On-line measurements of soot aggregates in a near-traffic urban environment – with applications to surface area and lung dose estimations

J. Rissler¹, E. Z. Nordin¹, A.C. Eriksson², M.E. Messing, P.T. Nilsson¹, B. Svenningsson², M. Frosch², A. Wierzbicka¹, J.G. Hemmingsen³, S. Loft³, S. Sjögren², J. Pagels¹, E. Swietlicki²

¹Division of Ergonomics and Aerosol Technology, Lund University, Box 118, 22100, Lund, Sweden
²Division of Nuclear Physics, Lund University, Box 118, 22100, Lund, Sweden
³Section of Environmental Health, Dept. of Public Health, University of Copenhagen, Denmark

Keywords: effective density, urban environment, health, aggregated particles

In traffic-dense urban environments, soot (black carbon) is often dominating the emissions by mass. The soot cores carry different degrees of coatings. As soon as the particles are emitted to the atmosphere, the atmospheric processing begins. When estimating exposure, or dose to the lung, with respect to surface area or mass from mobility number size distributions, information about the particle shape and effective density are needed.

In this study two on-line instruments; a DMA-aerosol particles mass analyzer (DMA-APM; Park et al., 2003) and an aerosol mass spectrometer equipped with a laser vaporiser for soot detection (SP-AMS, Onasch et al., 2012), was brought to a traffic-dense urban environment (Central Copenhagen). Complementary measurements were also performed at a rural background site nearby. From the DMA-APM data the effective density was determined, defined as: 

\[ \rho_{\text{eff}}(d_m) = \frac{6m}{\pi d_m^3} \]

where \(d_m\) is mobility diameter. From the data the lung deposited particle mass and surface area was estimated (as described in Rissler et al., 2012) and the results compared to that when assuming spherical particles.

The measurement showed that the particles found at street level were externally mixed, with one group of dense particles with effective density \( \sim 1.4 \text{ g/cm}^3 \), and one group of highly aggregated particles, mainly soot (confirmed by electron microscopy). The aggregates had the typical behavior of decreasing effective densities with size, ranging from \(0.94 \text{ g/cm}^3\) for 50 nm particles down to \(0.26 \text{ g/cm}^3\) for 400 nm (Figure 1). The particle effective densities found at the street level were almost identical to those found for freshly emitted diesel particles generated under well controlled lab-conditions (Park et al., 2003; Rissler et al., 2013), with no signs of atmospheric aging under winter conditions (January-February), and well described by a power law function as a function of size.

Whereas the particle effective densities were stable over time, the relative number fraction of the two types of particles varied considerably. Two types of time variations were observed; that over time of day, and that depending on the air mass origin. The diurnal variation in agglomerated soot particle concentration was associated with the traffic pattern – showing the lowest concentrations at night (00:00-04:00). The fraction of “dense” particles increased during occasions with trajectories from polluted areas. Thus, these particles were likely dominated by long range transport, while the aggregated soot particles were from local sources. This hypothesis was further supported by the measurements at the rural background site.

This work was supported by the Swedish Research Council FORMAS, the Swedish Governmental Agency for Innovation Systems, VINNOVA.


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This work was supported by the Swedish Research Council FORMAS, the Swedish Governmental Agency for Innovation Systems, VINNOVA.

Characterisation of nanoparticles from pilot-scale reactor producing metallic nanoparticles – exposure of workers

J. Lyryläinen\(^1\), J. Hokkinen\(^1\), A. Auvinen\(^1\) and J. Jokiniemi\(^1\)\(^,2\)

\(^1\)VTT Technical Research Centre of Finland, P.O. Box 1000, 02044 VTT, Finland
\(^2\)University of Eastern Finland, Department of Environmental Science, P.O. Box 1627, 70211 Kuopio, Finland

Keywords: Nanoparticle, characterisation, Cl-process, pilot-scale, exposure.

Materials made of nanoparticles and nanostructures generally possess different kind of properties than bulk material. Therefore, the interest towards products made of these materials is increasing. At the same time the possible health effects and worker exposure during manufacturing is also increasing. In this study Co nanoparticles (primary particle size 50-100 nm) were produced by hydrogen reduction reaction from cobalt chloride precursor powder in nitrogen carrier gas in a pilot-scale reactor (Hokkinen, et al., 2014). The reactor set-up is isolated from the experimental hall inside an enclosure. The aim of the study was to characterise the produced particles with aerosol measurement devices and find out the particle exposure levels at different locations of the reactor: reactor, control and filter collection station.

The particle number concentration was measured with a TSI 3775 CPC, the number size distribution with a TSI 3082 (3080) electrostatic classifier with a TSI 3081 and 3085 DMA connected with a TSI 3788 water (3775 butanol) CPC and controlled by the SMPS software, NanoScan SMPS 3910, Optical particle sizer (OPS) 3330 and electrical low-pressure impactor (ELPI). The mass concentration was measured with a TEOM 1400a. Individual particle samples for electron microscopy (EM) were collected with an aspiration EM sampler.

During the reactor heat-up the particle number concentration by CPC and SMPS levelled out to 2.0-3.5·10\(^3\) #/cm\(^3\), and by NanoScan to 8.0·10\(^4\) #/cm\(^3\) when the target temperature of 900 °C was reached (Fig. 1a). This indicates that fraction of particles smaller than 30 nm (lower detection limit of NanoScan) is quite high. These particles originate from the heating elements and insulation material of the furnace.

During the production of Co nanoparticles the particle number concentration in the reactor room by CPC and SMPS varied from 0.6-9.0·10\(^3\) #/cm\(^3\), and by NanoScan from 0.1-1.1·10\(^4\) #/cm\(^3\) (Fig. 1b). Thus during production of the Co nanoparticles the main source for measured particles is the heating elements and insulation material of the furnace.

The number concentration at the control room isolated from the reactor room varied from 1.0-6.0·10\(^3\) #/cm\(^3\) by SMPS, CPC and NanoScan. The background concentration during reactor operation in the experimental hall outside the reactor enclosure varied typically between 1.0-6.0·10\(^3\) #/cm\(^3\) thus being almost equal to control room concentration (Fig. 1b). The background concentration was mainly caused by assembly and research work at the hall. Hardly any particles escape the reactor enclosure because of slight underpressure.

![Figure 1. Number concentration measured with CPC, SMPS and NanoScan a) overnight at the reactor room during furnace heat-up b) at different locations during measurement campaign (rea, reactor; cont=control room, bckg, backg=background at the hall).](image)

The contribution of Labtronic and TSI is greatly acknowledged for providing measurement devices. This work was supported by the EU Seventh Framework Programme MARINA under grant agreement 263215.

Robust passive sampling materials for use with DNATrax aerosol simulant

C.J. Kaeser1,2, S.B. Hall2, A.D. Jones1,3, E.K. Wheeler2, G.R. Farquar2

1Department of Chemistry, Michigan State University, East Lansing, MI, USA
2Lawrence Livermore National Lab, Livermore, CA, USA
3Department of Biochemistry and Molecular Biology, Michigan State University, East Lansing, MI, USA

Keywords: passive sampling, particle deposition, airflow monitoring, spatial variability, indoor air

As the average time spent indoors increases, the need to monitor the airflow and quality in such environments also increases. Computational modeling methods can provide a theoretical understanding of particle deposition in turbulent airflow patterns but still require experimental validation using simulant aerosols (King, et al., 2013). Considerations that complicate experimental designs for model validation include high background aerosol levels, reproducing environmental conditions for multiple experiments, and detecting the simulant with disruption of natural airflow.

Use of DNA Tagged Reagents for Aerosol eXperiments (DNATrax) as the aerosol simulant can solve some of these concerns. DNATrax are particles of food-grade maltodextrin tagged with a unique 100 base pair oligonucleotide and use a TaqMan polymerase chain reaction (PCR) as the detection scheme, effectively amplifying and detecting only the DNA tag used in the simulant and eliminating the issue of background aerosols. By using simulants with different DNA tags multiple experiments can be performed in a large space without expensive or time-consuming decontamination. This also allows for experiments to be performed simultaneously, ensuring the same environmental conditions are experienced by both experiments.

For accurate endpoint deposition detection, multiple locations throughout the space must be sampled without disrupting the natural airflow. In order to accomplish this, small removable surfaces for particle collection can be used as passive sampling materials. Materials such as microscope slides (Leith et al., 2007), SEM stubs (Wagner and Leith, 2001; Ott et al., 2008), and polyethylene film (Sze To et al., 2009) have been reported as adequate passive samplers for aerosol collection, each useful for the detection scheme utilized. However, these materials can be costly or cumbersome to work with for experiments that require a large number of sampling locations. Several inexpensive and robust materials such as popsicle sticks, glass microscope slides, Post-It notes, transparency film and dry filter unit (DFU) filters were tested for their PCR compatibility through inhibition and recovery studies. Of these materials, the transparency film was found to inhibit the PCR reaction and, although no inhibition was observed, DNA recovery was decreased in popsicle sticks (Figure 1). Glass microscope slides, Post-It notes, and DFU filters were then utilized as passive sampling materials during a multiplexed experiment (Figure 2), dispersing DNATrax material from two locations within the same space using different DNA tags at each location.

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Estimating number emission rates of nano-particle sources by “Concentration Peaking” method

S. Anand¹, M. Joshi², B.K. Sapra² and Y.S. Mayya³

¹Health Physics Division, ²Radiological Physics & Advisory Division, Bhabha Atomic Research Centre, Mumbai-400 085, ³Department of Chemical Engineering, Indian Institute of Technology-Bombay, Mumbai-400 076, India

Keywords: Workplace exposure, number emission rate, coagulation, Engineered nanoparticles, One-box model.

Mass and number emission rates are two important parameters that characterise particle emission from sources such as those encountered during combustion, material synthesis and Engineered nanoparticles. These sources are of considerable concern in the context of climate change and health effects. Several techniques have been implemented for assessing mass emission factors. However, methods to assess number emission rates are virtually non-existent. This is mainly because of the difficulties associated with near source monitoring and effect of coagulation which rapidly decreases number concentration as one moves away from sources. It is suggested that number concentration, rather than mass concentration, is a superior summary index of climatic or health effects. Several techniques have been implemented for assessing mass emission factors. Also, aerosol dynamics models generally require near-source number emission as inputs. There is thus a fundamental need to develop methods to estimate this quantity.

In this paper, we propose a technique to estimate the number emission rate by locating the number-peak characteristics of nanoparticles injected continuously from source into a well stirred/ ventilated-chamber. The rate of change of aerosol number concentration (n(u, t)) in the chamber due to source injection, coagulation and removal processes is given by

\[ \frac{\partial n(u, t)}{\partial t} = \frac{1}{V} S(u', t) + \frac{1}{2} \rho D(u' - u) n(u', t) n(u - u', t) du' - n(u, t) \rho D(u', t) n(u', t) du' - \{ \lambda + \lambda_d(u) \} n(u, t) \]

(1)

where, \( u - \) particle volume, \( K(u, u') - \) coagulation kernel, \( \lambda - \) ventilation rate, \( \lambda_d(u) - \) removal rate, \( S(u, t) - \) particle number emission rate (number s⁻¹), and \( V - \) chamber volume. Using numerical and semi-analytical solutions, we scaled the number concentration and time in terms of emission rate and primary particle coagulation coefficient (Anand et al, 2012) as follows:

\[ N^* (t^*) = N(t)/N_c \text{, and } t^* = t/t_0 \]

(2)

where, \( N_c = \sqrt[3]{S/V K(u_0, u_0)} \) characteristic number concentration, \( t_0 = 1/(S^* K(u_0, u_0)/V) \) characteristic time, and \( u_0 \) volume of the emitted primary particle. It turns out that regardless of source strength, \( N^*(t^*) \) always peaks at \( N^* \approx 1 \) for \( t^* \approx 2 \). Using this simulation observation and Eq.(2), we can estimate the source strength from an experimentally measured peak number concentration \( (N_p) \) at a time \( (t_p) \):

\[ S^* = V N_p / t_p = 2 V N_p / t_0 \]

(3)

The experimental test was carried out using metal particles generated from electrically heated Tungsten/Nichrome wire source, injected into stirred chambers of three different volumes (450 cc, 40 l & 500 l). The concentrations were measured continuously using SMPS (Fig. 1). After locating the peaks from Fig.1, the number emission rates (Table 1) are estimated. The inherent uncertainty in locating the peak time and concentration appears to be about 30% each and the overall uncertainty of the emission rate estimates may be about 50%. However, this estimate may be considered quite acceptable for a difficult parameter like the number emission rate. Smaller chambers showed lower emission rates implying the possibility of higher wall loss effects on peak values.

![Figure 1. Experimental measurements. Inset figures. Y-axis is in linear scale to show peaking effects.](image)

Table 1. Number emission rate estimates.

<table>
<thead>
<tr>
<th>Chamber</th>
<th>Volume (V), m³</th>
<th>Np, #/m³</th>
<th>tp, sec</th>
<th>Emission rate (S*), #/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.5E-4</td>
<td>6.3E13</td>
<td>214</td>
<td>2.63E8</td>
</tr>
<tr>
<td>B</td>
<td>0.04</td>
<td>2.2E12</td>
<td>496</td>
<td>3.48E8</td>
</tr>
<tr>
<td>C</td>
<td>0.5</td>
<td>3.9E11</td>
<td>858</td>
<td>4.58E8</td>
</tr>
</tbody>
</table>

As a future application, the simple technique of locating the peak concentration and time, appears quite promising to characterize the number emission rates from combustion sources, widely used in homes in India.

Measurements of aerosol emissions during underwater laser cutting of steel equipment as part of decommissioning

S. Peillon*, S. Fauvel*, C. Chagnotb and F. Gensdarmesa

a Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES/SCA/LPMA, Saclay, Gif-sur-Yvette, 91192, France.
b Commissariat à l’Energie Atomique (CEA), DEN/DM2S/SEMT/LTA, Saclay, Gif-sur-Yvette, 91191, France.

When a nuclear facility reaches the end of exploitation, it is dismantled after a more or less long period of waiting for the level of radiation to decrease. The decommissioning consists in cutting the active parts of the installation piece by piece, in order to remove the waste thus created in the corresponding spinner and restore the infrastructure and/or soils to a level of radioactivity consistent with a possible return in the public domain. Assessing the risk of loss of containment of radionuclides during the decommissioning of a nuclear facility requires therefore to predict how much aerosols will be collected on the HEPA filters which may lead to its clogging and rupture. For this, we must characterize aerosols emitted upstream from filters based on the type of operation to be performed and the proposed tool. Studies of cutting tools used for decommissioning are designed to test the performance of these gears in configurations specific to each installation and characterize particulate emissions generated by these cuts (Pilot et al., 2008).

In this context, our goal is to provide results on aerosol emissions of different cutting techniques used for the decommissioning of nuclear installations. In particular, the study aims at characterizing the aerosol emitted during the cutting of steel specimens of different thicknesses and to study particulate emissions for cuts under water. These experimental tests are then compared with other cutting techniques which have been the subjects of previous studies. In this context, we calculate the airborne released fraction defined by the ratio between the mass of aerosol produced and the mass of loss material of the specimen as well as the emitted aerosol mass per unit length of cut.

Tests performed on the DELIA facility (Chagnot et al., 2010) show that the use of a high power laser, necessary for rapid cutting of large thicknesses (1 m/min up to 30 mm thickness), does not induce the increase of aerosol emissions compared to other cutting techniques (see Figure 1). In general, it was found that the mass of aerosol emitted per unit length of cut decreases with the increase of the laser cutting speed and laser power.

Figure 1. Mass of aerosol per unit length of cut for various underwater cutting techniques

The same applies when the water level in the test chamber increases, the airborne released fraction varying from $4 \times 10^{-2}$ to $7 \times 10^{-5}$ when the water level increases from 0.5 meter to 4 meters. Furthermore, the mass loss of the specimen with the laser cutting technique is lower than with the plasma torch.

The process of laser cutting can be easily compared to other methods already tested (plasma torch, consumable electrode, Contact Arc Metal Cutting (CAMC), high pressure water jet and lasers with different powers) and is sometimes better in terms of reduction of aerosols emission, especially compared to other thermal processes as the consumable electrode or CAMC.

Aerosols generated in hospital operating rooms

S.A. Grinshpun¹ and R. H. Koehler²

¹Department of Environmental Health, University of Cincinnati, Cincinnati, OH 45267-0056, USA
²Critical Fit Technology LLC, Tisbury MA 02568, USA

Keywords: surgical smoke, ultrafine particles, concentration, exposure

Aerosol hazard in health care environments is often associated with viable biological particles, including airborne bacteria and viruses. However, in an operating room setting, healthcare providers and patients are exposed to a unique aerosol referred to as surgical smoke. It contains combustion particles generated from the destruction of tissues through the use of thermal energy, common to essentially all of modern surgery, during dissection. Virtually any surgical procedure involving electrocautery, laser, argon beam, or high frequency ultrasonic instruments generates surgical smoke. The Occupational Safety and Health Administration (USA) recognizes the hazards of this aerosol and estimates that half a million American surgeons, nurses, anesthesiologists, and surgical technologists are exposed to laser or electrosurgical smoke each year (OSHA, 2008).

Studies have been conducted to measure and qualitatively characterize the chemical and biological composition of surgical smoke. Most of the studies, however, involved the sampling and analysis procedures, which did not allow the investigators to properly differentiate the gaseous and particulate components. We reviewed few available reports that were concerned with the concentration of particles generated by surgical procedures. Measured using a condensation particle counter, Brüske-Hohlfeld et al. (2008) found that electro-cauterization and argon plasma tissue coagulation produced concentrations in excess of $10^5$ cm$^{-3}$ in the particle diameter range of 10 nm to 1 μm. Andreasson et al. (2009) reported similar results. Among other limitations, the quoted studies did not address the size distribution of particles generated during surgical activities.

In this study, we conducted a series of aerosol measurements in a 6000 ft$^3$ (~170 m$^3$) operating suite equipped with a positive pressure HEPA-filtered closed airflow circulation at $T = 15^\circ$C and RH=55%. A tissue area of about 1000 cm$^2$ served as an operative specimen. With a cautery level set at 40 W, we utilized a standard surgical electrocautery unit (Valleylab Force FX, Covidien, Boulder, CO, USA) to perform dissection using a electrosurgical pencil (Valleylab E2516, Covidien). A P-Trak particle counter (model 3007, TSI Inc., St. Paul, MN, USA) and a Nanoparticle Spectrometer (Nano-ID, NPS500, Particle Measuring System Inc., Boulder, CO, USA) were deployed in parallel while sampling at approximately 30 cm from the source over a time period of 3 hours. Separate tests were conducted with the sampling inlet located at greater distances from the source (40–120 cm). A 10-fold dilution was used if the particle concentration was expected to exceed the upper threshold of $5 \times 10^5$ cm$^{-3}$.

The background total aerosol concentration varied approximately from $4.3 \times 10^3$ to $7.7 \times 10^4$ cm$^{-3}$ (as measured with the P-Trak) or from $3.0 \times 10^3$ to $4.0 \times 10^4$ cm$^{-3}$ (as measured with the Nano-ID). The cautery dissection generated significantly higher aerosol concentrations: from $5.0 \times 10^5$ to almost $1.1 \times 10^6$ cm$^{-3}$ (P-Trak) and from $6.7 \times 10^4$ to $1.3 \times 10^6$ cm$^{-3}$ (Nano-ID).

Two particle generation regimes were distinguished producing intermediate and high levels of exposure in the proximity to the source. The surgical smoke featured the size distribution curves that peaked between 40 to 200 nm particle diameter; most peaks were recorded between 50 and 150 nm. More than 50% of particles (by number) in the measured surgical smoke represented the ultrafine fraction. The background particle size distribution curves showed peaks at a narrower range of 60 to 100 nm. The analysis of time series suggested that the surgical smoke exhibited very high spatial and temporal data variability as compared to the background aerosol.

The results of this pilot study call for a more extensive investigation of the physical, chemical and biological characteristics of aerosols generated in operating rooms by both conventional and laparoscopic surgical procedures. Considering unexpectedly high levels of exposure to aerosol hazards observed in this study (as well as the previously published evidence of high toxicity of these aerosols), a more efficient respiratory protection methods and techniques should be implemented to reduce health risks for hospital personnel and patients.


Indoor Aerosol Concentrations in a Nanoparticle Synthesis Laboratory

L. Chassapidis¹, E. Papaioannou¹, A.G. Konstandopoulos¹,²

¹Aerosol and Particle Technology Laboratory, CPERI/CERTH, P.O. Box 60361, Thermi 57001, Greece
²Department of Chemical Engineering, Aristotle University, Thessaloniki, Greece

Keywords: indoor aerosols, engineered nanoparticles

While some nanomaterials have been in use since decades (e.g. silica, titania, carbon black), other nanomaterials are quite new and manufacturing and handling occurs only on the laboratory scale. In comparison to those nanomaterials already investigated (Maynard and Kuempel 2005), information on workplace exposure to new nanomaterials is very limited. The aim of the present study is therefore to assess indoor aerosol nanoparticle concentrations in our laboratory where synthesis of nanosized and nanostructured particles and powders takes place for various environmental and energy applications.

Indoor nanoparticle measurements were performed in several locations of our facilities. Laboratory space is separated from office space by a corridor, therefore measurements were conducted at the corridor and at the laboratory space where nanomaterials are synthesized and handled. Baseline measurements were taken in a nearby office during night time with no human or lab activity. The corridor also hosts two low to medium activity laser printers. Based on past studies (e.g. Morawska, 2010) laser printers can be nanoparticle sources.

Measurements were performed with a Diffusion Size Classifier (DiSC) which measures nanoparticle concentration and mean diameter from 20 nm to 200nm. DiSC is a lower accuracy instrument compared to a Scanning Mobility Particle Sizer (SMPS) but is well suited for working environments measurements as it does not include a radioactive source or hazardous operating liquids such as butanol.

In Figure 1 the bar charts present the results for 8 hour average concentration and mean diameter. The baseline measurement is as expected the lowest. In the corridor there is a 120% rise mainly due to the printing activity and possibly from particle transfer from the laboratory as these are adjacent rooms connected with a door.

In the laboratory there is a rise in the concentration clearly indicating that the workspace is more aggravated with particles. Although the laboratory is an adequately ventilated area with a very low total particle concentration (~1.2x10⁴ #/cm³), this is nevertheless 200% higher than the concentration of particles that was measured in the office (which is taken as the baseline measurement). This can be attributed to the presence in the same area of several laboratory and pilot units for the production of aerosols and the synthesis of nanostructured powders, as well as to the use of electrical furnace units that may be a source of nanoparticle emissions from the ceramic materials that are used as insulation.

The mean diameter is the same for the office and the corridor at 80nm and slightly higher in the laboratory at 82nm.

Continuous monitoring of the workplace nanoparticle concentrations and potential source identification for our laboratory is an ongoing task and forms an integral measure of responsible nanotechnology practice.

Exposure and risk assessment to carbon nanotubes and nanodiamonds in an industrial facility

K. Hämérı1, Koivistı2 A. J., J. E. Palomäki2, Viitanen2 A.-K., Yu1 M., Siivola2 K., Kanerv2 T., Norppa2 H., Alenius2 H., Hussein1,4 T., Godinho5 A. S.

1University of Helsinki, Department of Physics, P.O. Box 48, FI-00014 Helsinki, Finland
2Finnish Institute of Occupational Health, Nanosafety Research Centre, Topeliuksenkatu 41 a A, FI-00250 Helsinki, Finland
3Karlsruhe Institute of Technology, Institute for Mechanical Process Engineering and Mechanisms, Karlsruhe, Germany
4The University of Jordan, Faculty of Science, Department of Physics, Amman, JO-11942 Jordan
5Institute of Environmental Assessment and Water Research (IDAEA), Spanish Research Council – CSIC, 08034 Barcelona, Spain

Keywords: CNT, nanodiamond, exposure, workplace,

Industrial processes utilizing materials that are engineered on the nanometer scale are rapidly growing worldwide. Nanotechnology is identified as being one of the most promising technologies in OECD countries and other high technology centres. Only in Europe, nanotechnology sector is believed to employ 400 000 persons by 2015. However, during the last decade, there has been a growing amount of evidence that some engineered nanomaterials (ENMs) may be potentially very toxic to humans (e.g. Savolainen et al. 2010).

The ENM exposure occurs most likely when the materials are produced and handled (Hämérı et al. 2009, Savolainen et al. 2010). In such exposure, inhalation is the most relevant pathway for ENM uptake. Currently, there are no metrics for airborne ENMs that could be measured at workplace and directly linked to the health effects. Thus, the health effects of occupational ENM exposure need to be estimated by using traditional risk assessment techniques and conventional instruments. However, currently there are no health-based exposure limits or OECD guidelines for nanomaterial safety testing. Thus the risk assessment of ENM exposure currently relies on available toxicological (i.e. dose-biological response) data. This is usually studied with in vivo experiments where the dose-response is extrapolated to human equivalent dose-response.

In this study, we characterise the exposure of workers in two production processes dealing with nanodiamonds (ND) and carbon nanotubes (CNTs). Experimental results are studied in detail in order to understand the role of process-based particles to those existing in the background air.

Further, we utilized existing methods to assess workers risk to suffer pulmonary inflammation while working with nanodiamond powder. The NDs cytotoxicity was studied with THP-1 cell line by assessing cell death of macrophages and ability to produce reactive oxygen species (ROS) and IL-1β, IL-8, and TNF-α cytokines. The in vitro dose-response was extrapolated to human equivalent human dose-response according to Hinderliter et al. (2010).

We measured workers ND exposure levels which were used to calculate inhaled dose rates. The dose rates were used to estimate annual doses in work scenarios including ND handling, sieving, and cleaning. We will also discuss exposure metrics, particle emission rates from processes, exposure assessment, and dose rates, and dose-response, which all are essential for quantitative risk assessment of ENM exposure.

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Economically Viable Smell Abatement using Gas Phase Advanced Oxidation

C. Meusinger¹, A. Feilberg², C. Andersen¹, A. Butcher¹, L. Nannerup³ and M.S. Johnson¹

¹Chemistry Department, University of Copenhagen, 2100, Copenhagen, Denmark
²Department of Engineering, Aarhus University, 8830, Tjele, Denmark
³Infuser ApS, 4000, Roskilde, Denmark

Keywords: Farm emissions, smell abatement, air purification

Despite intense research, there is currently no cost effective way of removing many industrial odors, in particular for smells that are powerful even at extremely low concentrations (Blanes-Vidal et al., 2009). A series of compounds known to be components of obnoxious smell from pig farms, wastewater treatment and biogas production plants were treated using a combination of scrubbing and photochemistry. Here we report the removal efficiencies of these compounds using Photochemical Air Purification (PAP).

PAP is a new method that oxidizes gaseous compounds and drives them into the condensed phase forming particles (Johnson and Arlemark, 2009). The generated particles are removed, leaving the airstream clean of both pollutants and particulate matter. Unwanted pollutants are mainly oxidized by the OH radical formed by added ozone and UV-C light (OH concentrations are approximately 5x10¹⁰ l/cm³). Treatment times of common pollutants are on the order of seconds. Particles are filtered from the air stream using an electrostatic precipitator. Other potential products might be gaseous and if unwanted can be treated in a second step using UV light. An optional scrubber treats water-soluble compounds, e.g. ammonia, separately. Finally the air passes an ozone catalyst leaving the air stream exiting the PAP with lower concentrations of the unwanted compounds, particles and ozone. Different number of UV lamps, flows and ozone concentrations were tested for the removal of a range of compounds (e.g. hydrogen sulfide, 1-butene, dimethyl sulfide).

Table 1. Excerpt from the list of compounds tested in PAP (all UV lights on), experimental conditions, and removal rates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Flow/m³/h</th>
<th>Inlet conc./ppb</th>
<th>Outlet conc./ppb</th>
<th>Removal/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>600</td>
<td>847.6</td>
<td>54.4</td>
<td>94</td>
</tr>
<tr>
<td>H₂S</td>
<td>900</td>
<td>603.7</td>
<td>98.1</td>
<td>84</td>
</tr>
<tr>
<td>H₂S</td>
<td>1200</td>
<td>382.4</td>
<td>99.7</td>
<td>74</td>
</tr>
<tr>
<td>1-butene</td>
<td>600</td>
<td>60.8</td>
<td>0.9</td>
<td>99</td>
</tr>
<tr>
<td>1-butene</td>
<td>1200</td>
<td>41.6</td>
<td>1.1</td>
<td>97</td>
</tr>
<tr>
<td>DMS</td>
<td>1200</td>
<td>287.4</td>
<td>86.5</td>
<td>70</td>
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</tbody>
</table>

The removal of gas phase pollutants was monitored online using a Proton-Transfer-Reaction-Mass Spectrometer (Table 1) and the evolution of the population of particles was recorded with a Scanning Mobility Particle Sizer. Additional parameters including temperature, relative humidity, ozone and total trace gas concentrations were monitored with a suite of instruments. Information on the gaseous and particulate phases documents pollutant removal rates under different conditions.

Figure 1 shows data for H₂S oxidation in PAP at different flows. Lower flows translate into longer treatment times and result in higher removal rates. At the same time lower flows allow for longer particle growth times, increasing the mean modes of the generated particles leaving the PAP.

At around 3 kJ/m³ of treated air, PAP’s specific energy input is significantly lower than that of other air cleaning technologies. The particle and chemical removal data presented allows discussing PAP performance in light of energy consumption and economic viability.

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Ultrafine particle concentrations inside a car – cabin filter effects

D. Popescu, G. Ben-Haim and L. Tartakovsky

Faculty of Mechanical Engineering, Technion – Israel Institute of Technology, 32000, Haifa, Israel

Keywords: ultrafine particles, passenger cars, exposure, ventilation, cabin air filter.

Vehicle emissions that include particles and harmful gases negatively influence the cardiovascular, respiratory and immune systems, thus increasing the risk of stroke and cancer development. Ultrafine particles (UFP) were found to be penetrating through the blood cells into the human brain, liver etc with respective negative health effects (Knibbs et al., 2011).

Ultrafine particles, after being emitted from the vehicle's exhaust system, remain in the air and enter the vehicle's cabin, thus exposing the driver and the passengers. To reduce the exposure to ultrafine particles, extensive studies of filter effects and development of new efficient filters are required.

In this work measurement results of the ultrafine particle concentrations outside and inside passenger cars are reported. The measurements were made with various cars of different makers, under different ventilation conditions and different starting UFP concentrations in the vehicle cabin. UFP concentrations in the cabin of the vehicles without an adequate air filter, with genuine OEM-made filters of different types and a non-original air filter were studied. Influence of an additional high efficiency cabin air filter was investigated too.

Various parameters are known as influencing the ultrafine particles concentration inside a vehicle: ventilation mode, fan speed, cabin air filter, outside UFP concentrations, driving speed, vehicle age, etc.

In our work we studied the time required to reduce the in-cabin UFP concentration to the value of 4000 cm\(^{-3}\), typical for a clean office. This time was found to be changing from 6 to 12 minutes for different vehicles. An old car couldn’t reach these values, and a new car equipped with a non-genuine filter required a significantly longer time to reach the clean office UFP concentration. The results of our measurements suggest that in case of using the recirculation ventilation mode, acceptable CO\(_2\) concentrations inside a car are exceeded after approximately 6-7 min of driving (Tartakovsky et al., 2013). We studied UFP concentration values that may be achieved inside a vehicle's cabin after 7 min of driving in the recirculation ventilation mode at different initial UFP concentrations. It was found that UFP concentrations decreased after 7 min to values between 2500 - 22000 cm\(^{-3}\) from the initial in-cabin UFP concentrations of 45000 - 428000 cm\(^{-3}\), respectively.

Increasing the speed of the ventilation fan reduces the time required to reach the clean-office UFP concentrations, as shown in Figure 1.

![Figure 1: Time to reach the clean-office values of UFP concentrations from a starting value of 90000 cm\(^{-3}\) for various speeds the air exiting the ventilation channel](image)

Effects of a car retrofit with the in-cabin air purifier were studied. The purifier sucked the air from outside the vehicle, thus eliminating the problem of CO\(_2\) accumulation inside a vehicle. Our experiments showed that the in-cabin air purifier allowed reduction of the UFP concentrations in 7 minutes to the values below 3000 cm\(^{-3}\), with almost no influence of the initial UFP concentration in the cabin.

Application of the air purifier allowed a further reduction in the UFP number concentrations inside a car down to values below 500 cm\(^{-3}\), which are much lower than the UFP concentrations typical for a clean office. Along with this, some minimal time of 17-20 min was required to achieve maximal cleaning effect.

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Universal method for exposure assessment of spray applications

K. Schwarz, W. Koch

Department of Aerosol Technology, Fraunhofer Institute for Toxicology and Experimental Medicine, Nikolai-Fuchs-Straße 1, 30625, Hannover, Germany

Keywords: exposure assessment, spray application, inhalable aerosol release, aged aerosol, mass balance.

In recent years, spray products are widely being used. In the professional environment this comprises a broad range of applications (painting, surface treatment, biocide/pesticide application) as well as of spray technologies (spray gun, fogging device, pump spray). The issue of potential aerosol release is increasingly being addressed in regulation demanding an exposure assessment for hazardous substances. Therefore safety assessment of spray products requires information on the potential release of aerosols in health related particle size ranges under conditions of the use of the product.

Usually inhalation exposure characterization is based on droplet size distribution analysis of the native spray. However, the main fraction of the droplets is comprised of solvents and/or propellants. Therefore, in general, these droplets evaporate within a short period of a few seconds, so that the spray aerosol will shrink to the non-volatile constituents. This status is assumed to represent the real exposure situation of the spray user and needs to be considered for inhalation exposure characterization.

A mass balance method for determination of exposure risk from spray applications under real exposure conditions has been developed.

In this approach, the exposure risk is quantified in terms of release fractions, defined as mass of aerosol generated in the health-related size classes, normalized to total mass of liquid spray product released. Therefore, a well defined spray bolus is released into a control chamber followed by aerosol concentration measurement in the health-related size fractions (respirable, thoracic) according to international standards, European standard EN481 and ACGIH standard. This is performed using the RESPICON personal aerosol monitor (Helmut Hund GmbH, Wetzlar, Germany), enabling gravimetric and on-line light scattering analysis.

For various spray products and technologies, the aerosol release fractions were determined using the mass balance method.

The studies show that this method provides reliable information for a wide range of spray products and technologies with release fractions varying by orders of magnitude. From the data set generated, a simple, rough estimation on the expected thoracic release fraction can be derived, based on easily available properties of the liquid spray formulation and the spraying technology: the median droplet diameter and the concentration of the non-volatile compounds in the liquid spray formulation.

\[
R_{\text{thor}} = A \cdot \tilde{d}_{50}^{-q} \cdot c^{1/3} \quad [\mu m]
\]

A: Empiric pre-factor, 104
q: Parameter determining size distribution width, 2.6
c: Concentration of the non-volatile phase in formulation

For formulations containing non-volatile active compounds the mass balance approach is a simple, universal alternative to size measurement of the native droplet aerosol for exposure assessment:

- Consideration of realistic exposure scenarios and conditions of use: spray ageing (evaporation) and realistic application in simulated spray experiments (surface spraying, overspray formation)
- Consideration of droplet size spectrum of the spray as well as of concentration of the non-volatile phase in the liquid formulation
- Direct aerosol measurement in health-related size fractions according to international conventions
Airborne particulate release during spray application of nanoparticle-doped paints and varnishes

D. Göhler\(^1\) and M. Stintz\(^1\)

\(^1\)Research Group Mechanical Process Engineering, Institute of Process Engineering and Environmental Technology, Technische Universität Dresden, Münchner Platz 3, D-01062 Dresden, Germany

Keywords: nano-particle release, paints and varnishes, propellant spray can, spray gun, exposure assessment

Possible risk of substances to health, safety and environment depends on the coexistence of material toxicity and material exposure (NRC, 1983). In this context, systematic studies on nanomaterials in laboratory can provide basic information about the ability and the quantity of nanoparticle release into the air (Kuhlbusch et al., 2011).

Especially the coating industry processes numerous materials within their products (e.g. dispersing agents, pigments, fillers), which are covered by the definition of nanomaterials according to the recommendation of the European Commission (2011). Thus, several potential release scenarios for engineered nano-objects exist for this sector of industry and their products (Brower, 2010).

Despite a large production volume, little attention was spent on varnish spray application in the field of domestic and handcraft use. Merely, Hagendorfer et al. (2010) have analysed the nanometre size range of spray aerosols that originated from silver-nanoparticle suspensions, which were aerosolized by propellant and pump spray cans.

To estimate the (nano)-particulate release during varnish spray application, two different kinds of commercial propellant spray cans and a manual gravity spray gun were operated with four different types of varnishes that were combined with three kinds of metal-oxide tracer nanoparticle additives.

A suitable spray channel was developed for the spray aerosol conditioning. The spray-aerosol characterisation was performed according to the systematic of Göhler et al. (2013) using an Engine Exhaust Particle Sizer, an Aerodynamic Particle Sizer and a Condensation Particle Counter to determine number-weighted particle size distributions and particulate number concentrations over a size range from a few nanometres up to several micrometres. For the purpose of particle nature analyses, spray aerosol particles were electrostatically precipitated for scanning electron microscopy, transmission electron microscopy and energy-dispersive X-ray spectroscopy.

The presentation will give detailed information on the experimental conditions, the performed evaluation of the measurement data and results.

This work was supported by the German Paint Industry Association (VdL., representing about 180 German companies).

Determination of aerosol drug deposition by Raman spectroscopy


Wigner Research Centre for Physics of the H.A.S., Konkoly Thege M. st. 29-33, 1121, Budapest, Hungary

Keywords: In vitro, deposition, aerosol drugs, Raman spectroscopy,

The deposition of aerosol drugs - that are used for the treatment of lung diseases like asthma or COPD - in the human respiratory system is often presented as the results of an in vivo measurement (Newman, 2006). The drawback of this types of measurements are the poor resolution and the factors influencing the deposition are not adequately controlled. Consequently, one can get an integrated view of the particle deposition but the details remain invisible.

An experimental setup was built in our lab to study inhaled drug deposition in human respiratory airway models. A new methodology is presented here for the determination of the deposited particle concentration and its spatial distribution on the targeted surface. The complete system consists of a pulmonary waveform generator which is able to increase the correlation between the in vivo and the in vitro measurements, a BTPS simulator, a chamber holding the 3D lung models, and laboratory background for data evaluation and analysis. The digital versions of the respiratory models enable us to perform in silico experiments in the same geometries which extends our possibilities to validation test, etc.

Raman spectroscopy is not a widely used measurement method for in vitro deposition experiments because of the small scattered Raman intensities from the low amount of samples on the examined surfaces. The detection volume, which is determinated by the diameter of the excitation beam and the parameters of the sensing optics, can be increased limitedly. However, as it is shown on figure 1, the method is suitable for direct detection of the active substance of the inhaled drugs on a surface. The same area, which was affected by aerosol drug deposition, is shown as microscope image and Raman intensity map and the correlation is evident. The Raman spectra of four different pharmaceutical product are shown on figure 2. The spectra of the drugs were measured before deposition experiments, and clearly show that the different reagents can be distinguished easily by peak parameters. Peak intensities allow to determine the distribution of concentration by scanning the surface.

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Heterogeneous reactivity of internally mixed organic/inorganic aerosol particles with ozone

Estíbaliz Méndez, Lorena Miñambres, María N. Sánchez, Fernando Castaño and Francisco J. Basterretxea

Department of Physical Chemistry, University of the Basque Country (UPV/EHU), Barrio Sarriena s/n, 48940, Leioa, Spain

Keywords: ozonolysis, dicarboxylic acid, sodium halides, infrared spectroscopy

Atmospheric aerosols generally consist of inorganic species with a wide variety of organic compounds and elemental carbon. We have focused our attention in sea salt aerosols which are the second most abundant type of naturally suspended particulate matter in the troposphere after dust aerosol. An appreciable fraction of organic material is present in sea salt particles and it is known that the organic species at aerosols are extremely susceptible to atmospheric oxidation.

In the last years, the interest in the heterogeneous and multiphase chemistry in atmospheric aerosols has increased enormously. One of the most important reaction in the atmosphere is the ozonolysis, for this reason, general reactions with O$_3$ have been studied in depth for some time. However, there are not many studies about the reactions of unsaturated organic species in internally mixed organic/inorganic particles. These aerosols are likely to show important differences with regard to pure salt aerosols, because the mixture of components and the influence of competing processes can change particle properties, such as their water uptake (Y. Rudich, 2003).

In the present work we study the ozonolysis of some submicrometric sodium halide aerosols (NaCl, NaBr and NaI) internally mixed with maleic acid. Fourier-transform absorption infrared spectroscopy has been used to characterize particle composition, phase and water content, as well as gas-phase composition. With this study we aim to provide information about the reaction rate and mechanism of the ozonolysis of maleic acid in the presence of salt ions and the influence of hygroscopicity upon reactivity. In addition, we have studied the morphology of the internally mixed aerosol particles by Scanning Electron Microscopy (SEM) before and after the ozonolysis in order to study the structural changes in the submicrometric aerosols. The characterization of the ozonolysis reaction products has been supplemented with Electrospray Ionization Mass Spectrometry (ESI-MS) off-line analysis.

The ozonolysis of internally mixed maleic acid particles has been spectroscopically monitored at different relative humidities (RH): low (RH~0%), intermediate (RH~50%) and high (RH~100%). Preliminary results indicate that formic acid is generated as a product in the gas phase, and that it is produced at higher rate under high RH conditions, thus suggesting that a different mechanism operates in dry and aqueous particles. These results are in agreement with previous measurements in pure maleic acid aerosols (Nájera et al., 2009; Nájera et al., 2010). Also SEM pictures show that the internally mixed particles are not spherical and have complex forms.

Our results suggest that the surface properties of this type of aerosols may be more complex than model predictions. Further experimental work will be presented at the meeting.

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