dinner, meals were taken more frequently, distributed over the whole day.

In conclusion, the new developed method, based on thermal extraction GC-MS is a highly sensitive and precise method for the determination of Phenanthrene in human blood samples. It overcomes the time consuming and error prone sample preparation of standard PAH analysis of blood samples as well as the restrictions in sampling of blood by a medical doctor, due to the restriction to 1 µl blood and the use of selve lancing devices for capillary blood sampling. Future work will open the method to additional analytes.

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Aerosol Samplers and Semi-Volatile Organic Compound Aerosols: Particle Evaporation and Implications for Workplace Risk Assessment

George Dragan (HMGU), Erwin Karg (HMGU)

Introduction and objective

Aerosols of Semi-Volatile Organic Compound (SVOC) origin represent a big challenge to industrial hygienists with respect to toxicological and sampling issues. Sampling hazardous semi-volatiles at the workplace is problematic as they may appear in both particulate and gaseous phase. More attention has to be given therefore to the dynamics of aerosol systems as the particle-vapor fractionation may be considerably dependent on sampling conditions.

A project was carried out to address the issue of semi-volatile aerosol particle evaporation both theoretically and experimentally and to provide experimental data to show the extent of evaporation losses that might bias the workplace risk assessment.

Materials and Methods

Aerosols of several SVOC substances (C14 up to C20 n-alkanes) and particle diameters (0.5 to 4 µm) were generated, diluted with particle free dry nitrogen and monitored for particle evaporation losses. The aerosols were quantified using an "on-line" method as well as "off-line" methods that are usually used for workplace sampling. The on-line approach for SVOC aerosols was to account for the total mass (TM) with a flame ionization detector (FID) preceded by a heated transfer line (180°C). The Particle mass (PM) was calculated from particle diameter measured by an optical particle sizer, while vapor mass (VM) was calculated as the difference between measured total and particulate mass (VM=TM-PM). As off-line systems, two types of workplace filter- / adsorber-samplers were tested throughout the project. The first type (GGP) was used at a flow rate of 3.5 l/min and consisted of a 37 mm glass fiber filter for the separation of the particle phase and a 3 g XAD2 adsorber cartridge for the quantification of the remaining vapors. The second type (GGP-mini) was operated at a flow of 0.33 l/min and comprised of a 12 mm glass fiber filter to trap particles and 1 g of activated charcoal for vapor adsorption. To study SVOC particle evaporation an experimental apparatus comprising of a Sinclair-LaMer aerosol generator, a flow tube and the above mentioned aerosol sampling system was set up inside a temperature controlled chamber. Particle evaporation in the flow tube was assessed by measuring the particles' diameter at two different flow tube positions representing 1 second and 4 seconds of residence time. The flow tube evaporation results were compared to a theoretical computer model. Parallel measurements using the on-line and off-line methods were conducted to quantify for the amount of PM evaporated from filters during the sampling process.

Results

Figure 1 exemplifies the modifications in particle size distribution (PSD) driven by evaporation. The solid lines represent the measured PSD at

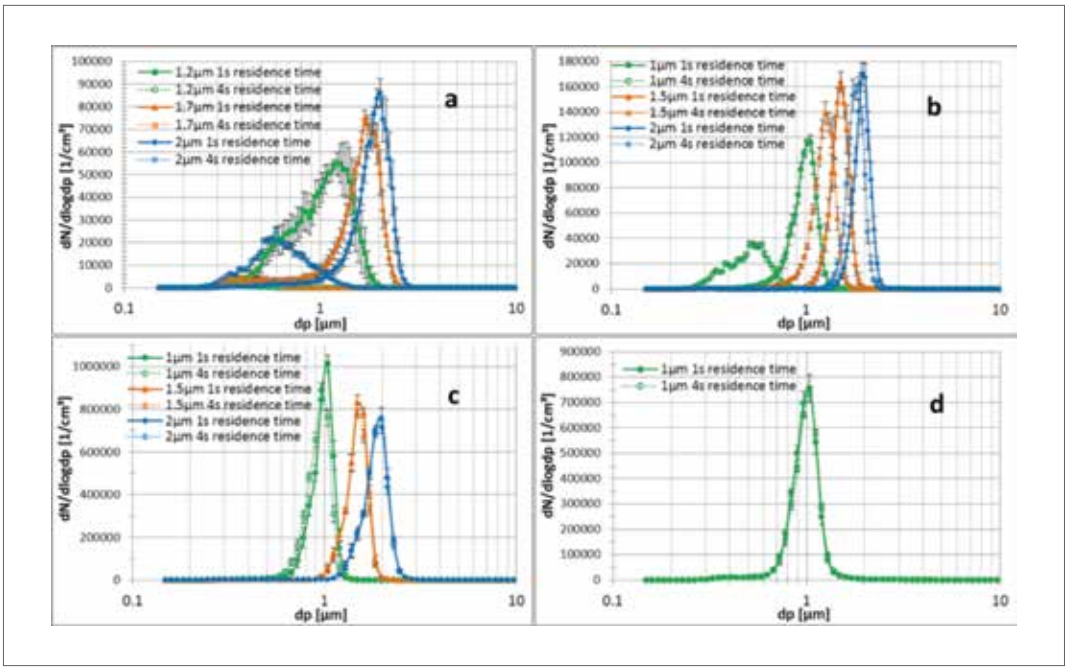


Figure 1: Comparison of particle size distributions measured at 1s (solid line) and 4s (dashed line) sampling points for Tetradecane (a), Hexadecane (b), Octadecane (c) and Eicosane (d)

about 1 second of residence time after the mixing region while the dotted lines show the measured PSD after additional three seconds of residence time. Flow tube measurements have shown that SVOC droplets can evaporate completely within 3 seconds as is the case for tetradecane or remain unchanged (octadecane), depending on substance volatility, vapor saturation degree, particle diameter and sampling temperature.

The experimental results correlate well with the numerical simulations (Figure 2). After 4s stabilization time, the relative deviation between numerical and experimental PM is less than 35% for all data sets. The experimental and model data were found to be in a good agreement for the flow tube experiments with less than 20% deviation for 80% of the data points.

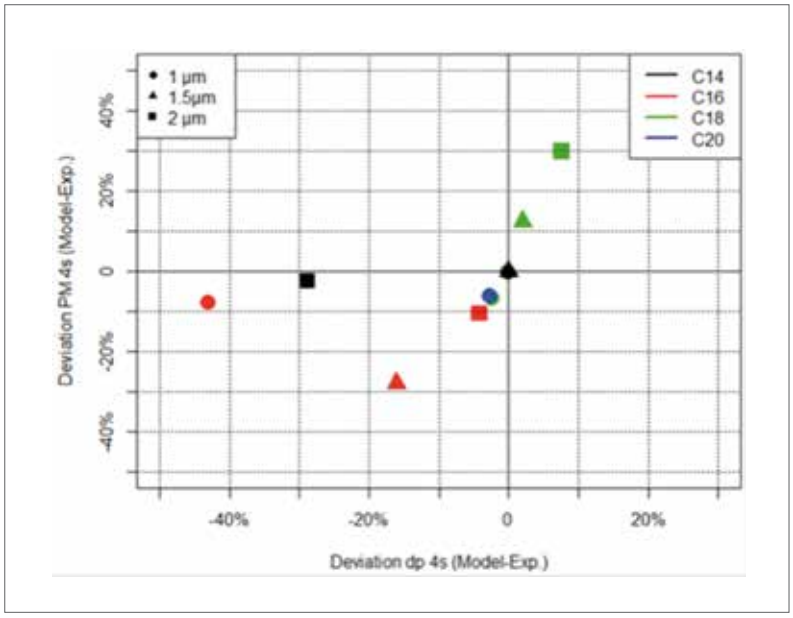


Figure 2: Model-experiment relative deviation (dp-particle diameter; PM-particle mass) after 4 s stabilisation time.Particle diameters (1 ... 2 µm) are shape-coded, particle substances (C14-C20) colour coded

Comparisons between the on-line method (Fig. 3, red columns) and the off-line method (Fig. 4, blue columns) have shows similar results for both methods with respect to TM. However the off-line method tended to lose a significant amount of particle mass due to evaporation, especially for more volatile compounds and small particles.

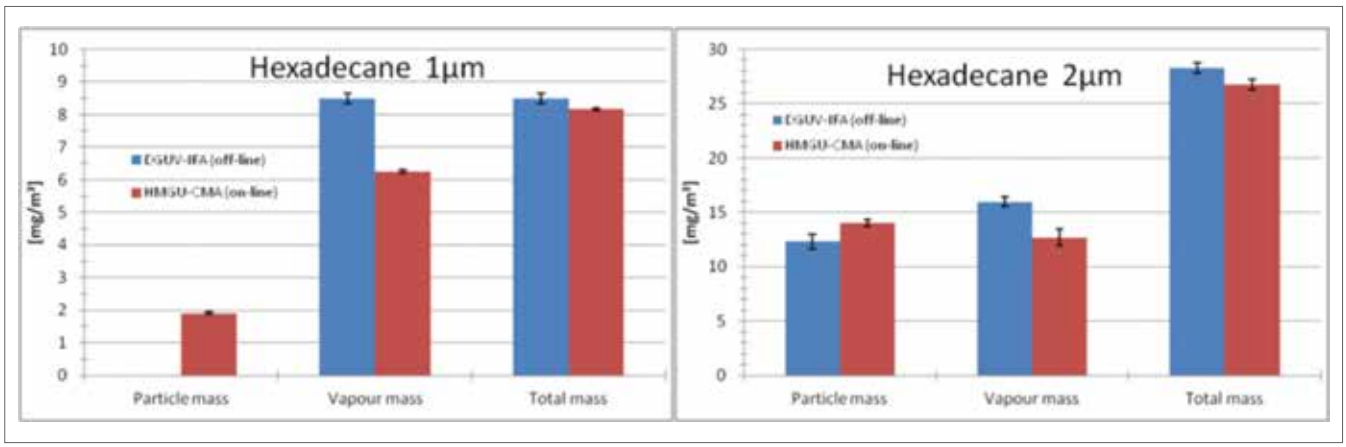
Conclusions

Our results show that the off-line method can be biased for SVOC particle measurement, but also that droplet evaporation can be predicted with good accuracy. The only comparable result that was independent of the sampling method is for TM. The off-line method systematically returns lower PM and higher VM values, a clear indication for particle evaporation loss. This effect is also expected to influence the workplace risk assessment; sampling using filters only can significantly underestimate the real aerosol concentration in the workplace.

The Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (MAK commission) in Germany already took notice of the projects' results. It introduced a new chapter concerning semi-volatile substances into the "List of MAK and BAT Values 2013" and marked 58 substances to potentially exist as particulate/vapor mixtures.

Funding and Cooperation: The project was funded by the German Statutory Accident Insurance (Deutsche Gesetzliche Unfallversicherung – DGUV), research grant FP 299

Figure 3: Comparison between on-line and off-line data for hexadecane droplets: 1 µm (left) and 2 µm (right)



New Technology for Fast Multidimensional Chemical Analysis of Thermal Processes

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The objective of the project is the development of a Thermal Analysis (TA) instrument, coupled to a fast-GC and Time-of-Flight mass spectrometer (TOFMS)

1. Applying TG-SPI-TOFMS to natural samples

The hyphenation of simultaneous thermogravimetry (TG) to single photon ionization time-of-flight mass spectrometry (SPI-TOFMS) for evolved gas analysis (EGA) is a thermal analysis technique for comprehensive characterization of thermal processes in carbonaceous materials. In addition to the complete thermal information from the TG, detailed chemical information can be extracted from the corresponding mass spectra[1]. The SPI mass spectra, in turn, are dominated by the molecular ions of the evolved gases, due to the soft character of this ionization technique. Natural sample releases a considerably amount of organic compounds during its thermal decomposition.

Discrimination different types of coffee

Coffee is one of the largest traded foods worldwide, with the dominant species being Coffea arabica (Arabica) and Coffea canephora (Robusta). Thus research on quality and optimization of the industrial processes is of great commercial interest. Roasting experiments were done laboratory -based on the micro scale using single beans in TG-SPI-TOFMS.

Analyzing the time-resolved SPI-mass spectrometric signature contour plots of the temperature resolved mass spectra of the roasting process in Fig. 1, some differences between the two coffee species are remarkable. At 20 min the signals at m/z 296 and 298 are dominant. These signals can be assigned to diterpene lipids anhydrous cafestol (m/z 298) and anhydrous kahweol (m/z 296). The difference between arabica (B) and robusta (D) during isothermal treatment are obvious and as Hertz-Schünemann et al. describe in “good accordance to the literature”; there is no anhydrous kahweol in the Robusta cultivar. Further experiments revealed the possibility of detecting Kahweol as a characteristic of the Arabica coffee also in powders and blends (roasted and grinded).

2. Rapid comprehensive characterization of crude oils by thermogravimetry coupled to fast modulated gas chromatography–single photon ionization time-of-flight mass spectrometry[2]

In this study, two crude oils from different origins have been investigated. In contrast to the previous described applications (coffee), a rapid chromatographic separation step has been included in to the TG-SPI-MS setup (Fig. 2) to result in TGxGC-SPI-MS. With this approach, fast isothermal GC separations with a cycle time of, typically, 30 s can be achieved. The eluted substances are subsequently analyzed by SPI-MS, leading to a comprehensive two-dimensional detection method (GC×SPI–MS).

Two distinct phases are clearly distinguishable for the Turkish oil. Starting from 40 °C to approximately 375 °C steady evaporation of the more volatile substances of this crude oil occurs. With rising temperature the mass/charge ratios of the evolved compounds also increase, so that a diagonal course of the pattern is observable (Fig. 3, red line on the left). The Greek oil undergoes a large mass loss over a relatively long period that results in a broad DTG peak from the beginning whereas the Turkish crude has only an intense peak on the DTG curve starting at approximately 100 °C, which can be partially ascribed to water, and a less pronounced mass loss with time in this phase. At approximately 375 °C pyrolysis and, thus, decomposition of heavier and less volatile components, starts; it ends at approximately 500 °C. Unlike the first phase, within the whole pyrolysis step the mass/charge distribution stays equal and does not rise with temperature, thus a vertical pattern is visible (Fig. 3, red line on the right). The second phase is much more distinct for the Turkish oil than for the Greek oil.

The inability to distinguish between isobaric and isomeric compounds was the main reason for enhancing the previous described TG-SPI-MS system. The additional GC step enables the possibility due to chromatographic separation prior to the MS detection. Two-dimensional plots of the observed GC peaks as a function of retention time and TG temperature for individual nominal m/z signals are depicted in Fig. 4.

Outlook of the project: More information will be achieved with ongoing development of the systems. The aim is to gain more resolution by additional, more sophisticated separation steps and high resolution mass spectrometry.

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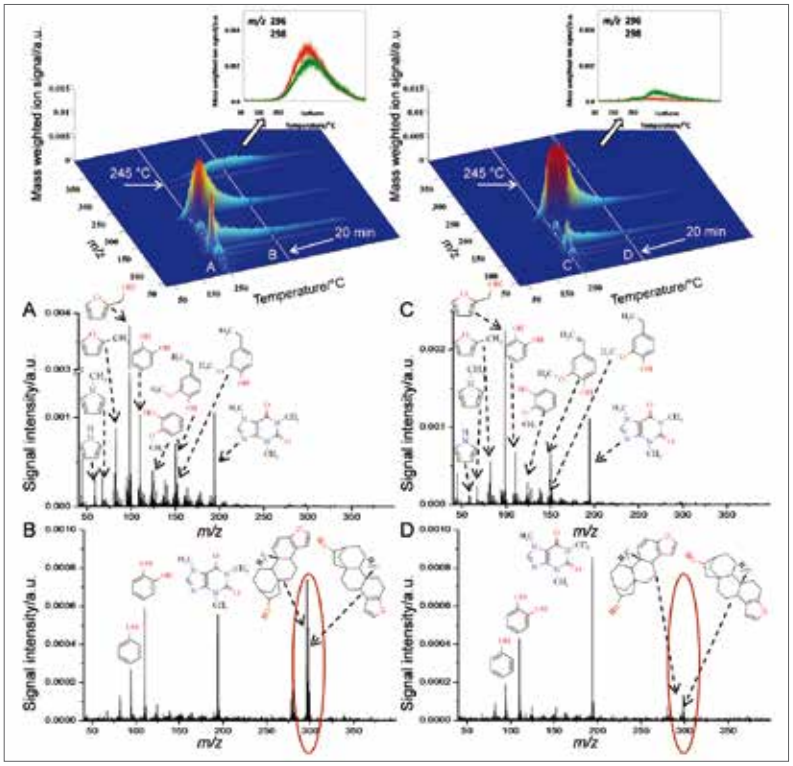

Fig. 1 Results of the simulated roasting process of a single Arabica coffee bean (left column) and an individual Robusta (right column) coffee bean. The extracted mass traces of the anhydrous diterpenes kahweol m/z 296 and cafestol m/z 298 as well as the mass spectra B and D after 20 minutes allow discrimination between Arabica and Robusta coffee. The mass spectra at 245 °C (A, C) reveal different composition ratios.

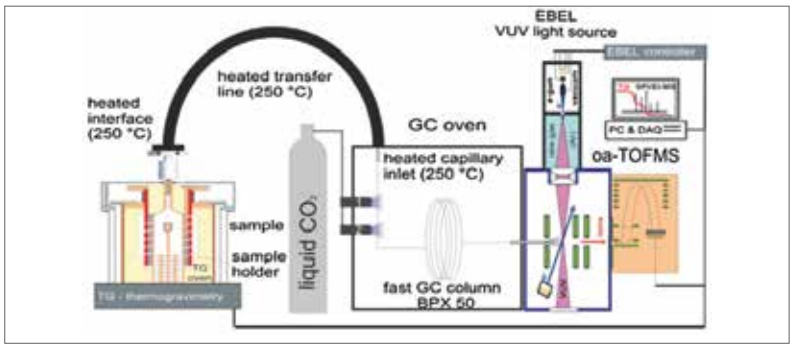

Fig. 2 Schematic diagram of setup of the TG–GC×SPI–MS device with thermobalance, GC×GC device including liquid CO2 modulator, EBEL VUV source, and TOF mass spectrometer

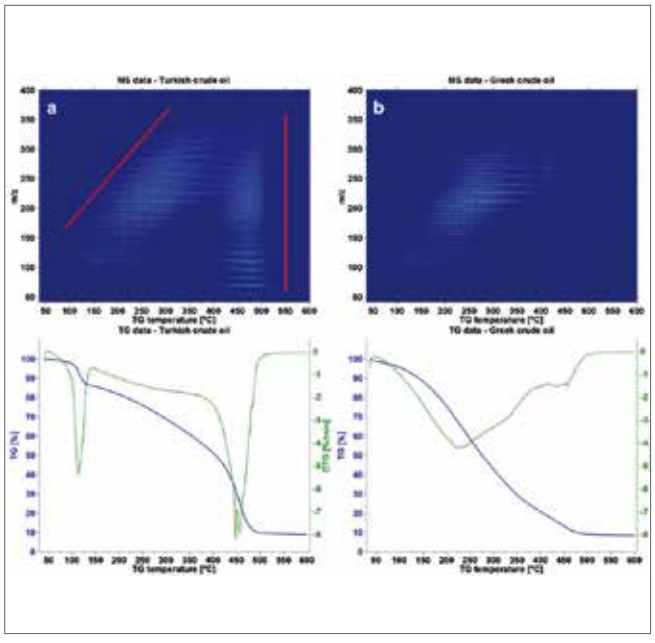

Fig. 3 Two-dimensional plots (m/z signal in relation to TG temperature) for a Turkish and b Greek crude oil from TG–GC×SPI–MS (upper part). The respective TG/DTG curves (solid blue line/dashed green line) are depicted in the lower part

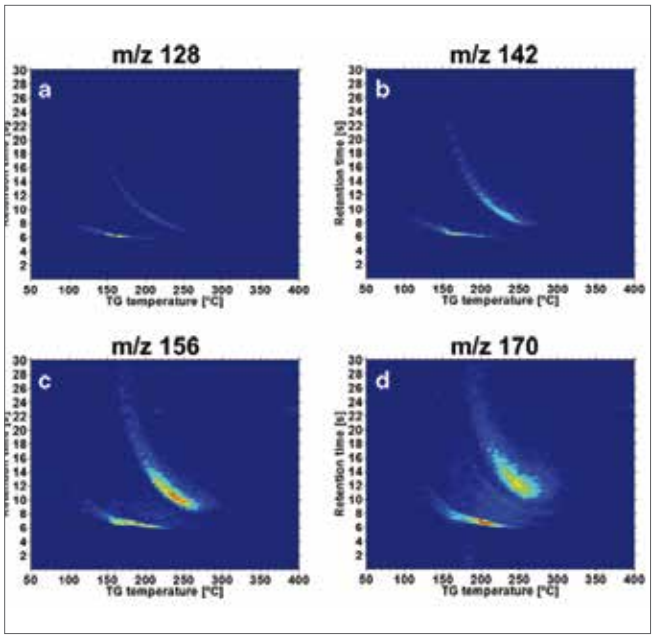

Fig. 4 Two-dimensional plots with dependence of retention times (s) on TG temperature (°C) for specific m/z signals from the "m/z 212±n×14" homologous series: a m/z 128, b m/z 142, c m/z 156, d m/z 170. The plots clearly confirm the occurrence of isobaric peaks. The figure illustrates the behavior of m/z 128, which is known to represent n-nonane and naphthalene.

Characterization of ship diesel soot particles using laser-desorption-ionization coupled to Fourier-transform-ion-cyclotron-resonance mass spectrometry – Comparison of feed fuel, direct particle measurements and filter extracts

Christopher Rüger (UR), Theo Schwemer (UR), Martin Sklorz (UR), Ralf Zimmermann (UR/HMGU)

Abstract: Due to high mass accuracy and high resolving power at the mass-to-charge dimension, high resolution mass spectrometry enables the chemical characterization of complex mixtures at the molecular level in terms of sum formula assignment. Laser-desorption-ionization as ionization technique offers several benefits such as rapid spectra generation and the capability of measuring solid samples directly without sample treatment. Nevertheless ionization parameter such as laser energy, spot size and shot number have to be carefully adjusted to avoid fragmentation and aggregation. It was shown that laser-desorption-ionization in the positive ion mode coupled to high resolution mass spectrometry can be a useful tool for the characterization of combustion aerosol as well as heavy fuel oil and is highly selective for high aromatic species with low heteroatom number.

Negative effects on the health caused by combustion aerosols are known for a long time. One of the most underestimated sources refers to ship diesel emissions [1], [2]. The chemical composition of ship diesel combustion aerosol is poorly investigated. Due to the extreme high complexity of combustion aerosols high resolution mass spectrometry (HR-MS) using laser-desorption-ionization (LDI) is one promising tool for revealing components with the same nominal molecular mass and assigning molecular sum formulas. As a result of the high aromatic content of heavy fuels used for ship diesel engines, the LDI is a favorable ionization technique cause of its selectivity for these compounds. The sensitive detection of a variety of alkylated nitrogen-containing aromatic compounds in fuel, such as carbazole- or acridine-derivatives, was recently shown by Cho et al. [3], [4].

The samples were taken during a measurement campaign at the Faculty of Mechanical Engineering and Marine Technology at University Rostock. The experiments were performed at a four-stroke one cylinder ship diesel engine with three liter cylinder capacity driven with heavy fuel oil (HFO). Particles were collected by impaction on stainless steel foils. Additionally, quartz fiber filters were taken and subsequently extracted with dichloromethane DCM/MeOH (1:1) three times using a supersonic bath. The extracts were filtered by a 0.2 µm PTFE-filter and flushed with DCM/MeOH (1:1).

The measurements were carried out by a solariX Fourier-transform-ion-cyclotron-resonance (FT-ICR) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 Tesla superconducting magnet. The setup was completed by a self-made MALDI-target to position the impactor foils directly in the ion source. The third harmonic of a Neodymium-YAG laser (355 nm) was applied with moderate laser power of 30 up to 60 % and various foci. Mass resolution was set to about 300,000 @ m/z = 400. The heavy fuel oil (HFO) was diluted with DCM to a concentration of about 500 ppm. The filter extracts and impactor foils were used without further preparation.

Various modifications in laser desorption ionization parameters, such as spot size, laser frequency and laser energy showed a high influence on the mass spectra and observed species. Figure 1 clearly shows the effect, that less photon density leads to weak or no signals, whereas to high laser energy leads to aggregation (dimer formation) and transformation processes forming species with increased double bond equivalent (DBE) and decreased hydrogen to carbon ratio (H/C), such as pure carbon clusters (e.g. C60 – C72).

Another important aspect that has to be taken into account when applying LDI for direct particle analysis is the non-uniformly spatial distribution of compounds and variations in sample spot height. Figure 2 shows the results of imaging experiments for impactor-sampled particulate matter. The inhomogeneous distribution of analyt species is clearly visible. Applying too high laser energy results in carbon clusters produced from graphite fragments. At lower particle density at the boundary of the impacted particle spots characteristic analyt marker, e.g. alkylated PAH, can be found. These effects leads to the result, that for the directly measurement of particulate matter with LDI the laser energy have to be reduced and additionally a larger laser spot size have to be chosen to avoid artifacts.

Three sample types, feed fuel (heavy fuel oil), particle extracts and impacted particle spots, were compared using the basic mass spectrometric approach. The mass spectra show several thousand distinct peaks, covering a mass-to-charge interval from about 150 to 700 amu,

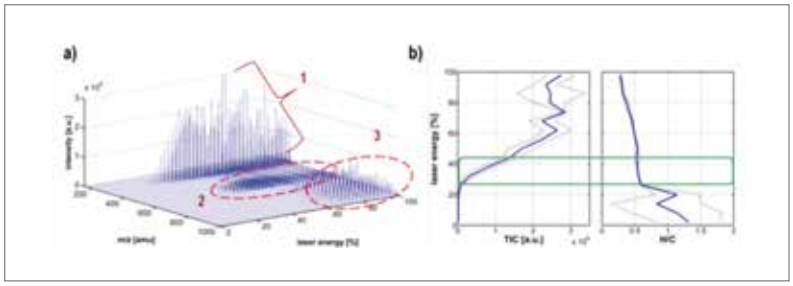

Figure1. laser energy dependency of the laser-desorption-ionization at fixed parameter of a 11 compound poly aromatic hydrocarbon (PAH) mixture, a) visualization of the influence to the mass spectra, 1 - PAH, 2 - aggregation, 3 - carbon cluster, b) influence to the total ion count (TIC) and hydrogen to carbon ratio (H/C), preferable measurement energy with this settings marked in green and error width in grey

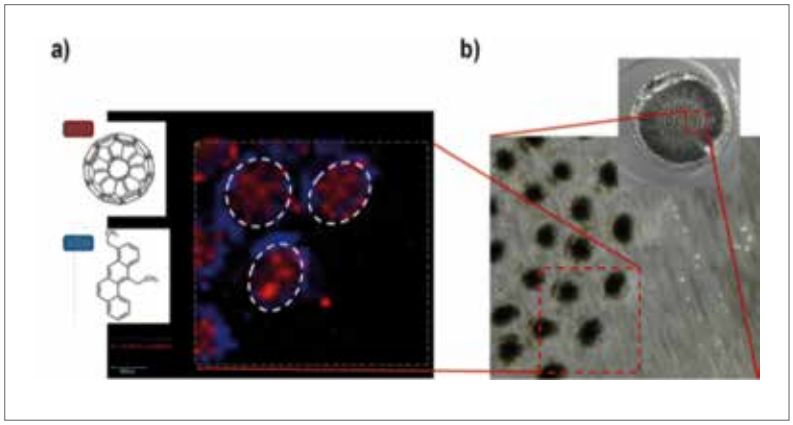

Figure2.b) photographical image of the low pressure impactor stage 9 (D50% 270 nm) with amplification of the measurement region, a) LDI-Imaging of a region of interest from the impactor stage with a lateral resolution of 100 µm, blue – 284.156 ± 0.002 amu C22H20 (e.g. C4-benz(a)anthracene), red – 719.994 ± 0.01 amu C60 (carbon cluster artefact)

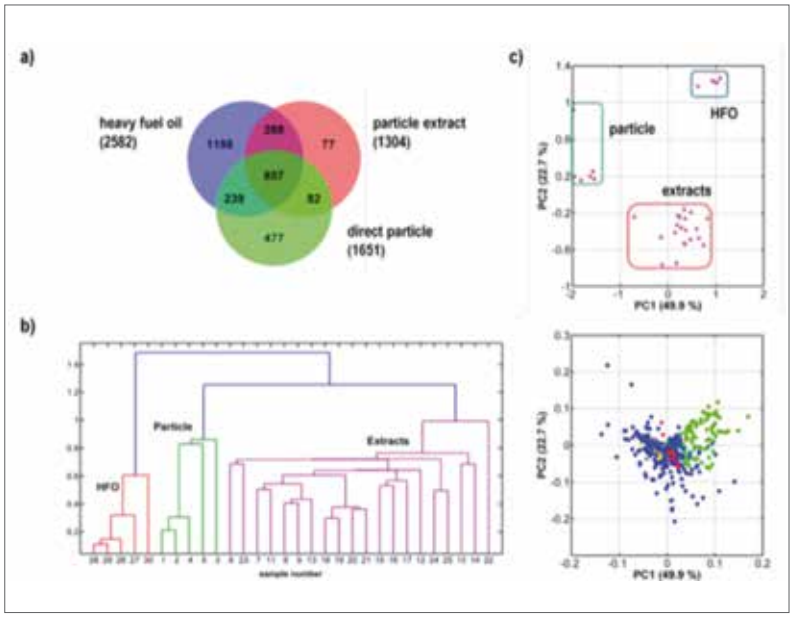

Figure 3. a) Venn-Plot comparison of the three sample types - approximately 900 species are shared between all samples and can be further used for statistics, b) hierarchical clustering analysis (HCA), c) principle component analysis with score (up) and loadings (down) plot - compound type color coded, CH – blue, CHN – green, CHO – red, CHS – yellow

peaking at roughly 400 amu. No significant shift between the sample types for the intensity weighted average mass-to-charge ratio was found. Nevertheless the average DBE value shifted from approximately 14 for the feed fuel to 12 - 13 for the aerosol samples towards lower values, whereas the average oxygen to carbon ratio increased significantly about a factor of two.

Deeper data exploration in high resolution mass spectrometry is usually done using Van-Krevelen-plots, plotting elemental ratio of the assigned sum formula, or interpretation of the DBE distribution versus the corresponding carbon number. Applying these strategies to the data set reveals on the one hand, that the shift in DBE refers to a high to the CHS and CHO compounds and on the other hand, that besides a general enrichment of oxygen and sulphur containing compounds the whole distribution shifted and the alkylation distribution is broadening for the CHO class.

The Venn Plot (fig. 3 a), as a first non-intensity weighted visualization of the data for further statistical purposes, reveal a high percentage of shared sum formula between all three sample types as well as between each pair. Nevertheless the direct particle measurements show appr. 500 unique species, whereas the extracts only exhibit a very small fraction of about 80 exclusive compounds. The feed fuel reveals over 1000 unique assigned sum formula, mostly high alkylated species from the CH and CHN compound class. For quantitative statistical purposes principle component analysis was carried out for 857 species found in all three sample types. It turned out that the three sample types could be well separated from each other, either using hierarchical clustering (fig. 3 b) or principle component analysis (fig. 3 c), and that the CH- and CHN-species mainly cause the partition along principle component (PC) 1 and 2.

Founding and Cooperation: We thank the DFG for funding of the Bruker SolariX FT-ICR-MS.

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Particulate emissions from medium-size ship diesel engine

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Abstract

The particulate emissions from a medium-size ship diesel engine operated at constant speed with heavy fuel oil (HFO) and diesel fuel (DF) under stepwise engine load progression were studied. Results showed that the average particulate mass for the whole test cycle is higher in HFO by a factor 6 than in DF. The main difference between HFO and DF was the significantly higher emission of organic matter (OM), sulfate (SO_4^{2-}), and inorganic elements in HFO. Elemental carbon (EC) and black carbon (BC), however, did not change significantly after switching from HFO to DF. For HFO, a higher emission factor was observed for OM at stable conditions for 25% engine load and the lowest for 75% engine load, and conversely for DF. OM emission was comparable for both fuels at 75% engine load, while they differed more than a factor of 100 at 25% engine load. The enhancement of OM with SO_4^{2-} was also load-dependent and significantly disproportionate at 25% load.

Introduction

PM is an important portion of the emissions from shipping activities. Aside from its suspected contribution to the global climate change, it also adversely impacts the health of the exposed population (Corbett et al., 2007). Carbonaceous compounds, classified as organic carbon (OC) and elemental/black carbon (EC/BC), are some of the major species of PM that are being emitted by shipping activities and dispersed into the local atmosphere at the coast line (Agrawal et al., 2008, Healy et al., 2009; Moldanova et al., 2009). Concentrations of EC/BC and organics have been found to be enhanced by 4-5 times in the port when ships are passing by (Lu et al., 2006).

This study aims to investigate the PM emission from a medium size ship diesel engine operated at constant speed. The engine was the basis of a measurement campaign within the framework of the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE) that took place at the Faculty of Mechanical Engineering, Department of Pistons and Internal Combustion Engine at the University of Rostock on November 19-30, 2012.

Experimental

The emitted aerosols were transported through a series of porous tube diluters downstream the exhaust to the particle measurement systems. The PM2.5 particle fraction was diluted by nominally a factor of 100 for HFO (1.6% fuel sulfur content, FSC) and of 40 for DF, were collected using a particle sampler (Partisol 2300, Rupprecht and Patashnik, USA), and analyzed gravimetrically (Sartorius AC 210, Germany). Particles collected from PTFE filters were analyzed for elemental content using (ICP-AES, Spectro Ciros Vision, SPECTRO Analytical Instruments GmbH & Co. KG, Kleve, Germany. The aerodynamic size distribution of the particles, diluted by 1000 for HFO and by 400 for DF, was monitored in real-time using a 12-stage Electrical Low Pressure Impactor (ELPI, Dekati, Finland). The mobility size distribution was measured by a Scanning Mobility Particle Sizer (SMPS, Differential Mobility Analyzer TSI 3080, Condensation Particle Counter TSI 3022) providing the mobility diameter (dm) of the submicron sized particles. Elemental and organic carbon samples were collected on a quartz fiber filter, heated stepwise to desorb the organic compounds and analyzed in an EC/OC analyzer (Desert Research Institute Model 2001 A, USA). Black carbon (BC) and brown carbon (BrC) were measured online using an Aethalometer (Magee Scientific Model AE33-7, Slovenia). The non-refractory particles were measured using a high resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS, Aerodyne Research Inc., USA).

Results and discussion

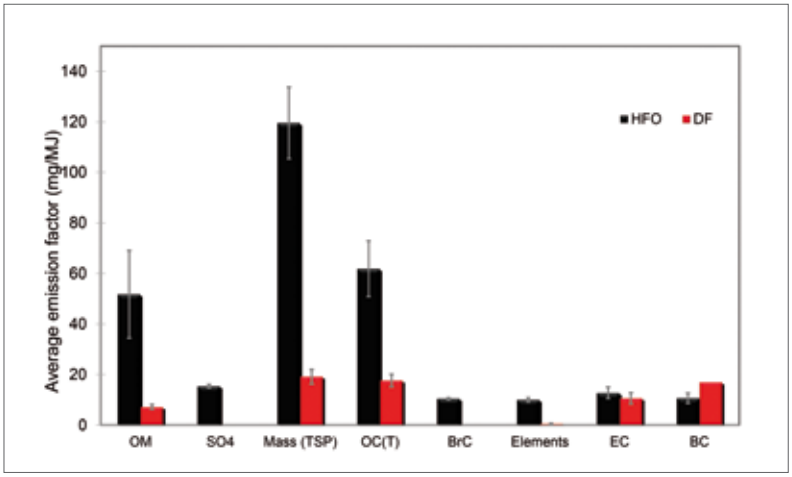

Figure 1. Average particulate emission factors of quantified components

The major species for the particulate fraction of the HFO exhaust consisted of organics (OC or OM), sulfate, soot (EC or BC) and inorganic elements, which is similar in DF, except for sulfate

and inorganic elements, as shown in Figure 1. The OM/BC ratio is 10 times higher in HFO than in DF due to the high residual content of the former. BC and EC have similar concentrations for both HFO and DF.

As presented in Fig. 2 (top), the evolution of non-refractory particles during a two hour test cycle, from 100% to 25% engine load, showed a characteristic emission pattern for each load. At 100% engine load, the OM emission factor for HFO indicates nearly steady state conditions while for DF most of the OM emission occurred at the beginning of the operation and consistently decreased with load. For HFO, first a drastic decrease followed by a slightly on-going decrease of the OM emission was observed as the engine load was reduced from 100% to 75%. In contrast, the combustion of diesel fuel is typified by slightly increasing and plateauing of the OM-emission for the whole one hour duration. Thus, at this operation point, the emission factors of OM stabilized to a lower amount in HFO and to a higher amount in DF. For the 50% load, the OM slightly increased in HFO and decreased substantially in DF. Both emission profiles showed stable factors during this time suggesting that at this operating point, a predictable emission of OM could be achieved in a very short time. When the load was changed to 25%, the highest emission factor was observed for HFO and the lowest for DF. Since for HFO the highest and lowest stable emissionfactors were observed for 25% and 75%, respectively, and inversely for DF, their mass spectra are presented in Figure 2 (bottom). The main difference between both spectra is the presence of sulfate fragments in HFO. They contribute higher in 75% than in 25% load. The OM dominant fragments, including m/z 29, 41, 43, and 55, are characteristics of hydrocarbon-like organic aerosols (HOA). They are similar to the dominant fragments from freshly emitted ship plume (Murphy et al., 2009).

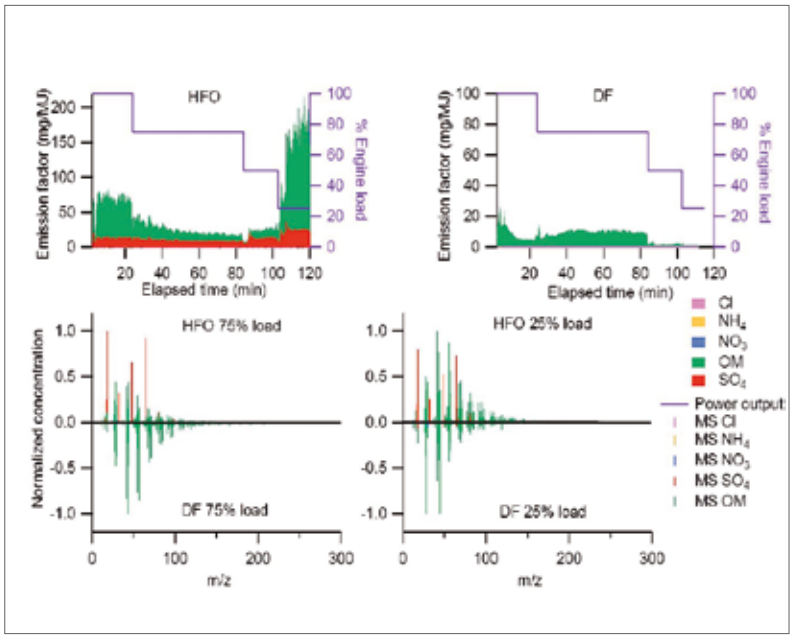

Figure 2. Time series trend of evolved non-refractory particles (top) and differences in mass spectra (MS) for 75% and 25% engine load (bottom)

Conclusion

This study showed that with lower sulfur content in fuel, the PM significantly declined for the overall duration of the test cycle employed. Our results showed furthermore, that organics, SO42-, and inorganic elements declined significantly with a lower FSC, but not the EC/BC concentrations. Also the power output seemed to play a role in the particulate emissions. It was shown here that under constant speed the 75% engine load produced approximately the same amount of particulate emissions for both HFO and DF. This may have an implication to the emission controlled area regulation: although ships are not allowed to operate there with HFO of high FSC, they might still emit PM comparable to HFO for a certain load.

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KANTIVA Bioenergy Research Center
Prof. J. K. Jokiniemi, Dr. O. Sippula
www.kantiva.fi/en/index.shtml

University of Ferrara
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Prof. Dr. C. Pietrogrande, Prof. Dr. F. Dondi
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University of Gothenburg
Gothenburg, Sweden
Prof. Dr. J. B. C. Pettersson
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University of Göttingen
Interdisziplinäres Zentrum für Nachhaltige
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Esch-Belval, Luxembourg
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Prof. Dr. E. Rohwer, Dr. P. Forbes
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University of Rostock
Department of Anaesthesiology and Intensive Care Medicine
Rostock, Germany
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University of Rostock
Department of Chemistry
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University of Rostock
Department of Piston Engines and Internal Combustion Engines
Dr. U. Schümann, Dipl.-Ing. C. Fink, Dipl.-Ing B. Stengel
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China University of Mining and Technology
Department of resources and Earth Sciences
Beijing Campus
Ph. D Professor Longyi Shao
Head of Department
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Peking University Health Science Center
Dept. of Occupational and Environmental Health
Professor Xiao-chuan Pan
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Public and State Institutions

Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto (ARPAV)
Belluno, Italy
Dr. R. Bassan
www.arpa.veneto.it

Bavarian Environment Agency (Bayerisches Landesamt für Umwelt)
Augsburg, Germany
Dr. H. Ott, Dr. M. Rössert
www.lfu.bayern.de/index.htm

Bayerische Landesanstalt für Wald und Forstwirtschaft (LWF)
Freising, Germany
Dr. H.-P. Dietrich
www.lwf.bayern.de

Bundeskriminalamt (BKA)
Wiesbaden, Germany
Dr. M. Pütz, Dr. R. Schulte-Ladbeck
www.bka.de

Federal Environment Agency Austria (Umweltbundesamt)
Vienna, Austria
Dr. Weiß
www.umweltbundesamt.at

Federal Environment Agency Germany (Umweltbundesamt)
Global Atmosphere Watch (GAW) - Globale Überwachung der Atmosphäre
Dr. L. Ries
Garmisch-Partenkirchen, Germany
www.umweltbundesamt.de/gaw

Funding and Scholarships

List of Funded Third Party Projects of the JMSC (April 2012 – March 2014)

Funding Institution	Grant period	Title	Total HMGU/UR Grant [€]
Netzsch Gerätebau GmbH	10/09–09/12	TG-Skimmer-MS: Charakterisierung und Optimierung der Jet-Eigenschaften	141.372 (UR)
BAT Research Centre	12/10–06/13	In-Situ Sampling/Mapping of Selected Toxicants inside a Burning Cigarette and Fractionation of Tobacco and the Effect on Selected Toxicants using Combustion Simulator	225.672 (UR)
Ministry for Science and Culture of lower Saxony	01/09–01/14	Nachhaltige Nutzung von Energie aus Biomasse im Spannungsfeld von Klimaschutz, Landschaft und Gesellschaft – TP Schadstoffemissionen bei der Energiegewinnung aus Stroh, Holz und Biogas	118.782 (HMGU)
Wissenschaftsgemeinschaft Gottfried Wilhelm Leibniz e.V.	03/11–02/14	Abbaubarkeit von arktischem, terrigenem Kohlenstoff im Meer	135.700 (UR)
DGUV – Deutsche Gesetzliche Unfallversicherung	04/10–03/14	Untersuchung von Messfehlern bei der Probenahme von Gefahrstoff-Aerosolen	404.000 (HMGU)
BFS / Netsch gerätebau GmbH	10/12–03/15	Mehrdimensionale Analyse thermischer Prozesse	658.600 (HMGU)
Sasol Technology (Pty) Ltd.	12/08–08/15	Application of REMPI-/SPI-TOFMS for on-line analysis of coal pyrolysis products and Fischer-Tropsch micro reactor streams and Comprehensive analysis in Fischer-Tropsch related systems	178.500 + 233.240 (UR)
DFG	04/13–03/16	Primary aerosol emissions from wood combustion and shipping engines and their potentials for formation of secondary aerosols	323.250 (UR)
Öl-Wärme-Institut e.V.	01/14–06/16	Untersuchung der Einflussgrößen auf die Messung der Partikelemission von Kleinfeuerungsanlagen	204.304 (HMGU)
DFG	01/13–08/16	ATOF-PIMS Verbesserung der Online-Charakterisierung von Aerosolpartikeln durch laserbasierte Ionisierungstechniken in einem Flugzeitmassenspektrometer	159.550 (UR)
HGF	01/12–12/16	Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE)	1.000.000 (HMGU) + 500.000 (UR)
DFG	2014–2017	Chemische Zusammensetzung und Herkunft von atmosphärischem Brown Carbon Aerosol	150.000 (UR)
Total funding sum:			**EUR 4.432.970**

List of Funded Scholarships of the JMSC (April 2012 – March 2014)

Name of beneficiary	Funding institution	Title
Christopher Rüger PhD student	Land Mecklenburg-Vorpommern – Landes-graduiertenstipendium	Entwicklung und Anwendung von laserdesorptionsbasierten Verfahren zur schnellen molekularen Charakterisierung komplexer petrochemischer Produkte, gesundheitsgefährdender Stoffe und anderer relevanter Proben mit hochauflösender Massenspektrometrie
Fengxia Li Peking University Health Science Center, Beijing, China	Chinese Scholarship Council (CSC)	Long term sampling of environmental nanoparticles in Augsburg and spacial-temporal variation characterization based on chemical composition measurements
Hilda Huang Institute for the Environment, Hong Kong University of Science & Technology, Hong Kong, China	Ministry of Education of the People's Republic of China	Integrated Assessment on Roadside Air Quality
Raeed Qadir University of Duhok, Dept. of Chemistry, College of Science, Irak	Deutscher Akademischer Austauschdienst (DAAD)	Analysis of Organic Molecular Markers in Airborne Particulate Matter: Application for Emission Source Apportionment
Ahmed Reda Al-Nahrain University, Bagdad, Irak	Deutscher Akademischer Austauschdienst (DAAD)	Development and application of methods for sampling and characterization of volatile oxygen containing compounds in emission aerosols
Abudula Reyimuguli Chinese Academy of Sciences, Urumuqi, China	Chinese Scholarship Council (CSC)	Impact of fuel type and fuel moisture content on wood emissions at different operation conditions
Yuting Huang Chinese Academy of Agricultural Sciences, Beijing, China	Chinese Scholarship Council (CSC)	Investigation of formation of secondary organic aerosols and health effects of wood combustion and ship emission
Sevinj Hajiyeva Institute of Petrochemical Processes, Azerbaijan National Academy of Sciences	Ministry of Education of Azerbaijan Republic	Comprehensive analysis of crude Naphtalan oil distillates
Sevil Khalilova Institute of Petrochemical Processes, Azerbaijan National Academy of Sciences	Ministry of Education of Azerbaijan Republic	Comprehensive analysis of crude oil distillates by means on STA-SPI-MS
Annamaria Poletti Department of Analytical Chemistry, Ferrara, Italy	LLP/Erasmus Placement A. A. 2013/14	Quantification of semi volatile organic compounds in Beijing samples
Rasim Alosmanov Baku State University, Chemical Department, Baku, Azerbaijan	Deutscher Akademischer Austauschdienst (DAAD)	Application of thermogravimetric analysis to the evaluation of aminated solid sorbents for CO2 capture
Xiao Wu Shandong University, China	Chinese Scholarship Council (CSC)	Development and application of HPLC and LC-MS methods for the determination of markers of oxidative stress in biological samples

Conferences

International conferences and workshops 2012 - Highlights

60thAnnual Meeting of the American Society for Mass Spectrometry (ASMS), 2012, Vancouver, Canada:
- Zimmermann et al., *Real-time analysis of flavors and pyrolysis-gases inside of individual coffee beans during the roasting process by microprobe-sampling photo-ionization mass spectrometry*

American Association for Aerosol Research (AAAR), 2012, Minneapolis, USA:
- Elsasser et al., *Dynamic Changes in the Aerosol Composition and Concentration during Different Burning Phases of Wood*
- Oster et al., *Comprehensive single particle analysis by aerosol mass spectrometry with different desorption and ionisation techniques*

Analytica 2012, Workshop on Light and Molecular Ions – Photo Ionisation in Mass Spectrometry, Munich, Germany:
- Session Chair: R. Zimmermann, *Light and Molecular Ions - Photo Ionisation in Mass Spectrometry*
- Ehlert et al., *Laser-Desorption for Real-Time Detection of Security Relevant Substances at Ambient Conditions,*
- Streibel et al., *Laser Based Single and Multi-Photon Ionization Mass Spectrometry for Characterization of Combustion and Pyrolysis Processes*

Analytica China, 2012, Shanghai, China:
- Gröger et al., *Hyphenated techniques for comprehensive characterization of the metabolom: Applications, Processing & new technology*

European Aerosol Conference 2012, Granada, Spain:
- Dragan et al., *First field application of a thermal desorption resonance-enhanced multiphoton-ionisation single particle time-of-flight mass spectrometer for online measurements of particle bound polycyclic aromatic hydrocarbons and source identification*
- Orasche et al., *Organic Emissions from Modern Small Scale Wood Combustion Appliances –Chemical Characterization and Toxic Potential of Fine Particulate Matter*
- Zimmermann et al., *Impact of wood combustion on the ambient aerosol in Augsburg, Germany: A joint measurement campaign using innovative on-line and off-line mass spectrometric systems for chemical profiling*
- Zimmermann et al., *Unraveling the molecular organic signature of the EC/OC fractions of PM: Coupling of an EC/OC-carbon analyzer to photo-ionization*

International Congress on Thermal Analysis and Calorimetry (ICTAC), 2012, Osaka, Japan:
- Zimmermann et al., *Thermal analysis coupled to on-line modulated fast gas chromatography-photoionisation TOF-mass spectrometry for comprehensive characterization of complex organic materials such as crude oil-fractions or polymers*

Petrophase, 2012, St. Petersburg Beach, FL, USA:
- Zimmermann et al., *Thermal analysis with evolved gas analysis by photo ionisation mass spectrometry for thermal and chemical characterisation of crude oils*

Pyrolysis 2012, Linz, Austria:
- Streibel et al., *Analytical Pyrolysis of Biomass and Fossil Fuels Applying Time-of-Flight Mass Spectrometry with Soft Photo-Ionisation*

Analytisches Seminar an der Bundesanstalt für Materialforschung (BAM), Berlin, Germany:
- Zimmermann et al., *Enhancing the selectivity of on-line mass spectrometry and gas chromatography-mass spectrometry based analytical methods*

University of Washington, Seattle, WA, USA:
- Zimmermann et al., *Enhancing the selectivity of mass spectrometry for on-line and off-line analysis of complex samples*

ChromSaams-Conference 2012, Dikhololo, South Africa:
- Zimmermann et al., *Enhancing the selectivity of gas chromatography-mass spectrometry for analysis of complex matrices: High resolution mass spectrometry, soft and hard ionization techniques and comprehensive separation*

SASOL-lecture series, Rhodes University, Grahamstown, South Africa:
- Zimmermann et al., *Small particles with a big impact: Methods to characterize chemical and physical properties of ambient and process aerosols*

Nelson Mandela Metropolitan University, Port Elizabeth, South Africa:
- Zimmermann et al., *Fuels, combustion and pyrolysis: Application of mass spectrometry based technologies to characterize complex mixtures*

IUMRS-ICEM congress 2012, Yokohama, Japan:
- Zimmermann et al., *On-line coupling of Thermal Analysis (TA) to soft Photo Ionisation-Mass Spectrometry (SPI-MS) for organic profiling of evolved gases: New instrumental concepts and applications*

Air Liquide GmbH (Lurgi), Frankfurt, Germany:
- Zimmermann et al., *Mass Spectrometry with Soft Photo Ionisation Technology for On-Line Characterisation of Organic Products from Industrial Combustion and Pyrolysis Processes*

CNRS, Nancy, France:
- Zimmermann et al., *Mass Spectrometry with Soft Photo Ionisation: Technology and Applications*

Bilbao Talks on Aerosol Science, Bilbao, Spain:
- Zimmermann et al., *On-line and off-line chemical profiling of aerosols by mass spectrometry: Unraveling the cause of aerosol-induced health effects*

GDCh-Seminarvortrag. Universität Hamburg, Germany:
- Zimmermann et al., *Aerosolmassenspektrometrie: Organische Verbindungen in Aerosolen – Eine Herausforderung für die chemische Analytik*

36th ISCC - Int. Symposium of Capillary Chromatography, Riva del Garda, Italy:
- Zimmermann et al., *Detection of tracers for wood combustion aerosols in ambient air by on-filter derivatization – direct thermal desorption – gas chromatography – time of flight mass spectrometry*
- Gröger et al., *Gas chromatography hyphenated to high resolution and accurate mass spectrometry: technical utilization, benefits and application*

ZHAW - Zurich University of Applied Sciences, Switzerland:
- Zimmermann et al., *Photo Ionisation Mass Spectrometry with Lasers and incoherent VUV light sources*

International conferences and workshops 2013 - Highlights

61thAnnual Meeting of the American Society for Mass Spectrometry (ASMS), 2013, Minneapolis, USA:
- Gröger et al., *Fast switchable single-photon/electron ionization for time–of–flight mass spectrometry and its hyphenation to gas chromatography – mass spectrometry*
- Lintelmann et al., *LC-Q-TOF-MS and LC-HR-TOF-MS Methods for the Determination of Metabolites of Polycyclic Aromatic Hydrocarbons in Urine: A comparison*
- Zimmermann R. and Sysage J., *ASMS-Workshop: Photo Ionisation Mass Spectrometry-Light for Molecular Ions, Introductionary presentation and workshop co-chair*

ANAKON, 2013, Essen, Germany:
- Gröger et al., *Advanced compound classification for GCxGC-MS due to the integration of accurate mass information obtained by high resolution time-of-flight mass spectrometry*
- Schäffer et al., *Forensisches Profiling von Sassafrasölen basierend auf zwei-dimensionaler Gaschromatographie (GC×GC-TOFMS)*
- Streibel et al., *Kopplung eines Thermisch/Optischen-Kohlenstoffanalysators mit Photo-ionisierungs-Massenspektrometrie zur Bestimmung der organischen Zusammensetzung von Aerosolpartikeln*

European Aerosol Conference 2013, Prague, Czech Republic:
- Dragan et al., *A study on SVOC aerosol evaporation and its possible implications on workplace sampling*
- Mueller et al., *Primary aerosols from ship diesel engine exhaust within the framework of HICE measurement campaign*
- Orasche et al., *Particle-bound Methoxyphenols and their atmospheric nitration products as wood combustion tracers*
- Orasche et al., *Health relevant compounds in wood combustion and ship diesel aerosols: Evaluation of the toxicity due to polycyclic aromatic hydrocarbons*
- Qadir et al., *Long-term monitoring, chemical composition and source apportionment study of PM2.5 in Augsburg, Germany*
- Streibel et al., *Hyphenation of a Thermal/Optical Carbon Analyzer to photo-ionization mass spectrometry for determination of the organic content of aerosol particles*

- Zimmermann et al., *Studying the causes of health effects of combustion-derived aerosols in the framework of the Virtual Helmholtz Institute HICE: First results on ship diesel aerosols*
- Zimmermann et al., *REMPI-Laser-mass spectrometry: On-line and off-line analysis of the molecular signature of polycyclic aromatic hydrocarbons (PAH) in gas- and particle-phase of combustion aerosols*

Annual meeting of the German Society for Mass Spectrometry (DGMS), Berlin:
- Zimmermann et al., *Gas chromatography coupled to fast high resolution TOF mass spectrometry (GC- and GCxGC-HRTOF) or ultra-high resolution FT- ICR mass spectrometry (GC-APCI-FTICR) for analysis of highly complex mixtures*
- Oster et al., *First field application of a thermal desorption resonance-enhanced multiphoton-ionisation single particle time-of-flight mass spectrometer for detection of particle bound polycyclic aromatic hydrocarbons and source identification*

41st Annual Conference of NATAS 2013, Bowling Green, Kentucky, USA:
- Zimmermann et al., *Crude oil, Tobacco, Polymers, Coffee and Soot: Thermal Analysis of complex materials and thermal processes using Photo-Ionisation Mass Spectrometry*
- Fischer et al., *Thermal Analysis with Evolved Gas Analysis by Single Photon Ionization – Mass Spectrometry for the investigation of coffee and tobacco*

3rd European GCxGC Symposium, Nice, France:
- Gröger et al., *LECO Pegasus GCxGC-HRT: The missing link between GCxGC and high resolution and accurate mass spectrometry,* 3rd European *GCxGC Symposium, Nice, France*

InnMassSpec: Innovations in Mass Spectrometry Instrumentation, St. Petersburg, Russia:
- Zimmermann et al., *Application of Multi-Reflection, High Resolution Time-of-Flight-Mass Spectrometry as Detector for One- and Two-Dimensional Gas Chromatography & Soft Photo Ionization Mass Spectrometry*

Pittcon 2013, Philadelphia, PA, USA:
- Zimmermann et al., *Detection of the molecular composition of coffee roasting pyrolysis gases by thermal analysis of individual coffee beans coupled to evolved gas analysis (TG-EGA) by photo ionization TOF mass spectrometry*

Environment Canada, Toronto, Canada:
- Zimmermann et al., *Aerosol emissions from a ship diesel engine operated either with heavy or with light diesel fuel: Chemical composition of the aerosol and toxicological effects on human lung cells*

Pittcon 2013, Philadelphia, PA, USA:
- Zimmermann et al., *Detection of the molecular composition of coffee roasting pyrolysis gases by thermal analysis of individual coffee beans coupled to evolved gas analysis (TG-EGA) by photo ionization TOF mass spectrometry*

40th Int. Symposium on HPLC, Hobart, Tasmania, Australia:
- Zimmermann et al., *New Concepts in LC-MS: Ultra-fast, very-high resolution Time-of-flight mass spectrometry coupled to HPLC for applications on crude oil, metabolites and plant extracts & A low-pressure photo ionization MS approach for matrix-effect free ionization from liquid phase*

US-Environmental Protection Agency (EPA), Research Triangle Park, NC, USA:
- Zimmermann et al., *Health effects of combustion-derived aerosols: First results on ship diesel aerosols*

Leco Inc., St. Josephs, MI, USA:
- Zimmermann et al., *High mass-resolution multi-reflection-time-of-flight-mass spectrometer systems as detector for gas chromatography or liquid chromatography: Concepts and first applications*

The J.M. Smucker Company (Folgers Coffee), Orrville, OH, USA:
- Zimmermann et al., *On-line analysis of of coffee roasting-gases*
- Zimmermann et al., *Photo-ionization mass spectrometry for on-line analysis of the chemical signature of coffee roasting-gases and coffee products*

Symposium of "The Chromatographic Society", Southampton, GB:
- Zimmermann et al., *On-line Monitoring of Complex Mixtures by Photoionisation Mass Spectrometry*

International Symposium on Capillary Chromatography (ISCC), Palm Springs, CA, USA:
- Zimmermann et al., *High mass-resolution multi-reflection time-of-flight-mass spectrometer as detector for one-dimensional (GC) and comprehensive two-dimensional (GCxGC) gas chromatography: Characterization of highly complex mixtures and*

comparison to GC-APCI-FTICR
- Zimmermann et al., *Ultra-fast, high mass-resolution multi-reflection-time-of-flight-mass spectrometer systems as detector for one-dimensional and comprehensive two-dimensional gas chromatography as well as for liquid chromatography: Concepts and first applications*

Tchibo GmbH, Hamburg, Germany:
- Zimmermann et al., *Soft photoionization mass spectrometry: A powerful tool for on-line analysis of the chemical signature of coffee roasting-gases and products*

Clean Air in Ports-Workshop (NABU), Hamburg, Germany:
- Zimmermann et al., *Characterization of ship diesel emission in the framework of the "Virtual Helmholtz Institute HICE - Aerosols & Health"*

Mondelez-International Ltd., Banbury, UK:
- Zimmermann et al., *Photo-ionization mass spectrometry: A versatile tool for on-line analysis of the chemical signature of coffee roasting-gases and coffee products*

International conferences and workshops 2014 - Highlights

Analytisches Seminar, Universität Duisburg-Essen, Germany:
- Zimmermann et al.: *Abgase aus Schiffdiesel-Maschinen, Holzverbrennung und Co.: Chemische Zusammensetzung und Gesundheitseffekte*

The J.M. Smucker Company, Orrville, OH, USA The J.M. Smucker Company, Orrville, OH, USA:
- Zimmermann et al.: *Photo-ionization mass spectrometry for on-line analysis of the chemical signature of coffee roasting-gases and coffee products*

Bremen MS-Seminar, Bremen, Germany:
- Zimmermann et al.: *Combustion, tobacco smoke crude oil and coffee roasting: Analysis of complex materials and thermal processes by Photo-Ionisation Mass Spectrometry (PIMS)*

13th HTC Conference, Bruges, Belgium:
- Gruber et al., *Needle trap micro extraction combined with GCxGC-TOFMS for the analysis of breath gas during metabolic stress*
- Weggler et al., *Advanced scripting for automated fast screening of GCxGC-TOFMS data generated from anthropogenic aerosols*
- Zimmermann et al., *One-dimensional and comprehensive two-dimensional gas chromatography coupled to a multi-reflection, ultra-high resolution time-of-flight-mass spectrometer (and FT-ICR) for characterization of complex mixtures*

SASOL-lecture series – University of Western Cape, Cape Town, SA:
- Zimmermann et al.: *Combustion, tobacco smoke and coffee roasting: Analysis of complex materials and thermal processes by Photo-Ionisation Mass Spectrometry*
- Zimmermann et al., *On-line and off-line techniques for characterization of complex mixtures – Thermal analysis, Fischer-Tropsch process and analysis of petrochemical samples*

SASOL-lecture series – University of Stellenbosh, Stellenbosh, SA:
- Zimmermann et al.: *Methods in Environmental Health Studies:Health effects of Ship Diesel emissions-A combined physical,chemical and molecular biological study*

Meeting of the Section: „FT-MS and high resolution mass spectrometry" of the German Society for Mass Spectrometry (DGMS):
- Rüger et al., C*haracterization of heavy fuel oil and combustion aerosol with laser desorption ionization coupled to ultra-high resolution mass spectrometry (LDI-FT-ICR-MS)*

→ All contributions to conferences and workshops can be found here: www.helmholtz-muenchen.de/cma

Publications

Papers of CMA and HICE authors 1.4.12 – 31.3.14 sorted inversely by date (newest first)

1. D. Breuer, C. Friedrich, C. Möhlmann, G.C. Dragan; Development of a Miniaturised Sampling System for the Simultaneous Collection of Vapour-Droplet Mixtures of Semi-Volatile Compounds (Entwicklung Eines Miniaturisierten Probenahmesystems Zur Gleichzeitigen Erfassung Von Dampf-Tröpfchen-Gemischen Bei Schwerflüchtigen Verbindungen), Gefahrstoffe-Reinhaltung der Luft 74:129-134 (2014)
2. M. Leuchner, S. Gubo, C. Schunk, C. Wastl, M. Kirchner, A. Menzel, C. Plass-Dülmer; Can Positive Matrix Factorization Identify Sources of Organic Trace Gases at the Continental Gaw Site Hohenpeissenberg?, Atmos. Chem. Phys. Discuss. 14:8143-8183 (2014)
3. S. Skruszewicz, J. Passig, A. Przystawik, N.X. Truong, M. Köther, J. Tiggesbäumker, K.H. Meiwes-Broer; A New Design for Imaging of Fast Energetic Electrons, International Journal of Mass Spectrometry in press (2014)
4. G. John, K. Kohse, J. Orasche, A. Reda, J. Schnelle-Kreis, R. Zimmermann, O. Schmid, O. Eickelberg, A.Ö. Yildirim; The Composition of Cigarette Smoke Determines Inflammatory Cell Recruitment to the Lung in Copd Mouse Models, Clinical Science 126:207-221 (2014)
5. R. Winkler-Heil, G. Ferron, W. Hofmann; Calculation of Hygroscopic Particle Deposition in the Human Lung, Inhalation Toxicology 26:193-206 (2014)
6. P. Schroeder, C.A. Belis, J. Schnelle-Kreis, R. Herzig, A.S. Prevot, M. Raveton, M. Kirchner, M. Catinon; Why Air Quality in the Alps Remains a Matter of Concern. The Impact of Organic Pollutants in the Alpine Area, Environ Sci Pollut Res Int 21:252-67 (2014)
7. R.M. Qadir, J. Schnelle-Kreis, G. Abbaszade, J.M. Arteaga-Salas, J. Diemer, R. Zimmermann; Spatial and Temporal Variability of Source Contributions to Ambient Pm10 During Winter in Augsburg, Germany Using Organic and Inorganic Tracers, Chemosphere 103:263-273 (2014)
8. M. Kirchner, W. Fegg, H. Römmelt, M. Leuchner, L. Ries, R. Zimmermann, B. Michalke, M. Wallasch, J. Maguhn, T. Faus-Kessler, G. Jakobi; Nitrogen Deposition Along Differently Exposed Slopes in the Bavarian Alps, Science of the Total Environment 470–471:895-906 (2014)
9. M. Schäffer, S. Dieckmann, M. Pütz, T. Kohles, U. Pyell, R. Zimmermann; Impact of Reaction Parameters on the Chemical Profile of 3,4-Methylenedioxymethamphetamine Synthesized Via Reductive Amination: Target Analysis Based on Gc-Qms Compared to Non-Targeted Analysis Based on Gc X Gc-Tof-Ms, Forensic Science International 233:201-211 (2013)
10. R. Hertz-Schünemann, R. Dorfner, C. Yeretzian, T. Streibel, R. Zimmermann; On-Line Process Monitoring of Coffee Roasting by Resonant Laser Ionisation Time-of-Flight Mass Spectrometry: Bridging the Gap from Industrial Batch Roasting to Flavour Formation inside an Individual Coffee Bean, Journal of Mass Spectrometry 48:1253-1265 (2013)
11. P.B.C. Forbes, E.W. Karg, G.-L. Geldenhuys, S.A. Nsibande, R. Zimmermann, E.R. Rohwer; Characterisation of Atmospheric Semi-Volatile Organic Compounds, Clean Air Journal 23:3-6 (2013)
12. S. Ehlert, A. Walte, R. Zimmermann; Ambient Pressure Laser Desorption and Laser-Induced Acoustic Desorption Ion Mobility Spectrometry Detection of Explosives, Analytical Chemistry 85:11047-11053 (2013)
13. P. Trefz, M. Schmidt, P. Oertel, J. Obermeier, B. Brock, S. Kamysek, J. Dunkl, R. Zimmermann, J.K. Schubert, W. Miekisch; Continuous Real Time Breath Gas Monitoring in the Clinical Environment by Proton-Transfer-Reaction-Time-of-Flight-Mass Spectrometry, Analytical Chemistry 85:10321-10329 (2013)
14. M. Schäffer, T. Gröger, M. Pütz, R. Zimmermann; Forensic Profiling of Sassafras Oils Based on Comprehensive Two-Dimensional Gas Chromatography, Forensic Science International 229:108-115 (2013)
15. T. Streibel, S. Mitschke, T. Adam, R. Zimmermann; Time-Resolved Analysis of the Emission of Sidestream Smoke (Sss) from Cigarettes During Smoking by Photo Ionisation/Time-of-Flight Mass Spectrometry (Pi-Tofms): Towards a Better Description of Environmental Tobacco Smoke, Analytical and Bioanalytical Chemistry 405:7071-7082 (2013)
16. J. Peters, M. Clemen, J. Grotemeyer; Fragmentation of Deuterated Rhodamine B Derivates by Laser and Collisional Activation in an Ft-Icr Mass Spectrometer, Analytical and Bioanalytical Chemistry 405:7061-7069 (2013)
17. Y. Hashiguchi, S.-i. Zaitsu, T. Imasaka; Ionization of Pesticides Using a Far-Ultraviolet Femtosecond Laser in Gas Chromatography/Time-of-Flight Mass Spectrometry, Analytical and Bioanalytical Chemistry 405:7053-7059 (2013)

18. C. Stader, F. Beer, C. Achten; Environmental Pah Analysis by Gas Chromatography–Atmospheric Pressure Laser Ionization–Time-of-Flight–Mass Spectrometry (Gc-Apli-Ms), Analytical and Bioanalytical Chemistry 405:7041-7052 (2013)

19. D. Riebe, R. Laudien, C. Brendler, T. Beitz, H.-G. Löhmannsröben; Laser Ionization of H2s and Ion-Molecule Reactions of H3s+ in Laser-Based Ion Mobility Spectrometry and Drift Cell Time-of-Flight Mass Spectrometry, Analytical and Bioanalytical Chemistry 405:7031-7039 (2013)

20. C. Brendler, D. Riebe, T. Ritschel, T. Beitz, H.G. Löhmannsröben; Investigation of Neuroleptics and Other Aromatic Compounds by Laser-Based Ion Mobility Mass Spectrometry, Analytical and Bioanalytical Chemistry 405:7019-7029 (2013)

21. K. Jorabchi, K. Hanold, J. Syage; Ambient Analysis by Thermal Desorption Atmospheric Pressure Photoionization, Analytical and Bioanalytical Chemistry 405:7011-7018 (2013)

22. A. Stindt, M. Albrecht, U. Panne, J. Riedel; Co2 Laser Ionization of Acoustically Levitated Droplets, Analytical and Bioanalytical Chemistry 405:7005-7010 (2013)

23. J. Klems, M. Johnston; Origin and Impact of Particle-to-Particle Variations in Composition Measurements with the Nano-Aerosol Mass Spectrometer, Analytical and Bioanalytical Chemistry 405:6995-7003 (2013)

24. S. Ehlert, J. Hölzer, J. Rittgen, M. Pütz, R. Schulte-Ladbeck, R. Zimmermann; Rapid on-Site Detection of Explosives on Surfaces by Ambient Pressure Laser Desorption and Direct Inlet Single Photon Ionization or Chemical Ionization Mass Spectrometry, Analytical and Bioanalytical Chemistry 405:6979-6993 (2013)

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Seminars

Seminar of the Joint Mass Spectrometry Centre and the Helmholtz Virtual Institute HICE

The seminar takes place at the Institute of Chemistry, Albert Einstein Str. 3a, 18059 Rostock, once a week. These lectures are transmitted to the Helmholtz Zentrum München as well as to the partners of the Helmholtz Virtual Institute HICE via video conferencing.

Summer term 2012			
#	**Date / Time**	**Speaker**	**Title**
1	10.04.2012	**Prof. Dr. Hans-Gerd Janssen** Unilever Ltd./Univ. Amsterdam, Niederlande	Modern analytical separation systems: Clever combinations of chromatographic dimensions with mass spectrometry and chemometrics
-	17. / 18.04.2012	*Lecture series and workshop „Light and Molecular Ions: Photoionisation in Mass Spectrometry" Invited speakers:* **Prof. K. Dreisewerd, Prof. T. Imasaka, Dr. J. Sayage, Prof. M. Johnston, Prof. B. Spengler, Prof. U. Boesl, Prof. L. Hanley, Prof. Qi, Prof. T. Benter, Prof. G. Suizdak, Dr. A.Walte, Dr. T. Streibel** – organized and moderated by **Prof. R Zimmermann** *Analytica Conference München and Helmholtz Zentrum München*	
2	24.4.2012 17:30 h	**Prof. Dr. Hartmut Herrmann** IfT, Leipzig *Invited by Prof. Detlef Schulz-Bull, Leibniz-Institut für Ostseeforschung Warnemünde (IOW)*	Tropospherical multiphase chemistry in laboratory studies, model development and field experiments
3	08.05.2012 10:15 h	**Prof. Dr. R. Zimmermann**	Das virtuelle Institut HICE: Hintergrund, Struktur und wissenschaftliche Ziele"
4	10:45 h	**Dr. Wolfgang Kreyling**	Gesundheitswirkungen von Aerosolen und Feinstäuben *Lectures in the framework of the inauguration of the Virtual Institute HICE at the IOW*
5	08.05.2012 17:30 h	**Dr. Hanns-Rudolf Paur** KIT, Karlsruhe	Measurement of Charged Nanoparticles in Flames and Plasma by Particle Mass Spectrometry
6	15.05.2012	**Dr. Andre Prevot** Paul Scherrer Institut (PSI) Villingen, Schweiz	Particulate Emissions and secondary organic aerosol formation potential of wood burning and vehicles
7	05.06.2012	**Prof. Alfredo Sanz-Mendel** Universität Oviedo, Spanien	Pulsed Glow Discharges- Mass Spectrometry: applications for integral speciation and nano-structure characterization
8	19.06.2012	**Dr. Riaan Becker** Sasol Ltd., Sasolburg, Südafrika	The application of comprehensive two-dimensional gas chromatography (GCxGC) for the analysis of Fischer-Tropsch process streams

Summer term 2012			
#	**Date / Time**	**Speaker**	**Title**
9	26.06.2012	**Prof. Dr. Stephan Denifl** Universität Innsbruck, Österreich	Low energy electron induced reactions in molecules and clusters
10	02.07.2012	**Dr. Gunnar Weibchen** Waters GmbH, Eschborn *Invited by Prof. Michael Glocker, University of Rostock (UR)*	Ion-Mobility Spectrometry coupled with Mass Spectrometry – Technical Background and Applications

Winter term 2012 / 2013			
#	**Date/ Time**	**Speaker**	**Title**
1	23.10.2012	*GDCh Fresenius Lecture:* **Prof. Dr Ulrich Panne** Humboldt Universität Berlin/BAM	„Nie wieder Dienstmagd“ – Analytical Sciences for real world problem solving
2	30.10.2012	**Prof. Dr Thorsten Hoffmann** Universität Mainz	Development and Application of Aerosol Mass Spectrometry for Atmospheric Research
3	06.11.2012	**Dr. Mark Libardoni,** NW-Laboratories, USA	The Role of Mass Spectrometry in Solar System Geochemistry and Planetary Atmospheres – Past Missions to State of the Art Instrument Development
4	20.11.2012	**Dr. Carsten Weiss** KIT-Karlsruhe Inst. für Technologie	Toxicology of inorganic nanoparticles
5	27.11.2012	**Prof. Dr. Michael Przybylski** Universität Konstanz	Ion Mobility- Mass Spectrometry and Affinity- Mass Spectrometry: New Tools for elucidation of structures and reaction pathways of “misfolding” – aggregating neurodegenerative proteins
6	11.12.2012	**Dr. Jonathan Williams** Max-Planck-Institut für Chemie	Atmospheric Chemistry of a forest and a football match, measured by mass spectrometry
7	18.12.2012	**Dr. Thomas Krinke** TSI GmbH, Aachen	Aerosols – Fundamentals and measurement approaches
8	08.01.2013	*GDCh Fresenius Lecture:* **Prof. Dr. Renato Zenobi,** ETH Zürich, Switzerland	The power of one - Single cell metabolomics by mass spectrometry
9	15.01.2013	**Prof. Dr. Douglas Worsnop** University of Helsinki, Finland	Mass spectrometry of atmospheric aerosols 1nm - 1µm
10	22.01.2013	**PD Dr. Bernd Scheider** Max Planck Institute Jena	Spectroscopic analysis of metabolite profiles in plant cells and on surfaces

Summer term 2013			
#	**Date/ Time**	**Speaker**	**Title**
1	16.04.2013	**Dr. Ales Svatos** MPI for Chemical Ecology, Jena *Invited by Prof. Peter Leinweber/UR*	Mass spectrometric imaging of metabolites
2	23.04.2013	**Dr. Thomas Zeuch** Universität Göttingen	Structure and dynamics of species that initiate soot formation and water aggregation
3	29.04.2013	**Dr. Claudia Maier** Oregon State University, USA *Invited by Prof. Michael Glocker/UR*	Chemical Strategies and Mass Spectrometry for Exploring the Oxidative Stress Response
4	07.5.2013	**Dr. Bert Ungethüm** Airsense Analytics GmbH, Schwerin	Ion mobility spectrometry: Technique and applications
5	21.05.2013	**Prof. Dr. Andrea Sinz** Universität Halle *Invited by Prof. Michael Glocker/UR*	Chemical Cross-Linking and Mass Spectrometry: A Fruitful Combination for Protein 3D-Structure Analysis
6	28.05.2013	**Prof. Dr. Hans-Gerd Löhmannsröben** Universität Potsdam	Laser spectroscopy and fibre-optical sensing for (bio) chemical diagnostics
7	04.06.2013	**Dr. Olli Sippula** Universität Rostock and University of Eastern Finland	Particulate emissions from a marine diesel engine - Chemical characterization and comparison to other combustion processes
8	25.06.2013	**Prof. Dr. Jorma Jokiniemi** University of Eastern Finland	Physical and Chemical Properties of Fine Particles Emitted from Small Scale Biomass Combustion
9	01.07.2013	*GDCh Fresenius Lecture:* **Prof. Dr. Oliver Schmitz** Universität Duisburg-Essen	Atmospheric-pressure laser ionization (APLI) in trace analysis: scientific findings, latest developments and outlook
10	02.07.2013	**Dr. Alexander Makarov** Thermo Inc., Bremen	Past, present and future of Orbitrap mass spectrometry

Winter term 2013 / 2014			
#	**Date/ Time**	**Speaker**	**Title**
1	22.10.2013 R 201	**Prof. Dr. Eric Reiner** Environment Canada, Toronto/ Canada	The Analysis of Persistent Halogenated Organics – Past, Present and Future
2	5.11.2013 R 201	**Prof. Dr. Detlef Günther,** ETH, Zürich/Switzerland	Micro to Nano-scale Analysis using ICP-MS and Lasers
3	12.11.2013 R 201	**Prof. Dr. Richard W. Vachet** University of Massachusetts/USA *Invited by Prof. Michael Glocker/UR*	*Using Mass Spectrometry to Study Protein Amyloid Formation*
4	26.11.2013 R 201	**Dr. Jens Kruse** University of Rostock/Germany	Synchrotron based X-ray absorption spectroscopy for speciation of C, N and P in environmental samples
5	10.12.2013 18:15 h R 201	**Prof. Dr. Jan Pettersson** University of Gothenburg/Sweden	Studying Aerosols with Surface Ionization Methods – New Tools for Atmospheric and Combustion Research
6	07.01.2014 R 201	**Dr. Antony Dufour** CNRS/INPL Nancy/ France	Analysis of biomass pyrolysis products by advanced mass spectrometry
7	14.01.2014 R201	**Prof. Dr. Caroline Huhn** University of Tübingen/ Germany	Capillary electrophoresis - mass spectrometry as a versatile tool for the analysis of complex samples
8	16.01.2014 Thursday HS 001	*Institute-Colloquium:* **Dr. Thorsten Streibel** University of Rostock/Germany	Photoionisierung-Massenspektrometrie für die Analyse organischer Spuren-komponenten aus thermischen Prozessen
9	21.01.2014 R 201	**Dr. Angela Vogts** Institut für Ostseeforschung-Warnemünde	NanoSIMS: principles and applications
10	23.01.2014 Thursday HS 001	*GDCh Colloquium:* **Prof. Dr. Christine Achten** University of Münster/Germany	PAK – Empfindliche Messmethode mittels GC-APLI-MS und Bioverfügbarkeit aus Kohle
11	27.1.2014 Monday R 201	**Prof. Dr. Ralf Zimmermann** University of Rostock / Helmholtz Zentrum München	Health effects of Ship Diesel emission: A combined comprehensive physical-chemical and molecular biological study in the framework of the HICE Project

HICE

HICE

Exposure to particulate matter (PM) decreases the life expectancy of every person by an average of 8 month in Europe, mostly due to increased risk of cardiovascular and respiratory diseases, and lung cancer.

(WHO Europe)

Facts:

- Helmholtz Virtual Institute in Aerosol & Health Research
- Funded by the Helmholtz Association with 3.000.000 Euros
- Led by the Helmholtz Zentrum München and the University of Rostock
- Cooperation with eight partners and six associated partners
- Started in January 2012 as a five-year project
- www.hice-vi.eu

Research goals:

- Elucidation of the molecular mechanisms and agents in combustion aerosols relevant for the observed health effects
- Identification of biomarkers for exposure and health effects
- Evaluation of the relative toxicological potential of different anthropogenic aerosol sources

Scientific hypotheses:

1. Reactive organic compounds in ambient aerosols, present either in the gas phase or the particle phase or in both phases, are particularly relevant for the induction of the observed adverse health effects.
2. Synergistic effects of reactive organic compounds in the gas phase and the particulate phase play an important role in causing these effects.
3. Expected increase of biofuel & biomass ("Energiewende") will change the composition and properties of aerosols and may enhance or modify aerosol-related health effects.
4. The nature of the refractory solid carbonaceous material (black elemental carbon/soot) has important effects on the biological and health effects of combustion derived particulate matter due to its ability to transport adverse chemicals into cells (e.g. via phagocytosis)

Innovative methodological concepts:

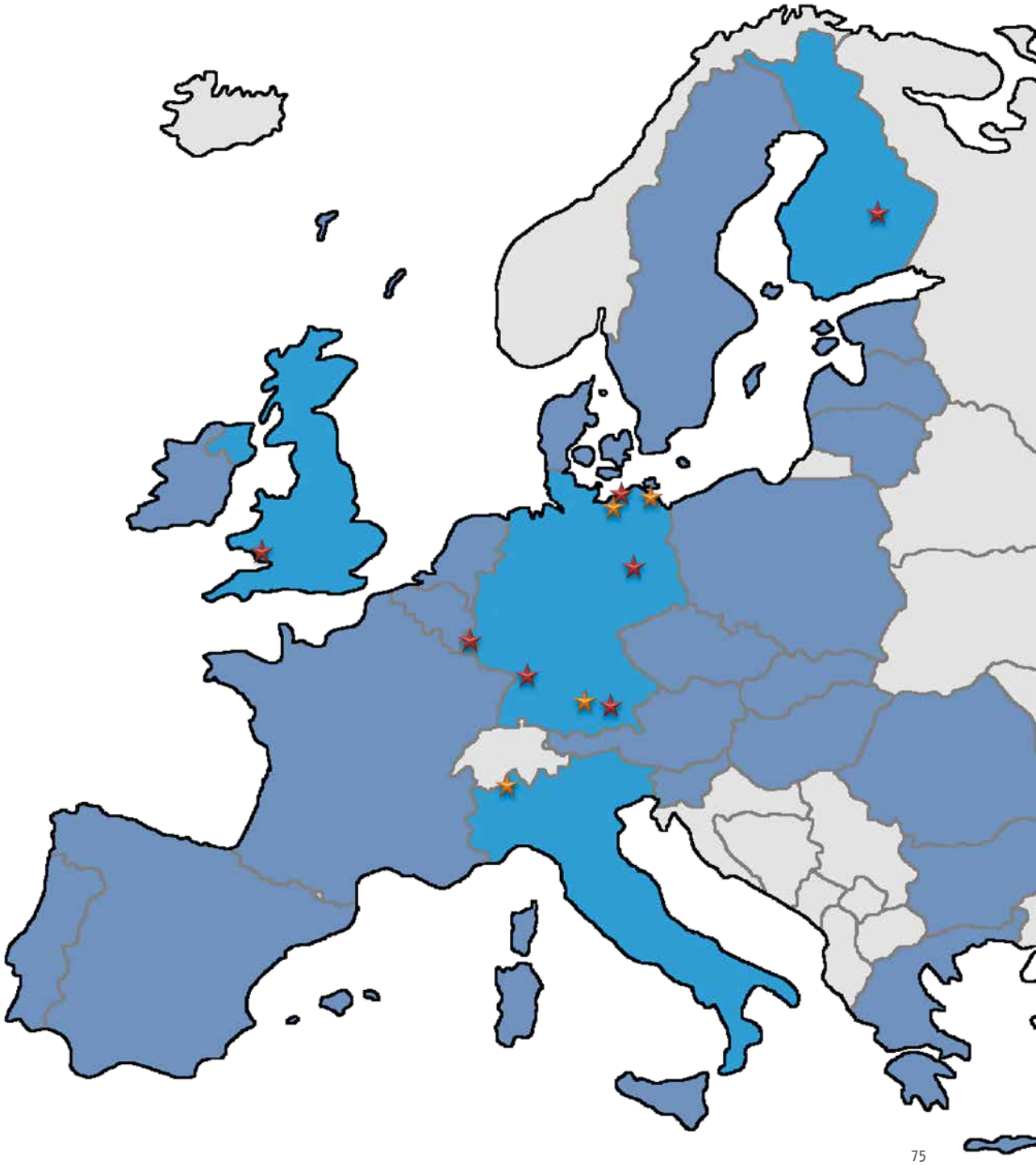
1. Health effect mechanisms can be studied by exposing human lung cell cultures to freshly emitted aerosols. The determination of the biological response is combined with a comprehensive chemical and physical analysis of the aerosol. The obtained data is subjected to a joint bio-statistical data analysis and leads finally by a systems biological mechanism and effect modeling.
2. Application and improvement of highly sensitive stable isotope-labeling methods for the detection of biological responses and elucidation of the underlying mechanisms
3. State-of-the-art exposure of human lung cell models at the air-liquid interface (ALI) provides a realistic model for aerosols inhaled into the lung by simulating the relevant primary effects in the lung tissue and can replace animal tests

Partners

- Helmholtz Zentrum München, DE
- University of Rostock, DE
- Technische Universität München: ZAUM – Center for Allergy and Environment, DE
- Karlsruhe Institute of Technology, DE
- Max Delbrück Center Berlin-Buch, DE
- University of Luxembourg, LU
- Cardiff University, GB
- University of Eastern Finland, FI

Associated Partners:

ASG Analytik-Service Gesellschaft mbH, DE; Decodon GmbH, DE; European Commission: Joint Research Center, IT; Leibniz Institute for Baltic Sea Research, DE; Photonion GmbH, DE; Vitrocell Systems GmbH, DE



Overview

Aims

The objective of the "Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health – Aerosol and Health" (HICE) is the establishment of a long-term, multi-disciplinary scientific research initiative for the investigation of the mechanisms of health effects and diseases caused by air pollution. In this respect, HICE focuses on a deeper understanding of the impact of anthropogenic aerosols on human health.

Adverse health effects caused by air pollution represent a serious worldwide problem. Combustion aerosols have been identified to be particularly potent in this context. Aerosols are suspensions of micro- or nanoparticles (fine dust) in gas. Based on current knowledge, particulate matter (PM), organic and inorganic or reactive organic compounds in the particles as well as in the gas phase of aerosols are suspected to be health relevant factors. Although such effects of aerosols are well documented, little is known about the exact mechanisms of health effects induction and the bioactive chemical species or factors. The investigation of aerosol induced biological effects is a challenging multi-disciplinary approach. This is due to the vast complexity of the anthropogenic ambient aerosol itself and the highly complicated interaction of particles and gases with the human lung tissue. However, the public health and socio-economic relevance of this environmental health topic motivates larger coordinated multi-disciplinary research activities in this field.

Consortium

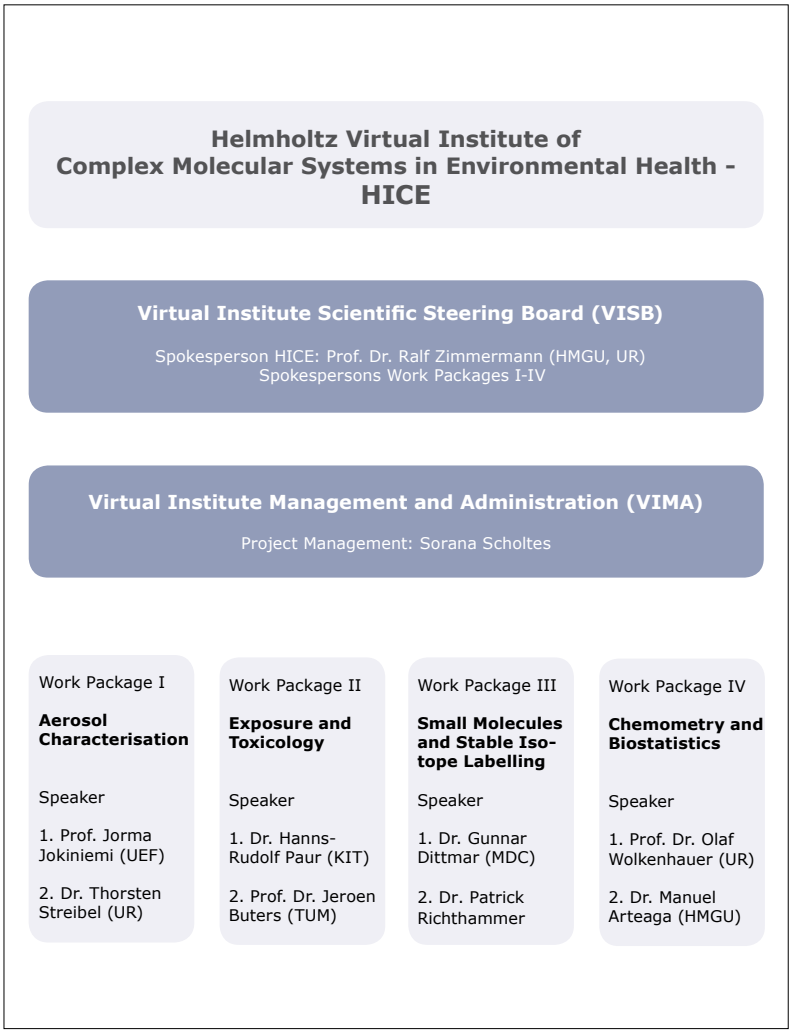
The multi-disciplinary consortium of the Helmholtz Virtual Institute HICE is based on the core cooperation (Joint Mass Spectrometry Centre) of the Helmholtz Zentrum München (HMGU) and the University of Rostock (UR). The consortium is augmented by the incorporation of outstanding further Helmholtz partners (Max Delbrück Centre, MDC and Karlsruhe Institute of Technology, KIT) and University partners (Technical University Munich, TUM) as well as by excellent foreign institutions (University of Luxemburg, ULUX, University of Eastern Finland, UEF and University of Cardiff, UCA). The consortium is further completed by associated partners from industry and additional research institutes. Researchers from a multitude of scientific disciplines are required to solve the scientific and technological challenges. Thus analytical-, environmental-, and technical-chemists, engineers, aerosol scientists, physicists, molecular biologists, medical scientists, biologists and toxicologists are working together in HICE. For the Virtual Institute HICE new organisational structures were implemented to ensure the successful amalgamation of the research groups from different scientific disciplines to one interacting multi-disciplinary institute.

Management Structure

The management structure is based on work packages (WP), exhibiting an own leading structure supervised by a joint HICE Scientific Steering Board. A project manager ensures proper administration of the scientific work in the WP and the educational measures implemented in HICE.

Scientific concept

The scientific concept of HICE is based on generation and joint analysis of comprehensive data on the properties of relevant anthropogenic aerosols and the molecular-biological response of lung cells on exposure to these aerosols. Therefore human lung cell cultures/tissue models are exposed to diluted combustion aerosols directly at the emission source, using a unique, mobile



Scientific and administration management of HICE

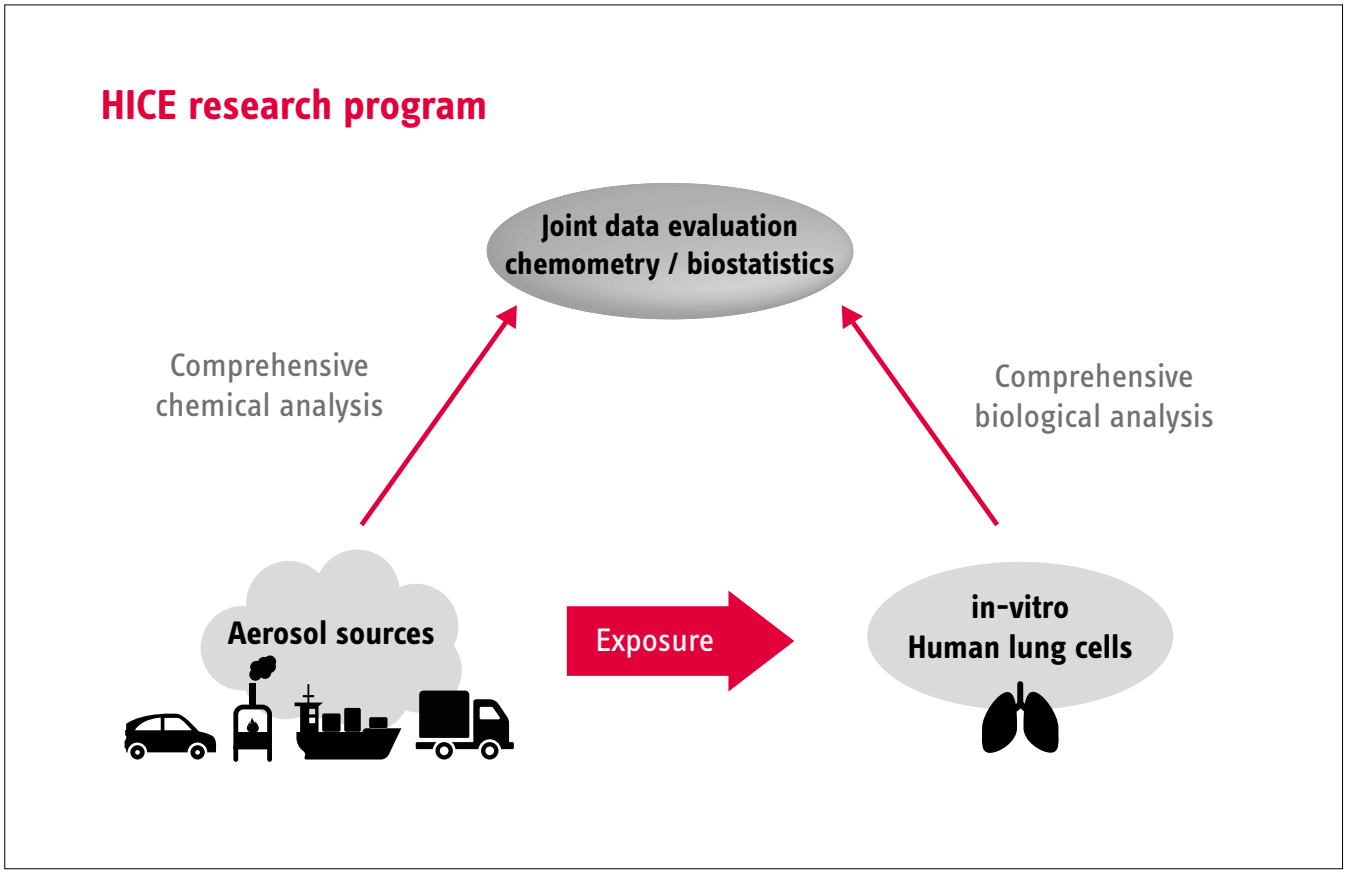
air-liquid interface (ALI) exposure unit and a mobile S2-biosafety laboratory (developed/build by HICE). The cells are differentially exposed to the full aerosol, the separated gas phase and clean air, respectively, in order to differentiate particle and gas phase effects. The composition and physical properties of the aerosol as well as the response of the biological systems are investigated comprehensively by state-of-the art analytical and bio-analytical techniques. The biological responses and the toxicological effects are comprehensively detected on different biological levels (transcriptome, proteome, metabolome, toxicological parameters). Innovative stable isotope labelling approaches are applied for detection of flux changes in the metabolism and precise detection of regulation in the proteome. The complex biological response data is bio-statistically analysed in conjunction with the chemometrical analysis of the comprehensive chemical and physical data of the exposure aerosol in order to identify biomarkers of exposure, harm and disease. The obtained multidimensional data sets are subsequently further exploited as input for a system-biological modelling of aerosol induced disease formation.

In summary the HICE approach is forging a bridge from understanding the chemical composition of aerosols to the comprehension of the adverse human health effects.

The vast complexity of ambient aerosols, of the lung tissue-particulate matter interaction and of the underlying health effects mechanisms as well as the importance of anthropogenic aerosols for public health render the research field to be of extreme complexity and multi-disciplinarity but also of large importance.

Strategic plan

In the future, HICE shall study important environmental health questions, in particular in the field of "Aerosol and Health". This includes addressing of further relevant aerosol sources, such as secondary aerosols (SOA) and non-combustion generated particles (e.g. entrainment), the development and application of improved cellular assays for health-effect evaluation, the improvement of analytical, molecular biological and instrumental methods and the application of statistical data analysis, data mining and system biological models.The strategic plan of the virtual institute HICE for the times after the HGF-INF funding period is based on the strengthening of the backbone cooperation between the Helmholtz Zentrum München and Rostock University (e.g. by establishing of a Helmholtz Institute) and on the other hand on keeping the consortium together and expanding it for future scientific cooperation in international projects.



Scheme of the HICE research program

Status and Results

HICE Test Measurement Campaigns on Wood Combustion (KIT 2012):

Two measurement test campaigns were performed at the KIT, investigating the effects of a wood combustion aerosol on two human lung epithelial cell lines (A549 and BEAS-2B). The objective of these test campaigns was to determine exposure conditions for the full, consortium-wide HICE campaigns. The cells were exposed for 4h (A549) and 2h (BEAS-2B), respectively, to 1:10 diluted beech wood combustion aerosol. LDH release was measured directly after the end of exposure, and showed no acute toxicity for A549and BEAS-2B cells. The cells were then subjected to cytotoxicological (KIT), metabolomics (ULUX) and proteomics (MDC) analyses. The cytotoxicological and 'omics results indicated that significant biological effects are induced, although no acute toxicity was observed.

HICE Test Measurement Campaign on Ship Diesel Emissions (UR 2012):

A first campaign on marine engine emissions was carried out in June 2012 at the University of Rostock, utilizing a single-cylinder research ship-diesel engine. The main objectives were to get insight into the emission levels from the engine and to find out how representative the engine would be in comparison to real-world ship emissions.

The experiments were conducted with heavy fuel oil (HFO) containing 2.7% of sulfur and 270 ppm Vanadium as well as with a conventional diesel fuel according to EN590. The engine was operated at nominal speed and at engine loads ranging from "idle" to 100 %. The exhaust gas was analyzed with single gas analyzers for O2, CO, NO_x and total hydrocarbons (THC). Volatile and semi-volatile organic species were measured online with a resonance-enhanced multiphoton ionization time-of-flight mass spectrometer (REMPI-ToF-

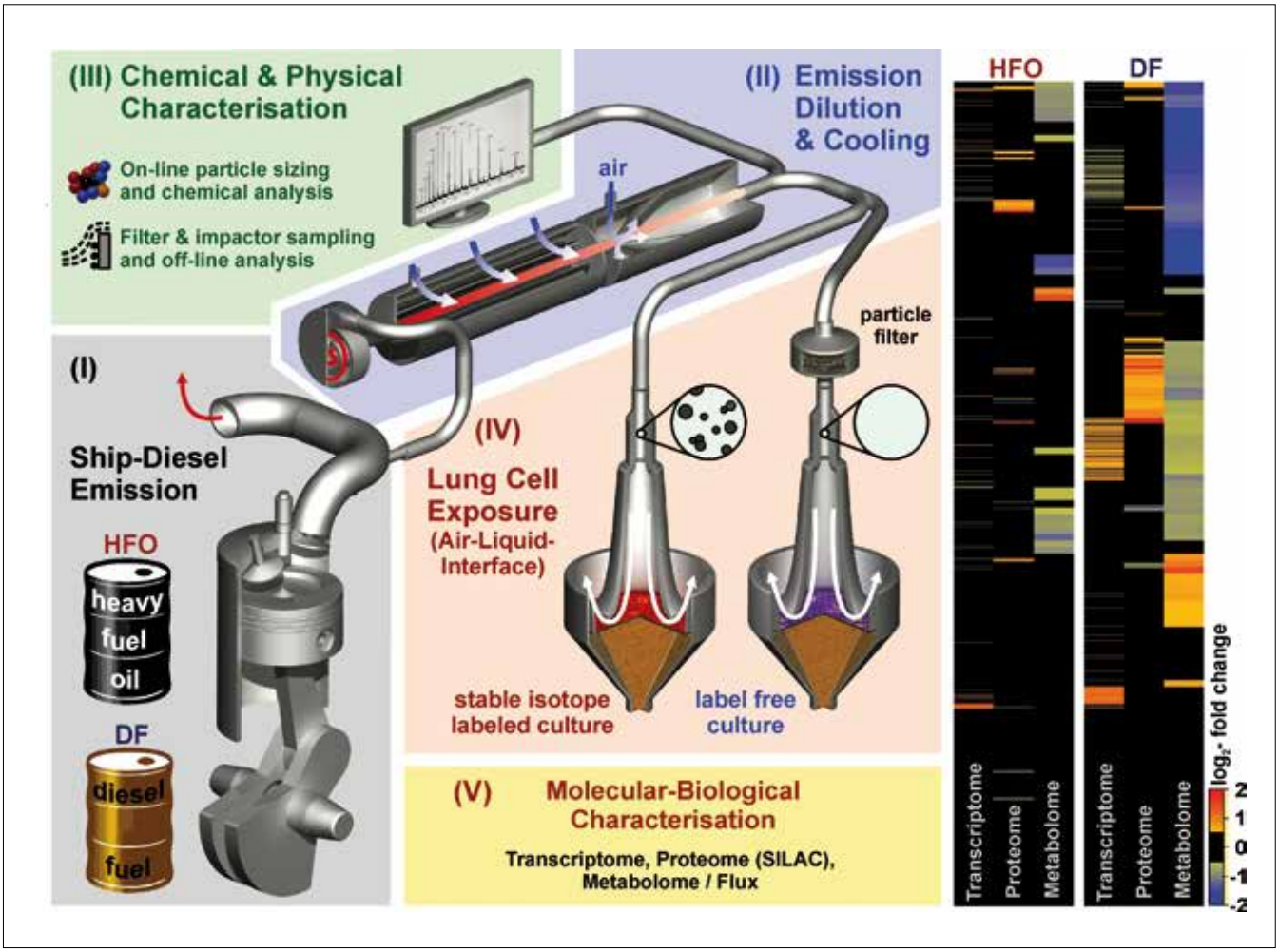


Figure 1: Experimental set-up und concept of the study. An 80 KW common-rail ship-diesel engine (I) was operated either with heavy fuel oil (HFO) or a highly refined diesel fuel (DF). The exhaust aerosols were diluted and cooled with clean air (II) and were synchronously subjected to physical and chemical analysis (III) as well to human lung cell exposure experiments at an air-liquid interface (ALI) (IV). Human bronchial cell lines were exposed for 4h and characterized using transcriptomics, proteomics and metabolomics (V). The vertical bars at the right depict the respective up- and down regulation for both fuel aerosols. DF shows more of such regulations than HFO for all investigated hierarchic 'omics levels.

MS) and a proton transfer reaction mass spectrometer (PTR-MS). Particulate samples were collected on filters and analyzed for inorganic and organic species by chromatographic and spectroscopic methods. Furthermore, a novel setup combining a thermal-optical carbon analyzer with a REMPI-ToF-MS was applied for simultaneous quantification of organic and elemental carbon and their molecular aromatic composition (Grabowsky et al. 2013). Measured particulate matter (PM) emission factors were generally on a similar level as the real-world emission factors reported in literature (Agrawal et al. 2008). The effect of load conditions on PM was found to be similar as in earlier studies performed with real large-scale marine engines (Sarvi et al. 2008). PM emissions from DF operation were mainly composed of relatively volatile organic species and elemental carbon (soot). PM emissions with HFO on the other hand, contained large amounts of low-volatile organic species, sulfuric acid and various transition metals originating from the fuel, while the soot emissions were relatively low. Depending on engine load, total PM emissions from HFO operation were 3-35 times higher than from DF operation, and inorganic species being released from HFO which generate substantial sulfuric acid and metal emissions. HFO usage also generated drastically higher emissions of known hazardous species (PAH, Oxy-PAH, N-PAH, transition metals), but, interestingly, lower soot emissions.

HICE-consortium-wide measurement campaign on ship diesel aerosol emissions (UR 2012)

The four-stroke research ship-diesel engine at the University of Rostock, which was used for the test campaign, was also taken for the consortium-wide campaign in November 2012. The engine was operated with either HFO (HFO 180) containing 1.6% sulfur, or DF containing less than 0.001% sulfur in compliance with the 2014 IMOSECA-legislation (DIN EN590). DF contained 3.2% plant oil methyl ester. The main objective of this campaign was to study the biological re-

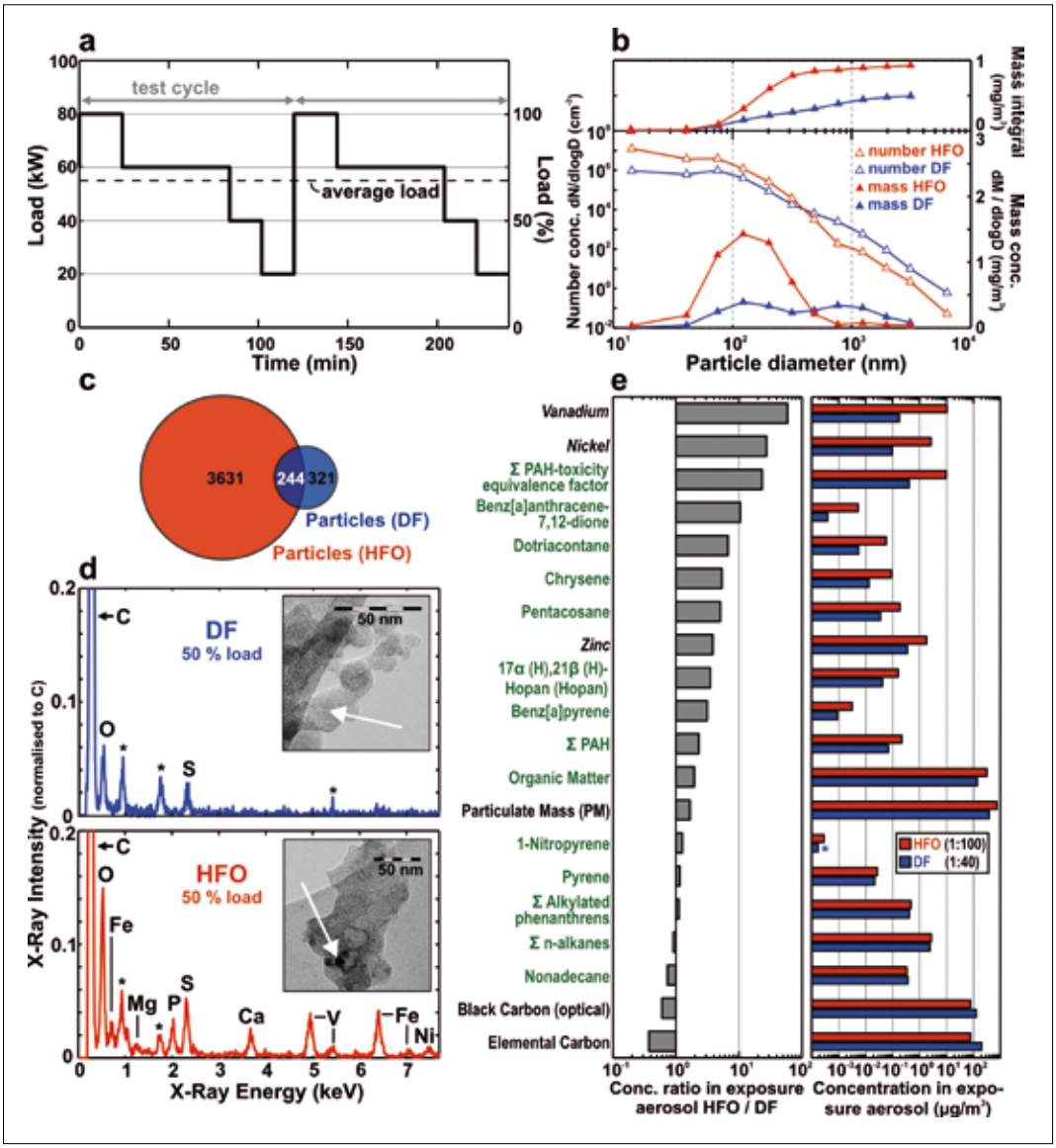


Figure 2: Chemical and physical aerosol characterization. a, The ship diesel engine was operated for 4h according to the IMO-test cycle. b, About 28 and 56 ng/cm2 for DF and HFO respectively were delivered to the cells with different size distributions. HFO contained predominantly particles with <50nm and DF predominantly with >200nm, both in mass and number. c, Number of chemical species in the EA particles. d, Transmission electron microscope-images (TEM) and energy-dispersive X-ray spectra (EDX) of DF-EA and HFO-EA; heavy elements (black speckles, arrow); contributions of elements V, P, Fe and Ni in HFO particles using EDX (= grid-material). e, Exemplary EA concentrations (right) and concentration ratios (left) for particulate matter bound species. All experiments n=3.*

sponse of human lung cell cultures when exposed to ship diesel-generated aerosols. This was accompanied by applying a wide range of analytical instrumentation for the chemical and physical characterization of both gas and particulate phases, covering as many substance classes and physical parameters as possible by applying selective methods. A new aerosol sampling setup was designed and taken into operation for the campaign. Cell exposure and monitoring of gaseous and particulate constituents of the aerosol was carried out on-line, and particles were sampled on filters for subsequent detailed laboratory analysis. The scheme depicted in Figure 1 gives an overview of the campaign setup. An overview of selected results of physical and chemical characterization of ship diesel aerosol is given in Figure 2.

For the cell exposure, HICE has built Europe's first mobile S2-biosafety laboratory hosting a mobile ALI cell exposure system (Paur et al. 2011) with 18 simultaneously exposable cell culture positions (for clean air reference, filtered aerosols (gas only) and whole aerosols (gas and particles) exposure).

It was shown that HFO-emissions contain more particle mass as well as higher concentrations of transition metals and organic chemicals, whereas elemental carbon-dominated particles (soot) prevailed in DF-emissions. Monitoring of the cellular response via transcriptomics, proteomics, metabolomics and flux analysis (see Figure 1 right bars) revealed biological effects for HFO-emission particles especially on inflammation and oxidative stress. Surprisingly, the effects of DF-emission particles were broader and towards basic cellular pathways compared to HFO-emission particles, suggesting that both, DF- and HFO-use evoke harmful health effects. The pathways are summarized in Figure 3. This result was highly unexpected, as the concentration of known toxic compounds in HFO-exhaust is much higher than in DF-exhaust. Currently switching from HFO to DF in coastal areas is promoted in order to reduce adverse health effects. The results suggest that this might be an insufficient strategy from a public-health perspective. At least reduction of soot particles from the emissions is highly recommended (e.g. via electrostatic precipitation or filters). Currently model experiments are conducted to further study the role of the soot core itself and the organic adsorbates on the soot particles, using a special model burner (combustion aerosol standard, CAST) and ALI exposure tests of human lung cells.

HICE Test Measurement Campaign on Passenger Car and Truck emissions (JRC 2013):

Effect	HFO	DF
Inflammation	↑	-
Oxidative Stress	↑	-
Cell homeostasis	↑	-
Response to chemicals	↑	↓↑
Cellular stress response	↑	↑
Motility	↑	↑
Cellular signaling	MAPK, TGF beta, PDGF, EGF, GPCR	ID, kinase cascade
Energy metabolism	-	↓↑[x]
Protein synthesis	-	↓
Protein degradation	-	↑
RNA metabolism	-	↓
Epigenetic modifications	-	↑
Cell junction and adhesion	-	↓↑[*]

*Figure 3: Summary of main biological effects (pathways) upon exposure with HFO- or DF-particles. Arrows indicate the direction of regulation for cellular functions derived from most statistically significant enriched gene- ontology terms of transcriptome, proteome, and metabolome (x - up BEAS-2B, down A549; * - down BEAS- 2B, up A549)*

In order to evaluate the specific technical challenges of highly variable vehicle emissions, online monitoring of gas phase aerosol constituents were conducted at the dynamometer installation of the Joint Research Centre at Ispra, Italy, in April 2013. Gasoline- and ethanol-powered passenger cars were investigated and were started at room temperature as well as at a temperature of -7°C. Gaseous emissions of PAH, aliphatic hydrocarbons and carbonyls were monitored in real time (Figure 4). High emissions were observed at the start of the engine, but dropped below the limit of detection after five minutes at the latest. Under cold start conditions, emissions were significantly higher and the decay of the signals took longer. Ethanol fueled cars also exhibited longer decay times compared to the use of gasoline fuel, and showed considerably enhanced carbonyl emissions. In this study, several innovative mass spectrometric techniques (PTR,SPI,REMPI) were directly compared and tested for suitability.

HICE-consortium-wide measurement campaign on wood combustion emissions (UEF 2013):

The third major aerosol source, on which HICE focuses, is wood combustion. A measurement campaign took place in October 2013 at University of Eastern Finland, Kuopio. Emissions from a masonry heater and a pellet burner were characterized. Three different sorts of wood, viz. beech, birch, and spruce, were combusted in the masonry heat burner. The fuel used with the pellet bur-

ner was soft wood pellets. In addition, aerosol was aged in a smoke chamber and characterized as well. Sampling strategy and cell exposure were similar to the ship diesel campaign.

The results from this campaign currently are still under analysis. A preliminary comparison of diesel exhaust and wood combustion emission suggests stronger biological effects in the case of diesel emission aerosol. In the remaining funding period, HICE will address further relevant emission sources such as passenger car- and heavy duty truck-emissions. The final joint analysis of the obtained comprehensive data on emission aerosol composition and the molecular biological response of human lung cells will be used for a system biological model of aerosol induced disease induction accompanied by limited animal exposure validation experiments. The results from the evaluation of in-vitro-lung cell and in-vivo-model exposures subsequently shall be translated to human studies. Finally, the search for significant biomarkers for exposure, harm and disease will be continued.

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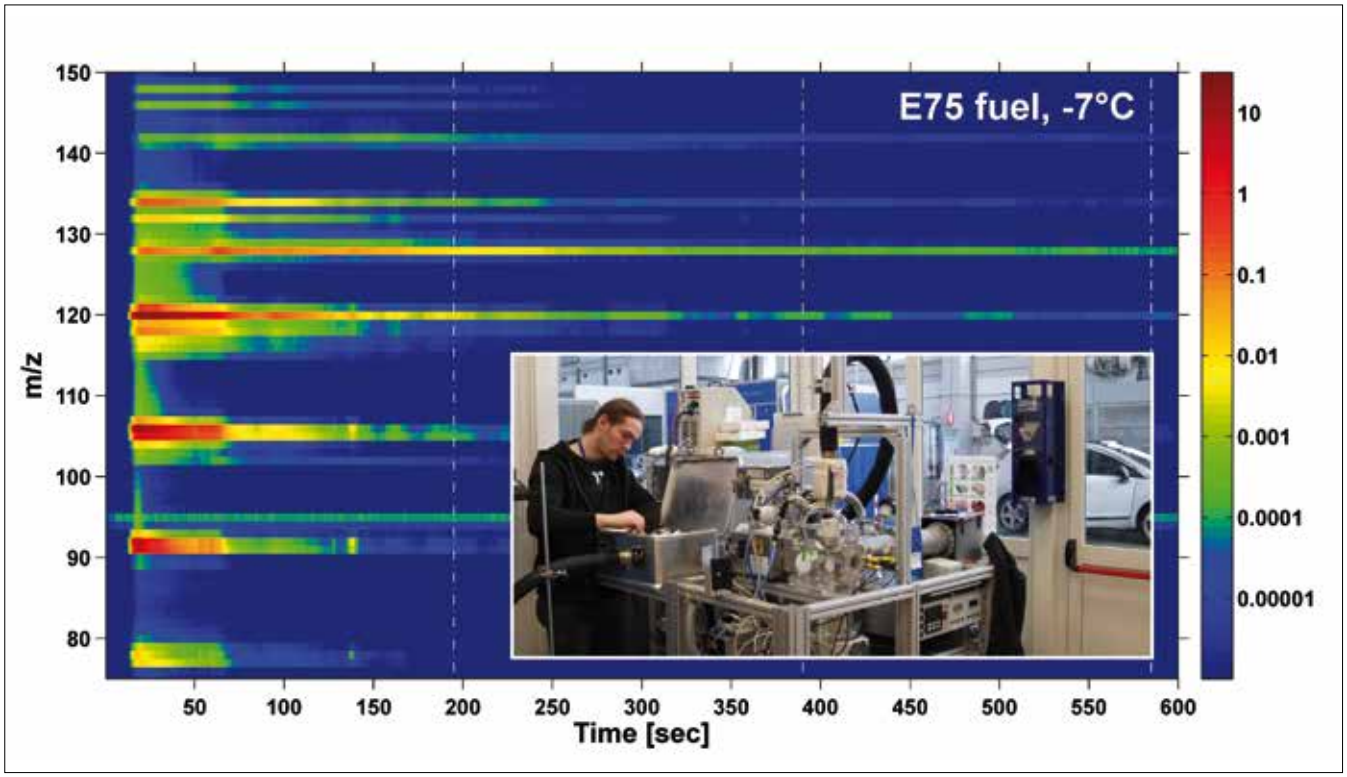


Figure 4: Time-dependent spectra of gaseous emissions using E75 in a car. At cold start conditions (-7°C), a variety of aromatic substances detected via REMPI-ToF-MS show strong signals which are several orders of magnitude higher compared to baseline concentrations during the driving cycle.

Outlook

2014: Focus on reproducibility experiments

HICE has obtained unexpected intriguing results in particular during the ship engine aerosol campaign. The data suggest a surprisingly prominent role of freshly formed carbonaceous soot for the induction of adverse biological effects in human lung tissue. Therefore the influence of freshly-formed combustion soot and gaseous combustion products on human A549 lung cells is currently being investigated using a special, custom-developed model burner for liquid and gas fuel combustion (L-CAST). The human alveolar cell cultures are exposed at the air-liquid interface with the currently optimized ALI exposure unit and the harvested material is subjected to the HICE-typical comprehensive 'omics characterization (i.e. proteomic, transcriptomic and metabolomic as well as metabolic flux analyses). Furthermore, a detailed chemical and physical characterization of the L-CAST aerosol is performed. For future HICE field campaigns the L-CAST burner will be used as reference combustion aerosol generator allowing a realistic and reproducible positive control. Therefore, special attention is placed on studying the reproducibility of the L-CAST aerosol generation in the remaining year 2014. Furthermore, experiments for the determination of the deposition dose are conducted, as the previous measurements suggest that striving for a better dose precision will support the upcoming large HICE consortium measurement campaign on automotive exhausts.

Several further methodological optimizations are also being performed in 2014, based on the experiences from previously conducted experiments. This includes better integration of the sampling of different biological molecules (RNA, proteins and metabolites) from the same harvested cell extracts. In order to increase precision of biological effect determinations on the proteome level, the stable isotope labeling approach (SILAC) is currently expanded to a triple-SILAC approach using two different labeled cultures in addition to the native culture. This allows a direct, high-precision comparison of three cases, namely the clean air, filtered aerosol (gas phase) and whole aerosol (gas phase and particles) exposure. Furthermore, the stable isotope labeling approach is currently extended from A549 alveolar epithelium cells (immortal cancer line) to the more realistically behaving BEAS2Bcell line which was immortalized by virus-transfection.

2015: Focus on car fuel and bio fuel – comprehensive data analysis

The third year of the HICE program (2015) will start with another large HICE-consortium-wide measurement campaign (about February 2015). In this campaign aerosol emissions of passenger cars and their biological effects are targeted. In particular, the effects of biofuel bends are addressed. The increased content of chemically bound oxygen in the biofuel fraction is suspected to increase reactive oxygenated species in the

The Air-Liquid Interface (ALI) system in which the cells are exposed to emissions is constantly improved for the needs of HICE

aerosol (e.g. compounds such as formaldehyde or acrolein). Two diesel- and one gasoline-powered (flexi-fuel) passenger cars (or engine-test benches) operated reproducibly on a dynamometer are on the test program. The gasoline car/engine will be operated with different gasoline and ethanol mixtures ranging from pure petrochemical gasoline (E0) to 80% ethanol (E80). The fuel of the diesel car (Euro 4/5) will be also varied, from pure petrochemical diesel (B0) to biodiesel (RME)/petrochemical diesel blends (B10 etc.). Furthermore, a different diesel car/engine will be used with different concentrations of biodiesel in the blend (B0, B50, B100). A549 and BEAS2B human lung cells will be exposed. In order to minimize the noise in the biological effects determination, the extended stable isotope-labeling concept (triple-SILAC) will be used. An improved ALI-system (synergy with a technology transfer project between the HICE partners Vitrocell and KIT) will allow a better referencing.

After the consortium campaign in the beginning of 2015 the comprehensive and joint analysis of the 4 large data sets (i.e. i) ship emission, ii) wood combustion, iii) reference burner/soot, iv) car emission/bio fuel) and several smaller data sets from the test campaigns will be a major task. On the methodological side, the implementation of methods from systems biology in the joint data analysis is planned.

A more technological task is the implementation of an improved gas phase and particle separation technology. Beyond the scope of HICE, this is supported by a recently granted project by the Deutsche Gesetzliche Unfallversicherung (DGUV) to the HICE coordinator (HMGU). The implementation of primary differentiated human lung cell-based assays is further fostered as well. This HICE activity is supported by a currently granted EU-Marie Curie post-doc project between the HICE partners UEF and UCAR. The enhancement of the chemical and biological characterization methodology and the development of on-line toxicity assays for ALI exposure as well as extension of the HICE concept to further health-relevant aerosol sources is also the main topic of a recently submitted HICE-consortium-wide proposal for a large EU-Marie Curie International Training Network.

2016: Focus on truck emissions – comprehensive data analysis

Starting with the last INF-funded year 2016 the last projected, highly relevant emissions source, namely heavy-duty traffic is addressed in a full HICE consortium measurement campaign on truck emissions. In the last INF-funded year the focus will then be placed on the comprehensive analysis and data mining of all obtained aerosol composition/molecular biological response data sets and validation experiments for hypothesis testing and identification of potential biomarkers for exposure and disease induction. This will include selected animal tests (COPD mouse model) and human material analysis for biomarker candidate confirmation.

HICE will analyze car fuel with different concentrations of biodiesel

Expected increase of biofuel & biomass will change the properties of aerosols and may modify health effects

Education

The Virtual Institute HICE pays substantial attention to the education of young scientists. Young researchers from different disciplines considerably contribute to the project. The majority of the experimental and data processing workload is carried out by PhD students. They work together in the measurement campaigns, run the experiments and assemble the different analyses to the main focus of HICE. To ensure and enhance the quality of the PhD work, several measures have been put into effect. These educational measures are especially important to bridge the gap between the researchers from different disciplines and to bring together all specific tasks aiming one goal.

HICE Summer Schools

In 2012 all young scientists met during the HICE inauguration meeting in Rostock. The first Summer School took place at Charles University in Prague in August 2013. The students and young scientists got the opportunity to present their work and the goals they want to achieve in HICE – therefore four groups were created and delivered insights into their specific tasks: Chemistry, Aerosol Physics, Health, and Biostatistics. Furthermore, HICE organized a workshop together with the German Association for Aerosol Research on "Aerosol Emissions from Fossil Fuel and Biomass Combustion". The students and young scientists were organized in groups for preparing their lectures. Constructive critics helped to improve the scientific presentation skills. Leading experts from aerosol research and environmental health were invited for lectures. In discussion- and break-out-sessions, the impact of combustion aerosols on human health was evaluated. The summer school attendees and over 100 participants thus learned about the state-of-the-art characterization of aerosols by bioassays, on-line mass spectrometry and advanced molecular profiling techniques.

HICE Measurement Campaigns

Another important contribution to the education program for students and young scientists are the HICE measurement campaigns. In those the students and young scientists work together under guidance of experienced scientists. In particular in the four large HICE-consortium wide measurement campaigns, where all students and young scientists are involved in joint multi-disciplinary measurements for about 3–4 weeks, respectively, a large training effect is achieved: The students and young scientists are involved in several facets of the technical/engineering, the aerosol analytical and in the biological/toxicological aspects of the HICE program.

HICE Workshops

Internal HICE workshops have been organized that focused on questions and problems related to evaluation and interpretation of the data from the measurement campaigns. During such meetings, young researchers could discuss their data with the post-docs and scientists involved in the project and gather knowledge about the handling and manipulation of scientific data as well as its integration into a bigger scientific context.

Mentoring of students, PhD students and young scientists

In the first two years of HICE, three bachelor theses and three master theses were completed on HICE-related topics. All MSc graduates have been employed as PhD students within the HICE project or related/associated projects to continue their work in this scientific context. All HICE PhD-students and young scientists were embedded in the graduate and mentoring program of their host universities. In addition the Helmholtz Zentrum München organizes (in collaboration with the universities LMU and TU München) a graduate program called HELENA – Helmholtz Graduate School of Environmental Health which is open for all PhD students involved in HICE. International networking is promoted by offering financial support for attending conferences and for research stays at other consortium organizations. HELENA offers courses to foster independent scientific working. Furthermore soft skill training courses such as self-management, scientific writing and presentation trainings are conducted. PhD students are assigned a personal thesis committee for intensive guidance and mentoring. Finally, they can earn a certificate in environmental health research as an extra qualification. Post docs are advised and supported in their career-planning. This includes the young investigator group position in bio statistics which is held by Dr. M. Arteaga Salas. He has one co-worker from the HICE program and can access data from multiple other coworkers due to the central position of his work package.

Lab exchanges

The Metabolomics Group of the Luxembourg Centre for Systems Biomedicine (LCSB) led by Dr. Karsten Hiller invited the HICE students for a lab training course on profiling cellular metabolism in October 2012. During a one week course the parti-

cipants analyzed metabolic effects on human lung cancer cells caused by wood combustion-derived nanoparticles. To measure intracellular metabolic flux changes, the scientists applied stable-isotope tracers. After the cultivation of the cells, they extracted intracellular metabolites and prepared them for chromatographic and mass spectrometric measurement. Finally, they analyzed the data and detected particle-induced changes in metabolite amounts and intracellular fluxes.

The group at the Karlsruhe Institute for Technology (KIT) invited students from HICE on two occasions to learn about the handling of the air-liquid interface system for the exposure of human lung cell cultures. The basic operation principles were explained and the steps for the preparation of cells were demonstrated. Actual exposures were performed with aerosol from wood combustion and knowledge about extraction procedures was imparted to the students after the exposure.

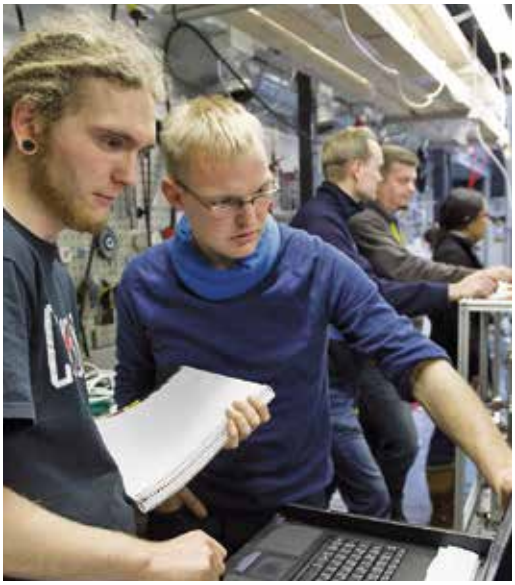
Weekly lecture program during teaching term

During the academic terms, weekly lectures are held on science and technology topics such mass spectrometry and its applications. Once in a week experts from universities and industry provide an overview on ongoing developments. The lectures are held at the University of Rostock and are transmitted to all HICE partners via video conferencing. Partially the presentations are transmitted to a public open seminar room (the Helmholtz Zentrum München).

Participants at the Workshop „Aerosol Emissions from Fossil Fuel and Biomass Combustion“ in Prague

Lab visit at the Metabolomics Group of the Luxembourg Centre for Systems Biomedicine (LCSB)

Scientists analyzing the effects of aerosols from ship diesel emissions in the HICE mobile lab



PhD students working at the HICE measurement campaign on wood combustion in Finland

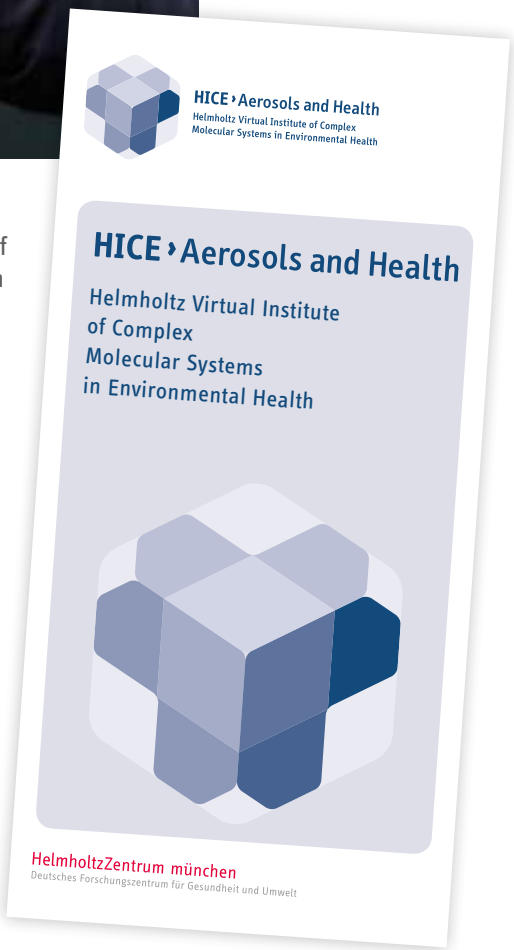
Public Relations

The official opening ceremony of the Helmholtz Virtual Institute HICE at the Leibniz Institute for Baltic Sea Research Warnemünde in May 2012 was well covered by the media. The collaboration of the Helmholtz Zentrum München and the University of Rostock evoked the interest of the public. The scientific aims of HICE –research on the adverse health effects of anthropogenic aerosols – are frequently picked up by journalists.

HICE consistently informs the public through press reports on its campaigns and on the obtained and published results. All HICE events can be found on the website **www.hice-vi.eu**. Information on the project is also available on the website of the Helmholtz Zentrum München as well as on the website of the Helmholtz Association in Berlin. A HICE flyer and a brochure were created to inform the public on conferences and events about the scientific goals of the project. Furthermore the project logo and a broad variety of pictures help to increase the visibility of the project and to visualize the work of the scientists.

The official opening ceremony of HICE at the Leibniz Institute for Baltic Sea Research Warnemünde

In November 2012 the first HICE measurement campaign took place at the University of Rostock where one of the few research ship engines in Germany is located. The scientists ran the ship engine and exposed human lung cells to different fuels in a mobile laboratory, which was build in HICE.. The local media reported about the experiments. The press conference at the University of Rostock was attended especially by local journalists from TV, radio and newspapers. Rostock with its Baltic Sea harbor is particularly interested in the research of the HICE scientists: The reports created public attention and Prof. Ralf Zimmermann received several interview requests from the media. An NDR documentary on cruise ships and their emission in ports included an interview with Prof. Zimmermann and illustrated the work of the project. Other media such as the ZDF, the WDR and the newspaper "Wirtschaftswoche" also reported on the topic. The public awareness of the



Prof. Ralf Zimmermann, spokesperson of HICE, gives an interview on the research of ship diesel emissions

Press conference at the HICE measurement campaign on ship diesel emissions at the University of Rostock

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