Third Progress Report of the Joint Mass Spectrometry Centre of the University of Rostock and the Helmholtz Zentrum München

Summer Term 2010 and Winter Term 2010/2011
Dear reader,

Herewith we present the third progress report of the Joint Mass Spectrometry Centre (JMPC). The JMPC represents a long-term cooperation of the Helmholtz Zentrum München (Institute of Ecological Chemistry, now Cooperation Group Comprehensive Molecular Analytics, CMA) and the University of Rostock (Institute of Chemistry, Chair of Analytical Chemistry). Similar to the two preceding progress reports, which were written in German providing English summaries only (available for download at the JMPC web site www.jmsc.de), this report surveys the concept and structure of the JMPC. In addition, new developments of the past year are addressed and illustrated by a photo series. Scientific highlights are presented in the framework of 16 reports. Finally, the co-workers in the JMPC are introduced and performance parameters, such as publication output and acquired third-party funds, are tabulated.

I wish to express my gratitude to all supporters of the Joint Mass Spectrometry Centre at the University of Rostock and the Helmholtz Zentrum München. In this context, particular mention must be made of the Rector of the University of Rostock, Prof. Dr. Schareck, and the CEO of the Helmholtz Zentrum München, Prof. Dr. Wess. Furthermore, I would like to thank the former director of the Institute of Ecological Chemistry (IEC), Dr. Schulte-Hostede, for his continuous support during the last few years. Last but not least, I would like to acknowledge the excellent contributions in research and in education of the meanwhile more than 50 co-workers and senior scientists of the Joint Mass Spectrometry Centre. Without their outstanding performance the achieved progress would not have been possible.
Towards the end of the reporting period on March 31st, 2011, some organisational changes became effective. Dr. Schulte-Hostede, the former head of the Institute of Ecological Chemistry (IEC), retired. The management board of the Helmholtz Zentrum München had previously decided to discontinue the IEC. In the framework of the closure of the IEC, the “Cooperation Group for Analysis of Complex Molecular Systems” was converted into an independent research group of the Helmholtz Zentrum München on March 1st, 2011, and was renamed as “Comprehensive Molecular Analytics” (CMA). The cooperation of the University of Rostock and the JMSC was strengthened by this appreciation and we are looking forward to our first report on the progress obtained in the new structure in a year from now.

Rostock and Neuherberg, in June 2011

Prof. Dr. Ralf Zimmermann
Joint Mass Spectrometry Centre of the University of Rostock
Helmholtz Zentrum München
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Concept of the Joint Mass Spectrometry Centre of the University of Rostock and the Helmholtz Zentrum München
The Joint Mass Spectrometry Centre (JMSC) of the University of Rostock and the Helmholtz Zentrum München

Since April 2008, the University of Rostock (Chair of Analytical Chemistry) and Helmholtz Zentrum München (cooperation group “Analysis of Complex Molecular Systems” of the Institute of Ecological Chemistry) have been cooperating in the field of development and application of mass spectrometry-based analytical techniques for the characterisation of complex molecular substance mixtures. For this purpose, a cooperation contract between the University of Rostock and the Helmholtz Zentrum München was signed, creating the “Joint Mass Spectrometry Centre” (JMSC) as a joint research activity. The JMSC is headed by Prof. Dr. Ralf Zimmermann, who concurrently holds the Chair of Analytical Chemistry at the University of Rostock (UR) and directs the Cooperation Group at Helmholtz Zentrum München (HMGU).

Figure 1: Left: On July 3rd, 2009, the public inauguration of the Joint Mass Spectrometry Centre took place in the historical main building of the University of Rostock; right: Aerial image of the campus of Helmholtz Zentrum München.

In March 2011, the HMGU cooperation group was restructured to form the independent Cooperation Group “Comprehensive Molecular Analytics” (CMA).
The JMSC is formed by the CMA and the Chair of Analytical Chemistry (CAC) at the University of Rostock. Research topics of the JMSC are structured in three research areas with corresponding research groups at UR and HMGU (Figure 2).

The first research area of the JMSC is focused on environmental aspects and their impact on human health. The main objective of the research group “Environmental and Process Analysis” in Rostock is the analysis of chemical signatures of significant technical and environmental processes. The corresponding group at the HMGU is “Health Relevant Environmental Analysis – Aerosol Research” (HAR). It is embedded in the framework of the HMGU “Environmental Health” POF program and focuses its research activities on ambient aerosols and their health effects.

The second research area of the JMSC is concerned with biomedical and health-related applications. One focus of the unit “Biomedical Analysis” in Rostock is the comprehensive analysis of breath gas which is performed in cooperation with, e.g., the Rostock University Hospital. The corresponding research area in Munich is named “Comprehensive Molecular Profiling” (CMP). It develops and applies
novel multidimensional profiling techniques for non-targeted metabolic characterisation, for instance in diabetes research or in cell-based toxicological studies on the effect of inhaled aerosols. Moreover, this unit develops statistical data analysis tools for this purpose.

The third research area of the JMSC is “Analytical Method Development” (AMD). It is identically named at both institutions. In Rostock the AMD focuses on the advancement and implementation of single and multiphoton ionisation technologies. The photon sources consist of laser or lamp-based light sources, such as electron-beam pumped rare-gas excimer light sources (EBEL). At the HMGU, research is concerned with the development and application of joint analytical systems. Examples include comprehensive two-dimensional gas chromatography and thermogravimetry (TG) coupled to single-photon ionisation time-of-flight mass spectrometry.
Presentation of the Joint Mass Spectrometry Centre at the Chair of Analytical Chemistry (UR) and the Cooperation Group “Comprehensive Molecular Analytics“ (HMGU)

At the University of Rostock, the Joint Mass Spectrometry Centre (JMSC) is represented by the Chair of Analytical Chemistry. It is located in the buildings of the University of Rostock at Dr.-Lorenz-Weg. Currently 17 academic staff members (senior scientists, postdocs, PhD students and diploma students) are employed at the Chair of Analytical Chemistry. Three members occupy permanent academic positions, while nine members have temporary third-party funded employment contracts. There are also three scholarship holders. Facilities in Rostock comprise 515 m² of laboratory space (200 m² for teaching) and 125 m² of office space, including an office container.

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). 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). Moreover, two LC-MS systems and several GC-MS are being 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 interconnectable 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.
Thermodesorption equipment is available to study carbon content in solid samples. It is coupled to a photo ionisation mass spectrometer. Finally, a laboratory reactor used to study Fischer-Tropsch synthesis (heterogeneous catalysis) was implemented.

In addition, the research group of PD Dr. Gerd-Uwe Flechsig, conducting research in electrochemical analytics, is located at the Chair of Analytical Chemistry. It currently consists of three PhD students.

The cooperation group “Comprehensive Molecular Analytics” (CMA) at Helmholtz Zentrum München in Neuherberg consists of 25 scientists. Thirteen scientists are permanently employed at Helmholtz Zentrum München. Two are exempt employees, working as Helmholtz employee representatives for half a day. 10 PhD students are employed on a temporary basis with contracts through third-party funding. The cooperation group also has four technical staff members and two retired scientists serving as associated scientific consultants. Members are currently dispersed in several buildings on the campus of the Helmholtz Zentrum München (bldg. 16, 24, 38c and 57), but reconstruction and renovation work in building 24 is being carried out. The renovated building will bring together all members of the research group in the future.

The cooperation group in Neuherberg operates two HPLC-MS/MS systems, two HPLC systems equipped with a diode array and fluorescence detector, one system for multi-dimensional gas chromatography - time-of-flight mass spectrometry (GC x GC - TOFMS), four GC-MS systems (one TOF, three for thermo desorption) and several instruments coupled for thermal analysis (TG, DSC, etc.) with EI – quadrupole mass spectrometry and FTIR.

Physicochemical characterisation of particulate matter and aerosol particles is performed using a high resolution aerosol mass spectrometer (AMS, WTOF), various particle sizing instruments (a scanning mobility particle sizer (SMPS), two electric low pressure impactors (ELPI), an aerodynamic particle sizer (APS), a white light optical particle sizer (WELAS) and 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 / thermodesorption - resonance enhanced multiphoton ionisation - single particle - time of flight mass spectrometer (LD-/TD-REMPI-SP-TOFMS) for the online characterisation of aerosol particles;
- A laser-desorption ionisation / laser-desorption resonance enhanced - multiphoton ionisation / single-photon ionization - time of flight mass spectrometer (LDI/LD-REMPI/SPI-TOFMS) for the analysis of solid samples, sampled aerosol particles and biological samples;
- A thermal analysis - single-photon ionisation - quadrupole mass spectrometer (TA-SPIxMS) and
- A thermal analysis - single-photon ionisation - time of flight mass spectrometer (TA-SPI-TOFMS) for the determination of organic signatures in thermal processes.

Three instruments for the multi-dimensional analysis of highly complex samples in bio and environmental science are available in the group:

- Thermal analysis - single-photon ionisation comprehensively coupled with gas chromatography time of flight mass spectrometry (TA-GCxSPI-TOFMS);
- Gas chromatography - EBEL-single-photon ionisation - time of flight mass spectrometry (GCxSPI-TOFMS) and
- Comprehensive two-dimensional gas chromatography - EBEL-single-photon ionisation - time of flight mass spectrometry (GCxGC-SPI-TOFMS) including two thermodesorption - photo ionisation - ion trap - mass spectrometers (TD-SPI-ITMS) for the determination of security-relevant compounds (drugs, explosive substances etc.).
The bifa Environmental Institute: Cooperation and Projects

The Joint Mass Spectrometry Centre cooperates with the bifa Environmental Institute, founded in 1991, through a contractual partnership with the cooperation group “Comprehensive Molecular Analytics” (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.

Figure 5: The bifa Environmental Institute in Augsburg. The bifa is a close cooperation partner of the Joint Mass Spectrometry Centre.

The basic institutional funding of bifa is approx. 20% of the volume of sales. Hence it is close to the financial concept of the German Fraunhofer-Gesellschaft, to give an example. The bifa is located at Augsburg, has about 40 employees and is equipped with an efficient infrastructure (chemistry, microbiology laboratories, pilot plants, experimental workshop, etc.). Prof. Dr.-Ing. Wolfgang Rommel has been CEO of the bifa Environmental Institute GmbH. Prof. Dr. Ralf Zimmermann has served as external director of the subject area “chemistry” at the bifa. The cooperation with the Helmholtz Zentrum München and the Joint Mass-Spectrometry Centre is based on a cooperation agreement.

The priorities of joint research are aerosol research and process analysis, to name a few. In the beginning of the reporting period, the joint investigation of aerosol components in raw gases from waste incineration plants was completed. A major new collaborative research project to study the distribution of harmful substances between the particle and gas phase of an aerosol was approved and the first experiments on particle generation, ageing and characterisation were performed. One employee of the bifa currently works as senior scientist in a third-party funded project of the JMCS on the fundamentals of work place aerosol characterisation.
Technology Transfer: Photonion GmbH

Ongoing developments in online single-photon ionisation mass spectrometry (SPI-MS) in our cooperation group 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 single photon ionisation-mass spectrometry (SPI-MS) techniques and expertise present at the JMSC.

The used SPI-MS technique involves an electron-beam pumped excimer light source (EBEL), which allows the efficient and soft ionisation of organic compounds. 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, 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.

Figure 6: Photonion GmbH. The company is located in Schwerin and in Munich. Left: In the buildings of Airsense Analytics GmbH in Schwerin the CEO and administration are located; right: Research and production of Photonion GmbH are housed in a container building on the premises of Helmholtz Zentrum München. Note that the geographical structure of Photonion (Mecklenburg-Vorpommern and Bavaria) reflects that of the JMSC.
The partners of Photonion GmbH are Ascenion GmbH (patent realisation 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.

In the currently running HEF phase, demonstration instruments are developed, partly in close cooperation with prospective customers, and prototyping tests are carried out. 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, etc.) may be a key technique for further fields of application. As an example, it is used in medical technology for the online analysis of breath gas.
News and Highlights from Summer Term 2010 and Winter Term 2010/2011: Progress Overview
Overview of Summer Term 2010 and Winter Term 2010/2011

After the official foundation of the Joint Mass Spectrometry Centre as a long-term cooperation of Helmholtz Zentrum München (HMGU) and the University of Rostock (UR) on July 3rd, 2009, the ensuing year, i.e., the reporting period from April 1st, 2010, to March 31st, 2011, was characterised by the establishment and development of the JMSC and intensive, successful scientific research. From the organisational point of view, the Munich part of the JMSC at Helmholtz Zentrum München, called Cooperation Group for Analysis of Complex Molecular Systems, represented a research area of the “Institute of Ecological Chemistry” (IEC) until February 28th, 2011.

The alliance of the Helmholtz Zentrum München and the University of Rostock was further strengthened in the period under report. The regular online transmission of the seminar series “Modern Methods in Mass Spectrometry and Chromatography” held in Rostock commenced in summer term 2010. These seminars, which were now also available at the Helmholtz Zentrum München via video conference, have attracted attention beyond the members of the JMSC.

During the reporting period, three PhD students defended their dissertation theses. Werner Welthagen defended his thesis on June 6th, 2010, on the topic “Development and Evaluation of Multidimensional Gas Chromatographic and Mass Spectrometric Techniques for the Analysis of Highly Complex Chemical Mixtures”. In his studies, new ways of interpreting analytical data from existing techniques and new analytical techniques with increased separation capabilities were developed for the analysis of highly complex chemical mixtures. Data interpretation methods introduced unique chemical and physical interactions of compound classes with the stationary phase of a two-dimensional gas chromatographic system and the unique fragmentation pattern observed for different compound classes. Newly introduced analytical techniques include the use of mass spectrometry as a separation dimension coupled to one-dimensional and two-dimensional gas chromatography. On June 29th, 2010, Maren Mieth successfully
defended her thesis on the topic “Development of Analytical Procedures for the Determination of Volatile Organic Substances for Clinical Breath Analysis - Sampling, Preconcentration and Analysis.” This thesis was jointly supervised by Prof. J. Schubert from the Medical Faculty of the University of Rostock. In her work, the influence of different breath gas sampling procedures on test results was determined. The Needle Trap technique was modified to meet the requirements of breath gas analysis. Desorption was automated and practical application in a clinical setting was examined. New analytical methods were developed for complex clinical breath gas samples by means of Heartcut-GC-MS and comprehensive GCxGC-TOF-MS.

The third candidate, Mohammad Reza Saraji-Bozorgzad, passed his dissertation defense on July 14th, 2010. The title of his dissertation is “Development of a Hyphenation for Simultaneous Thermogravimetry and Single Photon Ionisation Mass Spectrometry in Polymer Analysis.” The objective of his work was to design and to develop a gas detection system for thermal analysis by means of the hyphenation of a thermo balance with mass spectrometry using electron-beam pumped excimer lamp sources. This technique provides brilliant VUV radiation for single-photon ionisation (SPI). The advantage of SPI is reflected in the absence of fragmentation due to soft ionisation, which allows the correlation of measured signals to organic molecular ions. Extension to a two-dimensional analytical technique by prefixed gas chromatography additionally improves the information content. The functionality of the built prototypes with the novel SPI-MS hyphenation was proven by investigation of well-known problems in the organic speciation in thermal analysis of (co)polymers.

Besides these excellent results of our ambitious young scientists, the Joint Mass Spectrometry Centre conveyed its scientific competence at numerous international conferences and workshops. Only a selection of the most prominent examples can be given here.

June 15th 2010
2nd Sino-German Workshop
Aerosols and Health
Beijing, China

June 21st 2010
Start of one-year sampling campaign for ambient PM_{2.5}
in Beijing, China

June 29th 2010
Defense of dissertation of Maren Mieth, UR

July 14th 2010
Defense of dissertation of Mohammad Reza Saraji-Bozorgzad, UR

July 22nd 2010
Joint seminar of JMESC and hiking in the Alps
On June 15th, 2010, the 2nd German-Sino Workshop on “Aerosols and Health” was held in Beijing. A prominent aspect of this workshop was the continued discussion of future joint activities of the Chinese Academy of Sciences (CAS), universities and Helmholtz centers. A pilot study monitoring ambient particulate matter (PM) on a daily basis started on June 21st, 2010. The major aims of this study include the characterisation of the meteorological impact on PM concentration and composition, the identification of the main sources for PM$_{2.5}$ as well as toxicological investigations and epidemiological time series analyses. Partners of the pilot project are, in addition to the HMGU and the JMSC, the Karlsruhe Institute of Technology (KIT), China University of Mining and Technology Beijing (CUMTB), China University of Geosciences Beijing (CUGB) and the Peking University Health Science Center (PUHSC).

In the framework of the Analytica China Conference in Shanghai (September 15th-16th, 2010), a small invited workshop on “Aerosols and Health” was organised by Prof. Dr. Ralf Zimmermann. This event represented a continuation of the successful international workshop on aerosols and health held in April 2010 in Munich (Analytica Conference Munich and HMGU).

The invited lectures of Dr. BéruBé, U Cardiff, UK; Dr. J. Chow, DRI-Reno, USA; and Dr. Hoffman, U Mainz, Germany, were the highlights of the workshop. Dr. Schnelle-Kreis, JMSC, focused on the characterisation of organic compounds in source and ambient particulate matter. Following the workshop at the Analytica China Conference, the participants joined a discussion meeting specialised in carbonaceous aerosols. It was conducted at the famous UKIST University in Hong Kong.
In November 2010, the JMSC participated in the workshop “The Use of Receptor Models in the Source Apportionment of Air Pollutants” at the Joint Research Centre (JRC) in Ispra, Italy. This workshop aimed at planning and organising a European intercomparison for receptor modelling of air pollutants.

On a cold winter’s day on December 12th, 2010, the foundation stone for the new research building for the study of Complex Molecular Systems at the Department Life, Light & Matter of the Interdisciplinary Faculty was laid on the Rostock university campus. After its completion, the JMSC will operate the Mass Spectrometry Centre, which is one of the permanent facilities in the research building.

Access to high-end laboratory equipment was further increased. In particular, the Leibniz Institute for Baltic Sea Research (IOW) received the authorisation to purchase an analytical nano-secondary ion mass spectrometer (Nano-SIMS). This instrument will be jointly operated with the JMSC and shall finally be placed in the above-mentioned new research building currently under construction.

Through a new cooperation with Thermo Scientific, a 7 T FT-IRC-MS system will be allocated to the Munich part of the research group. Moreover, a new GCxGC-HR TOFMS was bought and installed in Rostock in March 2011 after successfully passing the evaluation of the German Science Foundation (HBFG project). In the same month, a cooperation with the ASG Analytik-Service Gesellschaft was initiated and an additional routine GCxGC-TOFMS was provided to the HMGU part of the JMSC.

Outside the JMSC laboratories in Rostock and Munich, several measurement campaigns were performed during the reporting period. On June 21, 2010, a one-year sampling campaign for ambient PM$_{2.5}$ started in Beijing, China.

On the campus of the CUGB, two high-volume samplers daily collected PM$_{2.5}$ samples. Chemical characterisation of PM samples will be performed at KIT and...
HMGU. Toxicological and epidemiological investigations will be carried out by Chinese partners.

In October 2010, a three-week measurement campaign was conducted at BESSY II synchrotron facility in Berlin (Berlin Electron Storage Ring Society for Synchrotron Radiation) in the framework of a large network project for security-relevant research funded by the Federal German Ministry for Education and Research (BMBF). Both the Rostock and the Munich part of the JMSC participate in this project. It is aimed at the development of new photo ionisation mass spectrometric methods for the detection of traces of security-relevant compounds, such as explosives, drugs of abuse and medical drugs.

The last months of 2010 and January 2011 were devoted to the development of the concept for a proposal of a large joint research project. In detail, a Helmholtz Virtual Institute was proposed. The Helmholtz Virtual Institutes are announced by the Helmholtz Association and are dedicated to the development of a strategic research cooperation between Helmholtz centres and universities.

The proposed Virtual Helmholtz Institute addresses the origins of the health effects of anthropogenic aerosols from combustion sources. In addition to providing an innovative research program, a particular intention of the proposal is to further intensify the signature cooperation between the Helmholtz Zentrum München and the University of Rostock in the framework of the Joint Mass Spectrometry Centre as well as to establish a new scientific cooperation with other Helmholtz and university partners relevant for the field of research (MDC-Max Delbrück Center for Molecular Medicine, KIT-Karlsruhe Institute of Technology, TUM-Technical University Munich, ULUX-University of Luxembourg, UEF-University of Eastern Finland, UCA-University of Cardiff).
In February 2011, a measurement campaign in cooperation with colleagues of the Bavarian Center for Applied Energy Research (ZAE Bayern) was performed at the laboratories of the Bavarian Technology and Support Center (TFZ) to study the emissions of wood combustion.

Besides intensive research activities, some time remained for social experiences. In July 2010, the annual joint seminar of the JMSC was held in Bavaria. It was combined with a hiking tour in the Berchtesgaden Alps. In winter 2010, the research group in Munich arranged a skiing event at the Bavarian Spitzingsee.

As mentioned before in this report, the organisational structure of the HMGU-part of the JMSC changed on March 1st, 2011. In the framework of the closure, the cooperation group “Analysis of Complex Molecular Systems”, which was a part of the IEC, was transformed into an independent research area at the HMGU. The new name of this area is “Cooperation Group of Comprehensive Molecular Analytics” – CMA. On March 3rd, 2011, a farewell party took place for Dr. Schulte-Hostede, the retired former director of the IEC.

The last month of the reporting period was characterised by instrument installations and project starts. In the framework of a cooperation project with ASG-Analytik-Service Gesellschaft mbH, a comprehensive two-dimensional gas chromatography – time-of-flight mass spectrometer (GCxGC-TOFMS, DANI Inc.) of ASG was installed at the HMGU (loan for project duration). In Rostock, a comprehensive two-dimensional gas chromatography – high resolution time-of-flight mass spectrometer (GCxGC-HR-TOFMS, TOFWERK AG/ZOEX Inc.) was installed. The site preparation for the installation of a Fourier Transform Ion Cyclotron Mass Spectrometer (FT-ICR, Bruker Inc.) with a 7 Tesla superconducting magnet was finalised at the University of Rostock. The FT-ICR system, also acquired via an HBFG large instrumentation grant, is due to be installed in April 2011.
Reports on Current Research
Funding by the Helmholtz Zentrum München via the "Environmental Health" program in the framework of the program-oriented POF funding mechanism of the National Helmholtz Research Centres by the BMBF (Federal Ministry of Education and Research) and/or by the University of Rostock via the Federal State of Mecklenburg-Vorpommern is involved in all projects presented here and is thus not specifically acknowledged in the individual reports.
Health Relevant Environmental Analysis – Aerosol Research (HAR)
Impact of wood combustion on ambient aerosol in Augsburg during wintertime: Comparison of on-line and off-line mass spectrometric methods

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The impact of wood combustion on aerosol composition in wintertime was studied in Augsburg in 2010. On-line analysis by means of aerosol mass spectrometry and off-line analysis of PM$_1$ and PM$_{2.5}$ filter samples were carried out. High variability of aerosol composition and diurnal courses of source contributions has been observed.

Ambient organic aerosol is of increasing interest due to its suspected effects on climate and human health. During winter season, wood combustion (WC) is one of the major organic aerosol sources in Europe. Nowadays, novel on-line measurement techniques make it possible to observe highly dynamic processes during WC emission events and their contributions to ambient aerosols. Monitoring of WC markers such as levoglucosan, potassium and retene and the application of source apportionment methods like positive matrix factorisation (PMF) provide the basis for a better understanding of the impact of WC.

A measurement campaign to examine WC aerosol was set up in Augsburg in the winter season of 2009/2010. Different on-line and off-line mass spectrometry-based analytical methods were applied at a central measurement site of the Helmholtz Zentrum München (Figure 1), located at the University of Applied Sciences close to the city centre of Augsburg (urban background). On-line analysis of the aerosol composition was carried out by a high resolution time of flight aerosol mass spectrometer (HR-TOF-AMS, Aerodyne Research Inc.). The sodium and potassium content of aerosol particles was determined size resolved by an alkali aerosol mass spectrometer (Alkali AMS) [1] operated by the University of Gothenburg.

Figure 1: Instrumentation at the permanent aerosol measurement site in Augsburg, Germany, including innovative on-line aerosol mass spectrometers.
For particle size resolved detection of polycyclic aromatic hydrocarbons (PAH) and PAH derivatives detection, a single particle mass spectrometer, i.e., a single-particle thermal-desorption resonance enhanced multiphoton ionisation mass spectrometer (TD-REMPI-SP-TOF-MS) [2] was applied. This instrument, which was previously developed at the CMA (first progress report, II. 4, p. 35-38; second progress report, III. 2, p. 35-39) was used here for the first time in a field campaign. In parallel to the on-line mass spectrometric measurements, PM$_1$ and PM$_{2.5}$ samples were collected on quartz fibre filters on an hourly basis and on a daily basis, respectively. Samples were analysed for organic composition with in-situ derivatisation thermal desorption gas chromatography time of flight mass spectrometry (IDTD-GC-TOFMS). For method details (see report number 11) special emphasis was put on the correlation of WC marker results from on-line and off-line analyses. Analysis of non-refractory compounds measured by the AMS and black carbon (BC) measured by an aethalometer aerosol resulted in an average aerosol composition of 35% organics, 28% nitrate, 16% sulphate, 10% ammonium and 11% BC (Figure 2).

Source apportionment calculations by means of PMF identified three factors (Figure 3) determining the organic aerosol measured by AMS: The first factor, assigned to “wood combustion organic aerosol (WCOA)”, provides a mass spectrum similar to spectra from primary wood combustion. The second factor, assigned to “hydrocarbon-like organic aerosol (HOA)”, represents primary emission sources, such as traffic. The third factor, assigned to “oxidised organic aerosol (OOA)”, is associated with secondary organic aerosol from photochemical processes, agglomerations and transport. The OOA fraction additionally contains parts of aged (atmospherically oxidised) primary organic aerosol including WCOA. On average, the organic aerosol consists of 23% WCOA, 34% HOA and 42% OOA.

Diurnal variations of the PMF factors (Figure 4) show that OOA is the major fraction of the total organics during a day, especially in the afternoon. HOA contribution is mainly driven by the rush hours in the morning and in the evening. WCOA is strongly increased during the evening period from 6 a.m. to 9 p.m. after the end of regular working hours and the rush hour. During this time people arrive at home and start
wood combustion for domestic heating.

Figure 4: Diurnal variation of the PMF factors OOA (green), HOA (grey) and WCOA (brown) during the whole campaign.

A correlation between the WCOA results from PMF analyses of the online AMS data and the off-line IDTD-GC-TOFMS results from the PM$_1$ filter samples on an hourly basis was performed (Figure 5a). The concentration variation of WCOA and levoglucosan, a molecular marker for wood combustion, provides a good correlation of $R^2 = 0.84$ (Figure 5b). The high time resolution (hourly) allows observing the dynamic changes in the contribution of WC emissions to the ambient aerosol with both methods. Further data analysis, including data from the other aerosol mass spectrometers and correlations with the presented data is currently under way.

Figure 5: (a) Time series of the hourly mean PMF WCOA factor (brown) and the hourly PM$_1$ GC-MS levoglucosan data (blue) during the week from February 15th to February 19th. (b) Scatter plot of hourly mean PMF WCOA factor versus PM$_1$ GC-MS levoglucosan.

Cooperation: The study was carried out in cooperation with the Paul Scherrer Institute, Villigen, Switzerland, and the University of Gothenburg, Sweden.

Evaluation of aging biomass combustion aerosols:
Comparison of on-line aerosol mass spectrometry
and off-line chemical analysis data

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The atmospheric stability of polycyclic aromatic compounds and levoglucosan in wood combustion aerosols has been studied in smog chamber experiments. Fast decay of PAH has been observed, whereas no significant changes in levoglucosan concentrations were found.

Receptor models are used to determine the origin of ambient particulate matter (PM). In recent years, the use of organic molecular markers has become a popular approach for PM source apportionment. However, major sources of uncertainty, such as the atmospheric oxidation of organic molecular markers, need to be considered. Studies with the increasingly more popular aerosol mass spectrometer (AMS) from Aerodyne Inc. may be hampered by the atmospheric formation of compounds with mass fragments in the AMS-mass spectra, overlapping with the marker signatures [1-3].

The goal of this study was to investigate the stability of organic compounds and molecular markers in a series of controlled smog chamber experiments carried out in the 27 m³ smog chamber of the Paul Scherrer Institute (PSI) in Switzerland. Emissions from a logwood burning beech wood stove were investigated. Emissions were sampled from the chimney of the stove and introduced into the humidified smog chamber (~50% relative humidity) using a heated dilution system. All experiments were performed with primary organic aerosol concentrations at atmospherically relevant levels (1-30 µg/m³). Separated experiments investigating emissions from the starting phase and the flaming phase of the combustion process were carried out.

Figure 1: Instrumentation at the smog chamber of the PSI.

Prior to switching on the lights for inducing the photochemistry, instruments sampled for approximately one hour to characterise the primary emissions and a filter sample were collected. Then, four xenon-arc lamps were switched on to replicate the sunlight and start photooxidation. Experiments were carried
out for six to eight hours. The chamber aerosol was analysed by several on-line instruments. Black carbon (used for correction of wall losses) was analysed with an Aethalometer and a Multiangle Absorption Photometer (MAAP). On-line analysis of chemical composition was carried out by two Aerodyne HR-ToF-AMS systems. Hourly filter samples for off-line chemical analysis were collected during all experiments. Chemical analysis was carried out by in situ derivatisation thermal desorption gas chromatography mass spectrometry (IDTD-GC-MS). Polar analytes are derivatised directly on the filters prior to desorption.

On the one hand, the starting concentrations of the organic PM-fraction were about ten times higher in starting phase experiments compared to flaming phase experiments (Figure 2, left). On the other hand, polycyclic aromatic hydrocarbons (PAH) had higher concentrations in flaming phase experiments. In all experiments, PM bound PAH showed a strong decrease. No significant differences in decay rates for PAH with different reactivity like benzo[a]pyrene and benzo[e]pyrene were observed (Figure 2, left). Most PM bound oxidised PAH showed a decrease in concentration as well. Polycyclic aromatic acids which could be formed from volatile PAH in the gas phase showed increasing concentrations during the first three to four hours after light on. The highest increase was found for a compound which has not yet been identified. From its mass spectrum it most probably is a naphthalic acid derivative. In most experiments, emissions showed strong and fast production of secondary organic aerosols (SOA) after the light was switched on, which could be observed in increasing AMS signal for organics (Figure 2, left). An increasing signal for the mass trace m/z 60 as well as fragment C_2H_4O_2^+ was observed during the whole time when the light was on in all experiments (Figure 2, right), an indication of ongoing formation of oxidised organics. On the other hand,
a decreasing signal for organics was observed one to two hours after the lights were switched on, indicating a loss of organic particulate matter due to volatilisation (Figure 3, left). A recently published study on the stability of levoglucosan, a molecular marker for biomass combustion, has found the atmospheric lifetime of levoglucosan in wood combustion particles to be 0.7–2.2 days when exposed to typical summertime OH radical concentrations [2]. In our investigation of the photooxidation of levoglucosan in wood combustion particles in the first six to eight hours after emission, no significant changes in levoglucosan concentrations were observed (Figure 3, right) when wall losses of particles were acknowledged. Due to increasing wall losses over time, longer experiment times than applied were avoided.

The question why we did observe fast decay of PAH but no significant decay of levoglucosan will be investigated in further experiments including further analytes. Higher light intensity and thus increased OH radical concentrations shall be applied in these experiments as well.

**Funding and Cooperation:** The study was carried out in cooperation with the Paul Scherrer Institute, Villigen, Switzerland, and with the support of the European Community within the 6th Framework Program, Section Support for Research Infrastructures – Integrated Infrastructure Initiative: EUROCHAMP.

Spatial distribution of ambient particulate matter and source contributions in Augsburg, Germany

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The spatial variability of PM$_{10}$ composition was investigated. Nine source factors including two traffic and two domestic heating-related factors were separated by the multivariate statistical “positive matrix factorisation” (PMF) approach. One factor includes cooking and shows significant contribution only in the city centre.

Ambient particulate matter (PM) has long been found to be associated with adverse health effects. In order to better understand and clarify the health impacts of different air pollution sources, there is a growing interest in the relationship between source-specific PM, spatial variability of PM and adverse health effects. The aim of the study was to identify sources of urban PM$_{10}$ in a winter season and to provide information on the temporal and spatial variability of PM composition and source contributions. The study location was Augsburg, a median sized city in southern Germany. In a previous study, five sources of organic compounds have been identified using the statistical “positive matrix factorisation” (PMF) and based on concentrations of organic compounds in PM$_{2.5}$ [1]. In the present study, daily PM$_{10}$ samples were collected from November 14$^{th}$ 2007, to March 31$^{st}$ 2008, at a central, mainly traffic influenced site (Traffic). In an intensified campaign from February 13$^{th}$ to March 12$^{th}$, parallel samples were collected at seven further sites. These sites are characterised as follows: industry (Industry), residential area with one-family dwellings (Residential), urban background (Urban background), tower in city centre with sampling site 100 m above ground (Tower), and three suburban sites (Suburb 1 to Suburb 3). Meteorological data including temperature, humidity, wind direction and speed as well as mixing layer height were determined at a central site. A total of 330 PM$_{10}$ samples were analysed for inorganic ions, elements, EC/OC and particulate organic compounds. In the intensified campaign with eight parallel sampling sites in operation, the temporal variation of PM composition was determined by the Pearson correlation coefficients ($r$) of individual PM constituents. The spatial variation was characterised by means of coefficients of divergence (COD) [2]. High correlations and medium to low COD values were found for most inorganic compounds including NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$, EC and OC, and some organic compounds like PAH or levoglucosan. Some elements, such as Ca, Mg, Na, Ti and Zn, and most organic compounds including hopanes showed medium or weak correlations and higher COD values. These compounds are most likely influenced by local sources at the respective sites. PMF [3] has been applied for source
apportionment analysis. Analyses with six to twelve factors have been carried out. The nine factor solution was the best interpretable model. These nine source factors can be sub-divided into three groups. The first group includes factors mainly consisting of secondary inorganic aerosol which exhibit very similar variation in time and concentrations at all eight sites (see Fig. 1).

Factor 1 (\(\text{NH}_4\text{NO}_3\)) is characterised by high concentrations of \(\text{NH}_4^+\), \(\text{NO}_3^-\) and 1,8-Naphthalic acid, and factor 2 ((\(\text{NH}_4\))\(_2\text{SO}_4\)), which is characterised by high concentrations of \(\text{NH}_4^+\), and \(\text{SO}_4^{2-}\) as well as medium concentrations of \(\text{NO}_3^-\), EC, OC, As, Cd, and Pb.

The second group also exhibits a very similar variation in time, but concentrations differ substantially between the differently characterised sites. The factors in this group are characterised by high concentrations of \(\text{Na}^+\), and \(\text{Cl}^-\) (factor 3. NaCl), high concentrations of Ca, Mg, Cr, Fe, Ni, Cu and Sb combined with medium concentrations of n-alkanes > \(\text{C}_{28}\text{H}_{28}\), some hopanes, EC and OC (factor 4, Soil and traffic resuspension). This factor shows highest values at the traffic site (Figure 2, top). Factor 5 is characterised by high concentrations of K, levoglucosan, 1,8-Naphthalic acid and medium concentrations of Cd, PAH, and n-alkanes (\(\text{C}_{26}\text{H}_{54} - \text{C}_{28}\text{H}_{58}\)).

![Figure 1: Variation in time of source factor 1, \(\text{NH}_4\text{NO}_3\) (top) and factor 2, (\(\text{NH}_4\))\(_2\text{SO}_4\) (bottom).](image1)

![Figure 2: Variation in time of source factor 4, soil and traffic resuspension (top) and factor 5, wood combustion (bottom).](image2)
This factor (wood combustion) showed highest values in the residential area during weekends (Figure 2, bottom). The 6th factor (Traffic 2) is characterised by high concentrations of lubricating oil originated n-alkanes (C_{22}H_{46} – C_{26}H_{54}) and hopanes. This factor showed highest values at the industrial site.

![Graph showing variation in time of source factor 9, traffic, tobacco smoke and cooking.](image)

Figure 3: Variation in time of source factor 9, traffic, tobacco smoke and cooking.

The 7th factor (wood and coal combustion) is characterised by high concentrations of PAH and oxidised PAH. Source specific markers with medium high concentrations in this factor are levoglucosan and coal combustion related hopanes. The 8th factor is characterised by high values of hopanes. It is characterised by a high spatial and temporal variation without any significant correlations between the sites. Factor 9 showed significant contribution to PM composition only at the traffic site in the city centre (Figure 3). This source factor consisted of high amounts of iso- and anteiso-alkanes, cholesterol, fatty acids including oleic and linoleic acid, and dehydroabietic acid. In addition, medium concentrations of n-alkanes (< C_{26}H_{54}), traffic related hopanes, and metals like Cr, Cu, Fe, Ni, and Sb characterise this factor as a mixture of traffic emissions combined with tobacco smoke and cooking.

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Reactive thermal extraction (RTE)-GC-MS method for the determination of levoglucosan in atmospheric aerosol samples

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A new in-situ derivatisation method based on tetramethylammonium hydroxide (TMAH) assisted thermal extraction for the determination of levoglucosan in atmospheric aerosol samples is developed. The method allows the determination of anhydro-sugars and non-polar components from aerosol samples within one measurement without any additional extraction/derivatisation step.

The monosaccharide anhydrides levoglucosan (1,6-anhydro-b-D-glucopyranose), mannosan (1,6-anhydro-b-D-mannopyranose) and galactosan (1,6-anhydro-b-D-galactopyranose) are formed exclusively during combustion of cellulose and hemicelluloses, respectively. Therefore, they are source specific molecular markers for biomass burning and should be found in residues of incomplete combustion of fuels containing cellulose or hemicelluloses\(^{[1-3]}\). Simoneit et al.\(^{[2]}\) were among the first to show that levoglucosan and related degradation products from cellulose could be used as molecular markers for the presence of emissions from biomass burning in atmospheric fine particles (PM). Thus during the last decade, the monosaccharide anhydrides, especially levoglucosan, mannosan and galactosan, have achieved increasing relevance as an important class of the water soluble organic compounds (WSOC) sub fraction of organic aerosols\(^{[3-5]}\). Although many studies reported on the monosaccharide’s content of organic aerosols, a limited diversity of applied analytical methods is observable\(^{[3,6]}\). The most frequently used methods are GC/MS methods, based on solvent extraction of the filter samples, followed by derivatisation using various silylating agents. Several studies using this analytical technique have revealed that the WSOC fraction is dominated by oxygenated multifunctional polar compounds containing hydroxyl, carbonyl and carboxyl as well as amide and amino groups\(^{[7]}\). A few studies on the performance of GC/MS analysis of non-derivative samples either reported poor chromatographic behaviour or did not include detailed methodology description. Although a recently published study that uses two dimensional GC-MS\(^{[8]}\) showed good results, derivatisation seems to be necessary and a fast, simple and reliable derivatisation method is required. However, due to the time consuming off-line derivatisation step, one of the key questions regarding routine chemical analysis of these important multifunctional polar compounds in PM samples is the development of faster analysis methods. One approach, an on-filter silylation method, is also discussed in the present progress report (see report number 11). The aim of this
A study was to develop a GC-MS based method for the quantification of levoglucosan and its isomers in air particulate matter using the in situ TMAH methylation reaction under thermal extraction conditions. In contrast to thermally assisted hydrolysis and methylation (THM), which occurs at temperatures above approx. 400 °C, thermal extraction conditions are below 350 °C. Several advantages over the current aerosol science status were expected:

1. Thermal extraction combined with an in-situ derivatisation is expected to be less labourious and time consuming since solvent extraction and derivatisation steps can be omitted.

2. The number of components to be quantified within one GC-run can be enlarged, since polar components can be determined besides non-polar components, both from one and the same sample.

3. The variety of chemical methods for the determination of anhydro-sugars will be increased. It is of great scientific value to compare results from different analytical approaches.

**Instrumentation and sample analysis:** RTE-GC-MS was performed on a Thermo Trace-DSQ single quadrupole GC-MS system (Thermo Scientific, Dreieich, Germany), equipped with a PAL thermal desorption autosampler TDAS 2000 (Chromtech GmbH, Idstein, Germany) and a cryo-trap (cold Trap 915, Thermo Scientific). Separation of the analytes occurred on a VF-XMS 0.25 mm x 0.25 μm x 30 m capillary column (Varian GmbH, Darmstadt, Germany). A schematic diagram of the RTE-GC-MS system is shown in Figure 1.

For each measurement of the target and reference compounds, a punch of a clean pre fired (500 °C, 12h) quartz fibre filter was first spiked with the compound solution, added by 1 µl 13C labelled levoglucosan internal standard solution (5 ng/µl), soaked by 30 µl of the TMAH solution and left to dry for 3 min at room temperature. After three minutes, the filter-punches were placed in the desorption tubes (glass tubes, 85 x 7 mm), sealed and stored in the auto sampler rack for analysis. For the thermal extraction step, the loaded tubes were taken, flushed for 10 s with helium at room temperature, moved to the TE oven which was then lowered into the injector. Splitless thermal extraction was achieved by heating the TE oven from 280 °C to 350 °C (ballistic heating) and kept there for 3 min. To ensure the necessary helium flow over the sample (30 ml/min), the bypass line downstream of the cryo-trap was opened during this step. The extracted analytes were trapped and

| Table 1: Method Cycle |
|---|---|---|---|
| Time / Event | GC | TDAS | Cold Trap |
| Prep Run | 40 °C | 250 °C; 350 °C; | -50 °C |
| | bypass line on | Hold 180 s | |
| Injected | 40 °C hold 1 min | Conditioning 350 °C, 30 s | -50 °C; 1 min |
| 0.1 min | PTV splitless of bypass line | | |
focused in the cold trap at -50 °C (liquid N2 cooling). Upon completion of the reaction/extraction step, the TE oven was removed from the injector, the bypass line closed and the trap heated to 340 °C (6 K/s), transferring the analytes to the analytical column. The separation of the analytes was performed by heating the GC-oven from 40 °C to 320 °C at a rate of 8 K/min. A complete cycle of the method is given in Table 1.

Results and Discussion

Calibration: Standard mixtures containing Lev, Gal and Man were prepared and diluted over a concentration range from 1 – 300 ng/µl and used for the RTE-GC-MS instrument calibration.

RTE-GC-MS application to SRM 1649a extracts: The NIST Standard Reference Material SRM 1649a (Urban Dust) was investigated for levoglucosan in several studies. To compare the results from different solvent extraction/derivatisation methods with the reactive thermal extraction method, we investigated extracts form SRM 1649a. For the extraction we placed about 5 mg of the SRM in a 5 ml flask and added HPLC-grade methanol (5ml). This mixture was treated with ultrasound for 15 min and left to settle for 24 h. The supernatant was investigated (n=9) using the same procedure as for the calibration standards. The result from this extraction (160 ± 8.6 µg/g) is similar to those mentioned above. Fig. 2 shows the results in comparison to the earlier studies.

Figure 2: Content of levoglucosan in SRM 1649a.

A novel simulation facility for workplace aerosols: Set-up, start-up and first characterisation

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The workplace exposure of employees to hazardous aerosols is a major concern in occupational health. Diesel exhausts, welding fumes and oil mist aerosols (OM) are common examples for aerosols found at an industrial workplace. OM is formed by mineral oil while used as coolant or lubricant in many industrial processes. OM consists mainly of a carrier gas (air) and semi-volatile oil components. Depending on their thermodynamic state, they can be present as droplets and as vapour. A shift in their gas-particle equilibrium can lead to errors in risk assessment. The aim of this study is to assess industrial aerosol samplers with respect to fractionated aerosols.

Gaseous and particulate components behave differently after inhalation. While the deposition of gaseous components depends predominantly on diffusion, absorption and solution at the lung surface, the particles are deposited at different locations in the respiratory tract depending on their aerodynamic diameter. Thus a particular problem in workplace aerosol measurement is posed by compounds which occur simultaneously in vapour and particle form. A typical example is oil mist aerosol. OM consists of air, gaseous oil fractions and suspended condensable components from mineral oil which can often be contaminated with other chemicals, bacteria and fungi. As OM is a non-equilibrium aerosol, long residence times are required to achieve thermodynamic equilibrium between droplets and vapour. The mass concentration in each phase mainly depends on ambient temperature and partial vapour pressure. Due to phase separation, artefacts are likely to occur in workspace aerosol samplers (filter blow-on, blow-off, evaporation, condensation, particle penetration) and may, as a consequence, lead to errors in risk assessment. Mineral oil is frequently used as a metal working fluid (MWF) in many industrial processes: as a coolant, a lubricant or a cutting fluid during the machining of metal components. It mainly consists of a mixture of straight chain aliphatic hydrocarbons from C_{12}H_{26} to C_{23}H_{48} [1, 2]. In the case of OM, the particulate phase is considered to be of greater toxicological concern than the vapour (due to particle deposition), even though the vapour is often present in much higher concentration [3].

Figure 1: Experimental set-up scheme.
The measurement of semi-volatile hydrocarbons in workplace air is rendered difficult by their readiness to condense and form particles or absorb onto surfaces. On the other hand, traditional filter sampling of the mist loses oil by evaporation. Our research objective is to evaluate the impact of sampling and analysis on the real phase distribution of dynamic gas-particle mixtures.

For this purpose, an experimental system was designed for in-situ gas-particle analysis inside of a twin set of environmental chambers (Fig. 1). They are operated independently from each other at temperatures ranging from 10°C to 40°C. The set-up allows simulation of the three phases in an aerosol life cycle: (1) generation, (2) transport/ageing and (3) deposition/analysis. The experimental system consists of:

- A Sinclair-La Mer type aerosol generator (Topas SLG 270, fig. 2) to produce aerosol particles from test substances often found in MWFs (decane to octadecane homologous series). The aerosol is generated by oil vapour deposition on separately produced salt condensation nuclei (Fig. 3).
- A dilution and mixing system consisting of a T-shape mixing head and lamination unit. It is employed for both atmospheric dilution and homogeneous aerosol-carrier gas mixing at ambient pressure. It facilitates both homogeneous mixing and particle loss (coagulation and turbulent inertial deposition) minimisation.
- A variable length flow-tube reactor is used to stabilise the aerosol and allow evaporation-condensation processes to take place. The flow tube reactor enables the study of dynamic processes, such as gas-particle partitioning immediately after the aerosol generator (< 1 s residence time) or after a pre-determined ageing volume (1 … 6 s residence time). The flow-tube reactor achieves a uniform “laminar-like” flow profile (Fig. 4) while aerosol number concentration across the tube is kept fairly constant (Fig. 5).
• A white light particle sizer (Palas WELAS) and an FTIR gas analyzer for in-situ characterization of particle phase and gas phase.

![Figure 5: Particle-size distribution in the centre (X1) and near the tube wall (X6-X9).](image)

• A 600 l Tedlar ageing bag to simulate aerosol ageing within a 10 ... 60 minutes residence time.

![Figure 6: Comparison between a freshly generated and a 10 minute aged DEHS aerosol. Not being in thermodynamic equilibrium, a part of the particle substance evaporates leading to a decrease in particle-size.](image)

The aged aerosol is re-circulated and analysed with the identical sampling equipment to assess the aerosol transformation during the ageing process (Fig. 6).

**Conclusions:** Errors in risk assessment can be studied by comparing the results obtained from the traditional filter/sampling equipment with the in-situ experimental system. In the first phase of the project an aerosol simulation facility was designed, constructed and tested for functionality. Preliminary tests have shown that the chosen equipment is well suited for the study of dynamic gas-particle mixtures. Aerosol from single components was generated with good reproducibility and stability over time. N-alkanes (C_{10}H_{22}-C_{18}H_{38}) were chosen as the first test substances, as they are found in the vast majority of MWFs. Each substance is tested to determine the suitability and stability for aerosol generation. Particle-gas phase partitioning represents a key parameter in this study. Tests are conducted to quantify the influence of dilution, flow rate, residence time, temperature and sampling on the aerosol real-phase distribution.

**Perspectives:** After the study of n-alkanes single-component behaviour and pattern, tests will be conducted for mixtures of substances that will represent a closer approach to actual MWF composition. Studies on carbonaceous agglomerates with semi-volatile organic compounds condensed on their surface can also be performed.

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Errors in BET specific surface area measurements for particulate matter samples near the detection limit of an analyzer

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To find a health-related metric for the impact of ambient particulate matter (PM), toxicologists and epidemiologists correlate data from physicochemical particle characterisation methods with toxicological or adverse-health-effect data. The specific surface area (surface area per mass of substance) has been shown to be an interesting parameter in this context. However, it is challenging to produce correct BET surface area results from aerosol particle samples, since the amount of collectable PM mass is usually close to the resolution limit of the BET-surface analyzer.

Epidemiological studies point out that airborne ambient particulate matter is relevant for human health. The desired metric properties for the correlation of physical metrics with health effects are: implicitness and cost efficiency, good reliability of the measurement method, achievability of a reasonable time resolution and a (linear) correlation with the biological response. In the past the particle mass concentration was considered to be this metric. However, it only works well for soluble or bulk particles and fails for agglomerates, aggregates and porous materials.

A parameter which may adequately reflect biological response is the (geometric) surface area of a particle. Via the surface area the particle and its chemical compounds get into contact with the environment. After inhalation and deposition, possibly followed by endocytotic uptake, the particle surface area contacts the epithelial lining fluid of the lung surface or the cytoplasmic membrane, respectively. A number of authors thus suggest that the BET specific surface area (SSA) is a very adequate metric for PM induced health effects [1].

Figure 1: Scheme of a BET analyzer for the static-volumetric method. In a first step, pressurised nitrogen gas is filled into the reference volume \( V_A \). Then the gas is expanded into the sample cell and condenses on the particle sample at liquid nitrogen temperature (77 K). The amount of condensed gas can be calculated from the mass balance equation of the analyzer. From the number of gas molecules condensed in a monolayer on the particle, the surface area of the particles is then determined using the BET equation and the projected surface area of one molecule (0.16 nm²).
The definition of the surface area of a particle is challenging. Depending on the method used, numerous diverging results can be obtained. The BET method, developed by Brunauer, Emmet and Teller [2] uses the adsorption of a monolayer of gas molecules onto the particle surface as a surface measure. This method is stable; it is widely used in material science represents the basic process of molecular contact with the particle’s substance via its surface area and it correlates well with biological response.

![Figure 2: Left: Adsorption and desorption isotherm of electric spark generated carbon particles. Right: Scheme of condensed gas molecules in an open pore of a material. Green: monolayer of gas molecules representing the BET specific surface area measured from the BET range of the isotherm.](image)

Depending on the size of the adsorbed gaseous probing molecules, the BET method (Fig. 1) yields a kind of geometric surface area which is independent of shape and porosity of aggregated particles. However, it neglects pores smaller than the probe molecule size as well as (blocked) inner cavities (Fig. 2).

In spite of these positive properties, only a few authors have measured the BET specific surface area of ambient and emission particulates. This is due to the relatively large amount of PM mass (up to 1000 mg) necessary to achieve reliable results.

As particle sampling is time consuming and expensive (typical PM concentrations in Germany are several 10 µg per cubic meter of air), we developed a method to estimate the minimum surface area threshold for particle samples. The method is contingent on the standard deviation of the BET analyzer and on a test for the accuracy of the analyzer’s calibration. A theoretical curve is derived from the mass balance equation (Fig. 3) which shows that the bias of the measured relative surface area (SSA_{m,b}) depends on the surface area of the sample A_s and a deviation from calibration, expressed in terms of an “erratic surface area” A_{err}. SSA_{m,b} is the measured SSA normalized by the true SSA_s. It is independent of the substance and is 1 for unbiased measurement but deviates up to a factor of 2 and more for decreasing sample surface / sample mass (see theoretical lines in Fig. 3).

The calibration error A_{err} mainly depends on room and instrument temperature and on the accuracy of the submersion of the sample in the coolant. It is the sum of all (systemic) errors and also includes the instrument noise. If A_{err} is made up by noise only, the measured data points will scatter between both the positive and negative theoretical lines in Fig. 3. If the measured data points follow one of these lines, a systemic error must be supposed in the instrument.

![Figure 3: Theoretical curves for positive and negative erratic surface area A_{err} in the analyzer. Measured data are for activated charcoal samples (AC).](image)
A threshold for the instrument can be defined at the place where both theoretical curves leave the standard deviation (SD) band. For \(|A_{err} / A_s|\) on the left hand side of this place, SSA_{m,b} will remain close to 1 within the instrument’s SD-band. For \(|A_{err} / A_s|\) to the right of this place, the bias of SSA_{m,b} will be remarkably larger than the SD of the instrument.

In our case, \(A_{err}\) was determined to be 0.42 m² from a number of 47 consecutive samples. For a SD of ± 6 \%, a threshold \(A_s = 7\) m² is calculated from Fig. 3. This means that the surface area of a sample measured in the sorptometer must not be smaller than 7 m² to achieve results with a SD of ± 6 %.

Depending on the SSA of a substance, these 7 m² correspond to a different mass. For instance, for road dust from a tunnel with an SSA of 5 m²/g, a mass of more than 1629 mg is necessary, whereas for Diesel emission particles (SRM 2975) with a SSA of 95 m²/g, 48 mg are sufficient.

**Funding and Cooperation:** The project is a cooperation of the Joint Mass Spectrometry Centre and the Comprehensive Pneumology Center, Institute for Lung Biology and Disease, both located at Helmholtz Zentrum München.

Redox activity of ambient particles:
Establishment of an ascorbate-based test system
using luminol-dependent chemiluminescence
analysis to determine particle-associated free radicals

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A method was developed to quantify the oxidative potential of ambient particles sampled on quartz fiber filters. Filter strips were incubated with an aqueous ascorbate standard (0.1 mM) solution used as radical scavenger followed by analysis of residual ascorbate by the photo chemiluminescence method (PHOTO-CHEM, Analytic Jena). The kinetic of ascorbate consumption showed a logarithmic trend. Pre-treatment of filter strips with the antioxidants iodide or 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) decreased the ascorbate-directed reaction. A marked variability of response to ascorbate was observed with 24 h filter samples collected on consecutive days within one week.

There is substantial evidence from epidemiological studies that airborne particulate matter is involved in adverse health effects, including cough and wheezing, and is strongly associated with hospital admissions and emergency-room visits for treatment of respiratory and cardiovascular diseases [1, 2]. Among the various properties of air-borne particles, their oxidative potential seems to elicit a significant impact on tissue homeostasis on a molecular and cellular level thus contributing to irreversible damages to target organs [3, 4]. Therefore, analysis of the oxidative potential of particulate air pollution has a high priority.

Ascorbic acid is one of the major antioxidants in most tissues like liver, lung, brain and kidney (2 -6 µmol/g) [5, see table 3]. Since ascorbate acts as a highly efficient scavenger for numerous reactive oxygen species, this compound seems to be suitable to establish a test procedure for quantifying particle-related oxidants in ambient particles. This concept was first described by Stoeger et al. [6] to determine the oxidative capacity of artificial carbonaceous particles in aqueous suspension. The objective of this project is to modify and optimize an existing test procedure to allow quantification of radicals in ambient particulate matter sampled on quartz filters.

Method
This procedure consists of 2 steps:
1. Incubation of filter strips: Filter strips (2.1 x 27 mm) were stamped out from 150 mm Digital filter discs. All incubations were performed with 4 bisected stripes submerged in 0.75 ml of a 0.1 mM ascorbate solution (reagent 4 of the PHOTOCHEM
ACW test kit from Analytic Jena AG) in 1.5 ml tubes for different times at 25°C with gentle mixing using an Eppendorf-Thermomixer. Thereafter, the reaction mixtures were centrifuged for 5 min at 13 000 g.

2. Measurement of remaining ascorbate: 25 µl of supernatants were assayed for ascorbate based on luminol-dependent chemiluminescence using a PHOTOCHEM device from Analytic Jena AG. The amount of ascorbate consumed during incubation of filter strips was calculated in nmol/25 µl supernatant.

In this study we investigated 24 h filters taken in 2008 between March 19th and March 25th in Augsburg on the campus of the University of Applied Sciences (campus location Rotes Tor, Augsburg, Germany).

Results

A) Time dependency of reaction with ascorbate

Figure 1: Kinetic study with test filter from March 19th, 2008. Four strips were incubated in 0.75 ml ascorbate standard solution (0.1 mM) at 25°C for 30 min, 2 h, 4 h and 24 h.

Incubation of filter strips with 0.1 mM ascorbate revealed a logarithmic trace of reaction. The initially very fast response (within 30 min) covered 50% of the overall reaction. Control incubations with strips from blanc filter elicited no response to ascorbate (data not shown).

B) Pretreatment of filter strips with antioxidants

Figure 2: Four bisected strips from a test filter (March 21st, 2008) were pretreated with KI or Trolox under different conditions followed by 3 x washing. Remaining redox activity on the strips was determined in supernatants from 24 h incubations with 0.1 mM ascorbate solution (standard test conditions).

We postulate that the ascorbate-consuming activity on filter strips is based on oxidation of ascorbate to dehydroascorbate. Pretreatment of strips with KI or Trolox, which both have strong antioxidant properties, lowered the ascorbate directed response. This finding suggests a redox-dependent mechanism which is responsible for ascorbate consumption by particulate matter on the strips (Fig. 2).

C) Variability of response by samples obtained from one location

We analysed strips from 24 h filters collected on consecutive days over one week. There was a high variability of ascorbate-directed response, suggesting substantial changes in daily redox activity of particulate matter from the same site. So far, no data from climate reports were found to correlate with these results.
Perspectives

The Asc-consumption is only weakly correlated with mass concentration (PM2.5, Figure 3b, \( R = 0.66 \)). A comparable study [7], e.g., suggests that the concentration of some organic compounds such as polycyclic aromatic hydrocarbons (PAH) and their oxidised derivatives (O-PAH) in the PM samples correlates with the ROS formation potential. In combination with data from anorganic and organic constituents, thus the method described here might further contribute (1) to better understand mechanisms by which oxygen-derived free radicals arise in ambient particulate matter and (2) to substantiate statements on their risk evaluation.

Funding and Cooperation: The project is accomplished by the Joint Mass Spectrometry Centre together with the Comprehensive Pneumology Center, Institute of Lung Biology and Disease, both at Helmholtz Zentrum München.

Organic components in ambient particulate matter (PM2.5) collected at an urban site before and after its conversion to a Low Emission Zone

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During two sampling periods, particulate matter (PM$_{2.5}$) was collected regularly at an urban site in the Munich inner city area. The first sampling period was in 2006/2007. In 2008 the Low Emission Zone (LEZ) was established. The sampling site is located within LEZ. A second measurement campaign was performed in 2009/2010. Organic components on PM$_{2.5}$ were analysed applying different chromatographic methods. Composition of the organic fraction is mainly dominated by traffic and residential heating.

In 2006 a high volume sampler (PM$_{2.5}$) was implemented at the monitoring station "Lothstraße". This site is part of the Air Hygienic Monitoring System of Bavaria consisting of more than 50 monitoring stations in Munich and the whole of Bavaria. It is conducted by the Bavarian State Office for Environment (BLfU). Lothstraße is situated in the inner city of Munich near to a main traffic road. It is a traffic-influenced station with approx. 41,000 passing vehicles per day. The local area is mainly composed of habitation, trade and commerce$^1$. Important parameters like NO$_x$, PM$_{10}$, BTX, O$_3$, CO, SO$_2$ and meteorology are collected and evaluated by the BLfU, but higher molecular organic compounds are not determined.

Recent studies underline the importance of the organic fraction of particulate matter for human health. Participation at the sampling site "Lothstraße" allows the characterisation of representative, health relevant organic substances by investigating concentration courses during seasons, evaluating influencing parameters like meteorology, sources, source variabilities and long range transports in a representative urban area. Regular sampling (every 3$^{rd}$ day for 24 hours) was performed in 2006/7 for 12 months, in 2009/10 for 6 months and started again in 2011. Particle-laden quartz-fibre filters were extracted and used for the determination of polycyclic aromatic hydrocarbons (PAH), nitro-PAH, alkyl-PAH, PAH-diones and – since 2009 – of azaarenes. The chromatographic methods applied were developed, validated and established in previous years$^{2-4}$. They are continuously expanded, meeting actual and future analytical needs.

The samples of the first measuring period (2006/7) were analysed, the results were partly evaluated and interpreted. The concentrations of the analytes are season dependant. Significant higher values and "extreme" days always appear in winter and autumn.

To gain more detailed insight into the contribution of potentially different
sources, two easily available multivariate source apportionment models (Environmental Protection Agency, USA), Unmix and positive matrix factorisation (PMF) were applied. PMF leads to reasonable results assessing four sources, which can be described as follows: Factor 1 exhibits a high load of coronene and 1-nitropyrene as well as of 3- and 4-ring PAH. 1-nitropyrene almost exclusively originates from direct diesel emissions. The substance profile and the observation that the factor contribution does not show a clear seasonal trend support the assumption that this source is mainly formed by traffic diesel emissions. In the opposite, factor 2 displays a clear seasonal trend and due to its composition (mainly PAH, small part of PAH-diones) it is regarded as emissions from residential heating. The identification of the remaining two sources is more difficult, because composition and seasonal trends are ambiguous. Factor 3 exhibits high loadings of PAH-diones, moderate loadings of 2-nitrofluoranthene and 2-nitropyrene with a clear seasonal trend. PAH-diones are emitted during combustion processes and generated by atmospheric photo oxidation processes. The two nitro-PAH are not emitted directly but formed via atmospheric gas-phase reactions of PAH. Probably this source is a kind of mixture from combustion/heating emissions which have partly undergone transformation processes. The seasonal trend for the fourth factor is not very distinct, and the profile (4 – 6 ring PAH, nitro-PAH) suggests a traffic (gasoline) source influenced by photooxidation processes and long-range transports. Unmix operations also led to a four factor solution exhibiting similar profiles. Advanced operations of the multivariate source apportionment models will help to improve the resolution of potential sources.

Within the scope of the “Air Monitoring Action plan” which was passed by the Bavarian State Ministry of Environment and Health in 2004, the consecutive establishment of a Low Emission Zone (LEZ) is one major measure to achieve a permanent reduction of pollution in the Munich city area. One important tool to control the success of the LEZ is the Air Hygienic Monitoring System of Bavaria. A main focus of the LEZ is the reduction of PM$_{10}$ to minimize its health effects on the inhabitants.

According to the view that the organic fraction of the particles may play a significant role in the observed health impairments, the analysis of various organic compounds is a relevant contribution to the constructive accompaniment of the establishment of the LEZ. If this measure leads to changes in air pollution, they must be reflected in the composition of the organic fraction and their main sources over the time course.
Figure 3: Box plots for the sum of hopane $31\alpha\beta R$ and $31\alpha\beta S$ ($\Sigma_{31\alpha\beta R+31\alpha\beta S}$), the sum of PAH ($\Sigma$ PAH), the sum of oxidised PAH ($\Sigma$ O-PAH) and 1-nitropyrene concentrations in 2006/7 and 2009/10.

To receive preliminary information on the efficiency of the LEZ to reduce traffic-related PM-adsorbed chemicals, samples collected in winter 2006/7 and winter 2009/10 were also analysed for alkanes, oxidised PAH (O-PAH) and hopanes. Some hopanes are used as traffic markers, therefore their concentrations are of special interest with regard to the impact of the LEZ on the reduction of traffic-related PM emission. To find out if there are significant differences in the concentration levels of PAH and selected hopanes, the results of the two sampling periods were compared and statistically approved.

Note that in this context the substance classes PAH and O-PAH are suspected to be involved in the induction of PM-related health effects.

The box plots depicted in Figure 3 visualize that there are no significant differences in the sum of PAH and 1-nitropyrene concentrations in 2006/7 and 2009/10. In contrast, differences for hopanes ($31\alpha\beta S + 31\alpha\beta R$) and the sum of O-PAH are obvious with higher concentration levels in 2009/10, showing a non-expected behaviour with respect to the LEZ effect. These results are confirmed by a t-test, which revealed statistically significant differences among the respective mean values.

However, these initial results need to be accompanied by future studies based on additional analysis results, taking into account further important external factors, such as meteorology and background concentrations, in addition to other PM sources, such as wood combustion.

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Polycyclic Aromatic Hydrocarbons (PAH) in particulate matter from outdoor and indoor air of elementary schools in Munich, Germany

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Within the PAMINA (Particulate Matter in Indoor and Ambient Environments) study the concentrations, elemental composition and cytotoxicity of PM collected in classrooms of six schools in Munich and the respective outdoor air were investigated to assess differences in the toxicological impact between classroom particles and outdoor particles. To obtain additional information about the organic content of the particles and its relevance to toxicity, PAH concentrations were determined in the cooperation group.

Exposure to outdoor and airborne particulate matter (PM) is associated with a broad range of health impairments, like chronic inflammatory processes, respiratory and cardiovascular diseases. To protect citizens, regulatory standards for PM with diameters of 10 µm or less (PM₁₀) in the outdoor air were passed. Although outdoor air is suspected to be particularly important for health effects, it must be considered that most individuals spend only approx. 15 % of their time outdoors[1]. Therefore, indoor air is a major contributor to personal PM exposure. Children represent a peculiar susceptible group because they are especially vulnerable to the effects of air pollution due to their developing respiratory and immune systems. Pupils spend an essential part of their time in schools where they are often exposed to high indoor PM levels[2]. Moreover, children receive higher doses than adults due to increased activities and differences in breathing rates. Outdoor particles originate mainly from traffic, residential heating, industrial processes and soil. In contrast, indoor PM in schools is a complex mixture of indoor-generated and transferred outdoor particles. To obtain an improved insight into children’s health risks as they are related to exposure to indoor PM on the one hand, and to develop protection strategies on the other hand, relevant studies are being performed. Within the PAMINA (Particulate Matter in Indoor and Ambient Environments) study, elemental composition and cytotoxicity of PM₁₀ collected in classrooms of six elementary schools in Munich and the respective outdoor air were investigated to find out if differences of the toxicological impact between classroom and outdoor particles exist[3,4]. The original study was amended determining PAH-concentrations of the particles in our cooperation group.

After collection (four weeks at school days for 5.5 hrs., respectively) the particle samples were prepared and systematically characterised applying various methods like scanning electron microscopy with X-ray spectroscopy, endotoxin determination, cat
allergen determination\textsuperscript{[3]} and PAH-analysis. The latter was performed with a liquid chromatographic separation and fluorescence detection after accelerated solvent extraction of the lyophilised particle samples\textsuperscript{[5]}. 14 PAH were detected, but due to losses during the freeze-drying process, only 10 compounds were quantified. In-vitro-test systems were used to investigate cytotoxicity and to conduct a genome wide analysis\textsuperscript{[3]}. PM\textsubscript{10} concentrations in the classrooms were on average 5.5 fold higher than in the outdoor air. In general outdoor air was characterised by calcium sulphate, indoor air by silicate and organic particles. In accordance to this, the PAH content of outdoor particles is mostly higher than that of indoor particles, as depicted in Figure 1.

This concentration gradient supports the assumption that indoor particles are a mixture of infiltrated outdoor and indoor generated PM. The sampling season is reflected by the respective outdoor and – less distinctive – by the indoor PAH concentrations: schools “ES” and “BE” were sampled in July/June, “IT” in October, “TP” in March, “PO” and “ER” in December/February. As expected, PM collected in the winter months exhibits the highest PAH concentrations. This concentration increase is commonly observed in urban heating periods (winter), which also represent the season with the lowest air-exchange. In addition to the seasons the geographical location of the school is a further determinant for PAH-concentrations. Elementary school “ER” is in the inner city of Munich, near to two main roads. The traffic-dominated, highly populated urban location in combination with the sampling month of February explains that highest PAH-concentrations were found here. “PO” is located at a semi-urban site. Here the PAH-concentrations are lower, although sampling time was December. For the remaining schools the PAH-concentrations observed are mainly determined by season. They are all in the north of Munich outside the inner city leading probably to similar ambient PAH-profiles. Lowest values were found in June and July.

In Figure 2 it can be seen that the patterns of single PAH in outdoor and indoor PM for the respective schools are nearly identical, meaning that the particle transport into the classrooms not only leads to a mixing but also to a dilution effect concerning PM adsorbed substances.

As mentioned above, toxicity of the collected particles was investigated with different test systems. Cytotoxic effects were only found after incubation with indoor PM\textsubscript{10}. A genome wide analysis revealed that exposure to PM\textsubscript{10} induces an expression of in-
flammatory genes and enzymes of the metabolism of xenobiotics. Whereas inflammatory genes were much stronger induced by classroom particles, metabolism of xenobiotics was significantly more induced by outdoor PM$_{10}$. It was found that especially the induction of CYP1A1 - a member of the superfamily of cytochromes P450 – is significantly correlated with the PAH-content of PM$_{10}$ samples ($r^2 = 0.75$)\(^{[3]}\). Cytochromes P450 own a high relevance concerning metabolism of xenobiotics because their enzymatic oxidation can lead to more reactive metabolites with a higher toxic potential compared to the native compounds. This is also true for PAH. Their cytochrome P450 induced transformation can produce carcinogenic metabolites\(^{[6]}\). Altogether PM$_{10}$ of elementary school classrooms had different characteristics, regarding composition and in vitro health effects, leading to different risks related to the exposure to the particles.

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Hyphenation of a carbon analyzer to photo-ionisation mass spectrometry to unravel the organic pattern of particulate matter

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A thermal/optical carbon analyzer for the determination of overall content of organic and elemental carbon of particulate matter is coupled to resonance-enhanced multi photon time-of-flight mass spectrometry. In doing this the molecular pattern of aromatic compounds of carbonaceous aerosol fractions can be detected.

The identification of the carbonaceous fractions of urban aerosol particles on a molecular level still provides an analytical challenge, yet knowledge of its composition may prove crucial in terms of understanding the adverse health effects of particulate matter. The determination of sum parameters such as the overall content of organic and elemental carbon (OC and EC) after thermal desorption of organic species and their oxidation to carbon dioxide provides information on an integral scale, however, nothing is revealed about the nature of the organic components that constitute the different thermal fractions. In the framework of a German Science Foundation (DFG) funded project, hyphenation between a thermal/optical carbon analyzer and photo-ionisation mass spectrometry has been developed, by which the desorbed organic compounds can be investigated prior to their oxidation to CO2. In a pre-study using a thermal desorption unit, it was shown that the concept is promising and may reveal interesting results, e.g., for oligomeric organic fractions in the secondary aerosol (SOA) [1]. Figure 1 shows a scheme as well as a photo of the setup of the EC/OC-Analyzer-photo ionisation mass spectrometer coupling. Samples including urban aerosol on quartz filters are placed inside an oven and heated up according to subsequently increasing temperature steps (e.g., 120 °C, 240 °C, 450 °C, and 550 °C for organic carbon fractions, referred to as OC1, OC2, OC3, and OC4, respectively) [2]. Carrier gas is helium, which is changed after OC4 to a mixture of 98 % He and 2 % oxygen for the determination of three EC fractions. The evolved gases are oxidised to CO2, which is catalytically reduced to methane in a second step. The formed amount of methane is then measured by a flame ionisation detector. An He/Ne laser is employed to determine the reflectivity and transmission to account for the part of OC that is transformed to char initially. By doing this, the distinction between OC and EC fractions is improved. Prior to the oxidation unit, a small amount of the desorbed gaseous species is side-lined to the ion source of the mass spectrometer via a heated deacti-
vated quartz capillary. Thus the EC/OC measurement can proceed undisturbed. Due to the nature of the applied soft photo ionisation, the molecular ion pattern of each carbonaceous fraction is obtained. Figure 3 shows a two-dimensional depiction of the whole EC/OC analysis of an urban aerosol sample representing roughly 1 m³ of air,

where resonance-enhanced multi photon ionisation time-of-flight mass spectrometry (REMPI-TOFMS) has been employed. This ionisation method is selective for (poly)aromatic compounds, at the same time providing a high sensitivity, thus reflecting the aromatic pattern of each carbonaceous fraction and its changes along the course of the analysis. The accompanying mass spectra of OC2 and OC3, respectively, depict the detected molecular ions of these fractions (Figure 2). The overall amount of organic carbon in OC1 is relatively low, and accordingly almost no aromatic compounds are observed. This changes when OC2 and OC3 emerge, revealing a large variety of aromatic species. Many of those can be assigned to homologue series of phenanthrene, pyrene, and chrysene/benz[a]anthracene. However, small phenolic compounds can also be seen. The prominent signal at 234 m/z is especially remarkable, which may be assigned to retene, a well-known marker for wood combustion, hinting at a considerable contribution of such emissions to the organic content of urban particulate matter. With OC3 the pattern shifts strikingly to smaller compounds. This can be explained by the onset of pyrolytic decomposition of larger, yet not desorbed organic molecules, which at the elevated temperatures of OC3 are thermally decomposed to smaller units. With OC4, despite exhibiting a relatively high organic carbon content comparable to OC2, the number of aromatic compounds decreases significantly. This gives rise to the conclusion that the organic constituents in this fraction and/or their thermal decomposition products are predominantly of non-aromatic nature. Elemental carbon fractions no longer contain aromatic compounds.
In connection with unravelling the various sources from which organic material on urban particulate matter originates, it could be of interest to investigate particle emissions stemming from these sources in the same manner as urban samples. Figure 4 shows the REMPI-TOFMS measurement of particles from biodiesel exhaust. In contrast to urban aerosol, the majority of the organic as well as the aromatic content already appears with the first organic fraction.

In the future, measurements with single photon ionisation (SPI) will be carried out to reveal the pattern of aliphatic substances, in addition to aromatic compounds. This may help to better understand the structure of oligomeric organic fractions in the secondary aerosol (SOA).

**Funding and Cooperation:** The project was performed with support of the German Science Foundation (DFG) support code ZI 764/3-1.

**Figure 2:** REMPI-TOFMS spectra of OC2 (left) and OC3 (right) of an urban aerosol sample.

**Figure 3:** Two-dimensional depiction of the EC/OC-Analysis showing the evolvement of the aromatic pattern of particles from urban aerosol (left) and biodiesel exhaust (right). Respective OC values are given.

**Figure 4:** REMPI-TOFMS spectra of OC2 (left) and OC3 (right) of a biodiesel emission sample.
In-Situ Derivatisation Thermal Desorption GC-TOFMS for direct analysis of particle-bound non-polar and polar organic species

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An in-situ derivatisation thermal desorption method followed by gas chromatography and time-of-flight mass spectrometry (IDTD-GC-TOFMS) was developed for the determination of polar organic compounds in PM samples on filters.

Polar organic substances play a major role in the characterisation of diverse atmospheric processes, for instance during formation of secondary aerosols. Once organic substances are released gaseous or particle-bound to the atmosphere they are exposed to UV radiation, to radicals and oxidants. Depending on further criteria on particles (e.g., pH value, possible reaction agents) reaction mechanisms and reaction velocities are affected. During aerosol ageing processes, particles grow and are getting more polar. Thus analytical methods for detection of formed polar organic compounds are of special scientific interest.

IDTD: An online silylation technique
An in-situ derivatisation thermal desorption method followed by gas chromatography and time-of-flight mass spectrometry (IDTD-GC-TOF MS) was developed for determination of polar organic compounds. This advancement of thermal desorption was introduced for anhydrous sugars, alcohols and phenols; fatty acids and resin acids were accessible by the derivatisation procedure. Derivatisation is based on silylation with N-Methyl-N-trimethyl-silyltri-fluoroacetamide (MSTFA) during the step of thermal desorption. The high temperature of 300 °C during desorption process is utilised for the in-situ derivatisation on the collection substrate (quartz fibre filters) and accelerates reaction rate. Thereby, analysis time is as short as without derivatisation. The first step is to dampen the filter surface with derivatisation reagent before insertion of the sample into the thermal desorption unit. To ensure ongoing derivatisation during thermal desorption, carrier gas is saturated with MSTFA until the desorption procedure is finished.

Validation of IDTD-GC-TOF MS
All validation experiments are described in detail in a technical note [1]. Besides comparisons with solvent extraction methods for preparing samples from precipitation on quartz fibre filters, a brief summary of analyses of Standard Reference Material (SRM) 1649a (Urban Dust) from the National Institute of Standards and Technology (NIST) is given here. The analysed values of certified non-polar compounds are comparable to...
the intra-day course of levoglucosan. The influence of wood combustion activities was clearly visible. The heating activities were focused on the evening hours. High concentrations of levoglucosan with a maximum at about midnight were observed. Maxima of levoglucosan prevailed for several hours. The highest day average value (640 ng m\(^{-3}\)) was found on the 18\(^{th}\) of February within the days of hourly sampling. The highest maximum values were observed shortly before and after midnight between the 17\(^{th}\) and 18\(^{th}\) of February (1400 ng m\(^{-3}\)).

Emissions of PM and organics were lowered significantly. The third reload is characterised by a smouldering phase with high emissions of PM and organics. Levoglucosan, syringic acid (specific hardwood tracer originated from lignin degradation) and the oxidised PAH 9H-fluoren-9-one, in particular, were strongly influenced by inflaming and a smouldering phase during the combustion of the third reload, whereas benz[a]pyrene was not affected in the same magnitude.

On the emission side, fig. 2 shows experiments with a log wood stove. It demonstrates the characterisation of a heating event typical for winter evening leisure time. The heating event is separated into four periods. The inflaming process showed high emissions of organics. Afterwards, two reloads of logs were sampled.

Conclusions

A novel fast in-situ derivatisation thermal desorption technique was developed for GC-MS for combined analysis of both particle-bound non-polar and polar organic compounds. The suitability of the method for a broad scope of applications was demonstrated.

On-line monitoring of polycyclic aromatic hydrocarbons in heavy duty diesel truck exhaust

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Polycyclic aromatic hydrocarbons (PAH) in heavy duty diesel truck exhaust were monitored in real time by resonance-enhanced multi photon time-of-flight mass spectrometry (REMPI-TOFMS) when different driving cycles were applied on a test facility in Ispra, Italy. Distinct transient emission behaviour of different aromatic species, such as pyrene and naphthalene, could be observed, hinting at varying formation processes.

Ground transportation by heavy duty diesel trucks contributes a substantial amount to the anthropogenic emission of nitric oxides, volatile organic compounds (VOC), particulate matter and carbon dioxide. The acquisition of analytical data of such emissions, especially when attempted on a real time basis, is still challenging. Vehicle exhaust is a complex and dynamic mixture consisting of a large amount of gaseous chemical compounds and particulate material, with many species present in both phases. At the Institute for Environment and Sustainability of the European Commission Joint Research Institute (EC-JRC) in Ispra, Italy, a new vehicle emission laboratory (VELA) has recently been established. The intention of VELA is to provide measurement facilities for on-line investigation of exhaust emissions of vehicles under simulated driving conditions. In the framework of a joint project, several sophisticated on-line techniques were applied together, comprising, among others, a Fourier-transform infrared spectrometer (FT-IR), a high-resolution time-of-flight aerosol mass spectrometer and a condensation particle counter. In addition, a resonance-enhanced multiphoton ionisation time-of-flight mass spectrometer (REMPI-TOFMS) of the JMSC was employed to monitor polycyclic aromatic hydrocarbons (PAH). The present report concentrates on presenting selected results from REMPI-TOFMS on truck exhaust. Additional results (e.g., FT-IR, particles, passenger cars) can be found elsewhere [1]. A medium-sized truck complying with EURO-III exhaust regulation (i.e., no exhaust gas after treatment was installed) operating with EN 590 diesel fuel has been investigated. A steady-state test was performed, in which velocity was changed from idle to 40 km/h, then 60 and 90 km/h, and back to idle, each state kept for 300 s. A photograph of the principal setup is shown in Figure 1, depicting only the REMPI-TOFMS part of the analytical equipment. The heated transfer capillary of the REMPI-TOFMS was attached orthogonally to the sample line of the FT-IR. Ionisation of PAH in the exhaust gas was carried out with pulsed laser beams at a wavelength of 266 nm. The laser operated at 20 Hz repetition frequency, and 20 consecutive mass spectra have been averaged yielding a time resolution of 1 Hz.
The instrument was calibrated by measuring 1 ppm gas standards of toluene, m-xylene, and trimethylbenzene. Naphthalene and phenanthrene were quantified by determining their ionisation cross sections relative to toluene. Figure 2 shows an averaged REMPI-TOFMS spectrum of the truck’s exhaust gas recorded at a velocity of 90 km/h. Obtained signals were assigned to benzene, phenol, styrene, indane, naphthalene, phenanthrene, pyrene and their respective alkylated homologues. The unique strength of REMPI-TOFMS is, however, the time-resolved monitoring of PAH concentrations. Since the exhaust volume flow was also constantly monitored at VELA, measured concentration values could be converted to mass flows. Figure 3 shows the respective trends of phenanthrene and pyrene for the steady state cycle. The velocity changes are depicted as gray steps in the figure.

At idle motor conditions, PAH concentrations are negligible. When the velocity is raised to 40 km/h, a sharp increase in phenanthrene and pyrene content is clearly visible. Afterwards, during the 40 km/h run, the concentration levels remain on a nearly constant level above zero. The velocity steps to 60 km/h and 90 km/h, respectively, again become noticeable via sharp emission peaks of the PAH. The emission behaviour during the 60 km/h phase resembles that at 40 km/h. At a velocity of 90 km/h, however, the situation changes drastically. In short time intervals, a series of emission peaks is observed for both PAH, indicating that combustion conditions at this velocity do not remain as stable as during the lower velocities. When the motor returns to idle conditions, PAH content in exhaust gas decreases sharply, returning again to almost negligible values.
If the behaviour of phenanthrene and pyrene is compared to that of smaller aromatic compounds, i.e., naphthalene and toluene (Figure 4), distinct differences are exhibited. For instance, the emission trend of naphthalene remains nearly the same for all velocities. A sharp increase at the point of velocity switching is followed by roughly steady exhaust content. Toluene shows strong signals only during the acceleration phases, with emissions comparably low while the velocities are kept constant.

The different emission behaviour, exhibited even by compounds which are structurally related, gives a hint on the complexity of the reaction mechanisms during combustion. Two main mechanisms are known for the formation of aromatic species in diesel exhaust. On the one hand, they are already present in the fuel and survive the combustion process due to partially incomplete combustion, which is referred to as the survival pathway. Secondly, aromatic compounds may be formed via pyrolysis from other organic constituents of the exhaust or the lubricating oil. Naphthalene is formed predominantly by pyrolysis, while larger PAH tend to originate mainly from the survival pathway. Howsoever, the interaction between gas phase formation and particulate matter must also be taken into account. Depending on the respective gas/particle partition ratio, a substantial amount of PAH could be emitted adsorbed to soot particles.

**Funding and Cooperation:** The project was accomplished in cooperation with the Institute for Environmental Health and Sustainability (IES) of the Joint Research Centre of the European commission (JRC) in Ispra, Italy.

Comprehensive Molecular Profiling (CMP)
Investigation of the alteration in the molecular pattern of heating oil – biodiesel blends induced by storage

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In the framework of the planned partial substitution of fossil fuel by renewable carbon sources (i.e. bio fuel) investigations targeting the practicability and changes in emission profiles need to be studied. The stability of fatty acid methyl ester (FAME) / Petroleum blends in this context is of great technical and commercial interest. The composition of FAME is prone to oxidation and the degradation products show adverse effects like increased acidity and higher viscosity. Samples from an ongoing long term study were analysed by comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry to uncover changes in the molecular patterns of the blends.

Biodiesel and its blends have become more and more common substitutes of purely crude oil based fuels. Due to legislative regulations mineral oil derived diesel/biodiesel blends or pure biodiesel are commercially available and their usage as car fuel (e.g. B5, 5% Biodiesel) or heating oil (e.g. EL A Bio 20, 20% Biodiesel) in particular are of great economical and technical relevance. While refined mineral petroleum is mainly composed of hydrocarbons, biodiesel is a composition of different fatty acid methyl (FAME) or fatty acid ethyl esters. The numbers of double bounds, which are prone to chemical reactions, such as oxidation, are important for the stability of the FAME. They are usually in allylic configuration and the relative rate of oxidation increases with the number of double bounds (oleic : linoleic : linolenic = 1 : 12 : 25). The typical degradation route is the oxidation of the fatty acid group and results in lower weighted products like aldehydes and acids, which cause an increase in acidity, and higher weighted products like oligomers, which are related to an increase in viscosity. Both effects (acidity, viscosity) are major issues for the use of biodiesel in combustion engines. The quality of biodiesel for commercial use is regulated by EN 14214 in Europe and ASTM6751 in the United States. The main issues for normalisation are basic physical and chemical parameters, such as water content, viscosity and the basic chemical composition of the FAME content. Fuel stability is tested also using basic physical and chemical parameters like iodine value, perox-
ide value, viscosity, structure indices and oxidisability. Only a limited number of studies target the molecular composition of the blend using mainly spectroscopic methods like infrared spectroscopy. To gain a deeper understanding of the degradation mechanism and its impact on the fuel properties, a study based on comprehensive two-dimensional gas chromatography – time-of-flight mass spectrometry (GCxGC-TOFMS) was initiated to investigate the changes of the molecular pattern. Within the feasibility study a GCxGC-TOFMS method was evaluated to detect changes in the very complex pattern of isomeric constituents of the petroleum-biodiesel matrix combined with a meaningful statistical analysis. The sample matrix was obtained from the Institut für wirtschaftliche Ölheizung e.V. (OWI). Four different blends of low sulphur heating oil (HEL), namely pure HEL, HEL with 5 and 10% FAME and adulterated HEL with 10% FAME was stored at elevated temperature (40°C) for one to 24 months in contact to air and cooper¹ (see Figure 1). For the pre-study, pure HEL samples and HEL + 10% FAME (with and without cooper) were analyzed with GCxGC-TOFMS. The sample Matrix was injected directly after centrifugation into the GCxGC-TOFMS. Differ-

¹ „Storage Stability Project II, IWO“
Different column combinations were tested, including recently released highly polar ionic liquid phases.

![Figure 4](image)

**Figure 4:** Summed up logarithmic significance plot. Significant areas ($p > 99.5\%$) are coloured on blue background. (A) no significant change for non-polar region (paraffines, isoparaffines, naphtenes). (B) volatile polar compounds (aldehydes, ketones, small acids) from FAME break down. (C) highly significant chances for main unsaturated FAME compounds. (D) changes within the mono aromatic region. (E) changes within the poly aromatic region. (F) long chain mono and dibasic acids (tailing in the first dimension) and first oligomeric products.

The focus was the separation of polar degradation products from the main constituents, such as paraffin. A “reversed” column combination (highly polar ionic liquid (SLB™-IL59, Sigma-Aldrich) x mid polar trifluoropropylmethyl poly-siloxane (Rtx200, Restek) showed a good separation pattern. For data analysis a recently developed routine based on MatLab was adapted to the data structure. In addition, the data matrix was adjusted to meet the requirements for multicore processing (see Figure 2). The statistical analysis was based on t-test statistics on pixel values of a two-dimensional data matrix. However, due to the small number of samples (one sample for each point, 3 times injected) a special filter had to be incorporated to eliminate the large number of possible false positives (Type 1 errors). The filter is based on the assumption that such errors (“false positive pixels”) are uniformly distributed over the complete data matrix and real positives are characterised by an accumulation of significant values (see Figure 3).

The analysis was done subsequently for each mass. For a first qualitative overview the significance values could be summed up over all masses and logarithmic plotted (Figure 4). For a first quantitative assessment, the highest positive or negative fold change could be plotted for the significant areas. While these plots give a rough overview over the major changes, a detailed inspection was done on the single mass traces, as shown in figure 3 c.

**Conclusion:** A method was developed to determine the storage induced alterations in the molecular pattern of heating oil/ biodiesel blends. The method allows an inspection on the molecular level and was specially designed and successfully applied for: fast processing of large data sets; very complex matrices like petroleum-biodiesel blends; the elimination of false positive errors.

**Perspectives:** This pre-study was performed on a small subset of the samples. The main study (pending) will include all samples and time points (until twelve months) to increase the significance of the statistic. The complete data set will also allow the investigation of secondary effects like the catalytic effect of cooper and the time dynamic behaviour of the adulteration. The methodology developed here, however, is also used in several other projects, for instance in metabolomic investigations on the onset of diabetes or in aerosol research.

Quantification of Phenanthrene and its metabolites in human body fluids

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Phenanthrene is present in various environmental samples and serves as a model compound for PAH exposure in human biomonitoring. Therefore, new, fast and reliable methods for the quantification of Phenanthrene in whole blood samples as well as its metabolites in urine have been developed.

It has been shown that diesel exhaust particles (DEP) are involved in the formation and strengthening of allergic diseases\(^1,2\). This may be due to several reasons: a boost of allergen specific IgE production, a shift of the Th1/Th2 immune balance towards a Th2 profile as well as the activation of mast cells and basophils. It is assumed that polycyclic aromatic hydrocarbons (PAH) are responsible for the effects caused by DEP, regardless of the nature of the particles, and that the production of reactive organic species (ROS) induced by PAH plays an important role (activation of NF-\(\kappa\)B). Phenanthrene (Phe) is a main component of environmental PAH and occurs in various sources (e.g., DEP). Since its metabolites are excreted in large amounts in the urine, Phe is of high diagnostic value in the biomonitoring of PAH exposure. Phe is a known substrate for cytochromes P450 (CYPs). However, the multiple and overlapping specificities of CYPs mask the role of individual isoforms in PAH metabolism\(^3\). Whole blood elimination studies may help to elucidate the role of individual CYPs.

**Phenanthrene from blood samples**

The determination of Phenanthrene in blood samples, especially from humans, requires physicians to take the blood sample and a time consuming and error prone sample preparation. The newly developed gas chromatography mass spectrometry method (GC-MS) is based on the thermal extraction of the Phenanthrene from a 1 µl blood sample, which can be taken by the test person itself using a lancing device for capillary blood sampling and a 1 µl disposal capillary pipette (see Fig. 1).

![Figure 1: Sampling tools and desorption tube.](image-url)
Calibration and quantification are carried out using an internal standard (Phenanthrene D10, 4 ng/µl) and calculating the ratio of the peak areas from m/z 178 and 188 ion traces. For the calibration a solution of Phenanthrene in DMSO was added to a blood sample in the range of 0.01 – 0.1 ng/µl (6 points). The calibration curve showed a good linearity in this range and a correlation coefficient of 0.95. The same test person, whose blood was taken for the calibration, later took part in a preliminary study for the evaluation of the method. In this study, a test person worked for about 8 h at a grill station at the Munich Oktoberfest. Blood samples were taken directly after work, 8 h later and again 2 weeks after the last working day. In Fig. 2, the Phenanthrene blood-concentrations are shown. As expected, a high concentration is detected directly after work, which decreases subsequently over a longer period. Eight hours later, the value is still considerably higher than the base level, which is reached again after two weeks\[4\]. Besides the determination of Phenanthrene in whole blood, the quantification of renally excreted phenanthrene metabolites serves as an indicator for the internal dose after exposure to PAH and is often used for biomonitoring. Main metabolites in urine are monohydroxylated phenanthrenes and dihydrodiol-phenanthrenes\[5\]. Almost two decades ago, a fast and reliable HPLC-method for the determination of five hydroxy-phenanthrenes was developed and applied in our laboratory\[6\]. Recent research work has renewed interest in and the importance of this method and a further development was started. Up to now, it has not been possible to separate all monohydroxylated phenanthrenes with liquid chromatography. At least two metabolites always co-elute. The application of a novel, modified HPLC column packing material allows the separation of the monohydroxylated phenanthrenes. Additionally, one of three dihydrodiol-phenanthrenes can be analysed with this HPLC-method (cf. Figure 3). The other two dihydrodiols are not yet commercially available.

Figure 2: Phenanthrene blood-concentrations after exposure at a grill station.

![Figure 2](image_url)

Figure 3: HPLC-Chromatogram of 5 phenanthrene metabolites excreted in urine after exposure to PAH. Trans-9,10-Dihydroxy-9,10-Dihydrophenanthrene (1), 2-Hydroxyphenanthrene (2), 3-Hydroxyphenanthrene (3), 1-Hydroxyphenanthrene (4), 4-Hydroxyphenanthrene (5).

The analytes are detected using their native fluorescence leading to low detection limits of approximately 5 pg/µl. Future work will focus on the combination of selective and practicable sample processing with chromatographic separation. The established method was distinguished by an HPLC-integrated, highly selective solid phase extraction allowing direct injection of urine samples. The implementation of this kind of sample processing shall also be achieved for the current method.
Funding and Cooperation: This project was carried out in cooperation with the Center of Allergy & Environment (ZAUM) of the Technical University Munich.

Analytical Method Development (AMD)
Determination of ionisation and fragmentation energies of security relevant substances by single photon ionisation using VUV-synchrotron radiation at the BESSY II

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The determined ionisation energies (IE) of security relevant substances set fundamentals of using VUV sources in single photon ionisation mass spectrometry (SPI-MS). Knowledge of the IE allows an adjustment of the detection scheme to specific analytes.

The BMBF-funded “Safe Inside” project aims at detecting security relevant substances via Single Photon Ionisation-Mass Spectrometry (SPI-MS). However, knowledge of molecular physical parameters of the target substances such as ionisation energies and fragmentation threshold energies are required for this particular application. In SPI the molecules are ionised by interaction with a single vacuum ultraviolet (VUV) photon [1]. Very often soft, i.e., fragment-free ionisation can be achieved by SPI.

Figure 1: Pictures of the BESSY electron synchrotron measurement campaign in October 2010. Top left: Building of BESSY II; top right: Sample preparation; bottom left: Model of BESSY II storage ring, accelerators and beamlines; bottom right: Ionisation chamber of TOF MS with U125/2-NIM fundamental beam; centre: Transport box of the explosives samples.
An energy adjustment of the VUV source to the ionisation energy (IE) of the analyte on the one hand allows ionisation of the analytes and on the other hand masks the matrix molecules with higher IE, such as nitrogen (IE = 15.58 eV), oxygen (IE = 12.06 eV), carbon dioxide (IE = 13.77 eV) or vaporous water (IE = 12.62 eV) [2] at the same time. In addition, the adjustment of the VUV photon energy also helps to reduce unwanted fragmentation of the analytes. Soft ionisation techniques are particularly suitable for direct analysis of complex substance mixtures without pre-separation. By reducing or avoiding undesired fragments, the identification of the other mass spectrometric signals is simplified. Furthermore, for structure determination of the molecular ions by tandem mass spectrometry can be applied. The measurements presented here were performed with a homebuilt reflectron time of flight mass spectrometer system (based on RT50 TOF, Kaesdorf, Munich) at the

![Graph](image)

**Figure 2:** Measurement of 2,4 Dinitrotoluene. **Left:** EI and VUV mass spectrum of 2,4-DNT; **right:** Molecular (182 m/z) and fragment (165 m/z) ion signal of 2,4-DNT (normalised on EI signal), with indicated ionisation energy (IE) and appearance energy (AE). The photon energy region for predominately soft ionisation is shaded in light blue, the one for maximal molecular ion signal in darker blue.

U125/2-NIM BESSY synchrotron VUV beam line (photon energies from 7 to 11.9 eV). In contrast to earlier work [3], the thermal stress of the samples during the measurements was reduced due to direct vapourisation in the ionisation chamber of the TOFMS. This allowed determination of ionisation energies of low-volatile narcotics such as heroin. Up to now, unknown ionisation and fragment appearance energies of nearly 100 compounds were determined. This included many narcotics, explosives and medical drugs. In Figures 2 and 3, two exemplary results show the IEs and the occurrence of the first fragment. The first example (Figure 2) is 2,4-DNT (2,4 Dinitrotoluene, representing the substance class of explosives). The signal of the molecular ion $M^+$ at 182 m/z can be observed starting at a photon energy rate of about 10.0 eV (IE). The first fragment 165 m/z appears significantly at 10.5 eV (AE). The 165 m/z fragment signal is the result of an OH elimination. Smaller fragment masses, start to appear in the VUV spectrum at 11.6 eV.
Figure 3 illustrates the ionisation energy determination measurement of a drug precursor. As an example for drugs and their precursor, benzomethylketone (BMK), a precursor of the amphetamine syntheses, was chosen. The ionisation energy was approximately 7.5 eV (IE). Due to the molecular structure and the absorbed excess energy at lower wavelengths during the scan fragment signals where also observed.

The 43 m/z fragment (acylium ion) reaches the significant level at about 9.8 eV (AE).

In conclusion, the homebuilt SPI/EI mass spectrometer can be used at synchrotron VUV beam lines for rapid determination of important physico-chemical parameters required, for example, for analytical applications of photo ionisation mass spectrometers.

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Investigation of the coffee roasting process by microprobe sampling - single photon ionisation time-of-flight mass spectrometry

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Soft photo-ionisation mass spectrometry (SPI-MS) in combination with a µ-probe sampling is a promising analytical method to investigate the evolution of chemical signatures of pyrolysis gases within individual coffee beans. Therefore, SPI-MS is a tool for studying, among others, the roasting flavour formation mechanisms.

Coffee is one of the food products with the richest flavour. During the roasting process at high temperatures over 200 °C, flavour compounds are formed from precursors which are already present in green coffee. Currently 850 volatile organic compounds (VOC) are identified in roasted coffee. 500 of them are produced by the predominant reactions of Strecker and Maillard. There are several reviews on the chemistry of coffee roasting and the formation of flavour compounds. Considering the complexity of the chemical and physical processes that occur during roasting, it is not surprising that knowledge about these processes is fragmentary and sometimes speculative. To ensure a constantly good quality, the roast master still uses a set of indicators, his or her senses and empirical experience for process controlling. On-line process control methods for coffee roasting are still under development. Nevertheless, a rational control of roast quality requires a real-time monitoring of properties relevant for the coffee flavour throughout the whole roasting process. Possible methods to realise this comprise Proton-transfer-reaction mass spectrometry (PTR-MS) and single photon ionisation time-of-flight mass spectrometry (SPI-TOF-MS), which allow the detection of VOC in complex matrices with high-time resolution and sensitivity (Figures I+II)[1]. The direct gas inlet into a mass spectrometer applying single photon ionisation allows ionisation without fragmentation for a wide range of organic compounds. With SPI-MS relative simple mass spectra without non-deconvolutable, overlapping fragment peaks are obtained. In combination with the high-time resolution of time-of-flight mass spectrometry, a fast chemical profiling can be achieved. The result is a considerably improved chemical description of the roasting process compared to other on-line analysis methods such as IR-spectroscopy, gas sensors or sensor arrays (“electronic nose”). For research and pilot plant applications in particular, SPI-MS has a large potential. In the future, even application for process control might be possible. To obtain a first overview of all produced VOCs during the roasting process of a single bean, the mass spectra of the first 15 min roasting time were examined.
In Figure 3 a resulting spectrum is presented. Additionally, a 3D-graph of the comprehensive SPI-TOFMS on-line monitoring of the whole roasting process is shown. The application of this technique allows for the detection of heterocyclic compounds as well as ketones. Furthermore, several compounds with masses higher than \( m/z \) 200 can be observed. Dominant peaks in the mass spectra are at \( m/z \) 43 (carbohydrate fragment), \( m/z \) 44 (acetalddehyde), \( m/z \) 58 (acetone), \( m/z \) 79 (pyridine), \( m/z \) 98 (furfurylalcohol), \( m/z \) 110 (dihydroxybenzenes) and \( m/z \) 194 (caffeine). In Figure 4 the variability of the release dynamics of selected compounds is depicted. For the four roasting experiments #1-#4 different release behaviours are observed. However, if phenol (\( m/z \) 94) is compared with caffeine (\( m/z \) 194) it becomes visible that sharp emission peaks formed during popping or cracking of the beans at different roasting times are observed for phenol solely. In contrast, the caffeine release profile does not exhibit such sharp emission peaks; here the signal increases with proceeding roasting time and after passing through a formation maxima the signal decreases steadily. This may be due to the different plant wall permeability of various chemical compounds. In summary, the results shown here demonstrate the potential of the µ-
probe SPI-mass spectrometry approach for on-line analysis of the chemical processes during the roasting-induced flavour formation.

Figure 3: Averaged mass spectrum (15 min roasting time, individual Coffee Arabica bean experiment, sampling within a coffee bean (µ-probe)). The time-resolved 3D-graph shows the release dynamics of chemical compounds during the roasting process.

Figure 4: Mass traces of caffeine (194 m/z) and phenol (94 m/z) for four single bean roasting experiments. While caffeine is released predominately in the early roasting stage, sharp phenol emission peaks are observed.

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Dr. R. Williams, Dr. U. Steiner, Dr. E. Almasi
Co-workers of the Joint Mass Spectrometry Centre

On the following pages the co-workers are introduced in alphabetical order.
Dr. Gülcin Abbaszade, Dipl.-Chem.
Helmholtz Zentrum München

Senior scientist
Development and validation of analytical methods for chemical particle characterisation; quantification of health-relevant substances in ambient aerosol particles.

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David Adelmann, Dipl.-Phys.
University of Rostock / Helmholtz Zentrum München

PhD student
Development and validation of an analytical system for thermal analysis (TA) coupled with evolved gas analysis (EGA) via mass spectrometry (MS) using photo ionisation (REMPI and SPI) and electron impact ionisation (EI). One main target is the characterisation and improvement of the skimmer-nozzle-coupling between MS and TA.

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Dr. Matthias Bente, Dipl.-Phys.
Helmholtz Zentrum München / Photonion GmbH

Scientist
Works at the JMSC spin-off company "Photonion GmbH". Development, validation and support of online and offline analytical systems based on mass spectrometry (MS) equipped with different ionisation techniques.

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Christian Busch, Dipl.-Chem.
University of Rostock / Helmholtz Zentrum München

PhD student
Fundamental investigation of the transient pyrolysis and combustion processes in cigarettes by application of a cigarette combustion simulator. Online, real-time analysis of organic combustion by-products is performed by photoionisation mass spectrometry (SPI/REMPI-TOFMS). Extracted tobacco and tobacco with additives are also included in the investigations.

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George-Constantin Dragan, Dipl.-Ing.  
Helmholtz Zentrum München / University of Rostock  
PhD student  
Development, setup and construction of a work place aerosol simulation unit, consisting of an aerosol generator, a flow tube reactor and an aerosol chamber. Current tasks are the characterisation of the physico-chemical behaviour of model aerosols in the flow tube reactor and the aerosol chamber.

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Sebastian Dresen, Dipl.-Ing. (FH)  
University Hospital Freiburg / University of Rostock  
PhD student  
Development of LC-MS/MS mass spectral libraries and LC-MS/MS methods for the screening and quantitative analysis of pharmaceuticals, drugs of abuse and other forensically relevant compounds and their metabolites in biological matrices.

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Sven Ehlert, Dipl.-Chem.  
University of Rostock / Helmholtz Zentrum München  
PhD student  
Detection of security relevant substances (explosives, narcotics, toxics and the related precursors) using Laser Desorption Mass Spectrometry. Short Laser Pulses are used for atmospheric pressure ablation of analytes from the surface. The volatilised neutral molecules are samples by a mass spectrometer. Either chemical or photo ionisation and tandem mass spectrometry are applied for detection.

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Michael Elsasser, Dipl.-Chem.  
Helmholtz Zentrum München / University of Rostock  
PhD student  
Stationary and mobile aerosol measurements with a high time resolved online aerosol mass spectrometer (AMS) in ambient and smoke chamber assays for determination of wood combustion markers in ambient aerosol.

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Markus Eschner, Dipl.-Chem.
Helmholtz Zentrum München / University of Rostock
PhD student
Development and investigation of multi-dimensional separation techniques based on the coupling of single-photon ionisation (SPI) mass spectrometry (MS) to gas chromatographic methods (GC, GC×GC) for online and offline applications.
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Ernst Feicht, Dipl.-Ing. Agr.
Helmholtz Zentrum München
Scientist
Characterisation of ambient aerosols. Running of aerosol characterisation and sampling sites in Munich and Augsburg.
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Alois Fendt, Dipl.-Chem.
University of Rostock / Helmholtz Zentrum München
PhD student
Investigation of biomass pyrolysis gases via time-of-flight mass spectrometry (TOF-MS) using two soft photo ionisation techniques (SPI and REMPI) as online detection method for organic compounds at a technical flash pyrolysis plant. The aim of research is the optimisation of a biomass to liquid process for the production of biofuels or base materials. To achieve this aim multivariate data analysis is applied for the characterisation of the pyrolysis gases.
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Dr. George A. Ferron, Dipl.-Phys.
Helmholtz Zentrum München
Associated Consultant
Modelling of the deposition of hygroscopic particles in the respiratory tract of humans and rats.
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Robert Geißler, Dipl.-Phys.
Helmholtz Zentrum München / University of Rostock

PhD student

Development of a combined analytical system for thermal analysis (TA) and subsequent evolved gas analysis (EGA) via quadrupole mass spectrometry (QMS) using alternating single photo ionisation (SPI) and electron ionisation (EI), allowing quasi-simultaneous sample analysis. The coupling is realised with a heated capillary system to ensure fast and uniform gas aliquot transition.

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Harald Grabow, Dipl.-Ing.
University of Rostock

Electronic Engineer

Hardware support and maintenance for chemical instrumentation, in particular nuclear magnetic resonance (NMR) spectrometer servicing, including cryogenics (magnet) and pneumatics (sampler). Professional engineering support for design and construction of dedicated electrochemical test setups for student and PhD projects.

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Jana Grabowsky, Dipl.-LMChem.
University of Rostock / Helmholtz Zentrum München

PhD student

Determination of the molecular signature of different carbonaceous fractions, organic (OC) and elemental carbon (EC), evolving during the thermo-optical analysis of combustion and ambient aerosols.

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Thomas Gröger, Dipl.-Ing.
Helmholtz Zentrum München

Senior scientist

Characterisation of complex molecular systems by chromatographic and mass spectrometric techniques. Special focuses are the conceptional research, further development and application of higher dimensional separation techniques. Main applications include health related research, such as metabolomics and the investigation of petrochemical samples.

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Anja Gummesson  
University of Rostock  

Graduaand  
Analysis of organic compounds in complex gas mixtures with PTR-MS. The aim of this research is the identification and impact of bacterial volatile organic compounds (VOCs) and volatile organic biomarkers in human exhaled air.

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Dr. Sabine Haack, Dipl.-Chem.  
University of Rostock  
Senior scientist  
Organisation and implementation of lectures, seminars and analytical practical trainings for students of chemistry, agriculture, biotechnology and for teacher trainees. The emphasis is on trace analysis with AAS, ICP and polarography. Development of the schedule for the Institute of Chemistry.

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Nanette Hacker  
University of Rostock  
Graduaand  
Characterisation of crude oils by pyrolysis-gas chromatography coupled to mass spectrometry using soft ionisation techniques.

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Romy Hertz, Dipl.-Chem.  
University of Rostock / Helmholtz Zentrum München  
PhD student  
Development of a heated microprobe sampling device coupled with photo-ionisation mass spectrometry (REMPI and SPI) that can be applied, for example, for sampling of (semi)volatile compounds within the glow of a cigarette or inside individual coffee beans during roasting. The aim of the study is a spatial resolved investigation of combustion and pyrolysis processes in burning cigarettes as well as chemical reaction pathways in flavour formation in coffee roasting.

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Jasper Nils Hölzer, Dipl.-LMChem.
Helmholtz Zentrum München / University of Rostock
PhD student

Development and validation of an analytical system for fast trace detection of security relevant substances based on an ion trap mass spectrometer coupled with an electron beam pumped excimer light source for internal vacuum ultra violet single photon ionisation and standard electron impact ionisation. The injection of the VUV radiation for ionisation is realised by a Lithium Fluoride coated vacuum mirror system.

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Evelyn Hübner, Dipl.-Ing.(FH)
Helmholtz Zentrum München
Engineer

Quantification of health-relevant substances in aerosols with GC, HPLC- and LC-MS/MS. Development of chromatographic methods for the identification and determination of organic compounds in environmental and biological matrices. Technical support of HPLC and HPLC-MS/MS-systems.

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Dr. Gert Jakobi, Dipl.-Chem.
Helmholtz Zentrum München
Scientist

Monitoring of organic and inorganic compounds in ambient air and deposition; experimental studies concerning their substance inputs in ecosystems. Monitoring of all relevant meteorological parameters. Monitoring of persistent organic pollutants (POPs) in ambient air and precipitation in the Alpine region, especially at high Alpine altitudes.

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Erwin Karg, Dipl.-Met.
Helmholtz Zentrum München
Senior scientist

Characterisation of particulate and gaseous atmospheric components; characterisation of particle surface area; experimental aerosol production, instrumentation and analysis; impact of particulates on human health.

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Kristian Kiersch, Dipl.-Chem.
University of Rostock / Helmholtz Zentrum München

PhD student

Development of an analytical system for the determination of pyrolysed organic matter in soil via mass spectrometry (MS) using soft ionisation techniques (field ionisation – FI and photo ionisation - REMPI and SPI).

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Dr. Manfred Kirchner, Dipl.-Met.
Helmholtz Zentrum München

Senior scientist

Management of environmental studies and projects in Central Europe and the Mediterranean area. Monitoring of inorganic and organic compounds in ambient air and deposition in the vicinity of roads and other sources and in remote areas. Investigations of the impacts of pollutants on ecosystems. Performance of climate change studies particularly in the Alpine region. Evaluation of implement studies in the field of alternative mobility.

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Juliane Kleeblatt, Dipl.-Chem.
University of Rostock / Rostock University Hospital / Helmholtz Zentrum München

PhD student

Direct detection of trace substances in breath gas using Photon Ionisation Mass Spectrometry. Study of the behaviour of drugs by means of their concentration in breath gas in cooperation with the study group breath gas (ROMBAT) at the Department of Anaesthesia and Intensive Care Medicine.

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Simone Krüger
University of Rostock

Technical assistant

Support and preparation of practical courses, assistance to scientific work and general laboratory work.

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Geza Kocsis  
Helmholtz Zentrum München  

**Technician**  
Monitoring of hazardous chemical compounds in the environment with special emphasis on POPs in high alpine altitudes.  
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Martina Kürsten  
University of Rostock  

**Secretary**  
Secretary of the Chair of Analytical Chemistry and of the Department of Physical Chemistry at the Dr. Lorenz-Weg facilities.  
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Dr. Jutta Lintelmann, Dipl.-Chem.  
Helmholtz Zentrum München  

**Senior scientist**  
Quantification of health-relevant substances in aerosols with HPLC and LC-MS/MS. Development of chromatographic methods for the identification and determination of organic compounds in environmental and biological matrices. Investigation and evaluation of air monitoring data.  
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Helmholtz Zentrum München  

**PhD student**  
Metabolic characterisation of different phases of type 2 diabetes by means of plasma and tissue samples of different mouse models. Integrative examination of the yielded dataset in relation with phenotypical and proteomic data of the same sample material.  
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Dr. Jürgen Maguhn, Dipl.-Chem.  
Helmholtz Zentrum München  
Senior scientist

Characterisation of ambient aerosol by physical and chemical analysis employing online particle counters, impactor probing and aerosol mass spectrometry (AMS).

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Dr. Konrad L. Maier, Dipl.-Biochem.  
Helmholtz Zentrum München  
Associated Consultant

Radicals in particles: oxidative and proteolytic mechanisms, induction of inflammatory reactions by aerosols.

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Dr. Georg Matuschek, Dipl.-Chem.  
Helmholtz Zentrum München  
Senior scientist

Development of personal sampling techniques for the organic-chemical characterisation of environmental aerosols. Quantification of selected targets in model and environmental aerosols of different origins by GC-MS and DTD-GC-MS. Development of analytical methods for environmental and biomedical analysis.

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Maren Mieth, Dipl.-LMChem.  
Rostock University Hospital / University of Rostock  
PhD student

Development of sampling procedures (“needle trap”) for bedside sampling and preconcentration of breath-gas in cooperation with the study group breath gas (ROMBAT) at the Department of Anaesthesia and Intensive Care Medicine (Rostock University Hospital).

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Christoph Mocker, M.Sc.
University of Rostock / Helmholtz Zentrum München
PhD student
Analysis of breath and inhaled/exhaled cigarette smoke with a Nd: YAG based laser system (original wavelength 1064 nm) for single photon ionisation (SPI) and resonance enhanced multiphoton ionisation (REMPI) coupled to time-of-flight mass spectrometry (TOFMS).

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Makhosazana Mthembu, M.Sc.
University of Rostock
PhD student
Characterisation of products of coal pyrolysis and Fischer-Tropsch process. The latter is investigated in a homebuilt laboratory reactor.
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Hermann Nordsieck, Dipl.-Chem.
bifa Umweltinstitut GmbH
Senior scientist
Material flow analysis and energy balances in conjunction with dispersion models are tools used for assessment of environmental impact of industrial emissions and consulting on emission control technology. Research on aerosols kinetics at workplace and in thermal processes.
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Jürgen Orasche, Dipl.-Chem.
University of Göttingen / Helmholtz Zentrum München / University of Rostock
PhD student
Comparison and assessment of stoves, boilers and plants fired by wood combustion as a module for sustainable and renewable generation of energy. Investigations are carried out on the analyses and characterisation of organic tracers in emissions and their behaviour in the environment.
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Markus Oster, Dipl.-Chem.
Helmholtz Zentrum München / University of Rostock

PhD student

Development of an improved inlet system for laser based single particle aerosol mass spectrometry using soft photo ionisation (REMPI) for selective detection of polycyclic aromatic hydrocarbons.

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Stefan Otto, Dipl.-Chem.
University of Rostock

PhD student

Characterisation of crude oils, oil contaminated soils and biomass using Pyrolysis-GC, Pyrolysis-MS, Pyrolysis-GC-MS and Pyrolysis-GCxMS analytical techniques. These techniques involve both hard and soft ionisation methods. The combination of different analytical techniques promises to give more information of the components of the samples being analysed.

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Dr. Konstantinos Oxynos, Dipl.-Chem.
Helmholtz Zentrum München

Senior scientist

Analysis and evaluation of analytical data. Analysis of relations between analytical data or data and external sample or sampling parameters.

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Annika Pommeres
University of Rostock

Graduand

Determination of relative ionisation cross sections for resonance-enhanced multiphoton ionisation.

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Raeed Megeed Qadir, M.Sc.
Helmholtz Zentrum München / University of Rostock
PhD student
Development and application of analytical methods for the characterisation of organic constituents of ambient particulate matter within and outside low emission zones related to health effects.

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Christian Radischat
University of Rostock
PhD Student
On-line detection of organic trace components in the exhaust gases during the combustion of wood by mass spectrometry (MS) using photo ionisation techniques like resonance-enhanced-multi-photon-ionisation (REMPI) and single-photon-ionisation (SPI).

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Jan Rittgen, Dipl.-Chem.
Federal Criminal Police Office / University of Rostock
PhD student
Development of lab-based analytical reference procedures, specially contactless and direct MS-techniques for the detection of hazardous materials (explosives, synthetic drugs). Besides the established combination of solid phase microextraction (SPME) with GC/MS, SPME-fibers are directly analysed by placing them into an ESI-sprayer (SPME-ESI-MS). A further rapid technique, desorption electrospray ionisation mass spectrometry (DESI-MS) is applied.

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Dr. Mohammad Reza Saraji-B., Dipl.-Phys.
Photonion GmbH
Scientist
Works at the JMSC spin-off company "Photonion GmbH". Development, validation and support of online and offline analytical systems bases on mass spectrometry (MS) equipped with different ionization techniques.

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Petra Sattler, Dipl.-Ing.
University of Rostock

Laboratory assistant

Organisation and realisation of analytical practical courses. Planning and supervision of experiments.

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Marion Schäffer, M.Sc.
Helmholtz Zentrum München / University of Rostock

PhD student

Development of analytical methods for the chemical characterisation of illicit and pharmaceutical drug samples under forensic aspects based on comprehensive two-dimensional gas chromatography mass spectrometry (GC×GC-TOFMS).

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Claudia Schepler, Dipl.-Chem.
University of Rostock / Helmholtz Zentrum München

PhD student

Design, construction and characterisation of coupling techniques to combine liquid-chromatography and mass spectrometry using photoionisation. Application for the molecular characterisation of complex samples, such as mineral oils.

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Dr. Jürgen Schnelle-Kreis, Dipl.-Chem.
Helmholtz Zentrum München

Senior scientist

Investigation of the impact of aerosols on human health. Chemical characterisation of source and ambient aerosols and source apportionment of ambient aerosols.

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Dr. Elisabeth Schramm, M. Sc.
Helmholtz Zentrum München / University of Rostock

Scientist

Development and testing of a novel instrument for trace detection of security-relevant substances in complex matrices. The device is a combination of thermodesorption of wipe pads, soft single-photon ionisation using VUV-EBEL-photons and tandem mass spectrometry using an ion trap mass spectrometer.

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Henny Usmawati-Schwoebel, Dipl.-LMChem.
University Hospital Rostock / University of Rostock / Helmholtz Zentrum München

PhD student

Development of proton transfer mass-spectrometry (PTR-MS) for online monitoring of VOC’s (Volatile Organic Compounds) in human breath. The research aim is the investigation of VOC’s in connection with performance diagnostic in sports medicine and propofol online drug monitoring in cooperation with the study group breath gas (ROMBAT) at the Department of Anaesthesia and Intensive Care Medicine.

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Dr. Martin Sklorz, Dipl.-Geoökol.
University of Rostock

Senior scientist

Development of analytical methods and tools basing on mass spectrometry. Special interest in high resolution mass spectrometry, photoionisation sources and coupling techniques to chromatography for getting a deeper insight in environmental and biological processes.

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Dr. Thorsten Streibel, Dipl.-Chem.
University of Rostock

Senior scientist

Improving the comprehension of the formation of organic trace compounds originated from thermal processes such as pyrolysis and combustion. Investigation of the thermal behaviour and characterisation of fossil and regenerative fuels. The analytical methodology comprises direct mass spectrometry applying soft photo ionisation.

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Philip Trefz, Dipl.-Ing. (FH)
Rostock University Hospital / University of Rostock

PhD student

Development of sampling techniques based on needle traps for sampling and preconcentration of breath-gas in cooperation with the study group breath gas (ROMBAT) at the Department of Anaesthesia and Intensive Care Medicine (Rostock University Hospital).

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Jochen Weh, Dipl.-Chem.
University of Rostock

PhD student

Development of a time and size-resolved analysis for ambient aerosols based on laser-desorption/laser ionisation time-of-flight mass spectrometry. The sampling is done with a three-stage rotating drum impactor system.

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Anita Wüst
Helmholtz Zentrum München

Technician

Sampling, sample preparation and GC/MS-analyses of target components in aerosols. Routine analysis of health relevant organic substances in environmental samples. Technical support of GC/MS- and DTD-GC/MS-systems.

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Prof. Dr. Ralf Zimmermann, Dipl.-Chem.
University of Rostock / Helmholtz Zentrum München

Professor of Analytical Chemistry
Head of the Cooperation Group “Comprehensive Molecular Analytics”
Head of the Joint Mass Spectrometry Centre

Main research interests include mass spectrometry and in particular photoionisation mass spectrometry, general organic analysis, comprehensive multidimensional separation, environmental and health related research, such as aerosols.

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Third-Party Funds and Scholarships
**Third-Party Funded Projects Since the Foundation of the Joint Mass Spectrometry Centre (JMSC)**

**08-14** Research and Development Centre, BAT Ltd., Southampton, UK
Study on the formation mechanisms of selected "Hoffmann-analytes"
*with project extension*
University of Rostock

**08-11** Sasol Technology Ltd., South Africa
Application of REMPI-/SPI-TOFMS for on-line analysis of coal pyrolysis products and Fischer-Tropsch micro reactor streams
University of Rostock

**08-11** Federal Ministry of Education and Research (BMBF)
Detection of safety-related substances in poorly accessible areas
(subproject: basic adjustment of ion trap mass spectrometers)
Helmholtz Zentrum München

**08-11** BMBF (Helmholtz-Enterprise-Fonds)
Helmholtz spin-off for the development and production of innovative devices for trace gas analysis based on spectroscopy and mass spectrometry using a novel ion source
Helmholtz Zentrum München

**08-11** German Research Foundation (DFG)
Development and application of a coupled thermodesorption photoionization mass spectrometer for the determination of the composition of the carbonaceous fraction and the oligomer/polymer content of ambient aerosol particulate matter
University of Rostock

**09-13** Federal Ministry of Education and Research (BMBF)
Grant by the German Center for Diabetes Research
Helmholtz Zentrum München

**09-12** NETZSCH Gerätebau GmbH, Selb
TG-Skimmer-MS: Characterisation and optimization of jet properties
University of Rostock

**09-11** Ministry for Science and Culture of Lower Saxony
Sustainable use of biomass energy in the area of tension between climate protection, landscape and society
Helmholtz Zentrum München
10-13 **German Social Accident Insurance (DGUV)**
Analysis of measurement errors in hazardous aerosol sampling in working areas
*Helmholtz Zentrum München*

10 **German Research Foundation (HBFG)**
Funding contribution (50%) of the federal government of Germany for large investment: Fourier Transform Cyclotron Resonance Mass Spectrometer, FT-ICR-MS (7 T) for ultra highly mass resolved mass spectrometric analysis of gaseous, liquid and solid samples
*University of Rostock*

**Total amount of third-party funds obtained since the foundation of the JMSC (2008):** € 2.308.606,-

**Newly Granted Third-party Funded Projects of the Joint Mass Spectrometry Centre (JMSC) in the Reporting Period**

11-14 **Bavarian Research Foundation**
Multidimensional analysis of thermal processes
*Helmholtz Zentrum München*
€ 648 700

11-14 **Bavarian Research Foundation**
Multidimensional analysis of thermal processes
*Photonion GmbH (cooperation with HMGU)*
€ 90 400

10-11 **German Research Foundation (HBFG)**
Funding contribution (50%) of the federal government of Germany for large investment: Multidimensional gas chromatography – High Resolution Time-of-Flight Mass Spectrometry, GCxGC-HRTOFMS
*University of Rostock*
€ 124 000

**Total amount of third-party funds obtained by the JMSC in the reporting period:** € 863.100,-
Granted Scholarships

Kristian Kiersch (Chemist)
Scholarship of the Faculty of Interdisciplinary Research, University of Rostock
(for the completion of a doctoral thesis in cooperation with Prof. Leinweber, Institute of Land Use, University of Rostock)

Juliane Kleeblatt (Chemist)
Scholarship of the Faculty of Interdisciplinary Research, University of Rostock
(for the completion of a doctoral thesis in cooperation with Prof. Schubert, Dept. of Anaesthesia and Intensive Care Medicine, Rostock University Hospital)

Claudia Schepler (Chemist)
Scholarship of the Federal State of Mecklenburg-West Pomerania
(for the completion of a doctoral thesis)

Makhosazana Mthembu (Chemist)
Scholarship of Sasol Ltd., Sasolburg, South Africa
(for the completion of a doctoral thesis)

Newly Granted Scholarship in the Reporting Period

Raeed Mageed Qadir (Chemist)
Scholarship of the German Academic Exchange Service
(for the completion of a doctoral thesis)
Teaching Activities of the Reporting Period
Lectures

SS 10  **Principles of Analytical Chemistry** (2 SWS)
Compulsory Lecture for Chemists
*PD Dr. G.-U. Flechsig*

SS 10  **Instrumental Analytical Chemistry I** (4 SWS)
Compulsory Lecture for Chemists
*Prof. Dr. R. Zimmermann*

SS 10  **Analytical Chemistry** (1 SWS)
Compulsory Lecture for Medical Biotechnologists
*Dr. S. Haack*

SS 10  **Analytical Chemistry** (1 SWS)
Compulsory Lectures for Chemists (Teacher Training Course)
*Prof. Dr. R. Zimmermann*

WS 10/11  **Instrumental Analytical Chemistry II** (2 SWS)
Compulsory Lecture for Chemists
*Prof. Dr. R. Zimmermann*

WS 10/11  **Environmental Analytics** (2 SWS)
Advanced Lecture for Chemists
*Dr. T. Streibel*

Practical Courses

WS 10/11  **Basic Practical Course in Analytical Chemistry** (6 SWS)
Compulsory Lab Course for Chemists

WS 10/11  **Practical Course in Instrumental Analytics** (4 SWS)
Compulsory Lab Course for Chemists

SS 10  **Practical Course in Area of Specialization** (12 SWS)
Advanced Lab Course for Chemists

WS 10/11  **Integrated Practical Course** (6 SWS)
Advanced Lab Course for Chemists

SS 10  **Analytical-Chemical Practical Course** (3 SWS)
Compulsory Lab Course for Chemists (Teacher Training Course)

WS 10/11  **Analytical-Chemical Practical Course** (1 SWS)
Compulsory Lab Course for Agroecologists

SS 10  **Analytical-Chemical Practical Course** (1 SWS)
Compulsory Lab Course for Medical Biotechnologists
Seminars

SS 10  
**Principles of Analytical Chemistry** (1 SWS)
Optional for Chemists
*Dr. T. Streibel, Dr. S. Haack*

SS 10  
**Modern Instrumental Analytics** (1 SWS)
Research Seminar for Master and PhD Students
*Prof. Dr. R. Zimmermann*

SS 10  
**Analysis of Complex Molecular Systems** (1 SWS)
Research Seminar for Master and PhD Students
*Prof. Dr. R. Zimmermann*

SS 10  
**Seminar of the Mass Spectrometry Centre** (1 SWS)
Interdisciplinary Seminar on New Methods of Mass Spectrometry and Chromatography
*Prof. Dr. R. Zimmermann*

JMSC Seminars

**Summer Term 2010**

22.03.  
14:30  
*Prof. Dr. J. Chow, Prof. Dr. J. Watson, Desert Research Institute, Reno, USA*
“New insights into aerosol sampling artifacts (Chow), PM$_{2.5}$ source apportionment study in Minnesota (Watson)”
(Seminar room 201, Dept. of Chemistry)

20.04.  
17:30  
*Prof. Dr. K.-H. Meiwes-Broer, Institute of Physics, UR*
“Mass spectrometry in cluster and nanoparticle research”
(Seminar room 201, Dept. of Chemistry)

27.04.  
17:30  
*Prof. Dr. G. Rehder, Institute for Baltic Sea Research, Warnemünde*
“Continuous flow combustion GC-IRMS to detect carbon stable isotopes of methane - technology and applications”
(Seminar room 201, Dept. of Chemistry)

04.05.  
17:30  
*Dr. E. Bahlmann, Institute for Biochemistry and Marine Chemistry, Univ. of Hamburg*
“Determining the carbon isotope ratios of atmospheric halogenated organic compounds”
(Seminar room 201, Dept. of Chemistry)
18.05.  
Dr. W. Dreher, BASF AG, Limburgerhof  
17:30  
“Use of mass spectrometry for pesticide analysis: Basics and applications”  
(Seminar room 201, Dept. of Chemistry)

08.06.  
Prof. Dr. E. Rohwer, BASF AG, Limburgerhof  
17:30  
“The development of a multi-purpose silicone rubber trapping device for improved trace organic analysis in a Chromatography and Mass Spectrometry laboratory”  
(Seminar room 201, Dept. of Chemistry)

15.06.  
Dr. M. Gonin, TOFWERK AG, Switzerland  
17:30  
„Metrology in Mass Spectrometry“  
(Seminar room 201, Dept. of Chemistry)

22.06.  
Prof. Dr. B. Spengler, University of Giessen  
17:30  
“Past and Future of MALDI-Imaging”  
(Seminar room 201, Dept. of Chemistry)

29.06.  
Prof. A. Amann, Innsbruck Medical University  
17:30  
“Breathing gas analysis: a tour d’horizon”  
(Seminar room 201, Dept. of Chemistry)

06.07.  
Dr. S. Mikkat, Proteome Center Rostock  
17:30  
“Detailed protein structure Characterisation with MALDI-MS and MALDI-MS/MS Analyses. How does it work?“  
(Seminar room, Biomedical Research Centre)

13.07.  
Prof. W. Schade, TU Clausthal  
17:30  
“Light in the future: Photonics for sensorics and materials”  
(Seminar room 201, Dept. of Chemistry)

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**Winter Term 2010/11**

19.10.  
Dr. W. Berneike, Cameca GmbH, Unterschleißheim  
17:30  
“High-resolution secondary ion mass spectrometry - technology and application“  
(Seminar room 201, Dept. of Chemistry)

26.10.  
Prof. Dr. M. Spiteller, Dortmund University  
17:30  
„Bioactive compounds from endophytic fungi: Isolation and analysis“  
(Seminar room 201, Dept. of Chemistry)

09.11.  
Dr. T. Arthen-Engeland, Bruker GmbH, Bremen  
17:30  
„New applications of ionization technology for atmospheric pressure, in particular APCI and APLI“  
(Seminar room 201, Dept. of Chemistry)
16.11. Dr. G. Dittmar, Max Delbrück Center for Molecular Medicine Berlin-Buch
17:30 „Post-translational modifications of the transcription factor C/EBP”
(Seminar room 201, Dept. of Chemistry)

23.11. Dr. K. Hiller, MIT, Cambridge, MA
17:30 „Non-Targeted Metabolomics: From biomarker discovery to the metabolic fate of compounds”
(Seminar room 201, Dept. of Chemistry)

14.12. Prof. P. Leinweber, Institute for Land Use, University of Rostock
17:30 „Mass spectrometric investigation of wine”
(Seminar room 201, Dept. of Chemistry)

11.01. Dr. U. Schümann, Chair of Piston Machines and Internal Combustion Engines, Univ. of Rostock
17:30 „Chromatographic and mass spectrometric analytical techniques in fuel and lubricant analysis”
(Seminar room 201, Dept. of Chemistry)

18.01. Prof. B. Piechulla, UR, Institute for Biosciences
17:30 „Biology and environmental chemistry of volatile metabolites in plants and bacteria”
(Seminar room 201, Dept. of Chemistry)
Lectures at Scientific Meetings and Colloquia
## Lectures at Scientific Meetings and Colloquia


2. **T. Streibel, M. Saraji-Bozorgzad, M. Eschner, T. Gröger, R. Geißler, R. Zimmermann;** *Characterization of fossil and renewable fuel by Thermal Analysis hyphenated to two-dimensional gas chromatography/mass spectrometry (TA-GCxMS),* ANAKON 2011, 22.03.3011


8. **R. Zimmermann, T. Gröger, M. Eschner;** *Perspectives of multidimensional analytical methods like "comprehensive" gas-chromatography (GCxGC) in process analysis,* 6. Kolloquium Prozesssanalytik der GDCh Fachgruppe, Waldbronn, 09.11.2010

9. **T. Gröger, S. Ly-Verdu, R. Zimmermann;** *Combined phenotypic-proteomic-metabolomic to re-investigate the role of the liver in T2D,* 4th Project Meeting Diabetes, München, Germany, 04.11.2010
10 T. Gröger, M. Eschner, T. Wilharm, R. Zimmermann; **Determination of changes caused by storage and oxidation in the chemical profile of fuel oil with biodiesel share based on higher-dimensional coupling of gaschromatopgraphic and massspectrometric analysis techniques**, DGMK-Annual Meeting of Analysts 2010, Hamburg, Germany, 26.10.2010

11 R. Zimmermann, R. Hertz, J. Hölzer, E. Schramm, J. Grabowski; **Application of on-line photo-ionisation mass spectrometry for investigation and monitoring of the coffee roasting process**, 23rd ASIC, Bali, Indonesia, 05.10.2010

12 R. Zimmermann, R. Hertz, T. Streibel; **On-line analysis of the gas-phase in the interior of individual coffee beans during the roasting process by microprobe-sampling photo-ionisation mass spectrometry**, 23rd ASIC, Bali, Indonesia, 04.10.2010

13 J. Schnelle-Kreis, G. Abbaszade, J. Orasche, Y. Liu, M. Sklorz, M. Elsasser, R. Zimmermann; **Application of thermal desorption-GC-MS for the analysis of particulate matter**, Peking University Health Science Center, Beijing, China, 26.09.2010

14 R. Zimmermann, J. Orasche, M. Oster, M. Bente, J. Weh, M. Elsasser, J. Schnelle-Kreis; **Aerosol mass spectrometric approaches for a better understanding of the organic fraction of the ambient PM**, Workshop at the HKIST: Analysis of carbonaceous ambient aerosols, Hong Kong, China, 24.09.2010


20 E. Karg, G. A. Ferron, X. Hecht, G. Schumann, O. Schmid; **The Accuracy of Specific Surface Area Measurements from Low-Mass-Carbon-Samples**, IAC 2010, Helsinki, Finland, 02.09.2010


23 T. Streibel, M. Saraji-Bozorgzad, M. Eschner, T. Gröger, R. Geißler, R. Zimmermann; **Characterization of coal, crude oil and wood pellets by Thermal Analysis hyphenated to comprehensive two-dimensional gas chromatography/mass spectrometry (TA-GCxMS)**, ESTAC 10, 27.08.2010

24 R. Zimmermann, J. Orasche, M. Oster, M. Bente, M. Elsasser, J. Schnelle-Kreis; **Analysis of PM from wood combustion in Augsburg and detection of source indicators as well as PAH by aerosol mass spectrometry**, Pre-IAC Aerosol Workshop, Kuopio, Finland, 27.08.2010


26 T. Streibel, M. Saraji-Bozorgzad, M. Eschner, T. Gröger, R. Geißler, R. Zimmermann; **Characterization of coal, crude oil and wood pellets by Thermal Analysis hyphenated to comprehensive two-dimensional gas chromatography/mass spectrometry (TA-GCxMS)**, 38th NATAS conference, 18.08.2010


31 J. Schnelle-Kreis, J. Orasche, G. Abbaszade, R. Qadir, M. Oster, M. Elsasser, R. Zimmermann; **Sources apportionment of ambient aerosols – application of different methods**, Sino-German Air Quality and Health Research Workshop, Beijing, China, 15.06.2010

32 T. Gröger, M. Eschner, R. Zimmermann; **Single Photon Ionization - A valuable detection method for comprehensive two-dimensional gas chromatography applied to metabolic fingerprinting: Technique, benefits and obstacles**, ISCC 2010, Riva, Italian, 03.06.2010

33 M. Schäffer, T. Gröger, R. Zimmermann; **Impurity profiling of 3,4-methylenedioxymethamphetamine (Ecstasy) based on GCxGC-TOFMS combined with chemometric data analysis**, ISCC 2010, Riva, Italian, 03.06.2010

34 R. Zimmermann, M. Eschner, M. Saraji, T. Gröger, R. Geißler, T. Denner, T. Streibel; **Comprehensive Two-Dimensional On-Line Analysis of Complex Mixtures by Thermally or Valve Modulated Fast Gas Chromatography Coupled to Soft Photo-Ionisation Mass Spectrometry**, 7th GCxGC Symposium and 34th ISCC, Riva del Garda, Italy, 01.06.2010


37 R. Zimmermann, J. Schnelle-Kreis, J. Orasche, M. Bente, M. Oster; Analysis of wood combustion aerosols in ambient air using inorganic and ambient air using inorganic and organic tracer compounds, A&WMA, Air Quality Specialty Meeting, Xian, China, 13.05.2010

38 J. Lintelmann; Preparation and chromatographic investigation of phenylboronate affinity materials, Closing workshop of Sino-German Cooperation Research Group on Separation and Analysis of Complex samples, 12.01.2010
Publications of the Reporting Period

Peer-reviewed and ISI-web listed publications (published or accepted) of the reporting period are listed in this section.
### Publications of the Reporting Period


12 T. Gröger, R. Zimmermann; **Application of Parallel Computing to Speed up Chemometrics for GC x GC-TOFMS Based Metabolic Fingerprinting**, *Talanta* 83:1289-1294 (2011)


20 S. Dresen, N. Ferreiros, H. Gnann, R. Zimmermann, W. Weinmann; **Detection and Identification of 700 Drugs by Multi-Target Screening with a 3200 Q Trap® LC-MS/MS System and Library Searching**, *Analytical and Bioanalytical Chemistry* **396**:2425-2434 (2010)


## Abbreviations in alphabetic order

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>2D</td>
<td>two-dimensional</td>
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<tr>
<td>3D</td>
<td>three-dimensional</td>
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<tr>
<td>AAS</td>
<td>atomic absorption spectrometry</td>
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<tr>
<td>ACS</td>
<td>American Chemical Society</td>
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<tr>
<td>AG</td>
<td>working group / corporation</td>
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<td>AMS</td>
<td>aerosol mass spectrometer</td>
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<td>ANOVA</td>
<td>analysis of variance</td>
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<tr>
<td>APPI</td>
<td>atmospheric pressure photo-ionization</td>
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<tr>
<td>APS</td>
<td>aerodynamic particle sizer</td>
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<tr>
<td>ATM</td>
<td>Atmoslytic Inc., Calabasas, CA, USA</td>
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<td>AUF</td>
<td>Faculty of Agricultural and Environmental Sciences, University of Rostock</td>
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<tr>
<td>BAP</td>
<td>benz[a]pyrene</td>
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<tr>
<td>BAT</td>
<td>British American Tobacco</td>
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<tr>
<td>BB</td>
<td>biomass burning</td>
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<tr>
<td>BBOA</td>
<td>biomass burning organic aerosol</td>
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<td>BC</td>
<td>black carbon</td>
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<tr>
<td>BESSY</td>
<td>Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H.</td>
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<tr>
<td>BET</td>
<td>Brunauer, Emment and Teller</td>
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<tr>
<td>BFS</td>
<td>Bavarian Research Foundation</td>
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</table>
bifa bifa Environmental Institute
BKA Federal Criminal Police Office
BMBF Federal Ministry of Education and Research
BMK Benzomethylketone
BtL biomass to liquid
CE capillary electrophoresis
CEO chief executive officer
CHAMP Collaborative Harmonisation of Methods for Profiling of Amphetamine Type Stimulants
CI chemical ionization
CID collision induced dissociation
COD coefficient of divergence
CYPs cytochromes P450
DAAD German Academic Exchange Service
DAD diode-array detector
DEP diesel exhaust particles
DFG German Research Foundation
DGUV German Social Accident Insurance
DHA dehydroabietic acid
DPP diabetes pilot project
DRI Desert Research Institute - University of Nevada, Reno, NV, USA
DSC differential scanning calorimetry
DTD direct thermal desorption
DTG differential thermogravimetry
DZD German Diabetes Center
EBEL electron-beam pumped rare gas excimer light source
EC elemental carbon
EC-JRC European Commission Joint Research Institute
EI electron impact
ELPI electrical low pressure impactor
EPA Environmental Protection Agency
EPI II Institute of Epidemiology II, HMGU
ESI electrospray ionization
EU European Union
FAME fatty acid methyl ester
FI field ionization
FKZ grant application number
FNF filtered noise field
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>FT</td>
<td>Fischer-Tropsch</td>
</tr>
<tr>
<td>FT-ICR-MS</td>
<td>Fourier transform ion cyclotron resonance mass spectrometer</td>
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<tr>
<td>GC</td>
<td>gas chromatography</td>
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<tr>
<td>GC</td>
<td>two-dimensional &quot;comprehensive&quot; gas chromatography</td>
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<td>GC-MS</td>
<td>gas chromatography-mass spectrometry</td>
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<td>GDCh</td>
<td>German Chemical Society</td>
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<tr>
<td>GKS</td>
<td>Schweinfurt Joint Venture Power Plant</td>
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<tr>
<td>HBFG</td>
<td>Higher Education Institutions Act</td>
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<tr>
<td>HCA</td>
<td>hierarchical cluster analysis</td>
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<td>HEF</td>
<td>Helmholtz-Enterprise-Fonds</td>
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<tr>
<td>HEL</td>
<td>heating oil</td>
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<tr>
<td>HGF</td>
<td>Helmholtz Association of German Research Centers</td>
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<tr>
<td>HMGU</td>
<td>Helmholtz Zentrum München - German Research Center for Environmental Health</td>
</tr>
<tr>
<td>HMTD</td>
<td>Hexamethylene triperoxide diamine</td>
</tr>
<tr>
<td>HOA</td>
<td>hydrocarbon-like organic aerosol</td>
</tr>
<tr>
<td>HPLC</td>
<td>high performance liquid chromatography</td>
</tr>
<tr>
<td>HPLC-MS</td>
<td>high performance liquid chromatography-mass spectrometry</td>
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<tr>
<td>HRGC</td>
<td>high resolution gas chromatography</td>
</tr>
<tr>
<td>HRMS</td>
<td>high resolution mass spectrometry</td>
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<tr>
<td>HR-TOF-AMS</td>
<td>high resolution time of flight aerosol mass spectrometer</td>
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<tr>
<td>HZB</td>
<td>Helmholtz-Zentrum Berlin</td>
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<tr>
<td>I.D.</td>
<td>inner diameter</td>
</tr>
<tr>
<td>ICP</td>
<td>inductively coupled plasma</td>
</tr>
<tr>
<td>IDTD</td>
<td>in situ derivatisation thermal desorption</td>
</tr>
<tr>
<td>IDTD-GC-MS</td>
<td>mass desorption gas chromatography mass spectrometry</td>
</tr>
<tr>
<td>IDTD-GC-TOFMS</td>
<td>in-situ derivatisation thermal desorption method followed by gas chromatography and time-of-flight mass spectrometry</td>
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<tr>
<td>IEG</td>
<td>Institute of Experimental Genetics</td>
</tr>
<tr>
<td>IES</td>
<td>Institute for Environmental Health and Sustainability, Joint Research Centre of the EU (JRC), Ispra, Italy</td>
</tr>
<tr>
<td>IEs</td>
<td>ionisation energies</td>
</tr>
<tr>
<td>IFA</td>
<td>Institute for Occupational Safety and Health of the German Social Accident Insurance</td>
</tr>
<tr>
<td>iLBD</td>
<td>Institute for Lung Biology and Disease, HMGU</td>
</tr>
<tr>
<td>IMK-IFU</td>
<td>Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research/Atmospheric Environmental Research</td>
</tr>
<tr>
<td>IMS</td>
<td>ion-mobility mass spectrometry</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>INF</td>
<td>Faculty of Interdisciplinary Research, University of Rostock</td>
</tr>
<tr>
<td>IÖC</td>
<td>Institute of Ecological Chemistry</td>
</tr>
<tr>
<td>IOW</td>
<td>The Leibnitz Institute for Baltic Sea Research, Warnemünde</td>
</tr>
<tr>
<td>IPs</td>
<td>ionisation potentials</td>
</tr>
<tr>
<td>IRMS</td>
<td>isotope ratio mass spectrometry</td>
</tr>
<tr>
<td>ITMS</td>
<td>ion trap mass spectrometer</td>
</tr>
<tr>
<td>JMSC</td>
<td>Joint Mass Spectrometry Center</td>
</tr>
<tr>
<td>JRC</td>
<td>Joint Research Centre of the EU (JRC), Ispra, Italy</td>
</tr>
<tr>
<td>K-AMS</td>
<td>potassium aerosol mass spectrometer</td>
</tr>
<tr>
<td>KIT</td>
<td>Karlsruhe Institute of Technology</td>
</tr>
<tr>
<td>KT</td>
<td>Criminal Technical Institute</td>
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<tr>
<td>LC-MS</td>
<td>liquid chromatography-mass spectrometry</td>
</tr>
<tr>
<td>LD</td>
<td>laser desorption</td>
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<tr>
<td>LDI</td>
<td>laser desorption/ionization</td>
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<tr>
<td>LEZ</td>
<td>Low Emission Zone</td>
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<tr>
<td>LFU</td>
<td>Bavarian Environment Agency</td>
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<tr>
<td>LIAD</td>
<td>laser-induced acoustic desorption</td>
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<td>LIKAT</td>
<td>Leibniz Institute for Catalysis</td>
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<tr>
<td>LMU</td>
<td>Ludwig-Maximilians Universität München</td>
</tr>
<tr>
<td>LSD</td>
<td>lysergic acid diethylamide</td>
</tr>
<tr>
<td>LÜB</td>
<td>Bavarian Hygienic Air National Surveillance System</td>
</tr>
<tr>
<td>m/z</td>
<td>mass-to-charge ratio</td>
</tr>
<tr>
<td>MAAP</td>
<td>multi angle absorption photometer</td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix-assisted laser desorption/ionisation</td>
</tr>
<tr>
<td>MDMA</td>
<td>3,4-methylenedioxy-N-methylamphetamine</td>
</tr>
<tr>
<td>MEUD</td>
<td>Medical Faculty of the University of Rostock</td>
</tr>
<tr>
<td>MNF</td>
<td>Faculty of Mathematics and Natural Sciences, University of Rostock</td>
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<tr>
<td>MONARPOP</td>
<td>Monitoring Network in the Alpine Region for persistent and other Organic Pollutants</td>
</tr>
<tr>
<td>MOUDI</td>
<td>micro-orifice uniform-deposit impactor</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
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<tr>
<td>MSTFA</td>
<td>based on silylation with N-Methyl-N-trimethylsilyl trifluoroacetamide</td>
</tr>
<tr>
<td>MWF</td>
<td>metal working fluid</td>
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<tr>
<td>Nd:YAG-Laser</td>
<td>neodymium-doped yttrium-aluminum garnet laser</td>
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<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
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<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
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<tr>
<td>NTD</td>
<td>needle trap device</td>
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</table>
NZO-Maus  New Zealand obese mouse
oa TOF-MS  orthogonal acceleration TOF-MS
OC  organic carbon
OM  oil mist
OOA  oxidized organic aerosol
OPO  optical parametric oscillator
OWI  Institut für wirtschaftliche Ölheizung e.V.
PAH  polycyclic aromatic hydrocarbon
PAMINA  Particulate Matter in Indoor and Ambient Environments
PCA  principal component analysis
PETN  pentaerythritol tetranitrate
Phe  phenanthrene
PI  photo ionisation
PI-MS  photo-ionization mass spectrometry
PLS-DA  partial least squares discriminant analysis
PM  particulate matter
PM  particles <=10 μm aerodynamic diameter
PM  particles <=2.5 μm aerodynamic diameter
PMF  positive matrix factorisation
PMT  photomultiplier tube
PMx  particulate matter with aerodynamic diameter smaller than x μm
POP  persistent organic pollutants
POPALP  Evaluation of Persistent Organic Pollutants in the Bavarian Alps
Ppb  parts per billion
Ppm  parts per million
Ppt  parts per trillion
PROT  Research Unit Protein Science, Helmholtz Zentrum München
PSI  Paul Scherrer Institute
PTR-MS  proton transfer reaction mass spectrometry
Py  pyrolysis
Py-FIMS  pyrolysis field ionization mass spectrometry
PyOM  pyrolysed organic matter
QIT  quadrupole ion trap
QMS  quadrupole mass spectrometer
Q-TOF  quadrupol time-of-flight mass spectrometer
RDI  rotating drum impactor
RDX cyclotetramethylenetetranitramine, hexogen
REMPI resonance enhanced multi photon ionization
ROS Reactive organic species
RSD relative standard deviation
RTE reactive thermal extraction
SAFE-XUV Trace Detection of Security Relevant Substances within Complex Matrices
SD-band standard deviation band
SMPS scanning mobility particle sizer
SOA secondary organic aerosol
SOCAR State Oil Company of Azerbaijan Republic
SOFAZ State Oil Fund of Azerbaijan Republic
SOM soil organic matter
SP single-particle
SPE solid-phase extraction
SPI single-photon ionization
SPI-MS single photon ionisation mass spectrometry
SPI-TOFMS photon ionization time-of-flight mass spectrometry
SPME solid-phase microextraction
SRM standard reference material
SSA specific surface areas
SVOC semi volatile organic compounds
SWS weakly teaching hours per semester
TA thermal analysis
TD thermo-desorption
TD-REMPI-SP-TOF-MS thermo-desorption resonance enhanced multi photon ionization mass spectrometer
TE thermal extraction/extractor
TFMPP trifluoromethylphenylpiperazine
TFZ Bavarian Technology and Support Centre
TG thermogravimetry
THM thermally assisted hydrolysis and methylation
TIC total ion current
TMAH tetramethylammonium hydroxide
TNT trinitrotoluol
TOFMS time-of-flight mass spectrometry
TOF-MS time-of-flight mass spectrometer
Triple-Quad triple quadrupole mass spectrometer
TUM Technical University Munich
<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>UG</td>
<td>University of Goettingen</td>
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<td>UGOT</td>
<td>University of Gothenburg</td>
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<td>UR</td>
<td>University of Rostock</td>
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<td>VELA</td>
<td>Vehicle Emission Laboratory, JRC, Ispra</td>
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<td>VOC</td>
<td>volatile organic compounds</td>
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<td>VUV</td>
<td>vacuum ultraviolet</td>
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<tr>
<td>WELAS</td>
<td>welas® White Light Aerosol Spectrometer</td>
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<tr>
<td>WLC</td>
<td>wall loss corrected</td>
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<td>WSOC</td>
<td>water soluble organic compounds</td>
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<td>W-TOF</td>
<td>W-time-of-flight mass spectrometer</td>
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<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
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