AMT
Process- and Aerosol Measurement Technology Division

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1. Preface

This documentation is designed to give the reader insight into the activities of our department.

The teaching activities of the department are mainly in the fields of measurement and process technology. In research we are concentrating on the material system aerosol, liquid and/or solid particles suspended in a gas.

Of equal interest for us are unwanted aerosols emitted from technical processes and distributed in the atmosphere and wanted product aerosols.

The work related to emission and immission of aerosols is mainly concentrating on the implications of the introduction of new EU particulate matter (PM<sub>x</sub>) Standards. Nanostructured materials and devices can be made using several synthesis technologies. We are concentrating on the synthesis of particles in the gas phase as a very promising route. We develop nanostructured materials with exiting properties, e.g. quantum dots in semiconductors and sensor materials.

As the application of aerosols are manifold the research activities of our department have been directed towards various other fields of application. Research priorities at our department are to be found in clean technology, filtration, aerosol measurement technology, physical and chemical characterization of aerosols, synthesis, transport behavior as well as characterization of properties of particles.

I would like to acknowledge and convey my gratitude to all those who contributed to the aerosol research work over the last year enabling the successful work of our department.

Duisburg, August 2001

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Anas Skiti
Thomas Krinke
Top Sezgin
3. Curriculum

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* L = Lecture,          E = Excercise,          P = Practical study
4. **Research**

4.1 **Research Areas and Projects**

**Basic Research:**

**Physical Properties:**
- Size and Shape
- Charge Level
- Particle Concentration Measures

**Physical Behavior:**
- Light Scattering
- Particle Transport in Flows
- Particle Deposition onto Surfaces
- Aerosol Dynamics

**Application Areas:**

**Aerosol Measurement Technology:**
- Test and Calibration of Aerosol Instruments
- Sampling and Conditioning Processes
- Development of Aerosol Measurement Technology
- Characterization of Aerosols in Technical Processes

**Clean Technology:**
- Contamination Risk Analysis
- Particle Control Concepts
- Quality Assurance of Filter Elements
- Particle Transport and Deposition in Clean Areas
- Development of Particle Flux and Deposition Meter

**Process Gas and Air Cleaning:**
- Analysis of the Structure of Fibrous Filter Media
- Effect of Filter Media Inhomogeneities on Filter Performance
- Optimization of Pleated Filter Media
- Collection of Agglomerates in Fibrous Filter Media
- Collection Efficiency of Fibrous Filter Media with Electric Fields

**Nanostructured Materials:**
- Nanoparticle Generation Technology
- Transport of Aerosols with Nanoparticles
- Deposition of Nanoparticles
- Characterization of Nanoparticles

**Ambient Aerosols:**
- Characterization of Ambient Particles
- Ambient Air Monitoring
- Source Apportionment
- Analysis of Factors Influencing Ambient Aerosol Concentration and Compositions
4.1.1 Physical Properties and Behavior of Particles in Aerosols

Particle Coagulation in Turbulent Flows

Co-operation with Kwangju Institute to Science and Technology, Kwangju, Korea
NRW

Dr.-Ing. F. E. Kruis

Aggregation phenomena often have a profound effect on the properties of an aerosol of particles and/or droplets. Frequently, turbulent motion causes the particles to collide and when they adhere, aggregation takes place. An expression for the turbulent collision rate is required in order to describe the evolution of the particle or droplet size distribution, for example in the aging of smoke particles in plumes originating from flaming and the growth of raindrops in atmospheric clouds and thus the influence of turbulence on initiating rain. In chemical reactor engineering the turbulent collision mechanism is important in aerosol reactors like the TiO2 production furnace or in short-contact-time catalytic cracking reactors.

A review of previous derivations of particle collision rates in turbulent fluid flow shows that these are applicable only to limited cases. A more general derivation is given, taking into account the effects of the inertia of the particles and the difference in densities of the fluid and the particles. A universal solution for the relative velocity of two particles due to turbulent accelerations in a gaseous or liquid system is presented. In gaseous systems the acceleration mechanism becomes predominant at particle sizes far below the Kolmogorov microscale of turbulence.

The time evolution of particle size distribution due to Brownian and turbulent coagulation (using the kernel of Kruis and Kusters, 1997) was systematically investigated. Using a new definition of dimensionless size distribution parameters based on the geometric mean values, self-preserving particle size distributions for turbulent coagulation were found to exist. The width of such distributions depends on the initial size distribution as well as the turbulence intensity. When starting with submicron aerosols, however, only the turbulence intensity plays a role in determining the final self-preserving form whereas the initial conditions have no influence. Typically, broad particle size distributions with in the 1.5-1.9 range are obtained. Because of the importance of scavenging by the largest particles in the size distribution, the possibility of developing a “run-away mass” exists, for which some experimental indications in turbulent systems exist.

Publications

Mixing of Nanoscale Particles by Electrical Bipolar Aggregation

SPP 1062 (Handling Highly-Dispersed Powders) of the DFG

Dr rer.-nat. A. Maisels, Dr-Ing. F.E. Kruis

Nanoscale materials are promising for modern technologies, but their production is complicated. For example nanoscale composite powder cannot be produced as a result of classical mechanical mixing. The solution of this problem could be found in the components mixing immediately after particles production in the gas phase. The aim of this work is to investigate the ability for aggregation of particles carrying opposite charges in bicomponent aerosols mixture. Opposite charge polarities on particles of different kinds lead to enhancement of attraction between different particles and in the same time to repulsion between particles of the same kind.

For the synthesis of composite Ag-PbS nanoaggregates two aerosols with oppositely charged quasi-monodisperse Ag and PbS particles have been mixed. The mixture was led to an aggregation tube and after some time, determined by the volume of aggregation tube used, the particle ensemble was studied. The fact that the initial aerosols contained only particles with charges of the same magnitude but opposite polarities with respect to each other allows to separate Ag and PbS particles by electrostatic filtering using their electrical neutrality. Particle deposition on TEM-grids in an ESP allows study in TEM. One can also analyse particle size distributions by standard aerosol measurement techniques (DMA, CPC).

Studies in TEM of deposited electrically separated particles have shown, that procedure proposed allows to obtain 1:1 mixed bicomponent particles. While the properties of primary particles (size, material, morphology) can be chosen independently, the amount of this particles is being determined by aggregation kinetics. As a characteristic of the aggregation kinetics, the number concentration of electrically neutral nanoaggregates was chosen in experimental studies. The dependency of the number concentration of electrically neutral nanoaggregates on the time for different particle size, width of the size distribution and morphology was studied.

Influence of the initial parameters (particle sizes, size distributions, particle morphology) on aggregation kinetics was studied numerically by specially developed theoretical model, based on Direct Simulation Monte Carlo method (DSMC). The method does not use particle trajectories but is based on the transformation of known collision frequencies into collision probabilities of particle pairs. The particle evolution is then defined in a stochastic game, computing the time step after each collision. This method looks especially attractive if not only integral particle characteristics as size and charge are the scope of interest, but also internal composition.

Because of solid nature of model substances (Pbs, Ag) some characteristic of aggregation effects must be taken into account. Colliding particles form non-spherical aggregates with fractal dimension between 1.4 and 2.4. This porous aggregate structure leads to increase of collision probability. To be capable to simulate such structures a diameter correction procedure was elaborated. Due to this procedure it is possible to get aggregates with fractal dimensions relevant to known experimental results. Comparing results of numerical simulations with experimentally obtained results one can see a good agreement.

From numerical simulations follows that for homogeneous component mixtures within aggregates high charge numbers on particles are required. The initially used radioactive charger is not sufficiently efficient, and a UV-lamp ($\lambda$=172nm) was taken as alternative charger. This charger was tested on aerosols with different particle number concentrations. Charge distributions obtained by photocharging depend, however, on aerosol parameters, like
particle number concentration, size and material as well as on parameters of the lamp irradiation (photon energy, irradiation intensity). In dependency of these parameters were obtained either bipolar or unipolar size distributions.

Publications


Controlled Deposition of Nano-Particles from the Gas Phase

ESF Nano-Program

Co-operation with the Division of Solid State Physics, Lund University, Sweden

Dipl.-Ing. T. Krinke

Nanometer sized metal and semiconductor particles can be regarded as potential components in future photonic or quantum electronic devices. This will require not only deposition but also positioning of nanoparticles on a substrate. We have developed a process for the arrangement of lines of nanometer-sized particles on oxidized silicon substrates by direct deposition from the gas phase of an aerosol. The particles were attracted onto charge patterns created on the plane surface by contact charging. The basic principle of which is that charges cross the interface between an insulator and a metal brought into contact. After the metal is removed, charges retain on the insulator. As substrates, we used silicon (111) with a 0.5 µm thick thermally-grown wet oxide and a plane surface. The underlying silicon was p+ doped with 0.01 to 0.02 Ωcm resistivity. After applying the charge patterns to the substrate, the deposition was carried out in an electrostatic precipitator (ESP), which is a vertical, cylindrical chamber designed to remove charged particles from the gas flow by means of a homogeneous electric field. As test aerosol we used monodisperse singly charged indium particles. Even without applying a voltage to the electrode of the ESP, the particles were attracted to the substrate and were collected on the charge patterns.

The deposition process has been investigated theoretically using a computer simulation program which has been developed in order to calculate the particle trajectories within the ESP. The program solves the equation of motion of the particle taking into account the flow field in the ESP, Brownian motion of the particle, Coulomb forces, van der Waals forces between the incoming particle and the substrate surface as well as with already deposited particles and image forces between incoming particle and substrate surface. The Coulomb force is calculated as a superposition of the homogeneous electric field in the ESP, the electric field due to the charge pattern and the electric field around already deposited particles.
4.1.2. Aerosol Measurement Technology

**Development of a Gas Particle Partitioner (GPP) for Highly Efficient Separation of Gas and Particle Phase with Minimal Changes in the Gas Phase**

Industry

Dipl. Ing. C. Asbach  
Dr. rer. nat. T. A. J. Kuhlbusch  
Dipl. Ing. F. Jordan  
Prof. Dr. Ing. H. Fissan

Measurements of particle mass concentrations in ambient air can be performed by manual and automatic samplers. In manual samplers, the air is pumped through a filter and the particles are deposited on the filter. If the total air flow through the filter is known, the particle mass concentration may be determined by weighing the filter in a conditioned room prior to and after filter loading. In automatic online samplers, the air gets pumped through a filter and the change of filter mass is measured simultaneously. To avoid meteorological influences, the aerosol is heated up inside the automatic sampler. This leads to an underestimation of particle mass concentration, due to loss of volatile and semivolatile material. The differences of particle mass concentrations measured by automatic and manual samplers reach up to 40%.

To avoid these discrepancies, the temperature inside the automatic sampler has to be reduced. Therefore a set up has been developed, containing a diffusion dryer, a GPP and a TEOM® automatic sampler. The GPP is developed and evaluated in this project (patent pending). It is a device that separates gas and particles with no or minimal effect to the thermodynamic properties of the aerosol. Inside the GPP, particles get charged due to a corona discharge and deflected by means of electrostatic forces. The total aerosol flow is isokinetically split into two flows, the sample flow and an excess air flow, which is used to dry the aerosol in the upstream diffusion dryer. By switching the corona and deflection voltage on, the sample air stream will be particle free, though maintaining all of its thermodynamic properties, such as pressure, gas composition, temperature and relative humidity. When no voltages are applied to the GPP, it acts as an isokinetic flow split, i.e. the total flow is divided into the sample flow and the excess flow with no changes to the particle size distribution.

To determine the artefacts, leading to the described underestimation of particle mass, the TEOM® is alternately operated with particle laden and particle free air, i.e. with and without voltages applied to the GPP. When operated with particle free air, the filter mass will decrease due to loss of semivolatile material. Provided the thermodynamic properties remain unaltered, the loss of mass is comparable to that when operating with particle laden air. By subtracting the negative mass difference, obtained with particle free air, from the positive mass change, obtained with particle laden air, the real particle mass concentration can be determined.
Development of PM 2.5 Inlets for Three Different Volume Flows

Industry

Dr. T.A.J. Kuhlbusch
LM-Chem. A.C. John

PM 2.5 inlets have to be designed and calibrated to measure PM 2.5 mass concentrations as required in the 1st daughter directive of the European Union related to limit values for sulfur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air (Council Directive 1999/30/EC, 22 April 1999)

The inlets have to be designed for different volume flows to enable variable sampling duration and adequate sampled mass for various chemical and physical analytical techniques. The inlets under development are designed for volume flow rates of 0.1 m³ h⁻¹, 2.3 m³ h⁻¹ and 4 m³ h⁻¹. The inlets will be calibrated with monodisperse, spherical Latex particles of known diameters. Six to seven different particle sizes ranging from 1-7 µm will be produced in the aerosol generator. Particle penetration in dependence of particle size will be determined by measuring particle number concentration in the inlet before and after the impaction plate. A field evaluation with other inlet systems may then give indication on the field performance of these inlets.

Assessment of the Processes in the Direct Vicinity of Emissions on Particle Mass and Size Distribution and Design of a Process Simulation Instrument

Landesumweltamt Nordrhein-Westfalen, Germany

LM-Chem A.C. John
Dr. T.A.J. Kuhlbusch

According to the 1st daughter directive "relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air" (Council Directive 1999/30/EC, 22 April 1999), mass concentrations of the particle size fractions PM 2.5 and PM 10 have to be measured in the European Union. So-called "action plans" will have to be set up to reduce ambient particle concentrations as first measurements indicate that the new limit values will be exceeded.

One of the major sources of PM 10 and PM 2.5 particles are industrial and combustion processes. So far, only total suspended particulate matter (TSP) are determined in particle emission measurements. These measurements are carried out in-stack at special conditions (e.g. high temperatures). Considering physical and chemical processes, substantial changes of particle number concentrations and particle mass concentrations will occur (e.g. by condensation and agglomeration processes and gas-to-particle conversion) when the process aerosol mixes with ambient air directly in the vicinity of the source. Thus using the in-stack data for source apportionment and dispersion modelling will lead to an underestimation of the contribution of the sources to ambient particle mass concentrations. The aim of this project is to develop an instrument which simulates the processes in the direct vicinity of these sources to determine the "real" emissions of point sources.

There to, the main processes which take place in the plume have to be determined. Additionally, dispersion modelling depending on the velocity of the exhaust gas and the diameter of the plume as well as wind speed will be conducted to define basic parameters for
the construction of the simulation device. Existing dilution systems will be evaluated for their use with regard to the design of the new simulation device. Later on, the instrument will be built and evaluated in the laboratory as well as in field measurements.

Development of a PM 1 Inlet for a High Volume Sampler

Industry

LM-Chem. A.C. John
Dr. T.A.J. Kuhlbusch

Mass concentrations of the particle size fractions PM 2.5 and PM 10 have to be measured in the European Union instead of total suspended particulates (TSP) as required in the 1st daughter directive “relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air” (Council Directive 1999/30/EC, 22 April 1999). However, from the point of view of health effects, even smaller particles are discussed and measurements of the size fraction < 1 µm (PM 1) might become a standard procedure. Additionally, the determination of PM 1 is useful concerning the identification of sources as fine particles are mainly produced by gas-to-particle conversion and e.g. combustion processes, whereas particles larger than 2.5 µm originate from mechanical processes as e.g. wind erosion. Particles in the size range between 1-2.5 µm can be derived from both processes. Thus, a new sampler inlet for the determination of PM 1 had to be developed. In order to collect enough particle mass to enable chemical analyses for the determination of the composition of the aerosols, the PM 1 impactor was designed for a high-volume sampler. The inlet was calculated, built and calibrated with monodisperse Latex particles in the laboratory. In a following measurement campaign, the PM 1 sampler was tested in the field where it was operated together with PM 2.5 and PM 10 samplers. The PM 1 concentrations showed reasonable results and the handling of the inlet was good.

Development of a New Instrument for Quasi Online Measurements of Particle Size Distributions Over a Range Between 3nm and 1000nm

Deutsche Bundesstiftung Umwelt (DBU) / Industry

Dipl.-Ing. Jun Luo
Dipl.-Ing. Peter Müschenborn
Dipl.-Ing. Frank Otten
Dipl.-Ing. Andreas Trampe

Investigations in the USA have shown, that there is a connection between an increasing mortality and an increasing concentration of submicron particles (nano-particles) in the atmosphere. As a consequence the influence of these particles on human health has become subject of considerations for new standards in the USA as well as in Europe. In order to understand the generation and effects of particles in the air, it is important to be able to estimate size distributions from 3nm to 1000nm. Since there exists no instrument, which performs such a measurement online (that means fast enough), we are working on an improvement of a so called differential mobility particle sizer (DMPS), a system which uses the differential mobility analysis (DMA) for the characterization of submicron particles.
A DMPS consists mainly of four parts:

1. A charger, a device which generates a cloud of ions passed by the (polydisperse) aerosol. Thus a certain number of particles gets charged because ions deposit on them.
2. A differential mobility analyzer to extract a (monodisperse) fraction from the aerosol by an electric field.
3. A counter for the particles fractionated by the DMA.
4. A microprocessor unit to control several adjustments and to evaluate the data, given by the counter.

The basic principle of the charger is the fact, that between two concentrical electrodes a zone of ionization is built (a so called corona), if the voltage between the electrodes reaches a certain value. However the charging efficiency especially for small particles is too small and has to be improved by modifications of the design.

Within the DMA the aerosol is lead into a gasstream and the diameter of the particles going through the outlet depends on the adjusted voltage. Here also a new design has to be found to cover the required range. In general big particles need a high voltage and need to stay relatively long in the electric field, whereas small particles are caught by a low voltage and must have a short residence int the DMA because they are effected by Brownian motion. Our investigations concentrate on a new inlet design to combine the features of narrow range mobility analizers.

One way to count the particles extracted by the DMA is to measure the current caused by the particles on a grid in the outlet of the DMA. Since the current is, especially at low particle concentrations, extremly small (about $10^{-17}$A), a new detector-circuit (electrometer) with a very high sensivity has to be developed.

The single components of the system have been designed that way, that they directly fit one onto another, which allows very short conection and a compact, integrated design of the whole apparatus.

After measurements in the laboratory with various test aerosols, first field measurements have been done within the scope of the "Feldex 2000" in October 2000, on the "Kleiner Feldberg", Taunus, organized by the DBU, where 26 groups of different universities participated. The measurements have been done in comparison to an already existing DMPS, to point out improvements and disadvantages.
Evaluation of the Effects of a Dryer on Particle Sampling and Mass Determination with a TEOM®

Industry

Dipl.-Ing. U. Drosten
Dr. rer. nat. T. A. J. Kuhlbusch

The discussion about the particulate matter measurement is revived by the information that an increasing fine particle concentration in the atmosphere increases the mortality rate. The new PM (Particulate Matter) standards for the measurement of particles less than 10µm, 2,5µm or even less then 1µm will be discussed in European countries. The development of standards towards smaller particle sizes increases the importance of eviting artifacts during sampling and conditioning.

Atmospheric aerosols consist of a combination of different substances such as organic and for a considerable part, in view of the mass concentration, of inorganic particulate matter. The artifact characteristics depends for volatile and hygroscopic salt particles on temperature and humidity. Ammonium nitrate and sulfate are representative in this study for theoretical and experimental modeling of volatilization characteristics during sampling and conditioning. Ammonium nitrate is of volatile nature while both of them are of hygroscopic nature.

All standards up to now recommend to collect particles with a filter at the thermodynamic state of atmospheric aerosols, to condition it at a certain temperature and relative humidity and to weight it off-line. In such a method the aerosol concentration is changed because of evaporation taking place at the filter and further changes during conditioning. The latter ones can be avoided by using a quasi on-line measuring balance like the Tapered Element Oscillating Microbalance-TEOM®. Since the thermodynamic state of the aerosol may change during sampling the measured aerosol concentration can be different depending on the history of the thermodynamic state during sampling.

First basic research experiments have shown that a zero point drift can be seen depending on different values of relative humidity. This tendency has to be investigated in more detail by several experiments. For this reason a laboratory setup has been build up to get defined thermodynamic conditions for long time experiments.

A suitable way to reduce the influence of relative humidity on artifacts is the use of a diffusion dryer. In this work experimental investigations show the efficiency of a Dryer-TEOM® system with regard to the stationary and dynamic behaviour of the drying process. The criterion of a successful drying operation is that the relative humidity level in the system is below the deliquescent point of important atmospheric substances. Under defined conditions in the laboratory experiments with particle free air give information about the limits of the drying process for several TEOM® operation modes. For practical applications further investigations with several aerosols should be done to show possible limits for particle mass concentration measurements in field measurements.

A further existing zero point drift has to take into consideration by a correction procedure. After we got informations about dynamic behaviour, losses and chemical behavior in our overall measuring system we should be able to design an online system for particle mass concentration measurements.
Publications

Developement of a Method for the Measurement of Particle Number Size Distributions in Industrial Processes for the Production of Nano-scale Powders

Deutsche Forschungsgemeinschaft / Industrie

Dr.-Ing. F. E. Kruis
Dipl.-Ing. P. Müschenborn

Nanotechnology is expected to become one of the key technologies of the very near future. In order to make the results of recent research on properties of nano-scale particles available for commercial applications, appropriate techniques for the control of processes and measurement have to be developed.

In cooperation between the DFG and DEGUSSA a so-called "Projekthaus Nanomaterialien" has been established, where the university of Duisburg as one of 9 universities takes part.

We have been developing a method to measure the particle number size distributions under the conditions of industrial production of nanopowders. These are namely:

- Low pressures (down to about 200mBar)
- High temperatures (up to about 1500°C)
- Presence of very corrosive gases (HCl, H₂O)
- Very high number concentrations (up to about 10¹² ccm⁻³)

We have built a measuring system basing on the differential mobility analyzer DMA. Since already available systems do not work under the mentioned conditions, modifications of the single components of ordinary differential mobility particle sizers are neccessary. These modifications concern charger, DMA and electrometer, which have to be vacuum-tight and resistant against corrosion. Besides, careful considerations as to the materials, tube connections, valves, etc. have to be made.

The measurement system is controled by a computer and runs fully automatically. Therefore we have developed adequate software and interfaces.

The work in the laboratory is completed by phases of investigations and tests at the research plants of DEGUSSA in Hanau.
4.1.3 Process Gas and Air Cleaning

Enhanced Filtration Efficiency in High Quality Fibrous Filters with Low Voltage Electric Fields

AIF-FLT

Dipl.-Ing. F. Jordan

The filtration efficiency of fibrous filters shows in the submicron particle regime a bold reduction. The reason for this behavior is the transition from interceptional to diffusional particle capture. Particle size dependent filtration mechanisms cause a minimum in filtration efficiency at particle sizes about 0.2 micrometer. Previous investigations have shown that a reduction of particle penetration, i.e. enhancement of filtration efficiency due to variation of the filterstructure (diameter of fibres, packing density, depth of filterlayer) results in a higher resistance to flow and causes a higher pressure drop.

Another way to improve filtration efficiency without changing the filter structure is the use of additional electric particle capture mechanisms. The main advantage is the higher filtration efficiency without increasing the pressure drop.

Today electric particle capture mechanisms are mainly applied in electret filters, which consist of electric inhomogeneous charged fibres. However, the fibres of electret filters loose their charge with time and particle loading. The electric field inside the filter layer will be neutralized so that filtration efficiency decreases.

To avoid this disadvantage a new type of filter can be used, in which dielectric fibres become polarized by an external electric field. This field maintains an inhomogeneous electric field inside the filter layer. Aim of this project is the development of a new filter, which will be optimized for filtration efficiency without increased pressure drop in conjunction with external electric fields.

The new filter will be produced with alternating thin translucent conducting layers and filterlayers of dielectric fibres. In that way it will be possible to obtain strong electric fields at low applied voltages inside the filter layers. The applied voltage should be in the range of 220V. The flow direction is perpendicular to the layers and parallel to the direction of the electric field.
Investigations of Deposition and Generation of Aerosols for Optimisation of Wet Smoke Gas Cleaner

AiF 11756

Dr.-Ing. St. Haep
Dipl. Ing. J. Lindermann
Dr.-Ing. M. Luckas
Dipl. Ing. A. Trampe

Wet smoke gas cleaning is a basic technique with a broad field of applications in the area of exhaust gas cleaning. The type and dimension of the plant and the combination with other cleaning stages vary with the concrete task. High rate of mass deposition are obtained. In state of the art plants the mass concentration of dust can be reduced down to a few mg/m³. However, aerosols in sub-micron size range can pass through the plant insignificant amount. The total mass of these particles is small but their number concentration is very high. These small particles can be used in wet smoke gas cleaners as condensation nucleus. Water and also pollutants will condensate on these particles. These particles will as a result grow up to larger sizes, which are easier to remove from the gas. The efficiency of the cleaning plant depend not only on the absorption of the solution but also depends on the number and size distribution of the particles in the exhaust flow.

In this project, a model for describing this process is to be developed. It should give an exact knowledge of generating, growing and transportation of aerosols in wet smoke cleaners. To verify the model a large scale experimental set-up was built.
Particle Deposition close to Air Outlets – Analysis and Reduction

AIF-FLT

Co-operation with Lehrstuhl für Wärmeübertragung und Klimatechnik, RWTH Aachen,
Prof. Dr.-Ing. M. Zeller

Dipl.-Ing. S. Neumann
Dipl.-Ing. F. Jordan

Primary goal of the project is to understand the particle deposition process in the vicinity of the outlets of air conditioning systems, especially the influence of outlet air velocity and turbulence grade on deposition. The results will be used to design optimal deposition free air outlets.

The investigations take place in a realistic room with original outlets. Test aerosols with properties based on observations in the field will be introduced. To reduce the necessary time for deposition and also increase the sensitivity of detection fluorescent particles and particles will be used. The methods of generating appropriate fluorescent particles and their detection has to be established. Furthermore the flow fields will be measured with Laser-Doppler-Anemometry. The flow fields as well as the resulting particle deposition will be modeled. The model results will be compared with the measured particle deposition. The evaluated model allows prediction of the deposition behavior for different operating conditions.

Publications


4.1.4. Nanostructured Materials

Synthesis of Nanoparticles

SFB 445 - A7 / NRW

Dr.-Ing. F.E. Kruis
Dr. K. Nanda

Nanostructured materials are receiving increasingly interest as building blocks for nanotechnological applications, such as nanoelectronics, quantum electronics, sensor technology, non-linear optics and solar technology. Our synthesis technique consists of modified standard aerosol technologies to generate monodisperse size fraction. In a furnace a specific solid material is heated, and during the cooling of the vapor nanometer-sized particles are formed. A specific size-fraction is selected based on the size-dependent electrical mobility (Differential Mobility Analyzer). In a second furnace the particles, which might consist of aggregated primary particles, can be sintered in order to reach a more spherical form. An electrostatic precipitator is used to bring the particles on a specific surface, e.g. a TEM grid, mica, glass etc.

A study was made of the sintering behavior of PbS which was shown to be necessary to obtain spherical and crystalline particles. The optical properties of thin films of PbS nanoparticles were studied in cooperation with the Low Temperature Physics section (Dr. M. Acet). As the sintering temperature is increased the band gap first decreases and then increases. The decrease in the band gap is associated with the recrystallisation of small particles to form large particles and the increase in the band gap is associated with the partial evaporation of larger particles. The same band gap is found for spherical particles and aggregates of smaller primary particles which suggests that the coupling between nanoparticles reduces the band gap.

Two radial DMAs for two different size ranges have been developed and tested at low pressures (down to 30 mbar). The radial DMAs have been successfully employed for analyzing the size of SnO system. Present investigations focus on the development of a laser ablation set up and to produce GaN nanoparticles using the same.

Publications


Nanda, K.K., Kruis, F.E. and Fissan, H., “Energy levels in embedded semiconductor nanoparticles and nanowires”, accepted by Nanoletters
Preparation Of Nanostructured SnO\textsubscript{2} Thin Films For Gas Sensor Applications

DFG SFB 445/ Project C1

Dipl.-Ing. M. K. Kennedy
Dr.- Ing. F.E. Kruis

In recent years there has been an increasing interest in the study of nanostructured thin films, because these films possess special electrical, optical, chemical and magnetic properties. Tin oxide is one of the most important semiconducting materials for gas sensors. Its electrical properties change as a result of the adsorption of gases onto the surface. In view of the high specific surface and activity of nanocrystalline tin oxide thin films, considerable improvement in sensing properties is expected. In order to understand the relationship between behaviour and particle size better it is necessary to generate monosized nanoparticles, because a distribution of particle sizes will decrease the special properties and complicate the interpretation of the experimental results.

The most important parameters of the particle preparation are crystallinity, stoichiometry, particle size and morphology thickness of the deposited particles. The deposited nanoparticles should be sintered to generate a contact between the particles. The dependence on the electrical properties of the parameters mentioned above provides the opportunity to optimise the sensorical properties of the films.

The set-up to produce the SnO\textsubscript{2} nanoparticles is going to be developed in the project A7.

In this project C1 the deposition of the nanoparticles will be optimised. In addition, the sintering processes must be examined. The stoichiometry will be measured by using AES/XPS/UPS, EDX and with RBS. The depth profile will also be investigated by means of RBS, the crystallinity by X-ray diffraction analysis and the morphology by TEM/AFM and SEM. An apparatus for measuring the gas-sensing properties, such as response time, charged carrier concentration and electron mobility has been built.

Gas concentrations from 10ppm to 10000 ppm can be adjusted by applying mass flow controllers (MFC). Accordingly the electrical properties of thin films of different particle sizes were investigated. Examination of the time-dependent change of conductivity while changing the gas type or the gas concentration were taken place. First van der Pauw measurements with monosized particles were done to obtain information about the conductivity of the sensor material. Furthermore, first impedance spectroscopy measurements were performed. Hall-measurements are going to be processed because of their ability to measure the charged carrier concentration and the mobility of these charged carriers separately in the thin films.

Publications
Laterally Controlled Nanoparticle Deposition from the Gas Phase

DFG

Co-operation with the Solid-State Electronics Department,
University of Duisburg, Prof. Tegude

Dipl.-Ing. F. Otten

Quantum devices have minimum feature sizes of a few nanometers. Producing small structures (d< 50 nm) by high resolution lithography reaches the economical and physical limits. The use of simpler nanopatterning techniques result in loss of structure control and engineering design. The goal of this research project is to implement the gas-phase synthesis of nanostructures into microelectronic technology to fulfill the design control.

Lead sulfide (PbS) powder is evaporated in a tube furnace at ambient pressure and nitrogen gas flow. After cooling nanoparticles are formed from the supersaturated gas. The nanoparticles are charged in a neutralizer and size selected in a differential mobility analyser, followed by a reheating process for compaction and crystallization of the nanoparticles. Finally the nanoparticles are deposited in an electrostatic precipitator forming thin films onto test substrates.

Electrostatic lenses formed by charged and patterned photoresist are employed to control the deposition process of the nanoparticles. This technique is a parallel process and has therefore a big advantage compared to serial pattern definition e.g. by electron beam lithography.

PbS nanoparticles are used, since PbS already exhibits quantization effects at feature sizes at about 20 nm and PbS nanoparticle films can be patterned by standard lithography. First results of SEM measurements confirm that nanoparticles are focused into the windows where the n-doped GaAs substrate is not covered by photoresist. The deposition area width of the nanoparticle film is smaller than the employed photoresist pattern. This offers the possibility to create chains of nanoparticles with a width of a few nanoparticle diameters. A simulation of the electrostatic field of patterned and charged photoresist proved that the observed focusing effect is due to the strong lateral electric field. The results can be transferred to other materials.

Publications

CVS of Nanocrystalline Metaloxide Films by Means of Pyrolysis of Molecular Metalsiloxides

Co-operation with Lehrstuhl für Anorganische Chemie I, Ruhr-Universität Bochum

Project Number: DFG KR 1723/3-1

Dr.-Ing. F.E. Kruis
Dr. Abhijit Roy

Semiconductor nanocrystals have attracted much attention due to their fundamental importance in bridging the gap between bulk matter and molecular species. The small size of nanoparticles, which is responsible for unusual electrical, optical and magnetic properties of nanoparticles and nanostructured materials, makes them suitable for new technological applications. Zinc Oxide (ZnO) is a very important semiconducting material because of its applications in gas sensors, catalysts, varistors, photoluminescent device, and optical wave guides. In view of these technological applications and fundamental research, it is necessary to prepare size-classified nanocrystalline ZnO particles and thin films.

In this project the monosized nanoparticles of ZnO will be generated using modified aerosol technologies. A novel molecular precursor will be used to generate the aerosol of ZnO. A specific size-fraction will be selected based on the size-dependent electrical mobility (Differential Mobility Analyzer) of the particles. In a furnace the particles, which might consist of aggregated primary particles, can be sintered in order to reach a more spherical form. An electrostatic precipitator will be used to bring the particles on a specific surface, e.g. a TEM grid. The detail characterization of the deposited nanoparticles will be done using XRD, TEM, AFM and SEM. A thorough investigation will be done on the deposited thin film ZnO for its application as a gas sensor and optoelectronic material.
Surface Chemistry and Impedance Studies on Aerosol Films of Tin Oxide Nanoparticles

Humboldt-Stiftung

Co-operation with Dept. of Physics, University of Duisburg, Prof. Lorke

Dr. R. Ramamoorthy

The advancement of the nanomaterials science has been well realized in the past two decades in the fields of quantum electronics, energy storage devices, (e.g. batteries, fuel cells), sensors, and catalysis etc. In the field of gas sensors, metal oxide semiconductors such as SnO₂, ZnO, TiO₂, etc. are widely used both in bulk and thin film forms. The high surface area of the nanoparticles of such materials leads to an enhancement in the sensitivity of the sensor devices especially when the particle size is very homogeneous. Our aim is to study the electrical resistivity/conductivity behaviors of the thin/ultrathin films of size classified semiconducting tin oxide (SnO₂) nanoparticles. Impedance analysis is an interesting technique to study the resistive behavior of the materials at different frequencies. It gives an insight over different mechanisms of the electrical conduction in polycrystalline materials. This technique is employed on the thin films of tin oxide nanoparticles. The SnO₂ aerosol thin films comprising nanometer sized (10 – 50 nm) particles are deposited on different substrates by a gas phase technique. The chemical compositional analysis, of the particle surface, is being carried out by Auger electron spectroscopy. The sensitivity and the selectivity of these films for different gases are under study by their frequency response of the conductance and hence a correlation between the grain size and the sensing properties will be established.
4.1.5. Ambient Aerosols

Characterization of Fine Airborne Particles at Carbon Black Working Places in Industry

Dr. T.A.J. Kuhlbusch
Dipl.-Ing. S. Neumann

Carbon Black is an industrial product for use in e.g. tyres and Xerox machines. It nearly consists of pure elemental carbon with only minute amounts of trace elements and organic carbon and has an amorphous structure. The primary Carbon Black particle size is around 10 nm. The Particle size of the processed particles range from around 1-10 µm depending on the later use.

Black Carbon or elemental carbon in ambient aerosols is of similar origin as industrial Carbon Black. These kinds of carbon are produced by all incomplete combustion processes, e.g. the combustion of diesel in cars. Black carbon, in contrast to Carbon Black, is always associated with relatively high amounts of organic carbon such as PAH’s. The main particle size range of Black Carbon in ambient aerosols ranges from 30 nm to about 1 µm. Airborne Black Carbon, in Europe mainly emitted by diesel engines, is currently discussed to be a health hazard.

Three field measurements at different Carbon Black Factories will be conducted to study the influence of Carbon Black production, processing and packaging on particle concentrations at corresponding working places.

Particle characterization will be conducted by means of Differential Mobility Particle Sizer (DMPS), Scanning Mobility Particle Sizer (SMPS), and Aerodynamic Particle Sizer (APS) to determine influences on particle number size distributions (0.02-10 µm aerodynamic diameter) and number concentrations. Especially the employment of the DMPS and SMPS will allow the determination of influences of the working area on particles in the size range below 300 nm. Mass concentrations of the size fractions PM 1, PM 2.5, and PM 10 will be measured with manual and automatic systems parallel to the particle number concentrations. These data will be used to study influences of the working process on mass concentrations. The laden filters of the manual samplers will be analyzed for Black Carbon and organic carbon to also study possible influences of the working process on the chemical composition of the aerosols.
Evaluation and Comparison of manual and automatic PM$_{2.5}$ Filtration Samplers for the European Harmonisation of Air Quality Assessments

Europe, CEN

Dr. T.A.J. Kuhlbusch

PM$_{2.5}$ beside PM$_{10}$ was set as a new standard in the 1$^{\text{st}}$ daughter directive related to ambient air quality of the European Union. No European standard for PM$_{2.5}$ currently exists and a working group for setting a standard measurement method for PM$_{2.5}$ was established within the European harmonisation agency (CEN). To evaluate and establish a European standard for PM$_{2.5}$, field measurements have to be conducted at different sites in Europe. A six month field campaign comparing 8 different manual and 4 automatic filtration samplers for PM$_{2.5}$ is conducted. Soot, particulate nitrate, PM$_{10}$, and all meteorological conditions are measured along with PM$_{2.5}$ to assess the quality of the data and investigate possible influences on PM$_{2.5}$ mass concentration measurements by various factors.
4.2 Habilitation Theses

Kruis, Frank Einar

Universität Duisburg 2001

There is a great deal of interest today in the special properties of nanoparticles and their potential applications. An overview of the potential functional applications, which include electronic, optical and magnetic applications, based on these special properties shows the broad range of possible applications. Most applications demand some control over particle size, width of the particle size distribution, crystallinity, stoichiometry, inter-particle connections and mixing or doping with other materials.

Gas-phase processes, although having some drawbacks, have the largest means of control and are therefore the method of choice here. Processes based on pure physical processes are used more often than chemical methods as they allow to obtain the highest purity. The evaporation-condensation method is chosen in this work as synthesis method. The Brownian coagulation inherent to this method makes it impossible to obtain narrow particle size distributions but allows to obtain a mixing of particles of different materials for the synthesis of nanocomposites.

The formation of nanoparticles by the evaporation-condensation technique was analyzed using a moment model describing nucleation, condensation and coagulation. Using the model, it was shown that the temperature in the evaporation furnace and the cooling rate determines the mean particle size and that an aerosoldynamical model allows the prediction of the temperatures needed for nanoparticle formation.

For describing more complicated systems having more degrees of freedom, such as distribution of particle sizes, different chemical compositions, distribution of charges and distribution of number of primary in an aggregate, a newly developed Direct Simulation Monte Carlo method was shown to be suitable. Two examples of practical relevance containing multi-dimensional particle dynamics were given: coagulation with chemical reaction in droplets (microreactors) and the coating of solid particles with nanoparticles.

Aggregation of mixtures of charged nanoparticles is useful for obtaining composites. This was studied by means of the Direct Simulation Monte Carlo method. The selectivity of mixing is characterized by means of the fraction of symmetric aggregates. It was shown that for each charge distribution different conditions lead to a highest possible selectivity of mixing.

Two chemical compounds were selected for further experimental study based on a literature review. One component is selected for its potential quantum confinement effects. PbS is a narrow-gap IV-VI semiconductor with a cubic rock salt structure and is an attractive candidate for the study of quantum confinement effects as its hole Bohr radius is 9 nm. This results in strong confinement effects. The confinement results in a blue shift in the optical absorption spectrum. The other material, SnOx, is selected for its gas-sensing properties.

A size uniformity is important in order to study or make use of quantum size effects, as a distribution of particle sizes will decrease or smear out these effects. In view of the high specific surface and activity of SnOx nanoparticles, considerable improvement in sensing properties is expected. In order to understand the relationship between gas-sensing behaviour and particle size better it is necessary to generate monodisperse nanoparticles, because a distribution of particle sizes will decrease the special properties and complicates the interpretation of the experimental results. At the moment no gas sensors based on almost equal-sized nanoparticles are available. For this goal, size fractionation by means of a Differential Mobility Analyzer was applied. This decreases the yield, but for functional
applications the quality more than the quantity of the nanoparticles is decisive, as most of the functional applications need only thin films.

Several new instruments have been developed in this work which allow to obtain more control over processes which are essential for the synthesis method chosen here. They allow nanoparticle charging, nanoparticle size fractionation and nanoparticle deposition.

A newly developed nanoparticle charger, the twin Hewitt charger, allows a larger fraction of the nanoparticles to be charged, which is important to get a higher yield. A higher yield would result in a shorter deposition time, which is important because the deposition takes at present hours to days. The instrument has been extensively investigated experimentally in order to find the optimal charging conditions.

Differential Mobility Analysis at lower pressures than atmospheric pressure has been investigated theoretically. It was found that the lower particle limit is not changed fundamentally with lower pressures when keeping the mass flow rate constant, but that the higher particle limit is decreased due to decrease of the maximum allowed field strength. A Differential Mobility Analyzer design for low pressure has been presented. It is important to perform size fractionation at pressures lower than atmospheric pressure, as usually the system pressure is decreased in order to get a higher yield of smaller nanoparticles and to increase the cleanness of the system.

An Electrostatic Precipitator has been developed which allows the investigation of electrical properties of nanoparticle films under clean conditions direct after deposition. This is especially important for semiconductor nanoparticles, where the surface influences the optical and electronic properties.

Synthesis of the semiconductors PbS and SnOx in form of almost equal-sized monocrystalline nanoparticles is showed to be possible with the help of carefully controlled techniques such as size fractionation and in-flight sintering. The processes of sintering of PbS has been investigated with help of a quantitative model which allowed the determination of sintering parameters, which are usually unknown for semiconducting materials. The process should be controlled such that sufficient sintering and crystallisation but no evaporation and re-condensation occurs, as this destroys the monodispersity.

As examples of the suitability of synthesized PbS and SnOx nanoparticles for functional applications, the absorption spectrum of PbS and the gas-sensitivity of thin films composed of SnOx nanoparticles were investigated. As a first indication of changing physical properties with particle size, the absorption spectrum of PbS particles is shown to shift toward the blue, indicative for quantum confinement effects. The measurements also indicate that the optical properties are strongly influenced by the handling of the nanoparticles directly after their formation, such as sintering and/or evaporation processes taking place in the sintering furnace. By choosing suitable initial mobility diameters, it should be possible to attain the commercially interesting bandgap range around 1.3 eV, used for very fast optical data transfer by means of GaAs solid state lasers. Further investigations should be accompanied by careful observations of the actual particle diameter and crystallinity after sintering at different temperatures, preferably by means of high-resolution transmission microscopy.

First measurements show that it is possible to create thin gas-sensitive layers composed of equal-sized SnO2 nanoparticles. The experimental procedure allows to produce thin films, in which the properties of the nanoparticles can be independently controlled by size-fractionation and in-flight sintering and oxidation. Further properties of the films, such as the inter-particle contacts which are very important for the electrical conductivity, can be influenced by post-deposition annealing. This opens a way to investigate fundamental gas-sensing properties of a better controlled microstructure than available at present.

Finally, the possibility of gas-phase synthesis of tailored composite nanoparticles by means of aggregation of oppositely charged, size-selected nanoparticles of two different materials is
shown. Electrical effects are applied for size-selection, selective mixing, separating the composite nanoparticles from unaggregated nanoparticles and the deposition of nanoaggregates. Size, size dispersion and materials can be selected independently. As an illustration of the method, composite nanoparticles consisting of differently sized Ag and PbS nanoparticles have been obtained. The method allows the investigation of fundamental properties of composite nanoparticles both in-flight and after deposition in form of a thin film.

Concluding, the field of nanoparticles for functional applications is exciting and rapidly developing. Synthesis and handling methods are available, but the main challenge lies in obtaining a better control over the particle characteristics so that the desired properties of the functional applications can be attained.
4.3 PhD Theses

Franken, Dirk
Modellierung und Optimierung eines integralen Meßverfahrens zur Partikelgrößenanlyse durch gezielte Aufladung der Aerosolpartikel

Universität Duisburg 2000

Referent: Prof. Dr.-Ing. Heinz Luck
Korreferent: Prof. Dr.-Ing. Heinz Fißan


Aus dem Modell der Partikelaufladung wurde zum einen die untere Messgrenze bezüglich der Partikelgröße und der Partikelanzahlkonzentration abgeleitet. Zum anderen wurde anhand der Kernfunktion begründet, dass die momentane Realisierung des Messprinzips eine sehr gute Bestimmung der Partikelanzahlkonzentration und des mittleren Durchmessers erlaubt. Die

4.4 MSc Theses

**Asbach, Christof**
Erweiterung und messtechnische Überprüfung der Invertierungs- und Auswertesoftware des DMPS und APS
Mai 2000

Im Fachgebiet Prozess- und Aerosolmesstechnik stehen zur Messung von Anzahlgrößenverteilungen ein DMPS für den Bereich $0,02 \, \mu m < d_{ae} < 1 \, \mu m$ und ein APS für den Bereich $0,5 \, \mu m < d_{ae} < 10 \, \mu m$ zur Verfügung. Das DMPS bestimmt auf Grund der elektrischen Mobilität zuvor neutralisierter Partikel den Stokes Durchmesser, das APS nutzt die Trägheit der Partikel um so den aerodynamischen Durchmesser zu bestimmen. Mit den Geräten ließen sich bislang nur separate Tabellen mit Anzahlgrößenverteilungen erstellen. Aufgabe dieser Arbeit war, die Auswerteprogramme so zu erweitern, dass die Daten von DMPS und APS in eine gemeinsame Datei geschrieben werden. Hierzu ist zunächst eine Umrechnung von Stokes und aerodynamischem Durchmesser ineinander vonnöten um eine gemeinsame Basis zu schaffen. Des Weiteren müssen die Konzentrationen auf die Bandbreite der Messkanäle normiert werden um eine Vergleichbarkeit der Daten zu Gewährleisten.


In einem weiteren Schritt wurde das Programm SiDAC Pro neu geschrieben, das Werte von DMPS und APS einliest und in normierte Anzahl- und Massenkonzentrationen umrechnet. Diese Daten lassen sich entweder nach den jeweiligen Anfangszeiten der Scans zeitlich sortieren, oder als Stundenmittelwerte darstellen. Für jeden DMPS Datensatz werden zudem die Fraktionen PM 0,1, und PM 1 berechnet, für jeden APS Datensatz die Fraktionen PM 1-2,5 und PM 1-10. Für zeitgleich gemessene DMPS und APS Daten werden hieraus weiterhin die Fraktionen PM 2,5 und PM 10 berechnet. Mit diesen Tabellen lassen sich nun durchgehende Anzahl- und Massengrößenverteilungen für den Bereich $0,02 \, \mu m < d_{ae} < 10 \, \mu m$ , oder mittlere Tagesgänge der einzelnen Größenfraktionen zur Darstellung von Messwerten erstellen.

Im Zuge einer Messkampagne am Mörsenbroicher Ei in Düsseldorf wurden DMPS und APS eingesetzt und ihre Feldtauglichkeit überprüft. Die Invertierung und Auswertung der Messdaten mit der weiterentwickelten Software SiDAC 2000 und dem neu entwickelten Programm SiDAC Pro war ebenfalls Gegenstand dieser Arbeit. Hierbei zeigten sich im Überlappungsbereich von DMPS und APS ca. 1 \, \mu m, unter Annahme einer mittleren Partikeldichte von 1,8 g/cm³, gute Übereinstimmungen, sowohl in der Anzahl- als auch in der Massengrößenverteilung. Die Tagesgänge zeigen einen stark vom Verkehr beeinflussten Verlauf.

**Ewald, Martin**
Meßtechnische Bestimmung der Partikelmassenkonzentration und Kohlenstofffraktionen an Arbeitsplätzen in der Pigment-Ruß-Industrie
Januar 2001

Vor dem Hintergrund, daß luftgetragene Partikel insbesondere Dieselrußpartikel negative gesundheitliche Auswirkungen haben, wurden im Rahmen eines Projektes der „International Carbon Black Association“ (ICBA) Messungen der Luft an verschiedenen Arbeitsplätzen in

Hufmann, Holger
Meßtechnische Bestimmung der Partikelanzahlkonzentration an verschiedenen Arbeitsplätzen in der Pigment-Ruß-Industrie
Juli 2001

4.5 Student Reports

Grotenburg, Karl
Automatisierung eines Filterprüfstandes zur Beladungsmessung an elektrisch unterstützten Faserfiltermedien
April 2000


4.6 Publications

Fissan, H.

**Charakterisierung von Staubpartikeln**
Haus der Technik e. V, Essen.; Veranstaltungsunterlagen "Messen von Feinstäuben PM 10 / PM 2,5 2001

Fissan, H.; Borggräfe, P.; Trampe, A.

**Quantitative Charakterisierung der Störungen in der Messkette von optische Partikelzählern**

Fissan, H.; Kennedy, M.; Kruis, F. E.

**Nanostructured Sensors**

Fissan, H.; Kruis, F. E.

**Synthesis of Composite Nanoparticle Pairs**
Abstracts AAAR 2000, 19th Annual AAAR Conference, St. Louis,USA, 486, 14D2, 2000

Fissan, H.; Marijnissen, J. C. M.

**European Aerosol Assembly (EAA)**
Proceedings of the Symposium on the History of Aerosol Science, held in Vienna, Austria, August 31 to September 2,1999, 2000

Fissan, H.; Trampe, A.; Borggräfe, P.

**Quantitative Characterization of Noise Sources in Optical Particle Counters**

Horodecki, J.; Fissan, H.

**Influence of Temperature an Humidity on on-line Particle Mass Concentration Measurement**
Abstracts AAAR 2000, 19th Annual AAAR Conference, St. Louis,USA, 178, 4PM5, 2000

John, A. C.; Kuhlbusch, T. A. J.; Fissan, H.; Pfeffer, H.-U.; Gladke, D.

**Measurements of PM 2.5 and PM 10 in the Ruhr-Area, Germany**
J. Aersol Sci., Vol. 31, No.11, 1385, 2000

John, A. C.; Kuhlbusch, T. A. J.; Fissan, H.; Schmidt, K.-G.; Schmidt, F., Pfeffer, H.-U.; Gladtke, D.

**Sampling of PM 10, PM 2.5 and Chemical Analysis by Total-Reflection X-Ray Fluorescence Analysis**
John, A. C.; Kuhlbusch, T. A. J.; Schmidt, K.-G.; Schmidt, F.; Pfeffer, U.; Gladtke, D.
Quell- und Prozeßuntersuchungen zu PM 10-Massenkonzentrationen

John, C.
Entwicklung eines PM 10 PM 2.5-Kaskadenimpaktors zur Messung der Emissionen von Feinstäuben
Haus der Technik e. V, Essen.; Veranstaltungsunterlagen "Messen von Feinstauben PM 10 / PM 2,5, 2001

Jordan, F.; Fissan, H.
Influence of Particle Charge Distribution on Filtration Efficiency in Electrified Fibrous Filtermedia
Abstracts AAAR 2000, 19th Annual AAAR Conference, St. Louis,USA, 56, 3D3, 2000

Kennedy, M. K.; Kruis, F. E.; Fissan, H.
Gas Phase Synthesis of Size Selected SnO2 Nanoparticles for Gas Sensor Applications

Kennedy, M. K.; Kruis, F. E.; Fissan, H.
Structural and Electrical Characterization of Monosized SnOx Thin Films for Gas Sensing Applications

Krinke, T. J.; Fissan, H.; Deppert, K.; Magnusen, M. H. Samuelson, L.
Positioning of Nanometer-Sized Particles on Flat Surfaces by Direct Deposition from the Gas Phase

Krinke, T.; Fissan, H.; Deppert, K.; Magnusen, M. H.; Samuelson, L.
Theoretical and Experimental Investigation of Nanoparticle Deposition

Krinke, T.; Fissan, H.; Deppert, K.; Magnusson, M. H.; Samuelson, L.
Experimental and Theoretical Study of Nanoparticle Deposition Using Electrostatic Interactions

Krinke, T.; Fissan, H.; Jordan, F.; Deppert, K.; Magnusen, M. H.; Samuelson, L.
Structured Deposition of Nanoparticles from the Gas Phase of an Aerosol
Kruis, F. E.; Fissan, H.
**Nanoparticle Charging Efficiencies of a Twin Hewitt Charger**

Kruis, F. E.; Maisels, A.; Fissan, H.
**Direct Simulation Monte Carlo Method for Particle Coagulation and Aggregation**

Kuhlbusch, T. A. J.
**Einfluss der Partikel- und Gasphasenemissionen auf PMx-Massenkonzentrationen - zukünftige Anforderungen an Emissionsmessungen**
Haus der Technik e. V, Essen.; Veranstaltungsunterlagen "Messen von Feinstäuben PM 10 / PM 2,5, 2000

Kuhlbusch, T. A. J.; Asbach, C.; John, A. C.; Fissan, H.; Schmidt, K.-G.; Schmidt, F.; Pfeffer, H.-U.; Gladtke, D.
**Correlation Studies of Particle Characteristics and Trace Gas Concentrations at a Traffic Site in Düsseldorf, Germany**

Kuhlbusch, T. A. J.; John, A. C.; Fissan, H.
**Diurnal Variations of Aerosol Characteristics at a Rural Measuring Site Close to the Ruhr-Area, Germany**

Kuis, F. E.; Fissan, H.
**Nanoparticle Charging in a Twin Hewitt Charger**

**Unipolar and Bipolar Aerosol Charging by UV-Radiation**

Maisels, A.; Kruis, F. E.;
**Synthesis of Composite Nanoparticle Pairs**

Maisels, A.; Kruis, F. E.; Fissan, H.
**Theoretical and Experimental Study of Mixing of Charged Nanoparticles**
Materials Science and Environmental Science and Engineering”, Dublin, Ireland, September 6, 2000, pp. 54 – 57, 2000
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5. Selected Publications

5.1 Sampling and Chemical Analysis by Total-Reflection X-Ray Fluorescence Spectrometry of Size-fractionated Ambient Aerosols and Emissions

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Abstract

Concerning the monitoring of particulate matter in ambient air, PM 10 and PM 2.5 have been recently introduced as new standards in the European Union [1]. Different estimates reveal that the new limit values will be most likely exceeded at different locations in Europe, so that measures will have to be taken to reduce PMx particle mass concentrations.

Because of these new requirements, source apportionment is necessary demanding multielement analysis and comparable methods for ambient air and emission sampling. Therefore, a special ambient air sampler has been constructed, as well as a specially designed emission sampler.

Total Reflection X-ray Fluorescence Analysis (TXRF) was used as a fast method with low detection limits for multielement analyses. For ambient air measurements, a specially designed sampling unit was built where the particle size classes 10 \textmu m-2.5 \textmu m and 2.5 \textmu m-1.0 \textmu m are directly impacted on TXRF sample carriers. An electrostatic precipitator (ESP) is used as a back-up filter to collect particles <1 \textmu m also directly on a TXRF sample carrier.
As air quality is affected by natural and anthropogenic sources, the emissions of particles < 10 µm and < 2.5 µm, respectively, have to be determined to quantify their contributions to the so-called coarse (2.5 µm-10 µm) and fine (< 2.5 µm) particle modes of ambient air. Therefore, an in-stack particle sampling system was developed, according to the new ambient air quality standards and in view of subsequent analysis by TXRF.

The newly developed samplers together with TXRF analyses were employed in field campaigns and proved the feasibility and capabilities of this approach. Ambient air data show that a wide spectrum of elements has been quantified. From those concentrations, PMx ratios were calculated which are an indicator for different sources for elements present in different size fractions as for example sulphur and calcium. Another result useful for source apportionment are the elemental day/night-ratios calculated to determine local contributions to PMx mass concentrations.

With regard to the emission measurements, results of mass and elemental concentrations obtained at two industrial processes show that the new PM 10/PM 2.5 cascade impactor and measurements with TXRF give characteristic fingerprints for different sources.

Size-fractionated ambient air and emission sampling together with multielement analysis proved to be a useful approach to derive information for source-receptor-modelling, a method necessary to set up effective abatement strategies to reduce PMx mass concentrations.

Keywords: Ambient aerosols; emissions; particulate matter; PMx sampling; TXRF
1. Introduction

Aerosols are known to have various effects on visibility, climate, and health. Until recently, the total mass of airborne particulate matter was the only standard of particulates used for air quality assessments.

New developments in aerosol measurement techniques allow size dependent analyses of e.g. number concentrations and chemical composition of aerosols. These developments enabled better classifications and more detailed studies of the effects of ambient aerosols. The investigations along with epidemiological studies indicate that mainly fine aerosols are responsible for health problems ranging from coughing, asthmatic attacks, to higher mortality [2, 3]. The above findings led to the implementation of new European standards [1] for inhalable particles (PM 10) and the alveolar size fraction PM 2.5 (particles with aerodynamic diameters < 10 µm or < 2.5 µm, respectively). The mass of these size fractions is believed to be a better indicator of health related issues than the previously used mass of total suspended particulates (TSP).

As these new limit values will be exceeded most likely at several locations in Europe [4, 5], so-called "action plans" will have to be set up to reduce high particle mass concentrations. Detailed information about ambient air, as well as PMx sources is required to set up effective strategies for air pollution control.

Therefore, multielement analyses are needed for a subsequent source-receptor modelling. We decided to use Total-Reflection X-Ray Fluorescence Spectrometry (TXRF) as a fast multielement method with low detection limits which was already applied for aerosol analysis [6-8]. It requires nearly no sample pretreatment if the samples are directly collected on a TXRF sample carrier.

Following the new air quality standards, new samplers for ambient air and emissions had to be designed. They were used for sampling of PMx particles and subsequent TXRF analyses. Here we present these samplers and give first results of ambient air and emission analyses.
2. Sampling and Chemical Analysis

2.1. Ambient air sampling

Total-Reflection X-Ray Fluorescence Analysis (TXRF) as a multielement method with low detection limits was chosen for characterisation of the aerosol under investigation. For this purpose, a specially designed sampling unit (ISP: Impactor + ElectroStatic Precipitator) was built [9]. It consists of the EPA design specified PM 10 inlet as a preseparator and a 2-stage cascade impactor where the particle size classes 10 µm-2.5 µm and 2.5 µm-1.0 µm are directly impacted on Vaseline-coated TXRF sample carriers. An electrostatic precipitator (ESP) was used as a back-up filter to collect particles <1 µm also directly on a TXRF sample carrier.

Special care was taken for choosing the material of the impactor [10, 11]. The device was made from aluminium and the Ematal treatment was applied for surface coating. Conductive glassy carbon sample carriers have not only been used in the ESP, but also in the impactor instead of Plexiglass carriers as the latter turned out to greatly enhance particle losses due to electrostatic charges of the material [9]. Before using the sampling unit (ISP) for the field measurements to determine the elemental composition of the mentioned particle size fractions, it was calibrated in the laboratory [9, 12]. The calibration curves proved to be in good agreement with the US EPA standards for PM 10 and PM 2.5.

Various commercially available filtration samplers were employed parallel to the ISP for ambient air sampling to collect PM 1, PM 2.5, and PM 10 on quartz fibre filters. These filters were used for gravimetric and subsequent chemical analyses.

2.2. Emission measurements

A plane filter device [13] measuring TSP is normally used for emission measurements. Available size fractionated in-stack measurement data are most often already some years old and do not reflect the actual "state of the art" concerning emission reduction technology.
According to the new ambient air standards, where monitoring changes from measuring total dust to smaller particle size fractions, also in-stack measurements determining PM 10 and PM 2.5 emissions should be conducted. As commercially available cascade impactors for exhaust gas did not meet these new requirements, a new in-stack PM 2.5/PM 10 cascade impactor (GMU-Impaktor johnas) was designed, constructed and calibrated in the laboratory [14]. Particles in the exhaust gas are isokinetically sucked into the inlet of the impactor which is similar to the one of the plane filter device. Instead of filtering the aerosol, the airborne dust is separated according to its aerodynamic diameter in the size fractions > 10 µm and 10 µm-2.5 µm which are collected on filters of the impaction stages, and particles < 2.5 µm which are collected on the backup filter. Again, calibration curves were determined and found to be in agreement with the US requirements for PMx sampling of ambient particles. This design enables comparable sampling of ambient air and emission aerosols.

2.3. Multi-elemental analysis

Elemental analyses were performed using an EXTRA II instrument (Rich. Seifert & Co., Ahrensburg, Germany). It was equipped with an 80 mm² Si(Li)-detector and a Mo tube which was operated at 50 kV and 5-38 mA. The multichannel analyser system QX 2000 was provided by Link Systems Ltd. An yttrium solution was used for quantification as internal standard. Measuring time was 300 s.

The ambient air samples were already deposited on the TXRF glassy carbon sample carriers, so as a sample preparation, only the internal standard had to be added. For each set of samples, field blanks were determined, which means that the "blank sample carriers" have been subjected to the same handling as the sample carriers (e.g. placing them into the ISP) just without the sampling procedure. These blank values were subtracted from the sample values.
The emission samples were collected on quartz fibre filters (Munktell MK 360) which were digested by HNO₃/HF/H₂O₂ pressure digestion. An aliquot of the solution was dropped on a quartz glass sample carrier, dried, and the internal standard added. Concentrations have been corrected for blank values determined by analysing filters which had not been used for aerosol sampling.

3. Results and Discussion

3.1. Ambient air measurements

To answer some of the questions related to the new PMx ambient air standards, a research project was set up where various measurement campaigns at different locations in the Ruhr area were conducted [5, 15]. Particle mass and number size distributions have been determined as well as the chemical composition of the PM 10, PM 2.5, and PM 1 size fraction.

Here results of only one campaign will be presented in view of the feasibility and capabilities of the applied method. This measurement campaign was carried out at a traffic related site in Düsseldorf (Germany) during 04-29 November 1999. The measurement station was located on a traffic island, with approximately 35,000 vehicles passing by on weekdays.

3.1.1. Mass concentrations

The PMx mass concentrations which were obtained gravimetrically from the filters of various high and low volume manual filtration samplers are summarised in Table 1. The annual limit value according to the 1st Daughter Directive [1] is 40 µg/m³, and daily limit values are not to exceed 50 µg/m³ more than 35 times a year. The PM 10 mass concentrations were 45 µg/m³ at this traffic site and indicate that the annual limit value will most likely be exceeded assuming that the determined average concentrations obtained during the measurement campaign are
representative for a whole year. The PMx mass ratios are 73% for PM 2.5 to PM 10, and about 60% of the mass of PM 10 are already contained in the PM 1 size fraction. This means that a large fraction of the particles < 10 µm is fine mode aerosol.

11 mass concentration data out of the 32 which were obtained during the measurement campaign exceeded 50 µg/m³. Projecting these data for one year, 125 exceedences of the limit value would occur. Even if this projection is more or less uncertain, it clearly shows that the new standards will most likely not be met and measures will have to be taken to reduce PM 10 and PM 2.5 concentrations. Measurements and model simulations have to be conducted for source apportionment which means that a wide range of parameters, e.g. elemental concentrations, are needed. Therefore multielement analyses were carried out by TXRF.

3.1.2. Elemental analysis

Elemental concentrations were determined using the ISP as sampling unit and the TXRF as a multi-elemental analytical method. Table 2 shows the concentrations which were determined for the size fractions PM 10, PM 2.5, and PM 1. The concentrations are on average higher by factors 2-20 than those found in the TXRF literature. This is not surprising as a large part of the aerosol sampling and characterisation by TXRF was carried out in remote areas as the north sea [16-18] or a high alpine research station [19] whereas the measurement campaign in Düsseldorf was conducted in a highly polluted area where total mass concentrations were also higher than those at the other sites. Elemental analyses of urban aerosols have been conducted in Vienna by proton induced X-Ray emission [20] with elemental as well as aerosol mass concentrations being about half of those determined in Düsseldorf.

From the concentrations obtained during the measurement campaign, the elemental PMx ratios have been calculated. In Fig. 1 the contributions of the particle size fractions < 1 µm, 1 µm-2.5 µm, and 2.5 µm-10 µm to PM 10 are shown. The elements are arranged according
to the contribution of the fine mode to PM 10. These elemental size ratios help to distinguish between particles that mainly occur in the fine mode formed by gas-to-particle conversion and combustion processes, and particles which are found in the coarse mode which mainly stem from mechanical processes and wind erosion. There are also elements which have different sources and which appear in the fine as well as in the coarse mode. An example of an element which is formed by gas-to-particle conversion is sulphur, where nearly 90 % of the PM 10 mass is already contained in the PM 2.5 fraction. In contrast to this, looking at silicon, iron or calcium, most of the mass of these elements is coarse mode aerosol which means that they stem from a different kind of sources.

For a closer look at the elements which were discussed only as average concentrations up to now, the time series of sulphur and calcium are presented as examples in Fig. 2 and Fig. 3. Looking at the sulphur concentrations, again it can be seen that most of the mass is already contained in the PM 1 fraction, and PM 2.5 and PM 10 have only little higher concentrations. In contrast, the time series of calcium points out that there is only very little mass in PM 1, and most of the mass is found in the coarse fraction.

Sampling time was normally 24h which is standard for ambient air monitoring. To obtain data with a higher time resolution, samples were taken from 6 in the morning to 8 in the evening, and from 8 in the evening to 6 of the next morning from the 17th to the 21st of September. No distinct diurnal pattern can be observed for sulphur. In the case of calcium, the time period of day and night sampling reveals clear differences between the samples. This means that there are local to regional sources and processes which are more active during daytime than during the night. These activities have to take place more or less in the vicinity of the measurement station, because the diurnal pattern could not be observed if the source is far away as it takes time for the air parcels to travel from the source to the point of the measurements.

The calculation of the ratios of the daytime to the nighttime concentrations was carried out for all the elements and for the 3 size fractions. The results are shown in Fig. 4. For calcium for
example, the daytime concentrations of PM 10 are a factor of 7.6 higher than the nighttime concentrations. A factor of 1 means that there are no differences between the day- and night concentrations, and a factor less than 1 means that higher concentrations have been observed during the night.

The highest changes in elemental day- and night concentrations have been found in the PM 10 fraction. This effect can be explained by the atmospheric lifetime of coarse particles which is in the range of hours. So particles which are produced by daytime activities are removed from the atmosphere for example by dry deposition and lead to quite low nighttime concentrations. These diurnal variations can be used to calculate the contribution of local sources. Day/night variations are only seen if the sources or processes leading to particle formations are situated in the vicinity of the measurement station.

TXRF multielement analyses turned out to be a very useful tool for measuring ambient air aerosols. However, these measurements only explain about 11 % (PM 1) to 20 % (PM 10) of the particle mass concentrations. Further chemical analyses from the filter samples showed that almost half of the PMx mass was comprised of carbon-containing particles (elemental carbon and organic carbon), and about one third consisted of sulphate, nitrate, and ammonium, with ca. 20 % which could not be identified with the applied methods. This means that different analytical methods have to be combined to gain information about the bulk composition. Still, TXRF or another method for multielement analysis is necessary to obtain data for fingerprint modelling.

3.2. Emission measurements

Emission measurements are needed beside ambient air measurements to identify sources. Thus, the GMU-Impaktor *johnas* was built. It was employed by the State Environmental Protection Agency of North Rhine Westphalia together with the plane filter device to carry out emission measurements determining PM 2.5, PM 10, and TSP mass concentrations at
various industrial plants. Additionally, chemical analyses by TXRF were performed for samples of two different industrial processes, both related to steel industry. Samples were taken in parallel by the impactor and the plane filter device in the exhaust gas stream behind the waste gas purification systems.

3.2.1. Mass concentrations

Table 3 shows the mass concentrations and particle size distributions of the emission measurements for the two processes. Sampling time was between 5 and 15 minutes. Mass concentrations are given in mg/m³, referring to the dry exhaust gas at 0°C and 1013 mbar. The table gives the mass concentrations of the 3 impactor stages > 10 µm, 10 µm-2.5 µm, and < 2.5 µm and the sum which was calculated from these size fractions, together with the mass concentration of TSP determined by the plane filter device. Because of particle losses at the impactor walls, the values of a filtration sampler will always be higher than the ones obtained from size fractionated aerosol sampling [14, 21, 22]. The data from Table 3 confirm the results already obtained from the calibration experiments that these losses depend on the size of the particles. The aerosol of process 1 mainly consists of fine particles, with 85 % being smaller than 2.5 µm. In this case, the losses in the impactor compared to the plane filter device are relatively low (e.g. 2 % for process 1). If a considerable amount of the sample is coarse mode dust as this is the case in process 2 where 66 % of the particles are larger than 2.5 µm, the difference between the filter sample and summarising the impactor stages can be as high as 20 %.

Looking at the concentrations of the aerosols, we do not only see a difference in particle size distributions, but also in mass concentrations of the emissions which are about a factor of 5 higher for process 1, compared to process 2.
3.2.2. Elemental analysis

Fig. 5 and Fig. 6 show the elements measured by TXRF for the 3 impactor stages > 10 μm, 10 μm-2.5 μm, and < 2.5 μm and the plane filter device (TSP) as percentages of the determined mass concentrations shown in Table 3. The elemental distributions in Fig. 5 and Fig. 6 show a big difference between the two processes. Process 1 is dominated by emissions of potassium, with small amounts of sulphur, calcium, iron and lead. In contrast to this, the emitted particles of process 2 mostly contain iron and calcium as well as potassium and some sulphur.

These patterns are in accordance with the steps of steel manufacturing where the emissions stem from. Process 1 is a so-called "hot process" and is the slag formation for steel production, involving the burning of iron ore, coke and aggregates like lime and dolomite. The exhaust gas of this process which reaches up to 700°C is cleaned by electrostatic filters. When the flue gas cools down, evaporated metals form small particles by gas-to-particle conversion. If this condensation takes places behind the waste gas treatment, particles are emitted which contain large amounts of potassium and sodium (the latter not detectable by the TXRF instrument used). Process 2 is a more or less "cold process" where the emissions from different steps of crushing the slag are combined and cleaned. This aerosol contains much more coarse particles and mainly consists of iron- and calcium oxides.

Looking at the minor constituents of the emitted aerosols, we also see distinct differences in the elemental composition. In Fig. 7 and Fig. 8 the concentrations are shown in μg/m³ on a logarithmic scale. The scaling of the two processes differs by a factor of 10. The graphs show a wide spectrum of elements which are emitted in concentration ranges of 6 orders of magnitude. Again, the differences of the size distribution between the two processes can be seen. While emissions are highest for the fine particles < 2.5 μm for nearly all of the elements in process 1 (except for titanium, chromium, and strontium, which have not been detected in the fine fraction), a lot of elements in process 2 as e.g. calcium, chromium, manganese, iron,
nickel, copper and zinc have the maximum of their concentrations in the size range 2.5 µm-10 µm.

Because of the logarithmic scale, it can not clearly be seen from the graphs that also the ratios of the elements which are important for fingerprint modelling differ very much for both the particle size fractions and the two processes. Table 4 gives the copper/nickel and iron/manganese ratios as an example revealing the differences in the composition of the samples (e.g. a Fe/Mn ratio of 52 (process 1) and 122 (process 2), calculated for particles 10 µm-2.5 µm, or of 35 (process 1) and 99 (process 2) for particles < 2.5 µm).

The data that have been presented are some examples which show that the size fractionated emission aerosols together with multielement analyses as they have been done by TXRF show characteristic patterns ("fingerprint") for different sources. The results of these investigations can in a next step be used to identify sources of ambient air pollution by "fingerprint modelling".

**Summary and Conclusions**

Monitoring of airborne particles has changed from the collection of TSP-dust to the sampling of smaller particle size fractions PM 10, PM 2.5, and even PM 1. The newly introduced European standards set up annual and daily limit values for PM 10 mass concentrations in ambient air. As it seems that the new limit values will not be met at various locations in Europe, strategies for air pollution control have to be developed. Ambient air and emission data of a wide range of elements obtained by comparable methods are needed for source apportionment by fingerprint modelling. In view of these new requirements, new samplers were designed and employed in field campaigns.

The ISP, a sampler specifically developed for TXRF analysis, was tested during a measurement campaign carried out at a traffic related site in Düsseldorf, Germany, in
November 1999. This new method provides the concentrations of PM 10, PM 2.5, and PM 1 of a wide spectrum of elements. In a following step, the ratios of the size fractions have been calculated because they help to differentiate sources. Emissions from combustion processes or gas-to-particle conversion can be distinguished from those which are generated by mechanical processes as this is the case e.g. for sulphur of which nearly 90% of the mass were found in the particles smaller than 2.5 µm and for example calcium which was determined nearly completely in the coarse particle fraction. As a further step in source apportionment, differences between the day- and nighttime elemental concentrations have been calculated. Changes are more pronounced for PM 10 than for the smaller size fractions with highest ratios for elements like calcium and silicon mostly contained in the coarse particles. These differences mean that there are sources or formation processes for these elements which are active during the day and which must be situated in the vicinity of the measurement site, so the measurements can be used to calculate the contribution of local sources to the PMx mass concentrations.

Up to now, only few size fractionated emission measurements and chemical analyses of the collected dust have been carried out. By comparing the emission profiles of two different industrial processes, it was demonstrated that PM 10 and PM 2.5 in-stack measurements using the newly developed GMU-Impaktor *johnas* together with TXRF multielement analyses is a useful tool to obtain detailed information ("fingerprints") of the emissions of different sources. However, digestion of the quartz fibre filters used in the impactor is still necessary for TXRF analysis. To avoid this pretreatment step, the design of a special device to directly sample emission aerosols on TXRF carriers is planned.

Combining the data obtainable from the newly developed PMx sampling devices, ambient air and emission data will give the data basis for fingerprint modelling to derive detailed source apportionments. This will help to set up more effective abatement strategies for "action plans" in accordance with the 1st daughter directive for air pollution control.
Acknowledgements
The ambient air sampling campaigns were financed by the Ministerium für Umwelt und Naturschutz, Landwirtschaft und Verbraucherschutz des Landes Nordrhein-Westfalen (MUNLV; former MURL: Ministerium für Umwelt, Raumordnung und Landwirtschaft). The emission measurements were conducted in the framework of a project financed by the Landesumweltamt Nordrhein-Westfalen (LUA NRW).

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Fig. 8. Emissions of the elements, industrial process 2
Table 1

Average mass concentrations and ratios of the ambient air measurements

<table>
<thead>
<tr>
<th>PMx</th>
<th>mass concentration</th>
<th>mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM 1</td>
<td>26 ± 7 µg/m³</td>
<td>PM 1/PM 10</td>
</tr>
<tr>
<td>PM 2.5</td>
<td>32 ± 11 µg/m³</td>
<td>PM 2.5/PM 10</td>
</tr>
<tr>
<td>PM 10</td>
<td>45 ± 17 µg/m³</td>
<td></td>
</tr>
</tbody>
</table>
Table 2

Average elemental concentrations of the PMx-size fractions in ambient air in ng/m³

<table>
<thead>
<tr>
<th></th>
<th>PM 10</th>
<th>PM 2.5</th>
<th>PM 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>841 ± 530</td>
<td>200 ± 187</td>
<td>b.d.l.</td>
</tr>
<tr>
<td>P</td>
<td>294 ± 197</td>
<td>242 ± 149</td>
<td>226 ± 45</td>
</tr>
<tr>
<td>S</td>
<td>2719 ± 957</td>
<td>2634 ± 1311</td>
<td>2087 ± 728</td>
</tr>
<tr>
<td>Cl</td>
<td>643 ± 592</td>
<td>239 ± 336</td>
<td>b.d.l.</td>
</tr>
<tr>
<td>K</td>
<td>274 ± 136</td>
<td>173 ± 131</td>
<td>139 ± 97</td>
</tr>
<tr>
<td>Ca</td>
<td>907 ± 496</td>
<td>170 ± 171</td>
<td>20 ± 11</td>
</tr>
<tr>
<td>Ti</td>
<td>87 ± 84</td>
<td>36 ± 49</td>
<td>9 ± 14</td>
</tr>
<tr>
<td>V</td>
<td>1.1 ± 2.2</td>
<td>1.1 ± 2.2</td>
<td>1.0 ± 2.1</td>
</tr>
<tr>
<td>Cr</td>
<td>65 ± 53</td>
<td>52 ± 46</td>
<td>39 ± 31</td>
</tr>
<tr>
<td>Mn</td>
<td>46 ± 34</td>
<td>32 ± 27</td>
<td>19 ± 15</td>
</tr>
<tr>
<td>Fe</td>
<td>2843 ± 1486</td>
<td>767 ± 609</td>
<td>108 ± 52</td>
</tr>
<tr>
<td>Ni</td>
<td>11.1 ± 8.6</td>
<td>8.8 ± 7.0</td>
<td>5.9 ± 4.1</td>
</tr>
<tr>
<td>Cu</td>
<td>102 ± 87</td>
<td>64 ± 77</td>
<td>38 ± 74</td>
</tr>
<tr>
<td>Zn</td>
<td>284 ± 428</td>
<td>115 ± 180</td>
<td>36 ± 82</td>
</tr>
<tr>
<td>Br</td>
<td>8.8 ± 4.2</td>
<td>7.9 ± 4.1</td>
<td>6.6 ± 4.0</td>
</tr>
<tr>
<td>Rb</td>
<td>0.5 ± 0.9</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
</tr>
<tr>
<td>Sr</td>
<td>7.1 ± 3.6</td>
<td>2.2 ± 1.5</td>
<td>0.7 ± 1.0</td>
</tr>
<tr>
<td>Zr</td>
<td>6.0 ± 3.3</td>
<td>1.6 ± 1.1</td>
<td>b.d.l.</td>
</tr>
<tr>
<td>Pb</td>
<td>42 ± 56</td>
<td>29 ± 32</td>
<td>16 ± 15</td>
</tr>
</tbody>
</table>

Σ of elements 9182 4775 2751

Average concentrations for the measurement period ± standard deviation; b.d.l.: below detection limit.
Table 3

Mass concentrations and particle size distributions of the emission measurements

<table>
<thead>
<tr>
<th>Particle size fraction</th>
<th>industrial process 1</th>
<th>industrial process 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>impactor stage &gt; 10 µm</td>
<td>5.4 mg/m³ 5.6 %</td>
<td>1.3 mg/m³ 7.4 %</td>
</tr>
<tr>
<td>impactor stage 10-2.5 µm</td>
<td>9.2 mg/m³ 9.6 %</td>
<td>8.5 mg/m³ 48.6 %</td>
</tr>
<tr>
<td>impactor stage &lt; 2.5 µm</td>
<td>81.1 mg/m³ 84.7 %</td>
<td>7.7 mg/m³ 44.0 %</td>
</tr>
<tr>
<td>Σ impactor</td>
<td>95.7 mg/m³ 100 %</td>
<td>17.5 mg/m³ 100 %</td>
</tr>
<tr>
<td>plane filter device (TSP)</td>
<td>97.3 mg/m³</td>
<td>21.8 mg/m³</td>
</tr>
</tbody>
</table>

Table 4

Elemental ratios Cu/Ni and Fe/Mn for different particle size fractions for the two processes

<table>
<thead>
<tr>
<th>elemental ratio</th>
<th>industrial process 1</th>
<th>industrial process 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Ni 10 µm</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Fe/Mn 10 µm</td>
<td>41</td>
<td>140</td>
</tr>
<tr>
<td>Cu/Ni 10-2.5 µm</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>Fe/Mn 10-2.5 µm</td>
<td>52</td>
<td>122</td>
</tr>
<tr>
<td>Cu/Ni &lt; 2.5 µm</td>
<td>63</td>
<td>2</td>
</tr>
<tr>
<td>Fe/Mn &lt; 2.5 µm</td>
<td>35</td>
<td>99</td>
</tr>
</tbody>
</table>
Fig. 1. Contribution of the elements to the different particle size fractions of PM 10

Fig. 2. Time series of sulphur concentrations determined with ISP / TXRF
Fig. 3. Time series of calcium concentrations, determined with ISP / TXRF

Fig. 4. Elemental mass concentration ratios day/night
Fig. 5. Percentage of the elements, industrial process 1

Fig. 6. Percentage of the elements, industrial process 2
Fig. 7. Emissions of the elements, industrial process 1

Fig. 8. Emissions of the elements, industrial process 2
5.2 Quantitative Characterisation of Noise in the Measurement Chain of Optical Particle Counter

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Keywords: optical particle counter, noise, background light, scattering

Abstract

Optical particle counters are deployed for monitoring possible contamination in gases by particles. The counting and sizing of particles are affected by various kinds of interference encountered during measurement. Two sources of interference are background light in the measurement chamber and electrical noise. Such interference causes measurement errors, which stem from the measurement equipment itself and not from the measured object or from the sampling. For the evaluation of measurement error by the particle counter itself, interference for a typical optical particle counter is identified and its effects on the measured results are discussed qualitatively. For the reduction of measurement error, quantitative determination of interference is important. It is only by doing this that we can judge which kind of interference has the more significant influence on measurement error. A method has been developed which makes it possible to determine individual components of interference. This paper presents a experimental method which allows separation of components of background light consisting of light scattering by the molecules and surface. The results of these measurements can be used to optimise existing particle counters as well as new equipment design.
Introduction

For counting and sizing particles, optical particle counters are deployed. As with every measurement process, readings will be specified only with finite errors of measurement. Among other sources, these errors will be caused by the interference within the measuring chain. There are two substantial groups of errors:

- Errors caused by the electrical noise in the measuring chain, and
- Errors caused by changes in the background light.

It is interference, which constitutes the so-called noise; the noise changes the amplitude of the signal stochastic. Since the amplitude of the signal will be analysed to determine the particle size, the real particle size distribution from the particle counter will be broadened [1]. Depending on the detector applied, interference can consist of additive short noise impulses with relatively high amplitude. Among the sources of these impulses will be the thermal electron emissions from the cathode of photo multipliers. If the amplitude of noise impulse transcends a given value, it will be counted as a particle and allocated a particle size class.

With higher particle number concentration, these counts should be ignored. If, however, aerosols with very low particle number concentrations are to be investigated, the measurement will be to a great extent falsified. Higher concentrations will be detected and a distribution shown which will normally reflect small particle sizes [2]. This error is thus particularly noticeable, if, for example, optical particle counters are being used for clean rooms monitoring or determination of cleanliness classes. This illustrates the problem of false count rate in measurements [3, 4].

Optical particle counters normally operate under standard temperature and pressure (STP), i.e. at an atmospheric pressure of approximately 1000 hPa and a temperature of 20°C with normal air as the carrier medium. Calibration of the equipment is therefore done under these
conditions. There is equipment, which can be used for measurements at higher pressures and temperatures, and especially with different types of gases. Like other equipment, these are calibrated under normal conditions as mentioned above. For process gas monitoring (gases with high pressure and high refractive index) [5, 6], as in the manufacturing of semiconductors, interference in the measurement chain can change in such a way that the particles are graded into other size classes. The interference responsible for this is termed background light. In the literature [7, 8] light scattered by molecules and that scattered by the surface of the measuring chamber are seen as the sources of background light, whereby the scattering by molecules is considered to be more significant and is therefore taken as the lower detection limit of particle size.

To improve optical particle counter performance, we require information on the type of interference, which has significant effect on measurement error. The difficulty here is to measure each interference type individually. In this paper, an experimental method is to be presented, with which interference in the measurement chain of any desired particle counter can be quantitatively determined. This way, the dominant interference source can be localised and specifically reduced.

**Construction of an optical particle counter**

An optical particle counter makes it possible to measure the particle number and, in connection with the measurement of the sample flow rate, to determine the particle number concentration. For the particle size, an optical equivalent diameter will be determined [16]. In a particle counter, therefore (Figure 1), individual particles with the sample flow rate will be transported through the measurement chamber.
Figure 1  Diagram of how an optical particle counter functions.

Inside the measurement chamber, the particles scatter the light that is emitted by the high intensity light source. Scattered light will be received by the photo detector and transformed into an electrical signal. If a certain value in the measured amplitude of the scattered light exceeds the lower detection limit, the signal processor of the optical particle counter determines whether the measured signal describes a particle and, if it does, classifies it into a particle size class.

If the signal were to be measured without noise, the result would not contain errors ascribed to the equipment.
**Interference**

To address the issue of permissive equipment errors and at the same time develop steps to minimise those errors, individual interference in the measurement chain must be explained. Individual interference can be deduced from the typical set-up of the measurement chain shown in Figure 2.

![Figure 2: Typical measurement chain of an optical particle counter and its noise sources.](image)

Nowadays monochromatic laser diodes and polychromatic discharge lamps are used as light sources in optical particle counters while gas laser and halogen lamps are rarely used anymore. Light from these sources contains interference in the optical power emitted, which generally comes from the electrical supply of the light source. The second interference type is photons noise, the cause of which lies in unsteady discharging processes and in the quantified nature of photons. Noise from white light sources is mainly produced by the turbulence of the gases in the gas bulb [9], which are of very low frequency. Noise from laser diodes [10, 11] decreases proportionally with frequency in the lower frequency range to 100 kHz and increases with frequency above 1GHz. Interference as a result of ageing and power supply
fluctuations are factored out here. The time progression of such noise is so slow compared to
the noise considered here that it could be compensated for by using simple methods.

In the measurement chamber interference results from light scattering by optical surfaces,
especially the lens and light trap surfaces. Reflections off the casing surfaces of the
measurement chamber are normally neglected. What is important is the light scattered by the
molecules of the gas medium. Light reflected by the surfaces and light scattered by the
molecules are collectively referred to as background light. Since light scattered by the
molecules changes with the thermodynamics of the gas medium, the condition of the gas
medium plays a role.

Photo diodes and photo multipliers are used as detectors for the light scattered by particles.
Electronic noise exists in the detectors, the individual characteristics of which differ
depending on detector type.

The last component of the measurement chain is the amplifier, which must amplify the signal
from the photo detector to a level, which is easy to process. Depending on the amplification
factor and the bandwidth of the amplifier, additional electrical noise is further added to the
overall signal composition.
There are, therefore, five significant interference types:

- Noise in the primary light,
- Electronic noise from the amplifier,
- Electronic noise from the photo detector,
- Light scattered by molecules and
- Light scattered by surfaces.

When characterising interference, one must differentiate between the stochastic and systematic components of the interference. Figure 3 represents a signal and its interference.

**Figure 3** The systematic component (DC or offset) and the stochastic component (AC) of a signal and its interference

The systematic component is the DC component in the signal, also frequently termed *offset*. The straight red line shows the DC component of the noisy signal. The stochastic or AC component is the classical noise.
These differentiation is necessary since the effects on the measurement results are different. The DC component limits the utilisation of the measurement range of the measurement chain but does not necessarily limit the lower detection limit with regard to particle size. As the DC component increases, the absolute signal amplitude of the particle at the output of the detector increases in the same magnitude. (Figure 4)

Figure 4  Effect of the DC component of the noise on the particle counter.
Therefore, the real size distribution is shifted to larger particle diameters. The DC component of interference limits the measurement range with regard to particle size. In extreme cases, this can cause saturation of the photo detector and, as a result, make it impossible to measure particles.

The AC component, on the other hand, influences the number and classification of the particles. From the noisy particle signal (shown with a solid line in Figure 5) no representation of the amplitude of the signal can be derived.

![Figure 5](image_url)  
**Figure 5**  *Particle signals; ideal and measured signals*

Figure 5 shows the curve representing the measured signal of a particle and compares it to the curve of a true or ideal signal. Due to the lack of an unambiguous representative amplitude, the particle counter cannot assign the particles to any one class without error. Furthermore, if the interference in the signal is below the lowest threshold set, this may also result in a false count. The signal of a single particle will be counted as two small particles or not counted at
all. Together, both effects lead to variation in the particle size distribution, which provides the particle counter measurement result. Figures 6 shows the differences in measurement results for a measurement without interference and a real measurement with interference.

**Figure 6**  Effects of noise on the particle size distribution.

The particle size distribution for real measurements shows not only a significant broadening of the distribution, but also a second mode with very small diameters. The broadening is ascribed to the errors in size determination, while the second mode in this case is only caused by the false count. The amplitude of the interference between particle signals is, in part, so high and long that the particles are interpreted as small.

**Quantitative determination of individual interference**

Individual interference measurement requires a system, which can measure a small voltage with high time resolution. The intrinsic noise and the offset of the measurement system must be known. Additionally, the electrical input of the measuring system must be short circuited and a voltage measurement done. The DC voltage measured will therefore be deducted from
further measurements by simple arithmetic subtraction, and the noise by geometric subtraction. In the same way, other components of interference are respectively subtracted from one another.

The procedure for the quantitative determination interference mentioned above is subdivided into four steps:

- Determination of amplifier interference,
- Determination of photo detector interference,
- Determination of light source interference and
- Determination of background light and distribution of interference as a result of scattering by molecules and surfaces.

- Determination of amplifier interference

The electrical current of photo detector signals is normally so small such that it must be amplified using a trans-impedance amplifier and then transformed to voltage. The noise created by the trans-impedance amplifier depends critically on the components used and its frequency bandwidth. These measurements must be done analogously with the determination of the intrinsic noise of the measurement equipment. The input from the amplifier is short circuited, and the DC and AC components are measured.

- Determination of photo detector interference

First, the detector is darkened. Then, the Schrot noise caused by the dark current, the thermal noise from the inner resistor of the photo detector and the dark current itself must be determined. The next step involves irradiating the detector with a light source, whereby the light intensity must be varied by a neutral filter. The measurement results will give the Schrot
noise, which is caused by the photocurrent. Particularly with a photo multiplier, noise behaviour will vary greatly with the light intensity.

- Determination of light source interference

To describe noise in the light source the term RIN, or Relative Intensity Noise will be applied. The RIN-value is calculated from the quadratic ratio of rms power $RMS_{\text{lightsource}}$ and in relation with the constant light power $P_{\text{lightsource}}$.

$$RIN = \frac{RMS_{\text{lightsource}}^2}{P_{\text{lightsource}}^2}$$  \hspace{1cm} \text{Eq.(1)}$$

The noise from the light source should be measured with a photo diode since with these detectors, thermal noise is dominant. This type of noise is independent of the irradiated light power as long as no heat is produced. Consequently, it can easily be subtracted from the measured values, which still contain DC and noise components in the measurement chain.

Table 1 shows the result of RIN value for two different light sources.

<table>
<thead>
<tr>
<th></th>
<th>Laser diode</th>
<th>White light</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type Sony SLD201-3</td>
<td>Type Osram HLX 100W</td>
</tr>
<tr>
<td>Fluctuation</td>
<td>6.66 mV</td>
<td>5.5801 mV</td>
</tr>
<tr>
<td>DC component</td>
<td>3.876 V</td>
<td>2.998V</td>
</tr>
<tr>
<td>RIN</td>
<td>$2.5 \cdot 10^{-6}$</td>
<td>$3.46 \cdot 10^{-6}$</td>
</tr>
</tbody>
</table>

Table 1 \hspace{1cm} \textit{Relative Intensity Noise of two light sources}
The DC component in this case describes the effective signal of the light power. The small component of noise in the light power can be regarded as characteristic. Therefore the resulting deviations from true readings can normally be neglected.

- Determination of background light and distribution of interference as a result of scattering by molecules and surfaces.

In the measurement chamber of the particle counter, background light is produced by light scattered by surfaces and molecules in the measurement gas sample. Surface scattering is due to the fact that light is scattered by an optical system, which is not ideal, and thus the beams are not completely absorbed. The AC component of surface scattered light noise results from light source noise and the discrete nature of light. In the measurement gas sample, gas molecules scatter light like particles. Molecule scattering is dependent on the concentration of the molecules and the refractive index as well as the electrical susceptibility $\chi$ of the gas. The effect of molecule scattering was originally described by Lord Rayleigh. In this case, light scattered in the inner chamber of the casing is neglected. This component is part of the component of the scattered light already mentioned, which is in turn reflected on the inner surface of the chamber casing. Only the component detected by the optical detector is to be measured. The power of this component compared with others is so small that it is not to be taken into consideration.

Under standard conditions scattering of light by molecules can only be measured together with scattering of light by surfaces. It is only in an evacuated measurement chamber that one can measure individual components. At 0 bar pressure there are no molecules in the measurement chamber and background light exists only due to scattering of light by surfaces. Measurement in a vacuum is possible, however, but only for a relatively high expenditure of money and
manpower. However, another alternative exists due to the fact that measurement of the total background light is dependent on pressure. The scattered light by surfaces is independent of the thermodynamic state of the gas and remains constant at varying pressure. In fact, the light scattered by molecules increases proportionally with pressure (see equation 4 below). From the measured values a straight-line graph can be drawn and extrapolated to 0°bar. At a pressure of 0°bar only the light scattered by surfaces still exists. Besides the DC component, the noise from scattering by molecules also comprises an AC component. The AC component of light scattered by molecules is produced by the noise of the light source and the Brownian motion of the molecules in the laser beam. The AC component produced by the light source can be calculated by multiplying the DC component of light scattered by molecules with the RIN value of the light source.

\[ P_{Molecule,RMS} = P_{Molecule,DC\text{Component}} \cdot \sqrt{RIN_{\text{Lightsource}}} \]  \hspace{1cm} \text{Eq.(2)}

The AC component of the scattering of light resulting from the Brownian motion can be determined by geometrical subtraction of individual components. Additionally AC components of measurement chamber and surface scattering are deducted from the AC component of the background light. This gives us the AC component of scattering by molecules, from which the component in equation 2 is then subtracted. The end result is the AC component of light scattered by molecules as a result of Brownian motion. With this, all the components of the background light have been determined and can be evaluated individually.

However, the pressure in the measurement chamber of the optical particle counter cannot always be varied in a broad range to determine the scattering of light in the measurement
chamber. In this case, one has to apply a method in which individual measurements at a known pressure are sufficient. The process of light scattering by molecules as a function of the thermodynamic state of the gas medium is be described by other advanced theory approaches. As a starting equation for the development of an advanced model, the power density of the scattered light $I_{\text{total}}$ by $N$ Molecules in the measurement sample $V_{\text{Scattered}}$ is calculated as follows [11]:

$$I_{\text{total}} = I_0 \frac{\pi^2 \cdot \chi^2}{A^2 \cdot r^2} \cdot \frac{V_{\text{Scattered}}^2}{N} \cdot \frac{1 + \cos^2 \theta}{2}$$  \hspace{1cm} \text{Eq.(3)}

$N \triangleq \text{Number of molecules}$

$r \triangleq \text{Interval vector}$

$I_0 \triangleq \text{Power density of the light in the measurement sample}$

$\theta \triangleq \text{Steradian between molecules and detector}$

The electrical susceptibility and the number concentration of the molecules are both dependent on the thermodynamic state of the aerosol [13]. This dependency is calculated as follows:

$$\chi(p, T) = \chi_0 \cdot \frac{p}{p_0} \cdot \frac{T_0}{T} \cdot N = \frac{p}{k \cdot T}$$  \hspace{1cm} \text{Eq.(4)}

$p \triangleq \text{Pressure}$

$T \triangleq \text{Temperature}$

$k \triangleq \text{Boltzmann constant}$

$\chi_0 \triangleq \text{Electrical susceptibility at temperature } T_0 \text{ and at pressure } p_0$

The power density of the laser beam is calculated from the power $P_{\text{Laser}}$ and its cross-section in the measurement volume is $A_{\text{Laser}}$. This gives us the following equation for the light scattered by molecules:
The power density increases proportionally with pressure and decreases hyperbolically with temperature.

The size of the measurement volume is calculated from the optical configuration. This configuration consists of the optical system (including lenses, etc.), the size of the light sensitivity surface of the photo detector and the cross-section area of the light beam. Methods of calculating the measurement volume are outlined in the literature [14, 15]. By integrating the density of the light scattered by the molecules over the detector’s geometric area, the power of light scattered by the molecules measured by the photo detector can be calculated.

\[
P_{\text{Molecule}} = \int_{\text{Detector}} \int \left[ I_{\text{Molecule}}(r, \theta) \cdot dA_{\text{Detector}} \right] \\
\text{Eq.(6)}
\]

With the help of the detector’s data, the DC component of the signal of the light scattered by the molecules can be calculated as a function—the thermodynamic state of the gas medium. As described above, these components of the signal will be subtracted from the measured value of background light. For this reason, the measurement of background light in one thermodynamic state suffices.

Both methods used to calculate the components of the background light of the optical counter can now be compared. A special construction (Figure 7) has been developed for the purpose of analysing aerosols at high pressure and temperature. In it, only the optical system is situated within the measurement chamber, while other components, such as the light source and the photo diode, are situated outside the measurement chamber.
Figure 7  Measurement construction for determining light scattering by molecules depending on pressure and type of gas.

The primary light is directed to the measurement chamber by optical fibres, which are also used to direct scattered light out of the chamber. The measurement chamber is brought to a particular pressure by inflating in it particle free gas. A transient recorder is then used to measure the background light of different gases.

Figure 8 shows the results of these measurements; the measured light power of the background light less the power of surface scattered light.
The power of light scattered by molecules dependent on pressure for different gases.

The experimentally determined and calculated scattered power is contrasted dependent on pressure and gas type. The measured value of light power in the sample is 23.3°mW. Other measured parameters and those arrived at through calculations are compiled in table 2.
Table 2: Parameters of the measurements and calculation of the power of light scattered by molecules

In principle, it is noted that the power of scattered light by molecules increases proportionally to pressure and depends on the type of gas used. The larger the gas molecules are and the more molecules per volume available, the greater the power of the scattered light. The values calculated using the approach described above tally well with the measurement results.

To measure the dependency of scattering of light by molecules on temperature, a gas flow is filtered and passed through a flow controller at a constant flow rate. The gas is led into the measurement volume through a very thin steel tube. The steel tube is heated by a resistor coil, and the gas temperature to be measured is sensed by a thermocouple directly at the exit of the...
measurement volume. The construction is otherwise identical to the scattered light measurement equipment described above.

In the following figure, the measured power of background light is presented.

![Figure 9](image)

**Figure 9** Power of light scattered by molecules dependent on temperature for different gases.

The comparison shows the experimentally determined and calculated power of light scattered by molecules dependent on temperature and gas type. For the calculation, the same parameters as in the pressure dependent consideration have been used. It can be seen from the results that the power of scattered light decreases hyperbolically with temperature. The decline differs for each of the three gas types considered.
The two comparisons between experimentally determined and calculated power for scattered light shows sufficiently good conformity such that the theoretical approach can be applied to estimate individual components of the background light.

**Conclusion**

To reduce measurement error, this paper has identified five essential kinds of interference in a typical particle counter. A four step method has been demonstrated which can determine all interference. Interference in primary light and electronic measurement chains are determined using different measurement methods. What is known as background light consists of interference through light scattered by both molecules and surfaces. These two measurements cannot be separately determined by direct measurement. In an ideal vacuum, there are no molecules to scatter light; we have presented two methods that can nonetheless be used to separate light scattered by molecules and that scattered by surfaces. In the first case, background light at different pressures in the measurement chamber of the optical particle counter was measured and the curve was extrapolated to zero; the result represents the light scattered by the surface. If pressure variation is not possible, scattering of light by molecules can be calculated as a function of temperature and pressure. For this purpose, a model for light scattered by molecules was shown. This approach was compared with the readings for the light scattering by molecules and surfaces and the two correlated highly. If the necessary data for calculating light scattering by molecules is available, this method of determining interference is preferable. With the results, it is possible to predict which interference types are most relevant and where improvement is really worthwhile.
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Determination of particle size distribution – Single Particle Light Interaction Methods –

Part 1: Light Interaction Considerations
5.3 Dynamics of the Aerosol Particle Photocharging Process

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Submitted to Applied Physics Letters

In photocharging process aerosol particles become electrically charged by interaction with high energy photons, e.g. ultraviolet (UV) irradiation. Photon adsorption by particles leads to electron emission and, as result, particles become positively charged. While maximal achievable charges were being described in previous studies in dependency on particle and irradiation parameters, the influence of photo-emitted charges on the charging process was not taken into account.

In this work it is shown that these emitted charges interact with the particles which heavily influences the entire process.

This complex process (charging particles positively by photons and simultaneously negatively by ions) is described in the actual work by a set of differential equations. These differential equations are solved numerically and with simplifying assumptions analytically. The general case of a multi-component polydisperse aerosol is considered. Analytical results coincide with numerical ones for a wide range of initial parameters, as was found by comparison of the analytical and numerical solutions. The evaluated analytical expressions allow to quantify the influence of the guiding processes and limits of the process which is heavily influenced by the previously neglected free ions. Model results explain e.g. experimentally observed decrease of particle charge by increase of particle number concentration. As result of this work, the particle charge distribution obtained by photocharging process can be considered now as a known function of aerosol parameters and parameters of UV-irradiation.

PACS numbers: 82.70.R, 92.60.Mt, 92.60.Pw
I. INTRODUCTION

In the last two decades nanoparticles became the object of intensive interest in science and technology.\textsuperscript{1-3} While the importance of the aerosol phase based synthesis is increasing among techniques for nanoparticle production,\textsuperscript{4,5} it is required for the most applications to monitor the aerosol particles motion. The common way to solve this problem is to charge aerosol particles electrically introducing Coulomb force as a tool allowing to affect the particle motion in a well-defined manner. Electrical charges on the particles enable the study of particle size distributions,\textsuperscript{6} the particle sampling from gas flows and deposition on given surfaces,\textsuperscript{7} the improvement of the efficiency of particle removal from the gas by filtration or precipitation,\textsuperscript{8,9} the synthesis of particles of defined size and chemical composition\textsuperscript{10} etc. Though, particles may be charged after production process (combustion aerosols, particle synthesis in plasma etc.), it is often required to have some defined charge distribution in the aerosol.

The problem of particle charging is non-trivial. The most known possibility to charge particles electrically bipolar is to expose them to radioactive radiation. The main advantage of this procedure is a known charge distribution,\textsuperscript{11} which depends only on particle size and gas temperature. However, the fraction of charged particles is relatively low.

Unipolar electrostatic diffusion chargers,\textsuperscript{12,13} based on a corona discharge were considered as an alternative to the radioactive bipolar chargers due to a higher charging efficiency. Contrary to radioactive chargers the charge distribution in diffusion chargers depends as well on particle size and gas temperature as on technological parameters (charger geometry, gas flow, ion concentration, etc). For particles with sizes under 20 nm the charging efficiency of unipolar electrostatic chargers is known to be low.

An interesting approach was proposed in the range of works,\textsuperscript{14-16} where ultraviolet irradiation was applied for particle charging. High charging efficiencies were achieved in diluted aerosols due to photo-emission of electrons. Specially for nanometer-sized particles
the obtained charging efficiencies were much higher than that for unipolar diffusion chargers. However, the shape of the charge distribution was still unknown. Furthermore, assuming the ultraviolet irradiation as the only process influencing the particle charge, the authors neglected the flux of negative ions onto particles. This diffusion process, however, is very important as was proven later.\textsuperscript{17} The authors considered a monodisperse aerosol, coming out from an irradiated region containing positively charged particles (seven elementary charges pro particle) and negative gas ions with the number concentration of seven times the particle number concentration. It was shown neglecting ion losses in the system, that the aerosol reaches zero mean charge after some time, i.e. the aerosol becomes discharged. The time needed to achieve zero mean charge reduces for increasing particle number concentration.

Up to now, no model exists, describing the evolution of the aerosol charge distribution under simultaneous action of ultraviolet irradiation and diffusive (dis-)charging by gas ions. A model for this dynamic process, taking into account the simultaneity of photoelectric charging and adsorption of gas ions is presented in the actual work. Under practical conditions measurements of the particle charge distribution are hardly possible in the irradiated region. Connections between irradiated region and measurement equipment are unavoidable. While no photocharging in these connections takes place, diffusion (dis-)charging of particles continuously takes place. With the aim to make theoretically obtained results accessible for experimental studies, particle (dis-)charging in these connections (so-called irradiation-free region) is also considered. Diffusion losses of ions are neglected, but the model can be simply extended for that case. Particle number concentration is considered to be constant, neglecting in this way aggregation, sedimentation and diffusion losses. The influence of aerosol parameters (particle size, number concentration, particle material) and parameters of UV-irradiation (lamp intensity, wavelength) is studied numerically for the complex instationary case. An analytical solution is obtained with simplifying assumptions. The range of the
applicability for these simplifying assumptions is determined by comparison of the results of analytical and numerical solutions.

II. THEORETICAL MODEL AND SOLUTION

A. Model of photocharging process

A principal photoelectric charger is shown schematically in Fig. 1. Aerosol path can be divided in two different regions. In the first region, particles are exposed to UV-irradiation. If the photon energy is higher than potential barrier for electron emission, which depends on particle material, charge level and geometry, free electrons can be emitted from the particle surface to the environment. These electrons become rapidly captured by gas molecules and build up ions. The ions can be adsorbed by particles due to their diffusive motion and the attracting electric force. Therefore, the charge level on particles within the irradiated region is determined simultaneously by photoelectric and diffusion charging.

The second region includes the irradiation-free zone. Leaving the irradiated region, the aerosol contains positively charged particles and negative gas ions. The ions are tending to discharge particles; here only diffusion charging is the mechanism which changes particle charge level. The dynamic behaviour of the charging process for an aerosol containing chemically dissimilar particles of different sizes can be described by the following sectional system of differential equations:

\[
\frac{dn_i}{dt} = \sum_{c_n} \sum_{R_{p_{\text{min}}}} \sum_{q_{\text{max}}} (\alpha^{q_{\rightarrow q+1}} N_{q,R_p,c_n}^{q_{\rightarrow q+1}} - n_i \beta^{q_{\rightarrow q-1}} N_{q,R_p,c_n}^{q_{\rightarrow q-1}})
\]

\[
\frac{dN_{q,R_p,c_n}}{dt} = \left[\alpha^{q_{\rightarrow q-1}} N_{q-1,R_p,c_n}^{q_{\rightarrow q-1}} - \alpha^{q_{\rightarrow q+1}} N_{q,R_p,c_n}^{q_{\rightarrow q+1}}\right] + n_i \left[\beta^{q_{\rightarrow q-1}} N_{q+1,R_p,c_n}^{q_{\rightarrow q-1}} - \beta^{q_{\rightarrow q+1}} N_{q,R_p,c_n}^{q_{\rightarrow q+1}}\right] \tag{1}
\]

The first differential equation describes the balance of the negative ion concentration \(n_i\) taken over all particle size-material fractions. In photocharging process all ions have one negative
elementary charge and equal mass which depends on the gas. The concentration of ions grows due to photoemission of electrons and decreases due to absorption of ions by the aerosol particles in the diffusion charging process. The second set of differential equations in system (1) represents the concentration balance \( N_{q, m, c_\alpha} \) for particles of the radius \( R_p \) and chemical composition \( C_m \) carrying a number of elementary charges \( q \). \( \alpha^{q \rightarrow q+1} \) represents the combination coefficient for photocharging of particle from charge level \( q \) to \( q+1 \). For spherical particles \( \alpha^{q \rightarrow q+1} \) can be determined as:

\[
\alpha^{q \rightarrow q+1} = K_c \left( \frac{h \nu - \Phi^{q \rightarrow q+1}}{\text{quantum yield}} \right) m \frac{l \pi R_p^2}{h \nu \text{ photon flux}}
\]

with material-dependent empirical constants \( K_c \) and \( m \), \( h \nu \) - photon energy, \( I \) - irradiation intensity and \( \Phi^{q \rightarrow q+1} \) - potential barrier which must be overcame by an electron to escape spherical particle with \( q \) elementary charges. As calculated in:

\[
\Phi^{q \rightarrow q+1} = \Phi_\infty + \frac{e^2(q+1)}{4 \pi \varepsilon_\alpha R_p} - \frac{5}{8} \frac{e^2}{4 \pi \varepsilon_\alpha R_p}
\]

with \( \Phi_\infty \) and \( e \) being potential barrier for a plane surface of that material and elementary charge, respectively. Outside the irradiated region the terms corresponding to photoelectric charging are excluded from system of differential equations (1) by taking the zero values for all \( \alpha \)'s, i.e. the irradiation intensity is zero.

\( n, \beta^{q \rightarrow q-1} \) in system (1) is the combination coefficient for diffusion charging of aerosol particles by ions from charge level \( q \) to \( q-1 \). For spherical particles \( \beta^{q \rightarrow q-1} \) is determined as:

\[
\beta^{q \rightarrow q-1} = \frac{4 \pi R_p D_i}{4R_p D_i \delta^2 \sqrt{\alpha}} \cdot \exp \left( \frac{\phi(\delta, q)}{k_B T} \right) + \int_0^\infty \exp \left( -\frac{\phi \left( \frac{R_p}{\delta}, q \right)}{k_B T} \right) dy
\]
$D_i$ - diffusion coefficient for ions, $\bar{v}_i$ - ion mean thermal velocity, $T$ - gas temperature and $k_B$ - Boltzmann constant. $\phi(l,q)$ is the interaction potential between ion and $q$-charged particle and is determined by superposition of Coulomb and image forces:

$$\phi(l, q) = \frac{e^2}{4\pi\varepsilon_0} \left( \frac{q}{l} - K(l) \frac{R_p^3}{2l^2(l^2 - R_p^2)} \right)$$  \hspace{1cm} (5)

$K$ - material-dependent function, $l$ - distance from particle.

$\delta$ in Eq. (4) is the radius of Fuchs's adsorbing sphere:

$$\delta = \frac{R_p}{Kn_i^2} \left( \frac{(1 + Kn_i)^5}{5} - \frac{(1 + Kn_i^2)(1 + Kn_i)^3}{3} + \frac{2(1 + Kn_i^2)^{3/2}}{15} \right)$$  \hspace{1cm} (6)

$Kn_i$ - Knudsen number for ions.

Equations (2)-(6) allow to calculate combination coefficients for each size-material fraction of the aerosol charged, which is required for solving the system of differential equations (1).

**B. Analytical solution in general case**

The analytical solution of the system of differential equations (1) is in the general case nearly impossible. First of all, the combination coefficients for photocharging and, specially, for diffusion charging have an extremely complex form. However, it is possible to find simplified expressions for this combination coefficients: it is allowed to neglect the small influence of the image forces in Eqs. (3) and (5) for large $q$ and to consider the exponential term in the denominator of the right side of Eq. (4) as negligible compared to one. Taking combination coefficients in the simplified form it is obtained:

$$\alpha^{q \rightarrow q+1} = \frac{K_c l}{h \nu} n \left( h \nu - \Phi_0 - \frac{(q + 1)e^2}{4\pi\varepsilon_0 R_p} \right)^m; \quad n \beta^{q \rightarrow q-1} = 4\pi R_p D_i n_i \frac{qe^2}{4\pi\varepsilon_0 R_p k_BT},$$  \hspace{1cm} (7)
Now, formally replacing sums in the first equation of system (1) by integrals, which can be made for relatively broad charge-, size- and material- distribution functions, the balance equation of the ion concentration can be written as:

\[
\frac{dn_i}{dt} = \int \int \alpha_{c>q} c(C_m, R_p) dR_p dC_m - n_i \int \int \beta_{c>q} c(C_m, R_p) dR_p dC_m
\]

with \( c(C_m, R_p) \) and \( \langle q \rangle \) being the density distribution function of the size-material concentration and the mean charge, respectively. For a particle number concentration \( N \) this values are defined:

\[
\langle q \rangle = \frac{n_i}{N},
\]

\[
\int \int c(C_m, R_p) dR_p dC_m = N, \tag{9}
\]

The third and fourth equations in Eqs. (9) are definitions, useful for further calculations. Taking the combination coefficient in the form of Eq. (7) and using Eq. (9) for integration of Eq. (8) one obtains for the change in ion concentration:

\[
\frac{dn_i}{dt} = N \frac{K_e I}{hV} \pi \langle (R_p (hV - \Phi_\omega))^2 \rangle - 2N \frac{K_e I}{hV} \pi \langle (R_p (hV - \Phi_\omega))^4 \rangle \frac{e^2}{4 \pi \varepsilon_0} \frac{n_i}{N} \\
+ \frac{K_e I}{hV} \pi \left( \frac{e^2}{4 \pi \varepsilon_0} \right)^2 \frac{n_i^2}{N} - \frac{D_e e^2}{\varepsilon_0 k_B T} n_i^2 \tag{10}
\]

In calculations \( m=2 \) was taken, as was determined for metal particles and particles from combustion processes.\(^{22}\) Equation (10) is solvable with respect to the ion concentration \( n_i \). The ion number concentration in the irradiated region is obtained as:

\[
n_i = N \frac{\langle (\Delta \phi_{\omega} R_p)^2 \rangle}{\langle (\Delta \phi_{\omega} R_p) \phi_C \rangle} \frac{\tanh(Bt)}{K + \tanh(Bt)} \tag{11}
\]
with \( K = \sqrt{1 + (A_v - 1) \left( \frac{(\Delta \phi_{v,m} R_p)^2}{\phi^2_c} \right)} \), \( \phi_c = \frac{e^2}{4\pi\varepsilon_0} \), \( \Delta \phi_{v,m} = h\nu - \Phi_{v,m} \),

\[
B = \frac{\pi K_c I}{h\nu} \phi_c \left( \langle \Delta \phi_{v,m} R_p \rangle \right) K, \quad A_v = \frac{16\pi\varepsilon_0 h\nu D_i N}{K_c I e^2 k_B T}
\]

For the mean number of elementary charges \( \left\langle q(C_m, R_p) \right\rangle \) in each size-material fraction \((C_m, R_p)\) in the irradiated region can be derived from Eq. (8) following equation:

\[
\left\langle q(C_m, R_p) \right\rangle^2 - d \left\langle q(C_m, R_p) \right\rangle + \left( \frac{\Delta \phi_{v,m} R_p}{\phi_c} \right)^2 = 0
\]

(12)

with the factor \( d \) being defined as:

\[
d = \frac{\Delta \phi_{v,m} R_p}{\phi_c} + \frac{1}{2} \left( \frac{n_i A_v}{N} + \frac{16\pi\varepsilon_0^2}{K_c I e^4 n_i} \frac{d n_i}{d t} \right) = \frac{n_i A_v}{N} \Delta \phi_{v,m} R_p \left( \frac{\left\langle (\Delta \phi_{v,m} R_p) \right\rangle}{\left\langle (\Delta \phi_{v,m} R_p)^2 \right\rangle} \right) \left( \frac{K}{\tanh(Bt)} + 1 \right)
\]

(13)

Thus, for the mean charge in a size-material fraction is obtained:

\[
\left\langle q(C_m, R_p) \right\rangle = d - \sqrt{d^2 - \left( \frac{\Delta \phi_{v,m} R_p}{\phi_c} \right)^2}
\]

(14)

It was found, that the mean number of elementary charges can be also approximated with a high accuracy by:

\[
\left\langle q(C_m, R_p) \right\rangle = \frac{n_i}{2N} \left( \frac{\Delta \phi_{v,m} R_p}{\left\langle (\Delta \phi_{v,m} R_p) \right\rangle} + \frac{\left(\Delta \phi_{v,m} R_p\right)^2}{\left\langle (\Delta \phi_{v,m} R_p)^2 \right\rangle} \right)
\]

(15)

In the irradiation-free region the first of the integrals in Eq. (8) can be dropped because all \( \alpha \)'s are zero. Therefore, the mean number of elementary charges on a particle in each size-material fraction is a simple function of time:

\[
\left\langle q(C_m, R_p) \right\rangle = \frac{\left\langle q(C_m, R_p) \right\rangle_{\text{max}}}{1 + n_{\text{max}} \frac{D_i e^2}{\varepsilon_0 k_B T} t}
\]

(16)
with \( \langle q(C_m, R_p) \rangle_{\text{max}} \) being the maximal mean number of elementary charges for a size-material fraction \((C_m, R_p)\) and \( n_{\text{max}} \) the maximal ion number concentration reached in the irradiated region. Now, the mean charge of the particle charge distribution is a known function of time in the entire region including irradiated and irradiation-free zones. As can be seen from Eqs. (14)-(16), the mean charge of a size-material fraction charge does not depend in the explicit form on the shape of size and material distribution. The mean charge of a size-material fraction is a complex function of the mean and square mean values of the product of \( R_p \) and \( \Delta \phi_{\nu,m} \), calculated from size and material distributions, while the ratio of photocharging to diffusion (dis-)charging parameters is, in some way, expressed by the dimensionless factor \( A_\nu \). It follows from Eqs. (14)-(16), that the value of the mean charge in each particle size-material fraction increases with rising product \( \Delta \phi_{\nu,m} R_p \) for a given ion concentration in the irradiated region, while in the irradiation-free region the value of the mean charge in a size-material fraction is being completely determined by the maximal charge and maximal ion concentration reached in the irradiated region. The ratios of the mean charges become "frozen" after leaving irradiated region, and this fact can be useful by experimental studies of the charge distributions, which is difficult to carry out directly in an irradiated region.

It may be useful to obtain asymptotic solutions on the early stages in the irradiated region, when there are negligible gas ion concentration \( n_i \ll \frac{a_{<q>}}{\beta_{<q>}} \), and under stationary conditions. At the early stages of the charging process the mean charge depends only on the particle size and intensity of the irradiation and does not depend on the particle number concentration:

\[
\langle q(C_m, R_p) \rangle_{t \to 0} = \frac{K e I}{h \nu} \pi (R_p \Delta \phi_{\nu,m})^2 t
\]  

(17)

The stationary solution in the irradiated zone can be easily obtained from Eq. (14) for \( t \to \infty \). In this case the form of Eq. (14) remains the same, with the factor \( d \) modified to:
while the value of ion concentration under stationary conditions is being easily calculated from Eq. (11) as:

\[
n_{i,f \to \infty} = \frac{N}{\left\langle \left( \frac{\Delta \phi_{\nu,m}}{R_p} \right)^2 \right\rangle} \frac{1}{\left\langle \left( \frac{\Delta \phi_{\nu,m}}{R_p} \right) \phi_c \right\rangle (K + 1)}
\]

The value of the mean charge under stationary conditions indicates the maximal achievable charge level and shows the limits of the photocharging process. This value is of particular interest for the use in Eq. (16) as \( q_{\text{max}}(C_m, R_p) \), if the stationary state has been reached.

C. Solution in the case of mono-sized particles of one material

Equations (14) and (16) describe completely the dynamic changes of the mean charge in each size-material fraction with the time in general case using Eq. (11) for calculation of the ion concentration. Even though, they can be modified for the case of mono-sized particles of one material, it is possible to calculate the mean particle charge in this case directly from the Eq. (11) without solving Eq. (12):

\[
\left\langle q(C_m, R_p) \right\rangle = \left\langle q \right\rangle = \frac{n_i}{N}
\]

with the ion concentration taken according to Eq. (11) corrected for the case of mono-sized particles of one material. For the mean charge achievable in photocharging under stationary conditions is obtained:

\[
\left\langle q \right\rangle_{\text{stat}} = \frac{\Delta \phi_i R_p}{\phi_c} \left( 1 + \sqrt{A_v} \right)^{-1}
\]

with \( \Delta \phi_i \) being \( \Delta \phi_{\nu,m} \) for the case of one material. It should be mentioned, that Eq. (19) can be obtained by the direct matching of combination coefficients \( \alpha^{q_{\to \infty}} = n_i \beta^{q_{\to \infty}} \). Remarkable is, that the value obtained from Eq. (19) is lower than the previously used for description of
maximal possible charge,\textsuperscript{23} which was limited by pure electrostatic reasons and was derived without taking into account diffusive recharging. It is also clear, that the mean charge under stationary conditions for a given irradiation wavelength depends on particle radius, material properties, particle number concentration and lamp intensity contrary to assumed earlier dependency only on the particle radius and material properties. The particle mean charge in the irradiation-free region for mono-sized particles of one material is described by:

$$\langle q \rangle = \frac{\langle q \rangle_{\text{max}}}{1 + \langle q \rangle_{\text{max}} N \frac{D_i e^2}{e_0 k_B T} t}$$

with the value of maximal charge calculated from Eq. (18) or (19), if a stationary state has been reached.

It was proven,\textsuperscript{24} that the charge distribution obeys Gauss law under stationary conditions. The standard deviation of the charge distribution under stationary conditions for mono-sized particles of one material can be found by solving the following equation:

$$\left(\alpha^{<q>_{\text{stat}}^{-1} \rightarrow <q>_{\text{stat}}} + \beta^{<q>_{\text{stat}} \rightarrow <q>_{\text{stat}}^{-1}}\right) \exp\left(-\frac{1}{2\sigma_{\text{stat}}^2}\right) = \alpha^{<q>_{\text{stat}}^{-1} \rightarrow <q>_{\text{stat}}^{-1}} + \beta^{<q>_{\text{stat}} \rightarrow <q>_{\text{stat}}^{-1}}$$

which is obtained from the balance equation of the particle fraction with the charge $< q >_{\text{stat}}$.

Solving Eq. (21) for $\sigma_{\text{stat}}$ the following expression is obtained:

$$\sigma_{\text{stat}}^2 = \left[-\frac{1}{2} \ln \left( \frac{1}{4\langle q \rangle_{\text{stat}}^2 A_v^2} \right) + 1 \right]^{-1}$$

Unfortunately, it is difficult to find an analytical expression for the standard deviation of the charge distribution in the entire region due to complex form of system (1). However, considering the process as "quasi-stationary" one can use Eq. (22) with the charge values corresponding to the actual time point. Another way to estimate the value of the standard
deviation is to use the square root of the mean charge. Thus, in the range of low times it can be obtained from Eq. (15):

$$\sigma_{t \to 0} = \sqrt{\frac{K_c I}{hV} \pi (R_p \Delta \phi_{\nu,m})^2 t}$$  (23)

Even though Eq. (21) has been derived for the case of mono-sized particles of one material, it is valid for each size-material fraction in general case under stationary conditions. This fact allows to use Eqs. (22) and (23) with corresponding values \( \langle q(C_m, R_p) \rangle, R_p \) and \( \Delta \phi_{\nu,m} \) to calculate the standard deviation of the charge distribution in each size-material fraction.

Of course, use of combination coefficients in the simplified form introduces error in the range of small charges. This error can be studied solving the system of differential equations (1) numerically and comparing results of this solution with obtained analytically ones. To be able to describe the charge distribution in the aerosol in the entire region without simplifying assumption about the shape the particle charge distribution and combination coefficients, system (1) was solved numerically by a Runge-Kutta-Fehlberg method.\(^{25}\) The initial parameters for analytical and numerical calculations are: the wavelength of UV-irradiation \( \lambda = 172 \text{ nm} \), the product \( K_c I = 6.29 \cdot 10^{52} \text{ J}^{-1} \text{m}^{-2} \text{s}^{-1} \), the potential barrier of the plane surface \( \Phi_\infty = 2.5 \text{ eV} = 4 \cdot 10^{-19} \text{ J} \), the gas temperature \( T = 293.15 \text{ K} \) and ion diffusion coefficient \( D_i = 3.41 \cdot 10^{-6} \text{ m}^2/\text{s} \).

III. RESULTS

The influence of the particle size on the mean charge in a polydisperse one-component aerosol is presented in Fig. 2a. The total particle number concentration is \( 2 \cdot 10^{10} \text{ #/m}^3 \) with particle number concentration in each size fraction being 0.2 of total, while for the particle diameters in fractions values of 43 nm, 48 nm, 53 nm, 58 nm and 63 nm are taken. The mean charge, as calculated according to Eqs. (14) and (16) for irradiated and irradiation-free regions, respectively, is plotted in dependency on time for each size fraction. The symbols and
solid lines represent numerical results and results of analytical solutions, respectively. Analytically obtained results coincide with numerically ones with high extent of accuracy in the entire region. This coincidence justifies allowance of simplifications made for the charge levels studied. Dotted lines represent the mean charge in each size fraction as calculated from Eq. (17) and coincide with numerical results and results of Eq. (14) for small times. As mentioned above, fractions with larger particles have higher values of the mean charge, compared to the fractions with smaller particles. In Fig. 2b the same numerical results as in Fig. 2a (symbols) are presented compared to results obtained from Eqs. (15) and (16) for irradiated and irradiation-free regions, respectively (solid lines). The best agreement is found for the size fractions with small deviation between the particle size in the fraction and the mean particle size (48 nm, 53 nm, 58 nm in the case studied). The small deviation for two other size fractions can be explained by raising difference between particle diameter in fraction and mean diameter, which increases errors of approximation used to obtain Eq. (15).

The influence of the particle number concentration on the charge distribution was studied on the case of mono-sized particles of one material (Fig. 3a). The particle diameter of 53 nm was taken. Numerical results are presented by symbols, while analytical results are presented by solid lines. The best agreement between analytical and numerical results is at the lower particle number concentrations. In the case with the highest particle number concentrated studied a small deviation is detected. This deviation is not surprising due to use of the simplified form of combination coefficients for analytical solution. Even though the simplifications made by derivations of Eq. (7) are valid for particles with at least one positive elementary charge, it can be seen in Fig. 3a, that the influence of these simplifications draws attention on itself for the mean charges being about 0.5 elementary charges and below. The dotted line represents the mean charge as calculated according to Eq. (17) and shows a very good agreement in the range of small times. Even though mean charges of more than five elementary charges can be obtained in relatively diluted aerosols, concentrated aerosols
studied show mean charges slightly differing from zero by the same lamp intensity. Thus, the charge distribution by photocharging in concentrated aerosols will be bipolar similar to the charge distribution after aerosol charging by a radioactive preparat,\textsuperscript{11} however, with a different value of the standard deviation.

The standard deviation of the particle charge distribution as function of time as obtained by numerical simulations is plotted in Fig. 3b (symbols) for different particle number concentrations. As has been already mentioned, analytical solution of the system (1) with respect to standard deviation failed due to very complicated form of resulting equations. However, it was found, that Eq. (22) can be used with the actual value of the mean charge in the vicinity of the stationary state. This "quasi-stationary" value of the standard deviation (solid lines) coincides with results of numerical calculations. For the early stages of charging process the square root of the mean charge (dotted line) describes the value of the standard deviation with a good accuracy. The discrepancy between analytically and numerically obtained values of the standard deviation increases with the time in the irradiation-free region, especially for the concentrated aerosols. This discrepancy is caused by the error introduced by the simplifications made, which rises in vicinity of zero mean charge.

The comparison of numerical results for the mean charge and standard deviation with the analytically obtained values shows a good agreement in the range of the applicability of the simplifications made. Analytical expressions specify the charge distribution function of photocharged aerosol for mean charges being above 0.5 positive elementary charges, which allows to consider photocharging process as a procedure with a known charge distribution function and high charging efficiency.

IV. SUMMARY

In summary, it was demonstrated that in aerosol charging by UV-irradiation diffusion (dis-)charging by ions affects the particle charge distribution in the entire process. The general
case, an aerosol with chemically dissimilar particles of different sizes, is studied analytically and numerically. Analytical expression for the mean particle charge in each size-material fraction is obtained using a simplified form of the combination coefficients for the irradiated and irradiation-free zones. The justification of the use of the simplifications is found by comparison of analytical results with numerical ones. It was found that results are in a good agreement, if the mean charge exceeds the value of 0.5 positive elementary charges on particles.

The value of the mean particle charge is used for the estimation of the standard deviation of the charge distribution. This estimation shows a good agreement with numerically obtained values for the charge distributions with the most particles being positively charged.

The expressions derived for the mean charge and the standard deviation allow to describe the time-dependent charge distribution of aerosol particles obtained as result of the photocharging process. This enables to use the photocharging as a process with a high charging efficiency and a known charge distribution function.

ACKNOWLEDGMENTS

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FIG. 1. A principal photoelectric charger.

FIG. 2a. Mean charges of the size fractions in polydisperse aerosol in dependency on time. Solid lines represent results calculated from Eqs. (14) and (16), symbols correspond to results of numerical simulations. Dotted line show results of Eq. (17) for each size fraction.
FIG. 2b. Mean charges of the size fractions in polydisperse aerosol in dependency on time. Solid lines represent results calculated from Eqs. (15) and (16), symbols correspond to results of numerical simulations.

FIG. 3a. Mean charge of the charge distribution in mono-sized aerosol as a function of time for different particle number concentrations. Dotted line show results of Eq. (17) applied for the case of mono-sized particles of one material.
FIG. 3b. Standard deviation of the charge distribution in mono-sized aerosol as a function of time for different particle number concentrations. Dotted line show results of Eq. (23).
6. Equipment

**Aerosol generators**
- Palas Mage monodisperse aerosol generator
- TSI 3050 Bergland and Liu vibrating orifice aerosol generator
- Sinclair-La Mer generator
- Dräger VI mist generator
- Knauer HPN nebulizer
- Scheibel and Porstendörfer monodisperse aerosol generator
- Palas GFG 1000 graphite generator
- Environmental Research Corporation 7330 fluid aerosol generator
- TSI 3075 constant output atomizer
- TSI 3072 evaporation-condensation aerosol conditioner
- TSI 3433 small scale powder disperser
- TSI 3460 Tri-Jet aerosol generator
- TSI electrospray system

**Aerosol measurement systems**

*Sampling and collecting systems:*
- sampling systems (filters, TSI 3110 isokinetic dust sampler, TSI 3100 electrostatic aerosol sampler)
- impactor (Anderson stack sampler, Sartorius HV100 high volume sampler)
- small-scale cyclones
- mass measurement systems (TSI PMM 3200 particle mass monitor, TEOM)
- electrostatic precipitator
- High Volume Sampler DHA 80, Digitel, PM 10 and PM 2.5 inlets
- 2 Low Volume Sampler 3, Derenda, PM 10 and PM 2.5 inlets
- Cascade Impactor for TXRF Measurements, PM 10, PM 2.5, PM 1
- 2 β-Gauges, Kugelfischer

*Optical particle counters:*
- TSI 3755/3751 laser particle counter
- Met One 205
- Climet CI-7400 / CI208
- Polytec HC15
- PMS HS-LAS 32
- PALAS PCS 2000

*Condensation nucleus counters*
- TSI 3022/3022/3025/3760
- General Electric CNC-2
- Kanomax UPC 3861
- Expansion-type CNC Scholz
electrical mobility analyzers:
- TSI 3071 dynamical mobility analyzers and prototypes of different lengths
- Hauke EMK100
- TSI 3030/3070 electrical aerosol detector
- radial-type DMA

others:
- TSI 3300 aerodynamical particle sizer
- TSI 3077 neutralizer
- TSI 3040 diffusion battery
- PALAS VKL10 dilution system

Particle measurement systems
- Lightmicroscopes and image analysis system (SIS)
- Confocal Laser Scanning Microscope (CLSM)
- Atomic Force Microscope (AFM)
- On-line surface scanner (OSCAR)

Gas measurement systems
- Environment One Corporation diffusion denuder
- URAS 3G/7N/36 gasanalysator
- TSI 9100 Laser Doppler System
- Technolab helium flow visualizing system

Liquid measurement systems
- Lauda TD1 tensiometer
- Conductivity meters

Diagnostic systems
- Laser beam diagnostic system

Clean room technology
- clean rooms class 100, 10 and 1
- clean working benches class 10 and 1

Others
- Weather Station (Ambient rh, Temp, Pressure, Wind Speed and Direction, Solar Irradiance)
- 2 Climate Chambers for Ambient Aerosol Monitoring Systems
- Aethalometer, Measurement of Aerosol Black Carbon
- Edwards Auto 306 Vacuum Coater
- Polytec Nd-YAG Laser SL 800
- Sputter
7. **Other Activities**

7.1 **Cooperations**

**Institute for Environmental Technology and Analysis (IUTA, Duisburg)**
Prof. Dr. K.-G. Schmidt

**University of Minnesota**
Prof. D. Pui

**European Science Foundation Programme ‘Vapour-Phase Synthesis and Processing of Nanoparticle Materials (NANO)’**
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**Department of Physics, Indian Institute of Technology Delhi, India**
Prof. Dr. Bodh Mehta

**Kwangju Institute of Science and Technology, Kwangju, Korea**
Department of Environment Science and Engineering, Prof. K.W. Lee
7.2 Committee Activities

Gesellschaft für Verfahrenstechnik und Chemie (GVC)
Fissan - FA Partikelmeßtechnik
Kompetenzfeld Nanoprosessstechnik

Kommission Reinhaltung der Luft (KRDL)
Fissan - Vorstand / Beirat
Kuhlbusch – Arbeitskreis „Messen von Ruß“

Gesellschaft für Technische Gebäudeausrüstung (TGA)
Trampe - FA Reinraumtechnik

European Science Foundation
Fissan - Chairman of Nano-Program

Scientific Committee European Aerosol Conference (EAC)
Kruis – Member

European Aerosol Assembly (EAA)
Kruis - Chairman of the Working Group on Nanoparticles
Kuhlbusch – Co-chair of the Working Group Chemistry
Kuhlbusch – Co-chair of the Working Group PM10/PM2.5

Forum für Umweltforschung
Fissan - Mitglied (Sprecher)

European Committee for Standardization (CEN)
Kuhlbusch - Member of the CEN/TC 264/WG 15 “PM 2.5 sampling methods“

WMO Global Atmospheric Watch Programme (WMO-GAW)
Kuhlbusch – Committee member of the Aerosol Component of GAW

American Geophysical Union (AGU)
Kuhlbusch – Committee member of Biogeochemical Cycles

Coopération européenne dans le domaine de la recherche scientifique et technique (COST)
Fissan