

## Ultrafine particles from cruise ships and ferries in ports

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**Background:** Cruise ships and ferries without catalytic converters and particulate filters use huge amounts of dirty fuel (containing 100 times more sulphur than road diesel) in European ports. Cruise ships are large floating hotels with very high energy demands often spending a full day in port. Many ferries have frequent arrivals/departures and overnight stays idle running at berth. Cruise ships and Ferries thereby contribute significantly to local air pollution in the heart of many cities where still more port areas transform into modern residential areas. Shore power (and electric ferries) eliminate local air pollution from ships at berth but only few ports offer shore power. Usually, there are no air quality monitoring stations in ports. Hence, it is important to start monitoring air pollution from ships in ports. **Purpose:** To perform systematic screenings of air pollution with ultrafine exhaust particles from cruise ships and ferries in 10 larger Mediterranean ports in Malta, Italy, Spain, France and Greece to assess if this pollution affects the air quality in the surrounding cities. **Methods:** Newly calibrated P-Traks were used to measure ultrafine exhaust particles in ports. Wind speed, direction, temperature and humidity were taken from local weather forecasts and controlled locally (where possible) by a WindMate350. In each port was carefully planned systematic screenings of air pollution from cruise ships and/or ferries: Upwind and downwind measurements, measurements before/during/after ship passages, measurements during different weather conditions and in different distances from ships etc. Air pollution screenings were performed in 10 ports: Valletta, Piraeus, Barcelona, Marseilles, Livorno, Piombino, Savona, Civitavecchia, Genoa and Palma de Mallorca. **Results:** Cruise ships and ferries cause significant air pollution in port cities thereby exposing the local population to high levels of toxic air pollution. Port air (without local exhaust) typically contains 1,000-3,000 particles per cm<sup>3</sup> whereas air polluted by ship exhaust often contains hundreds of times higher pollution levels several hundred meters downwind ships during rather strong winds (> 7 m/s) where the pollution plume from the ships is quite diluted. Air pollution several hundred meters downwind ships thereby reaches much higher pollution levels than measured along streets in the cities. This clearly illustrates the intense air pollution from ships that can pollute large city areas downwind ships and thereby reach almost all residential areas close to the ports. **Acknowledgement:** These air quality screenings have only been possible due to the financial support of the EU Commission; project LIFE4MEDECA with the purpose to designate a Mediterranean Sea Emission Control Area. **Main author:** Kåre Press-Kristensen has a master and Ph.D. in environmental engineering from the Technical University of Denmark. He has been teaching air pollution for 20 years at the university (recent years as external). He works as senior air quality advisor in Green Transition Denmark. He works with pollution from wood burning, road traffic, shipping, non-road machinery, and aircrafts focused on emissions, ambient air quality, and the connected risk to public and occupational health. He mainly works on an international level. Contact info: [kaare@rgo.dk](mailto:kaare@rgo.dk) / (+45) 22 81 10 27.



## **Exhaust Emission Characteristics according to Load Factor of Construction Machinery in Real-work Mode**

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In recent years, the environment of downtown areas has become an increasingly important topic of human interest as urbanization continues to grow and more people move into cities. Particulate matter (PM) is a representative environmental problem in downtown areas. These particles come in various sizes, shapes, and chemical compositions, and are often referred to as "brown smog" when they are visible in the air. PM can be emitted directly from various sources such as power plants, vehicles, and construction sites, or it can be formed in the atmosphere from the reaction of other pollutants. Some common sources of PM include dust, soot, and diesel exhaust. Among them, construction machinery operates mainly in urban areas, emitting exhaust gases and noise, which negatively impact the urban environment. Therefore, the problem of emissions from construction machinery has become a severe social issue. There are solutions to address the problem of emissions in urban areas. First, the exact amount of emissions from construction machinery must be calculated. Second, policies can be established by setting accurate emission reduction targets. The engine load of an excavator is proportional to the magnitude of the load generated during operation, and changes in Load Factor (LF) can affect the emission inventory. Researchers are studying emission factors using a portable emission measurement system (PEMS) to improve emission inventories. However, no research on LF has been conducted. The purpose of this study is to investigate and compare the effect of engine load on the exhaust gas characteristics of excavator engines, to improve the method of calculating the emissions inventory of construction machinery. To achieve this purpose, real-work operation tests of construction machinery were conducted to calculate the average LF. Data were also compared with measurements taken at actual construction sites. Engine OBD data (power, torque, speed) were collected through an engine CAN communication device (neoVI FIRE2, Intrepid Control Systems), and exhaust gas was measured using PEMS (SEMTECH Ecostar, Sensors). Results suggest that emissions from construction machinery, specifically NO<sub>x</sub> emissions, vary depending on the type and characteristics of work being performed, despite having similar average engine loads. This finding highlights the impact of work and soil on discharge characteristics. Therefore, adjusting the load factor (LF) used in the emission calculation formula to reflect real-world conditions can prove to be a significant strategy for environmental improvement.

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## **Study on Effective Variables for CO<sub>2</sub> Prediction of Construction Equipments using Supervised Learning**

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Carbon neutrality is currently one of the most popular global issue. To achieve the carbon neutrality by reducing CO<sub>2</sub> emissions, various methods have been suggested across almost all of the industrial sectors. One of the methods is the implementation of 'Zero-Emission Construction Site(ZECS)', where the non-road vehicles operating on the site do not emit pollutants. It has already been successfully implemented in Oslo, Norway,<sup>1)</sup> and has gained significant attention as a result.<sup>2)-3)</sup>

For contributing carbon neutrality through implementing the ZECS, accurate assessment of CO<sub>2</sub> reductions on the site is important as much as setting strategies to build the site. However, such an assessment requires a CO<sub>2</sub> database from the construction equipments. To obtain CO<sub>2</sub> data of construction machinery under actual working conditions, considerable cost, manpower, and time are required. In addition, various operating types depending on vehicle types and wide rated power range would require uncountable number of tests. Therefore, we aim to study for methodology to build the CO<sub>2</sub> database of construction machinery, which is operating in actual-working conditions by monitoring CO<sub>2</sub> without test, using AI prediction.

For the research, we obtained variables from vehicle and CO<sub>2</sub> data for three types of construction machinery through the test using PEMS(portable emissions measurement systems). We chose two rated power range vehicles for each types, that forklift(73.6kW, 80.9kW), loader(106kW, 256.7kW), excavator(129kW, 202.3kW). The test cycle was built by analyzing each of vehicles' representative operating types. Data obtained through the tests was applied to Python open source supervised model. The model consists of extreme gradient boosting algorithm,<sup>4)</sup> which is classifying data using decision tree and predicts using gradient descent method. As a result of the research we found out effective variables for excavator CO<sub>2</sub> prediction are exhaust flow, exhaust humidity and air/fuel ratio. However, for forklift and loader, there were the three variables and fuel rate. Finally we could get method of monitoring CO<sub>2</sub> by storing the sorted variables at real operating of in-use construction equipments.

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## Algorithm for Determining Abnormal Signs of Ship Propulsion Engines Using Machine Learning

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Heat engine is the main engine that helps to propel a ship. Main engine uses a rotating propeller and is the most important part in the course of ship operation. If the main engine fails, the ship may be uncontrollable and may lead to accidents. Time-based maintenance (TBM) is a maintenance method applied in the engine room of ships. However, it has a low operational efficiency for maintenance, resulting in high maintenance work time and operation costs in the engine room. To solve the problem of the TBM maintenance method and increase the efficiency and economics of ship maintenance, a predictive maintenance system that can predict the occurrence of failure or defects by continuously monitoring the status of machines and systems is necessary.

To solve these problems and operate an advanced ship maintenance system, this study designed an algorithm for determining abnormal signs in ship's main engines using machine learning. A database of normal operating conditions was established to accurately identify anomalies by applying time-series analysis based on the operation time of the main engine using total and average data of navigation. Monitoring alarms of the alarm monitoring system and engine maintenance items of the planned management system were analyzed to select significant factors for identifying abnormal symptoms. The trend of selected significant factors was identified through data analysis. A formula that can represent the state reference value of the main engine was derived, and an abnormal symptom judgment algorithm was designed. In addition, considering the specifications and engine operation conditions, engine factors were divided into concern level (concern, 1) and an abnormal level (abnormal, 2) based on the state reference value of the main engine to determine engine abnormalities.

The results of this study reveal that the ship operation efficiency can be further improved by optimizing the ship maintenance system.

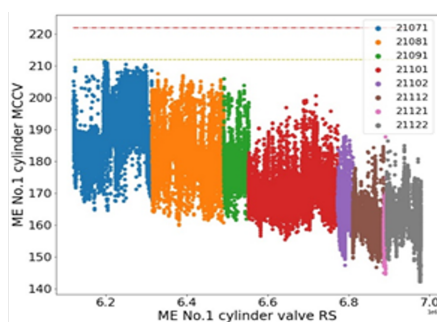


Fig. 1 Normal operation MCCV based on running hour

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## **Semivolatile fraction's characteristics from engine and car exhaust**

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Semivolatile compounds (SVC) in the exhaust from cars and vehicles are not well-known and they are not directly limited by emission standards. Additionally, SVCs partly pass the filters for collecting the particulate matter (PM). Phase partitioning of SVC compounds varies depending on their concentration and saturation pressure, the other constituents of exhaust gas, and the sampling parameters. Semivolatiles, besides volatiles and particles, are precursors of secondary aerosols, and they also carry many harmful exhaust species.

We studied polyaromatic hydrocarbons (PAHs) from PM and SVC fractions collected from the exhaust from heavy-duty diesel engine, Euro 2 car and Euro 6a cars. A high-speed heavy-duty, non-road common-rail diesel engine without exhaust aftertreatment system was operated with ISO 8178 RMC-C1 test cycle. Euro 6a passenger cars using diesel, gasoline, ethanol and natural gas, and Euro 2 diesel car, were tested with the European chassis dynamometer driving cycle (NEDC) at -7 °C. SVCs were collected with a membrane disks (HLB). For SVC from diesel engine, simulated distillation clarified its distillation range and thermal-optical analysis its carbon content. Additionally, GC-MS indicated which kind of compounds were present in the SVC fraction.

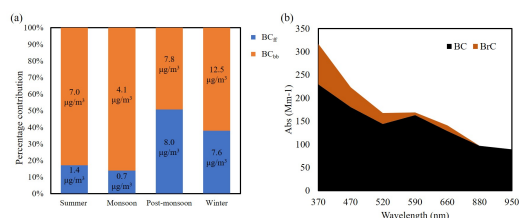
SVC fraction collected with HLB disks was substantial when compared to the PM fraction. PAHs were found in higher concentrations from the SVC than from the PM, however, PAH profiles were different. Results of this work show that incomplete combustion of fuel and lubricating oil leads to SVC emissions containing PAHs and other compounds.

## Sources and Light Absorption Properties of Black Carbon over Delhi

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Black carbon (BC) is an important constituent of the atmosphere formed during the incomplete combustion of fossil fuel and biomass. It perturbs the earth's radiation budget by absorbing incoming shortwave and outgoing terrestrial radiation and is recognized as the second-largest contributor to anthropogenic radiative forcing. In spite of its adverse climatic and health effects, the detailed information on BC sources and their light absorption properties is still not well documented in Delhi. Therefore, the observations were carried out to measure BC concentration in Delhi from January to December 2021 to study BC's sources and their light absorption properties using a seven wavelength aethalometer (Magee scientific® AE33). The BC is bifurcated into two sources i.e., biomass burning (BC<sub>bb</sub>) and fossil fuel combustion (BC<sub>ff</sub>). The BC, BC<sub>ff</sub>, and BC<sub>bb</sub> concentrations were  $5.89 \pm 4.09$ ,  $8.04 \pm 5.16$ , and  $4.07 \pm 4.75$   $\mu\text{g}/\text{m}^3$ , respectively, during the study period. The contribution of BC<sub>ff</sub> and BC<sub>bb</sub> to total BC was 65% and 35%, respectively, this represents the dominance of fossil fuel combustion sources in Delhi. The seasonal variation of BC<sub>ff</sub> and BC<sub>bb</sub> depicted the dominance of BC<sub>ff</sub> during summer, monsoon, and winter seasons, but during the post-monsoon season, BC<sub>bb</sub> concentration is higher than BC<sub>ff</sub> (Figure 1a). This could be attributed to the biomass burning events in northern India which influenced Delhi's air quality. The total light absorption (Abs) over Delhi is measured as 317, 223, 168, 169, 141, 96, and 89  $\text{Mm}^{-1}$  at 370, 470, 520, 590, 660, 880, and 950 nm wavelength, respectively. The spectral variation of (BC absorption) Abs<sub>BC</sub> and (brown carbon absorption) Abs<sub>BrC</sub> showed that BC absorbs light throughout the spectrum but BrC absorbs in the UV region. The mean fraction of Abs<sub>BrC</sub> in Abs during the sampling period was 28, 19, 14, 3, and 9 % at 370, 470, 520, 590, and 660 nm wavelengths, respectively (Figure 1b).



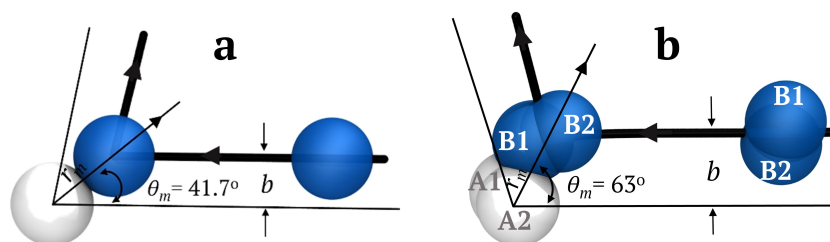
## Mean free path of air: The impact of inelastic molecular collisions

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The mean free path,  $\lambda$ , dictates if aerosol transport occurs in the free molecule or continuum regime. For eons, the kinetic theory of gases [1] has given  $\lambda$  assuming elastic collisions between spherical gas molecules. However, is this so with what we know about molecular shape and force fields today? Having reached a state of maturity today, molecular dynamics (MD) simulations can elucidate the fundamentals of basic aerosol processes that lead to understanding of natural phenomena and accelerating process scale-up [2]. Here the mechanics of gas collisions are studied by thoroughly-validated atomistic MD treating O<sub>2</sub> and N<sub>2</sub> as true diatomic molecules accounting for their shape and force field for the first time to our knowledge. The MD simulations were conducted for air (21/79 mole O<sub>2</sub>/N<sub>2</sub>) in the NVE ensemble at 300 K and 1 atm following Zambrano *et al.* [3]. Collisions were identified by the distance between colliding molecules, as in kinetic theory.

Treating O<sub>2</sub> and N<sub>2</sub> as hard spheres (Fig. 1a) by MD led to straight trajectories and collision densities in agreement with those from kinetic theory. Accounting, however, for the molecular shape and force field, trajectories were no longer straight, and these densities were much higher due to the attractive part of the force field and diatomic, thus more voluminous shape of N<sub>2</sub> and O<sub>2</sub> (Fig. 1b).



**Fig. 1** Collision trajectories by a) classic kinetic theory and b) accounting of attractive and repulsive forces between diatomic gas molecules (like N<sub>2</sub> and O<sub>2</sub>). The reference (stationary) molecule is in white, and the colliding one in blue. The bold line shows the trajectory followed by the moving molecule before/after collision.

Detailed analysis of the MD trajectories revealed complex collision patterns between colliding diatomic molecules, which, however, were never observed by treating O<sub>2</sub> & N<sub>2</sub> as hard spheres. These included the participation of three molecules in the same collision and the so-called spurious collisions, i.e., the successive collisions between the same pair of molecules without another molecule intervening in their interaction. Spurious collisions were systematically removed from the analysis to avoid overcounting collisions.

Due to the enhanced interactions between air molecules when these are treated as diatomic molecules their  $\lambda$  is determined as 38.5 nm almost 43% smaller than the currently known and widely used value in all aerosol textbooks of 67.3 nm at 300 K and 1 atm from the classic kinetic theory of gases.

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## Molecular dynamics simulations of fullerene and silica nanoparticles diffusion coefficients in air

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Knowing the diffusion coefficient of airborne nanoparticles (NPs) is important in nature and industrial applications that involve NPs diffusion and transport. Due to its fundamental nature, correlating NPs' diffusivity to NP size, pressure and temperature has attracted the interest of the scientific community over the years and several corrections to the kinetic theory or Stokes-Einstein relation have been proposed. Apart from the discrepancies often observed between them, especially regarding the dependence of diffusivity on temperature and/or NP diameter, they also fail to predict particles' diffusivity in the free molecular regime. This is mainly attributed to the difficulties encountered in experimental setups to include particles of a few nanometers, and usually large Knudsen numbers are achieved with particles in the range of micrometers under very low pressure conditions. However, the interactions between a particle and the gas molecules depend on the particle's size, and as this becomes comparable to the gas molecules size the collision type differs to the one that a large particle undergoes [1]. The so far used Cunningham-Millikan (CM) formulation has been derived based on experimental data that typically involve particles with diameter larger than 20 nm, and for this reason they might not describe adequately the transport dynamics of the particles in the free molecular regime.

Molecular dynamics (MD) simulations, however, provide useful insights of phenomena that take place in the atom or molecular scale and can contribute and supply data also for the tiny nanoparticles' diffusivity [2]. Therefore, in this study fully atomistic MD simulations are carried out in air of fullerene and silica particles with a diameter that extends from 0.4 up to 7 nm for estimating their diffusion coefficients at room temperature and pressure. Also, the temperature dependence of nanoparticle diffusivity is also explored over the 100 - 600 K span. The diffusion coefficient for each case is estimated from many independent MD simulations and subsequent averaging.

Our results are compared with the most known equations available in literature, i.e., the Cunningham-Millikan, the de la Mora *et al.* [3], the Chapman-Enskog and the kinetic theory of gases. The deviations observed between the MD-estimated diffusion coefficients and the CM equation are in accordance with the bibliography, where deviations of the CM formulation as the NPs' size becomes comparable to the gas molecules' size are reported (e.g., by de la Mora *et al.* [3]). Additionally, our study provides further information on the interactions with the gas molecules and the diffusion behaviour of NPs with a diameter smaller than 2 nm, where the observed deviations become even more prominent and the diffusivity dynamics of such small NPs cannot be described even by modifications proposed that include either corrected term for the particles' diameter and/or considers also the gas molecule size. Our MD simulations allow for better insights of how the size of these NPs should be treated in formulations that describe their diffusivity, while we propose a new modification of the Cunningham-Millikan formula that expresses the diffusion coefficients from the free molecular up to the continuum regime.

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## Optical and Chemical Properties of Wildfire Aerosol Plumes in the Free Troposphere

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Wildfires have become more frequent and more severe over the last decades due to climate change and land use and this trend is expected to continue. They are not only destroying land, lives and ecosystems but they also produce a large amount of primary particulate matter and gaseous aerosol precursors. When these biomass burning (BB) emissions are injected into the free troposphere (FT), they can be transported over long distances and thereby undergo chemical aging and influence the earth's energy budget. Due to increased backscattering of lower level clouds and longer residence times, the radiative forcing efficiency of PM in the FT can be higher than at ground level. Moreover, large concentrations of light absorbing aerosol in the FT can alter the vertical temperature profile with consequences for clouds and precipitation.

In this work, optical and chemical properties of wildfire plumes transported to the Jungfraujoch (JFJ) High Altitude Research Station, Switzerland (3571m a.s.l.) are investigated. From optical measurements, total and backscattering coefficients, absorption coefficients and their derived Ångström exponents as well as the single scattering albedo were retrieved. BB plumes were identified by using aerosol optical properties (in particular to exclude Saharan dust) as well as the gas phase concentrations of CO, CO<sub>2</sub>, benzene, toluene and CH<sub>3</sub>Cl. In addition, <sup>222</sup>Rn levels were used to distinguish between air masses from the planetary boundary layer and from the FT.

For the period between 2015 and 2019, more than 30 distinct plumes were identified at JFJ, many of them arising from Europe, but also some from North America. To complement this analysis with chemical information, the dataset was extended with data from 2012 to 2013 when an aerosol chemical speciation monitor was operated at JFJ. Figure 1 shows properties of the most prominent plume during that period. Non-refractory PM<sub>1</sub> of this plume was dominated by organics. A preliminary analysis revealed that the signal-to-noise ratio of the known BB tracer  $f_{60}$  (fraction of m/z 60 to all organic m/z) is very low throughout the year, but clearly increased during the plume. A more in-depth analysis of the identified plumes is ongoing aiming at the identification of other tracers for wildfire plumes as well as the distinction between different plume origin regions.

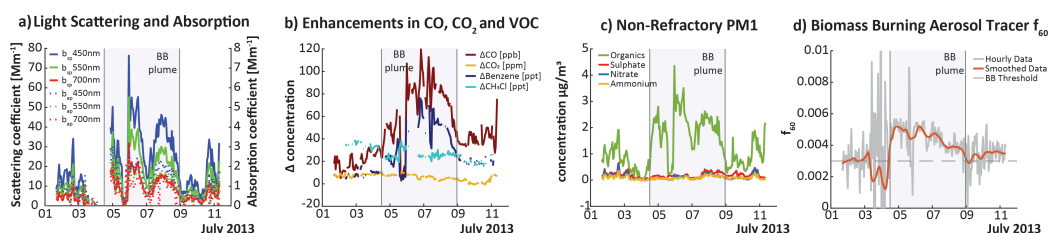


Figure 1: Optical and chemical characterization of the most prominent wildfire plume at JFJ in the period between July 2012 and October 2013. a) Total light scattering coefficients (solid lines) and absorption coefficients (dashed lines). b) Enhancements in concentrations of CO, CO<sub>2</sub> and VOCs. c) Chemical composition of non-refractory PM<sub>1</sub>. d) Fraction of m/z 60 of total organic aerosol concentration, a known tracer for biomass burning emissions.

## **Personal exposure monitoring of size-segregated aerosol and PAHs in recreational runners**

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Spatial and temporal concentrations of particulate matter (PM) and pollutants bound to the particle surface vary substantially. Therefore, individual exposures can be significantly different from concentrations measured at stationary monitoring sites. Personal monitoring using small portable battery-powered devices enables to measure exposure to pollutants comprising all daily activities and exposure sites of an individual. In the present study, we employed SKC Leland Legacy Pump with Sioutas Cascade Impactor enabling sampling of different PM size fractions (<0.25, 0.25–2.5, and >2.5 $\mu\text{m}$ ). Furthermore, 20 selected US EPA and EU 15+1 priority polycyclic aromatic hydrocarbons (PAHs) bound to the three different size fractions of PM were analyzed. A total set of 129 recreational runners from two localities of the Czech Republic: industrial area of the city of Ostrava (n=65) and a control area of České Budějovice city (n=64), participated in 24h personal air sampling taking place from August 2019 to August 2021. Personal monitoring data were accompanied by a detailed questionnaire and PM<sub>2.5</sub> measurements from the nearest stationary monitoring stations. Gravimetric analysis of the Teflon filters was carried out pre- and post-exposure to determine the PM size fractions masses. Extraction of the target PAHs was carried out by organic solvent extraction in an ultrasonic bath. An analytical method for PAH determination was developed using gas chromatography coupled to tandem mass spectrometry in electron ionization. As expected, all three PM fractions exhibited higher minimum, maximum and median concentrations in Ostrava than in České Budějovice, with maximum concentrations being approximately twice as higher for all three size fractions. The total amount of 20 PAHs ranged from 0.1 to 42.2 ng/m<sup>3</sup>. Concentration of benzo(a)pyrene, an air quality standard, ranged from 0.01 to 3.27 ng/m<sup>3</sup>. The EU daily averaged concentration limit of 1.0 ng/m<sup>3</sup> was exceeded in 20 out of 129 volunteers, especially those exposed in the industrial locality and the winter season. The particle size distribution showed 87% of the total amount of PAHs to be bound to PM<sub>0.25</sub> and only 1% to the fraction larger than 2.5  $\mu\text{m}$ . Comparing the industrial and control areas, Ostrava air contained twice as high mean concentrations of PM-bound PAHs compared to České Budějovice. The highest concentrations were observed in January and February in both areas, indicating the significant contribution of local heating and unfavourable meteorological conditions. The results of the personal monitoring contribute to the identification of local and seasonal sources of PAHs and specific activities with high PAH exposure. This work was financially supported by the European Regional Development Fund under Grant Healthy Aging in Industrial Environment HAIE (CZ.02.1.01/0.0/0.0/16\_019/0000798).

**The new real-time source apportionment feature of the portable AethLabs microAeth black carbon monitor**

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Black carbon (BC) is an aerosol byproduct of incomplete combustion with substantial implications for human health. Common sources include the combustion of biomass (e.g., wildland fires, woodstoves, cookstoves, and agricultural burning) and fossil fuel fuels. These sources are governed by a wide variety of natural and societal processes, and require distinct policy and regulatory approaches for mitigation. As a result, curbing BC emissions in an efficient and effective way requires specific knowledge of the mix of relevant sources and their contributions to exposure concentrations.

We present a software update that enables real-time source apportionment in microAeth portable multi-wavelength black carbon monitors. This update integrates the Aethalometer Model as previously validated by others for the delineation of measured BC concentrations arising from biomass combustion relative to those arising from fossil fuel combustion. We present the validated equations, parameters, and assumptions underlying this new feature. Source apportionment data collected with a beta version of this software feature during a short winter field campaign in an urban residential setting in Europe are presented, demonstrating distinct signals from biomass combustion and fossil fuel combustion.



## Reduced particle emissions from paraffinic diesel blended with polyoxymethylene dimethyl ether

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New synthetic and renewable-based fuels and oxygenate compounds are potential methods to reduce engine emissions. In previous studies, polyoxymethylene dimethyl ether (OME) has been observed to reduce particle emissions of a single cylinder test engine when blended with fossil diesel [1] and with fossil and paraffinic diesels [2].

We measured engine-out (no-aftertreatment) emissions from a turbocharged 4.4 L common-rail non-road diesel engine with different fuels: fossil EN590 diesel, paraffinic HVO-type diesel and paraffinic diesel blended with 10.6 vol-% of OME. The engine was run according to RMC-C1 test cycle. Additionally, emissions were tested from 5 different static load points. Due to large number of load points, engine emissions during static operation were mapped thoroughly. Engine torque was maintained at the same level with all fuels. Emissions were measured with comprehensive instrumentation including particle number (PN), black carbon (BC), and particulate matter (PM) as well as gaseous measurements with FTIR and sampling of semi-volatile organic compounds (SVOC). Elemental and organic carbon (EC/OC) was analyzed from the PM samples.

BC and PM emissions reduced when EN590 was switched to HVO and even more when switched to HVO-OME blend. EC/OC analysis from filter samples also indicated drastic decrease in EC emissions with HVO-OME blend. Particle number emissions (>23 nm and >10 nm, both non-volatile) reduced more than 50% with HVO-OME blend compared to EN590 or HVO. All the fuels produced similar particle size distributions but with OME, the concentrations were lower throughout the entire size range.

As a drawback, HVO-OME blend was found to produce significantly more formaldehyde emissions than EN590 or HVO and these emissions were the greatest at low load points. Results indicate that comprehensive emission analysis should be conducted when new fuel components are introduced. In further research, emissions with aftertreatment could be studied.

[1] Ahmad Omari, Benedict Heuser, Stefan Pischinger, Christoph Rüdinger, *Applied Energy*, **2019**, 239, 1242-1249.

[2] Matteo Parravicini, Christophe Barro, Konstantinos Boulouchos, *Fuel*, **2021**, 292, 120177.

## **Investigation of the influence of ammonia and hydrogen addition on soot formation in ethylene co-flow laminar diffusion flames**

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Ammonia is a promising carbon-free fuel for combustion. Co-firing ammonia with hydrocarbon fuels is an interesting strategy to improve combustion characteristics and reduce CO<sub>2</sub> emissions. Soot which is a dangerous airborne pollutant harmful to human health and the environment could still be generated during co-firing with hydrocarbon fuels. In this study, the soot-suppressing effect of ammonia addition was investigated using laser diagnostics and probe sampling from nitrogen diluted ethylene (24.7% by volume) co-flow laminar diffusion flames with increasing ammonia content (up to 15% by volume). Nitrogen dilution was lowered (from 75% to 45% by volume) with increasing ammonia content introduced to the fuel mixture while maintaining the molar balance. A type S thermocouple was used to measure the temperature along the flame centerline and identify soot deposition locations in the flame. Planar laser induced incandescence (PLII) was used to measure soot volume fraction (SVF). Planar laser induced fluorescence (PLIF) at different wavelengths was used to study polycyclic aromatic hydrocarbons (PAHs) which play a critical role in soot formation. Scanning Mobility Particle Sizer (SMPS) was used to measure soot particle size distribution and average particle diameter at several heights above the burner (HAB). Hydrogen is another attractive clean alternative to fossil fuels. Measurements were repeated with hydrogen addition (up to 45% by volume). Results indicate that ammonia addition suppresses soot formation while hydrogen addition promotes it.

**Exhaust and non-exhaust particle emission measurements using a road tunnel environment in Tokyo.**

H. Hagino<sup>1</sup>

<sup>1</sup>Senior Researcher

Exhaust and non-exhaust particle emission factors were estimated by measuring both PN and PM in a Tokyo road tunnel environment. Solid-PN correlated better with PM<sub>2.5</sub>, and Solid-PN was found to be more sensitive than Total-PN to real-world PM reduction. Exhaust-related compounds such as BC, NO<sub>x</sub>, and CO tended to decrease from 2012 to 2022, however, PM<sub>10</sub> and PM<sub>2.5</sub> seemed to bottom out due to the remaining non-exhaust emission particles.

## Brake wear particles: effects of braking intensity, frequency and temperature

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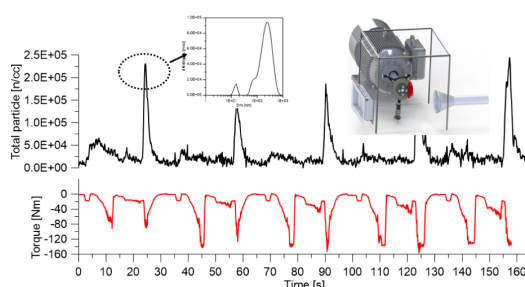
<sup>1</sup>Institute of Science and Technology for Sustainable Energy and Mobility (STEMS) - CNR

Traffic-derived emissions is the main source of particulate matter in the urban area. On road particle emissions can be classified in exhaust particles (EP), due to fuel combustion and lubricant volatilization during the combustion process, and non-exhaust particles (NEP), related to the mechanical abrasion of brakes and tires. The tightening of the emission regulations for gasoline and diesel vehicles has required the improvement of the exhaust emission after-treatment systems and the use of more environmentally friendly fuels driving down the exhaust particles. Consequently, the proportion of NEP has increased. In view of the intensification of the electrification in the road transport a further growth on the non-exhaust contribution is forecast because of the extra weight of the batteries.

The EP contains a variety of hydrocarbons and combustion by-products, whereas NEP are mainly composed of heavy metals, but not for this they are less dangerous. These metals, in fact, can form oxygen free radicals, which at high concentration can cause various diseases. Moreover, they are in the ultrafine range, thus, they can easily penetrate in the respiratory and in cardiovascular systems. Anyway, information on NEP is still inadequate. More studies are needed to broaden the knowledge on NEP to define a proper measure procedure for the emission legislation and above all to improve the technologies as well as the management of the braking events.

This study aimed to evaluate the effect of different brake profile and the temperature on the particle emissions. The investigation was performed on a brake typically used for light-duty vehicles. Different profiles representative of urban pathway, where typical braking events are more frequent because of the congested traffic and junctions, were performed. An EEPS and an OPS were used to measure the particle in the size range from 5.6 nm to 10mm. The disc temperature was measured by means of an InfraRed camera. The results highlighted that the extent and size of particles are affected by the brake profile: stronger the braking event, higher the temperature and larger the particle emissions.

Figure 1. Particle number and size distribution due to the brake wear.



## Formation and Morphological Appearance of Tyre Wear Particle Emissions

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Air pollution is a global threat to human health and poses a major challenge especially in urban regions. As one of the primary pollutants, particulate matter is increasingly becoming the focus of research and public interest, as it is responsible for a multitude of health risks and causes numerous deaths each year. While exhaust emissions produced by vehicle traffic are steadily decreasing, non-exhaust emissions such as tyre and brake wear are gaining in importance, as emissions from tyre wear, in particular, are increasing. These tyre emissions are especially relevant from a health perspective, as they are an important source of ultrafine particles (UFP).<sup>[1]</sup>

Motivated by the increasing contribution of non-exhaust emissions to air pollution, this study was performed to gain more knowledge about the formation of tyre wear emissions under different driving conditions.

As part of this study comprehensive driving tests of two types of tyres were conducted using a modified BMW i3 passenger car. The disc brake and rear wheel of one side were enclosed separately to ensure independent characterisation of the two emission types.

The driving tests and emission measurements were carried out on a chassis dynamometer. Different measuring devices such as fast sizers and condensation particle counters were used to characterise the particle number concentration and the size distribution between 5 nm and 10 µm. The measurements showed that the largest number of particles is formed below a diameter of 100 nm for both tyre types during acceleration events.

To get more knowledge about the formation and chemical composition of the tyre wear, particles were collected with a low-pressure impactor on aluminium and polycarbonate substrates, which were later investigated with a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). These investigations revealed various morphological features such as small rounded particles, larger flakes, and more elongated shapes and in particular showed differences between different particle sizes. The chemical analysis supported the assignment of tyre wear particles and helped identify particles originating from the pavement.

Acknowledgement: This work was conducted as part of the ZEDU-1 (Zero Emission Drive Unit-1) project and is supported by the Baden-Württemberg Ministry of Economy, Labour and Tourism.

[1] J. C. Fussell, M. Franklin, D. C. Green, M. Gustafsson, R. M. Harrison, W. Hicks, F. J. Kelly, F. Kishita, M. R. Miller, I. S. Mudway, F. Oroumihyeh, L. Selley, M. Wang, Y. Zhu, *Environ. Sci. Technol.* **2022**, 56, 6813–6835.

## **Study on the Effects of Operating Conditions on Nanoparticle Emissions in Direct Injection Ammonia Engines**

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According to Decarbonizing Maritime Transport reported in 2018, next-generation biofuels, liquefied natural gas, hydrogen, ammonia, and methanol can be applied as alternative fuels for propulsion of next-generation ships for decarbonization. And it was reported that if green ammonia using renewable energy is applied, it can be an eco-friendly fuel that can reduce carbon dioxide emissions by 100%. Because ammonia is judged as an alternative fuel with the highest growth potential in the future eco-friendly fuel market, considering the eco-friendly characteristics of ammonia fuel, its technical feasibility as an engine fuel, its applicability in terms of production and supply chain establishment, and economic feasibility, worldwide engine manufacturers are accelerating the development of ammonia fuel engines. There are many technical challenges to be solved as an alternative fuel, such as ammonia's low ignition characteristics and slow flame propagation speed, exhaust gas treatment problems due to ammonia slip, and difficulties in storage and management due to corrosiveness and toxicity. Therefore, in order to preoccupy eco-friendly transportation in the future and maintain the gap with competitors, it is very urgent to develop and localize core parts of ammonia alternative fuel engines. Until now, studies on ammonia engines have been aimed at developing combustion performance to secure stable combustion, and studies on exhaust gases including particulate matter have been very limited. Therefore, in this study, the emission characteristics of nanoparticles according to operating conditions was assessed as part of the preceding research on direct injection ammonia engines.

## **Comparison of particle number between the gasoline and hydrogen combustion engine and NOx reduction strategy in the hydrogen engine**

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Particle generation in internal combustion engines has been seriously dealt with, especially in diesel engines, and currently, including gasoline engines and gas fuel engines, not only the mass of particles but also the number of particles generated are regulated. This particulate generation is a major contributor to the movement to limit the use of internal combustion engines, including harmful emissions and carbon dioxide. Recently, in a situation where electric vehicles using batteries or fuel cells are gradually becoming popular, interest in hydrogen internal combustion engines using hydrogen as fuel, such as fuel cells, is prominent. This is because it is possible to significantly reduce carbon dioxide and harmful exhaust gases without major modifications to existing internal combustion engines. In the case of an internal combustion engine that burns hydrogen, the generation of particulate matter is expected to be extremely small compared to conventional hydrocarbon-based fuels. It is known that the components of the hydrogen fuel itself do not have any components necessary for particle formation, and extremely fine particles are generated through some combustion processes from the lubricating oil. However, there is very little related information because various research results have not yet been conducted or are not known.

Therefore, in this study, the number of particulate matter generated in gasoline and hydrogen direct injection engines was measured using the latest 2-liter gasoline direct injection engine. Measurements and results were analyzed through the Scanning Mobility Particle Sizer (SMPS) while operating the engine under the same 8 load and speed conditions. Despite the application of a direct injection engine that has unfavorable conditions for fuel mixing, the number of particles of the hydrogen engine were significantly lower than that of the gasoline engine

Meanwhile, in the hydrogen direct injection engine used in this study, in order to reduce nitrogen oxide, which is the only harmful gas component, an experiment was conducted to see if nitrogen oxide can be further reduced through the application of exhaust gas recirculation(EGR) and post fuel injection. Overall, the application of EGR showed some effect on reducing NOx due to the nature of the hydrogen engine that must be operated under lean operating conditions, but the NOx reduction effect through post-injection was very effective.

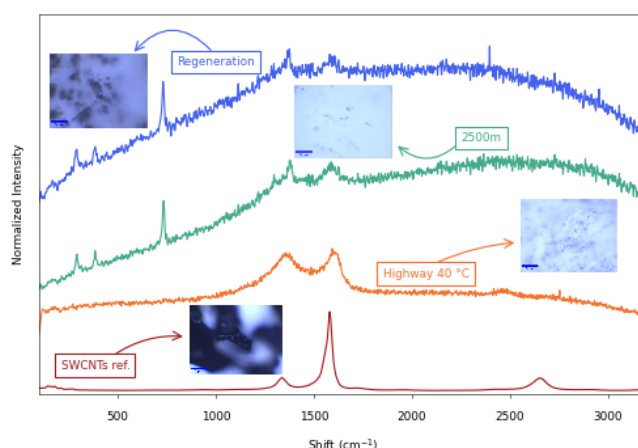


## Analysis of sub-micrometric particulate emitted by different types of internal combustion engines: a Raman Micro-spectroscopy study.

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<sup>1</sup>European Commission

The present research is focused on the development of an efficient and accurate approach for the physicochemical and morphological characterization of particulate samples collected at the exhaust of internal-combustion engine vehicles by means of optical microscopy and Raman spectroscopy. The study examines Raman spectra of micro, sub-micro, and ultrafine particles emitted by both light-duty and heavy-duty vehicles, with samples collected according to The European Commission Regulation 1151 (2017). Tests were carried out under standardized type-approval conditions and also under extended driving conditions, in which the driving style, ambient temperature and altitude were significantly varied. In this way one could check if the different testing conditions have any significant effect on the nature of the emitted particulate on a micrometric and sub-micrometric scale. Raman spectroscopy can identify various forms of carbon in the samples, particularly defective graphene rings in most cases, indicating its effectiveness in characterizing particulate matter deposited on filters, according to the procedure indicated in EC Regulation 1151 (2017), without further treatment. This approach, combined with numerous tests on different vehicles, allows for the development of a large database for statistical analysis. However, confirming the presence of carbon nanostructures detected by Raman spectroscopy is challenging and requires parallel techniques, such as transmission electron microscopy. The research also employed a correlative study using Hyper-Spectral Enhanced Dark Field microscopy and SEM/EDX analysis. A condensation growth tube aerosol sampler collected particles, and the scattering spectra of single nanoparticles were measured and analyzed using the Mie model for scattering, with size parameters obtained from SEM analysis. This study allowed measuring the refractive index of the single nanoparticles and, in combination with the EDX elemental analysis, obtaining insights on their material composition. Long-term goals of exhaust particulate analysis include determining a comprehensive approach to observing chemical species formed in exhaust particulate under specific driving conditions and characterizing their behavior in various circumstances. The possible formation of carbon nanotubes or sulfur-containing compounds will be studied in particulate matter produced by internal-combustion engine vehicles driven under various testing conditions. The impact of these species on air quality, the environment, and human health will be assessed in future studies.



## Influence of the type of soot generator on counting efficiency of PN-PTI instruments

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Aerosols emitted by the transport sector need to be better controlled and monitored [1]. To identify manipulated or broken diesel particle filters (DPFs), new particle number (PN)-based regulations were recently introduced across Europe for the periodic technical inspection (PTI) of vehicles [2]. In our previous work [3], the counting efficiency (CE) profiles of multiple diffusion charging (DC)-based PN-PTI counters depended strongly on the type and physicochemical properties. Combustion generated aerosols (CAST) were the best proxy for diesel soot, while spark discharge or NaCl particles led in some cases to remarkable deviations from particle concentrations reported by the condensation particle counter (CPC)-based reference instrument [3]. The aim of this study was to evaluate whether different CAST models can also result in such deviations of the measured CEs of DC-based PN-PTI counters. The particles were collected and analysed with EC/OC (elemental and organic carbon) thermo-optical methods. Morphology was analysed with scanning electron microscopy (SEM). In a first measurement campaign at Metas we explored the effect of four different combustion generators: bigCAST, miniCAST 5201 BC, miniCAST 6204 C (Jing AG, Switzerland) and Mini Inverted Soot Generator (MISG, Argonaut Scientific, Canada) on the CE of six DC-based PN-PTI sensors: AEM, HEPaC, DiTEST, CAP3070, DX280, Knestel. In the second campaign at JRC we studied the effects of diesel soot generated with Euro 5 and Euro 6 test vehicles with bypassed DPF on the same counters.

As depicted in Fig. 1, the CE of a DC-based PN-PTI counter HEPaC (FHNW, Switzerland) rises with increasing particle size. There is a notable influence of the type of soot aerosol, which could cause failure of the respective instrument in a verification test. These results will be compared to those obtained with the Euro 5 and Euro 6 test vehicles.

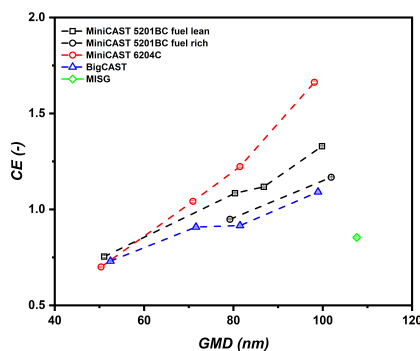


Figure 1 Counting efficiency profile of the HEPaC (FHNW, Switzerland) PN-PTI counter.

[1] Commission Recommendation (EU) 2023/688 of 20 March 2023 on particle number measurement for the periodic technical inspection of vehicles equipped with compression ignition engines; ELI: <http://data.europa.eu/eli/reco/2023/688/oj>

[2] Burtscher, H., et al. (2019), Emission Control Science and Technology 2019 5:3, 5(3), 279–287. <https://doi.org/10.1007/S40825-019-00128-Z>

[3] Vasilatou, K. et al., Preprint available at <http://dx.doi.org/10.2139/ssrn.4329822>

## **On-road & field measurement of exhaust flow of small engines**

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Real driving emissions measurements, after being successfully implemented on light and heavy on-road vehicles, are being considered for L-category vehicles such as moped and motorcycles, and for small non-road engines. Successful real-world measurement necessitates mastering both exhaust gas concentrations and flow determination. Neither of the two dominant approaches, direct flow measurement by Pitot tube and calculation from intake air flow measurements, is readily applicable for simplistic single-cylinder engines. Direct exhaust flow measurement by Pitot tube is subject to severe oscillations and reversals of the exhaust flow. Air flow and fuel flow meters are typically too bulky for installation on small equipment, and speed-density method lacks sufficient accuracy due to the relatively low volumetric efficiency of small engines.

In this work, different approaches for exhaust flow measurements on small engines will be reviewed, and improvised measurement setups developed by the authors will be presented. One such setup is an Improvised full-flow dilution tunnel, using a commercial vacuum cleaner turbine as a blower and a set of garage-grade gas analyzers, suitable for small garden machinery. Another setup is a Pitot tube with fast-response (kHz range) pressure sensors, measuring both forward and reverse exhaust flows, applicable to motorcycle engines. Yet another approach is the speed-density method, where the engine volumetric efficiency of a moped engine mapped on a chassis dynamometer using a direct fuel flow measurement. Examples of measurement setups and results of comparison measurements will be presented.

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## Performance Evaluation Methods for Air Cleaners

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In ANSI/AHAM AC-1-2020, Clean Air Delivery Rate (CADR) is a measure of the appliance's ability to reduce aerosol particles. The  $CADR_C$  measurement must be carried out in a standard AHAM chamber, following a tedious and time-consuming procedure. An alternative method is using the product of the flow rate and the filtration efficiency of the air cleaner. This product is named equivalent CADR or  $CADR_E$ . The present study compares and analyzes the pros and cons of these two methods. A small chamber was built to substitute the standard AHAM chamber. A constant output aerosol generator was used to generate DEHS particles. The initial concentration was controlled at about 100 or 5,000  $\#/cm^3$  when using monodisperse and polydisperse aerosol, respectively. The natural decay rate ( $k_n$ ) and the total decay rate ( $k_e$ ) were then measured using a condensation particle counter to determine the  $CADR_C$ . The aerosol number concentration and size distribution upstream and downstream of the air cleaner were measured using a scanning mobility particle sizer to obtain the filtration efficiency as a function of particle size. The flow rate of air cleaner was measured using a gas meter with a unique design to offset and balance the air resistance of the gas meter. For a given filter, the filtration efficiency increases with decreasing velocity because of a longer retention time within the filter media. This is particularly true for submicron aerosols because the primary filtration mechanism is diffusion. Notice that the  $CADR_E$  and  $CADR_C$  should be identical if the test aerosol is monodisperse. The  $CADR_E$  is always lower (41% in this work) than the  $CADR_C$  if based on the MPPS. If the whole size distribution of the challenge is included, the  $CADR_E$  is 13% higher than  $CADR_C$ . This mismatch becomes more significant if the spread of the test aerosol increases, i.e., higher geometric standard deviation. Through simulation, the longer the operation of the air cleaner, the particle distribution moves toward MPPS. Additionally,  $CADR_C$  would be overestimated if the testing aerosol is far from MPPS. The results show that both performance testing methods correlate well. The filtration curve should be measured to identify the MPPS. Hence, we can have a more conservative  $CADR_E$  based on MPPS. Overall, the  $CADR_E$  is more robust, conservative, universal, and faster than the  $CADR_C$ , based on the traditional chamber test method.

## **Comparison of charging mechanism, the efficiency of particle matter capture and generation of byproducts from different ionization based indoor pollution control technologies**

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Indoor air quality is a significant concern in the modern environment as people especially those in urban areas spend 80-90% of their time in living, working places a well different means of transportation and also due to the construction of tightly sealed buildings in developing and populated countries. Among different indoor pollutants, particulate matter (PM) is a significant concern to human health due to its smaller size and easy attachment to different chemical species. Although there are different PM control technologies in the market as well as in lab-scale they have several drawbacks like increased energy consumption due to pressure drop, sustainability issues regarding filter disposal, biofouling issues for filtration and lack of information regarding removal mechanism and performance in the real indoor environment as well as generation of byproducts for emerging PM control technologies like nonthermal plasma and biofiltration. In this regard, ionisation-based devices like electrostatic precipitators (ESP) as well as ionizers find their applicability in cleaning indoor environments with benefits like highly efficient PM capture, minimal energy consumption due to reduced pressure drop owing to their design, ease of maintenance as well as the flexibility of keeping as either stand-alone or duct unit as well along with its efficiency in removing multiple indoor pollutants like bioaerosols and hazardous volatile organic compounds (TVOC). Therefore, the current study is on comparison of charging mechanism, efficiency in PM capture, performance in removing multiple indoor pollutants and generation of byproducts like ozone, nitrogen oxide and ultrafine PM of different ionisation-based devices. Best performing ionisation-based products like wire plate ESP, brush type ionisers, ionising air guns, ion pens and static ionizing bars which work on different polarity, having different designs of ion emitters that emit different concentrations of ions while operating in different voltages were selected and compared in a closed chamber. This could help customers in selecting the most suitable technology based on their requirements. Additionally, the study also explored the most influencing factors which affect the performance of an ionisation-based technology which could assist in the design as well as the development of the most efficient ionizer for indoors. All tested ionisers and ESP captured standard aerosols as well as PM emitted from major real environments like candles, mosquito coils, incense sticks, mixed aerosols as well as bioaerosols like mycobacterium smegmatis as well as Escherichia Coli as well as ambient infiltrated PM have different size distribution ranging from 10nm to 5µm with efficiency range from 95 to 100%. Among all tested devices, the static bar showed the highest performance in PM capture and therefore was redesigned as per our requirement for a smaller diameter as well as an increased number of ion emitters in all directions. Even though the primary function of indoor control technology is to capture PM secondary consequences like energy cost, byproduct emission and removal of multiple pollutant removal affect the long run of usage. Unfortunately, many of the tested ionisers generated ozone above regulatory standards but it could be reduced by the use of a suitable adsorbent as the entire system is a closed enclosure. The energy cost/ efficiency of the designed static bar was found to be comparable with commercial HEPA air purifiers. The emission of ozone from the bar was far less than regulatory limits and there is no emission of other byproducts like nitrogen oxides and ultrafine PM. Additionally, the non-thermal plasma mechanism in ionisation-based devices was found to be capable of deactivating bioaerosols by 90% and degrading hazardous volatile organic compounds like formaldehyde to less toxic products by 70%. We are integrating ionisation with the photocatalysis process with nanomaterials for improved deactivation efficiency for bioaerosol capture and degradation efficiency for TVOC above 90% which will help in coming as a commercial indoor air purifier.

## **Online Quantification of Oxidative Potential from and Residential Wood Combustion (RWC) and Car Exhaust Aerosol**

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Air pollution particles are the single highest environmental health risk and have adverse effects on human health with over 7 million premature deaths per year. Despite these negative effects, many physical and chemical properties of particulate matter (PM) and their effect on human health still remain unclear. The oxidative potential (OP) has widely been suggested as proxy to measure toxicity in PM. Different assays have been developed to quantify OP over the recent years. Most of them measure the OP offline from aerosol that is collected on a filter and analyzed with a time delay from days to month.

We could show for a biogenic secondary organic aerosol using  $\alpha$ -pinene as precursor, that the OP-active compounds decay with a half-life from seconds to hours, leading to the assumption that the OP in filter samples, is potentially highly underestimated. Therefore, we built an online instrument that can quantify OP with a high time resolution using a physiological relevant assay. With this online instrument and the corresponding offline assay, we characterized several aerosol types, where we could show that there is not only an OP decay during the offline analysis, but that this decay is also highly variable for different aerosol systems.

With the online instrument we also measured primary (fresh) and secondary (aged) emissions from RWC and car exhaust to investigate the differences in aging times and compositional toxicity of the different aerosol systems. We could show a highly time resolved signal as well as that for RWC high photochemical ages lead to a lower mass-normalized OP, compared to car exhaust emissions where a higher aging leads to a slightly higher OP. Aged RWC gives, compared to aged car exhaust, an order of magnitude higher OP showing that aged RWC is potentially more toxic.

## **Microbial Indoor Air Contaminants and Its' Health Risk Assessment in different microenvironments of Lucknow: capital of most polluted State of India**

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Exposure to microbial organisms in indoor air has been related to effects on respiratory and overall health. The prevalence of mold in indoor spaces such as hospitals, households, etc. expresses worries about long-term negative health consequences and deterioration of existing lung conditions. The current study aimed to quantify the seasonal variation of microbial contaminants (bacteria and fungi) within households located in Industrial, Residential and Commercial areas and assessment of health risks. Temperature and relative humidity were measured to determine how they affected microbial survival. Bacteria and fungi in each microenvironment were assessed by different plates containing media using the gravitational settling method. Following the identification of microorganisms using conventional microbiological techniques, biochemical tests, and molecular approaches were used. The findings indicated that the substances in indoor air are a complex blend of physical, and microbiological contaminants in each area. The result reveals that the highest bacteria concentrations in the residential area ranged between 5045.73- 5019.52 CFU/m<sup>3</sup> in the spring season and fungi concentrations were found in the spring season in the commercial area 327.64 compared to the winter season 170.37 CFU/m<sup>3</sup>. Based on indoor fungal characterization, *Aspergillus niger*, *Aspergillus flavus*, *Cladosporium*, *Alternaria*, *Fusarium*, and *Penicillium*, were the most predominant genera found in an indoor environment. The proper rules should be followed for managed environments in residential settings. Furthermore, international regulatory agencies deny the presence of microbiological pollutants in indoor environments, which have been repeatedly linked to the transmission of lethal diseases in humans.

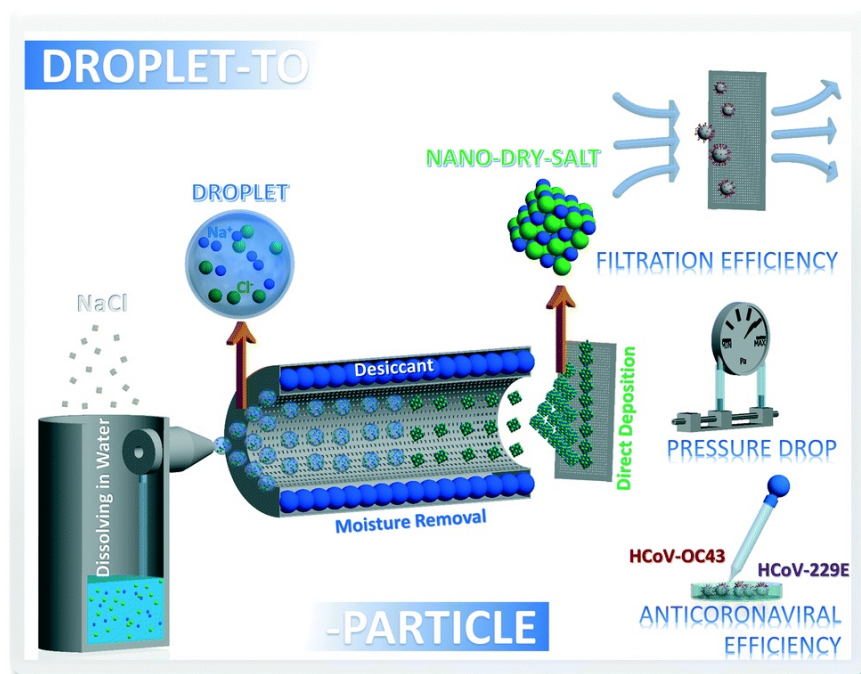


## Nano-dry-salt deposition on electret nonwoven confers anticoronaviral effect while retaining aerosol filtration performance

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Safe-by-design concepts for anticoronaviral functions are important in the production of air filters, face masks, and touch substrates because these interventions may be effective in allowing continued socioeconomic activity and alleviation of the global recession. Recent attempts to provide anticoronaviral functions have involved alternative compositions and architectures aimed at producing nanoscale compounds for highly effective anticoronaviral activities. However, translating the nanocompounds to the field requires considerable investment and time as well as actual trials; thus, they may not be a viable option for timely deployment during the COVID-19 pandemic. With these considerations in mind, we have used sodium chloride, which is generally recognized as safe (GRAS), to functionalize nonwoven sheets as frequently touched surfaces. Specifically, we produced nano-dry-salt (NDS) particles through Collision-type atomization and subsequent diffusion drying, and these NDS particles were finally deposited on electret meltblown nonwovens in a single-pass air flow. The resulting GRAS NDS deposited electret nonwovens were examined for effectiveness in anticoronaviral function and aerosol filtration with pressure drop. The treated nonwovens exhibited significant inactivation of airborne human coronaviruses (surrogates of SARS-CoV-2) while retaining the original filtration performance, even under saliva droplet and dust exposures. Several realizable platforms can thus be presented to quickly incorporate NDS deposition in conventional nonwoven production.



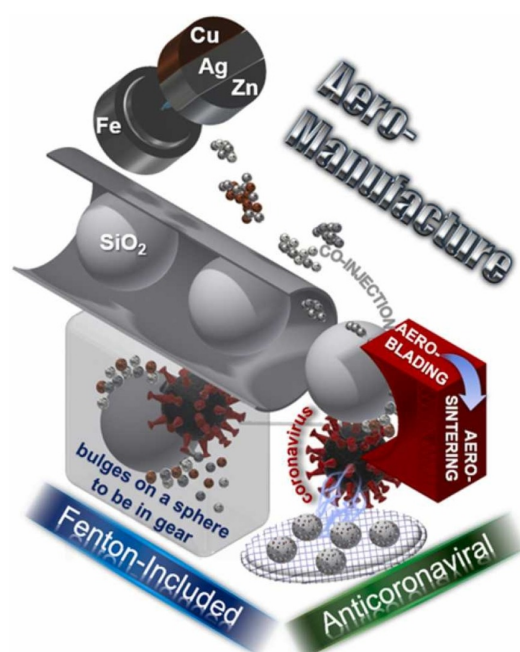
[1] Dae Hoon Park, Jisoo Choi, Amin Piri, Jungho Hwang, Jeong Hoon Byeon, *Environmental Science: Nano*, **2021**, 8, 2780-2791.

## Aero-manufacture of nanobulges for an in-place anticoronaviral on air filters

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The interest in removing contagious viruses from indoor air using ventilation and filtration systems is increasing rapidly because people spend most of the day indoors. The development of an effective platform to regenerate the antiviral function of air filters during use and safe abrogation of used filters containing infectious viruses is a challenging task, because an on-demand safe-by-design manufacture system is essential for in-place antiviral coatings, but it has been rarely investigated. With these considerations, an electrically operable dispenser was prepared for decorating continuous ultrafine Fe-Zn, Fe-Ag, or Fe-Cu particles onto SiO<sub>2</sub> nanobeads to form nanobulges (*i.e.*, nanoroughness for engaging coronavirus spikes) in the aerosol state for 3 min direct deposition on the air filter surfaces. The resulting nanobulges were exposed to human coronaviruses (HCoV; surrogates of SARS-CoV-2) to assess antiviral function. The results were compared with similar-sized individual Zn, Ag, and Cu particles. The nanobulges exhibited comparable antiviral activity to Zn, Ag, and Cu particles while retaining biosafety in both *in vitro* and *in vivo* models because of the significantly smaller metallic fractions. This suggests that the bimetallic bulge structures generate reactive oxygen species and Fenton-mediated hydroxyl radicals for inactivating HCoV.



[1] Jisoo Choi, Kishwor Poudel, Kang Sik Nam, Amin Piri, Adriana Rivera-Piza, Sae Kwang Ku, Jungho Hwang, Jong Oh Kim, Jeong Hoon Byeon, *Journal of Hazardous Materials*, **2023**, 445, 130458.

## Online Measurements of Oxidative Potential and Particle-bound Reactive Oxygen Species of Aircraft Turbine and Ship Engine Particulate Emissions

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Ambient particulate matter (PM) is one of the leading causes of premature deaths and is only surpassed by other risk factors like high blood pressure or tobacco use. As a widely suggested particle metric that might explain particle toxicity, the oxidative potential (OP) refers to the in-situ catalytic production of reactive oxygen species (ROS) in the lungs upon exposure caused by PM constituents like quinones, polyaromatic hydrocarbons (PAHs), redox-active transition metals (i.e. iron, copper), radicals, and peroxides. ROS can also be present in or on PM before inhalation.

We have developed two online instruments to quantify OP and particle-bound ROS. The Online Oxidative Potential Ascorbic Acid Instrument (OOPAAI) uses ascorbic acid (AA) oxidation which is highly sensitive towards PM components like redox-active metals and a range of organics. Whereas the Online Particle-bound Reactive Oxygen Species Instrument (OPROSI) utilizes the 2,7-dichlorofluorescein (DCFH) assay to detect ROS like H<sub>2</sub>O<sub>2</sub> and organic peroxides. These instruments can provide rapid (time resolution of 5-10 minutes) and accurate measurements. Traditional filter-based offline methods often have significantly longer time delays between sampling and analysis leading to potential sample degradation. This is of importance since some OP and ROS active compounds are highly reactive and short-lived. As part of the ULtrafine particles from TRansportation – Health Assessment of Sources (ULTRHAS) project a measurement campaign was conducted at the University of Rostock, Germany, to investigate PM emissions originating from the combustion chamber of an aircraft turbine operated with Jet A-1 fuel as well as from a marine four-stroke single cylinder research engine running on marine gas oil (MGO) and heavy fuel oil (HFO). In addition to measuring the emissions directly, the emissions were also directed through the Photochemical Emission Aging flow tube Reactor (PEAR) to simulate atmospheric aging by ozone and OH to achieve photochemical ages ranging from 0.5 to 8 days.

Both instruments observed dynamic changes in OP and ROS. For example, measuring aged ship emissions, the highest ROS concentrations were measured during the lowest load using MGO (Fig. 1). Both instruments also detected differences between fresh and aged emissions, where the ageing increased the OP and ROS. The OOPAAI and OPROSI demonstrated their capability to capture fast changes in PM toxicity characteristics that depend on fuel as well as combustion and ageing conditions.

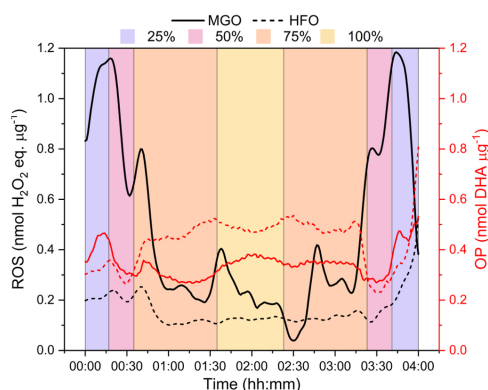


Figure 1. Online ROS concentration and OP per µg of aged PM: comparison of four measurements between MGO and HFO

## **Air to Liquid Interface (ALI) cell exposure under transient driving of gasoline vehicles.**

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### **Introduction and Background**

Air pollution, including exhaust emissions, especially in urban areas, has been suggested as one possible cause of the increased risk of respiratory and cardiovascular diseases, including asthma, lung cancer, and stroke. In particular, the ultrafine particles (UFPs) present in emissions are particularly harmful due to their small size, which allows them to penetrate deep into the lungs and even pass into the bloodstream, brain and placenta [US EPA, Health Effects of Air Pollution, **2021**] [Leikauf, G.D., et al., *Exp. & Mol. Medicine*, **2020**]. Health effects may be influenced by the vehicle's emission standard and the driving cycle used during the exposure [EU Env. Agency, Air quality in Europe, **2020**].

### **Methodology**

Two Air Liquid Interface (ALI) *in-vitro* cell exposure chambers of different designs are used in cell exposure experiments to emissions of other gasoline vehicles at transient driving conditions. The main difference between the exposure chambers is the direction of the exhaust flow concerning the cell surface. In the first one - the Multiculture *in-vitro* Cell exposure Chamber (MEC) [Asimakopoulou, A., et al., *J. of Physics*, 2013] - the flow is parallel to the biological samples, and particulates are deposited due to diffusion. In the second one, the flow is perpendicular, and particulates are deposited due to diffusion with minor enhancement caused by the stagnation point flow. A549 human epithelial cells were exposed to diluted exhaust emissions of two state-of-the-art passenger vehicles: a Gasoline Direct Injection (GDI) vehicle equipped with a Gasoline Particle Filter (GPF) and a gasoline Port Fuel Injection (PFI) hybrid vehicle. Two driving cycles were performed, each based on real driving conditions: a mild one (MRDE driving cycle) and a more dynamic one (Combined driving cycle). Each vehicle was tested at both cycles during cold start. The doses of particles during the cell exposure are determined according to the deposition efficiency of each system and are equivalent to human inhalation during realistic daily exposure [Paur, H.-R., et. al., *JAS*, **2013**].

### **Results and Conclusions**

Cell exposure with parallel flow (MEC) corresponds to lower particulate doses (equivalent to daily realistic ambient exposure), while cell exposure with perpendicular flow results in x8 particulate doses (equivalent to exposure in a more polluted environment). Dynamic driving of GDI vehicle caused 23% higher cell mortality than mild driving when cells are exposed to low particulate doses. Higher dosing (8x) - achieved within the perpendicular flow exposure chamber - resulted in 41 and 63% cell mortality at dynamic and mild driving, respectively. Differences in the dynamics of driving the hybrid PFI gasoline vehicle did not cause significant differences in cell viability. Although the dosing in the two exposure devices corresponds to inhalation at different pollution levels, mild driving caused 80% cell viability in both systems, while dynamic driving reduces cell viability to 60-70%.

## **Heavy metal characteristics and health risk assessment of PM<sub>2.5</sub> over Delhi, India**

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Human health risk assessment is the evaluation of the probability of adverse health effects impacting specific groups of the population over a specified time period. It is classified into hazard identification, toxicity evaluation, exposure assessment, and risk characterization. In order to identify the contribution of various emission sources to health risks, the present study aims to investigate annual and seasonal variations in PM<sub>2.5</sub> mass and concentrations of the associated trace elements over Delhi with complex pollution sources. The aim was to quantitatively assess the impact of heavy metals on human health. In this study, the chemical composition data were obtained to estimate the health risks (non-carcinogenic and carcinogenic) posed to children and adults via inhalation, ingestion, and dermal contact pathways, in an urban environment. The reference toxicity parameters (reference concentrations and doses for noncarcinogenic, inhalation unit risks, and oral slope factors for carcinogenic) have been retrieved from the EPA Integrated Risk Assessment System (IRIS) database. The source apportionment was also done to obtain the risk contribution of different sources for different seasons. The carcinogenic and non-carcinogenic risk values linked with all metals were within safe limits in this study except Chromium, Cadmium, and Vanadium (in some cases). The highest carcinogenic and non-carcinogenic risk is observed during the post-monsoon season. The study would help in identifying the contributions of individual sources and chemicals to health risks under different seasons, which can be understood to support the development of effective control strategies. Further detailed analysis of risks associated with sources during different seasons will be discussed during the presentation.

## Indoor particle pollution from residential wood stoves

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**Background:** Small residential wood stoves are a well-known source to outdoor air pollution with fine particulate matter (PM<sub>2.5</sub>), ultrafine particles (PM<sub>0.1</sub>), and other key pollutants. However, an increasing number of recent studies also document wood stoves as a significant source of indoor air pollution. This pollution is probably caused by particles escaping through an open stove door (when firewood is added), leakage from the stove and/or the stovepipe (occurring when hot and expanding), draught down the chimney into the living room (e.g. when opening a window or a door in the house – or when turning on the cooker hood), and/or dust burning on hot stove surfaces. Low indoor air pollution is crucial since people in Europe spend a significant part of their life inside their home. Still, new wood stoves have no limits for indoor air pollution. However, new technologies combining electrostatic precipitators with smoke extractors promise to reduce both outdoor and indoor air pollution from wood stoves. Several studies confirm reduction in outdoor air pollution but not much documentation exist for indoor air pollution. **Purpose:** To perform systematic measurements of indoor particle pollution (PM<sub>2.5</sub> and PM<sub>0.1</sub>) from wood stoves and to investigate if electrostatic precipitators with smoke extractors reduce indoor particle pollution from wood stoves. **Methods:** Indoor particle pollution in 23 houses with wood stoves was measured with newly calibrated P-Traks and DustTraks from TSI. Two of these houses had electrostatic precipitators with smoke extractors. In one house, measuring before/after installing an electrostatic precipitator with a smoke extractor was possible. Background measurements were done for 10 minutes in the living room before using the wood stove. Pollution measurements were done for about three hours during the normal use of the wood stove (by the house owner). Indoor measurements were taken in a realistic distance from the wood stoves i.e. at locations where the residents would typically stay when the stove was in use, e.g. on nearby coffee table or dining table etc. **Results:** This study confirms significant indoor air pollution with fine and ultrafine particles from some wood stoves and that the pollution can be caused by many different factors. New eco-labelled wood stoves were not found to pollute less than old wood stoves. Electrostatic precipitators with smoke extractors were not found to reduce indoor particle pollution. Residents cannot smell the indoor pollution (smoke) from their stoves and are not aware of the health hazardous air pollution they inhale. **Recommendations** Authorities should inform about the risk of toxic indoor air pollution from wood stoves. The EU Ecodesign requirements and other eco-labels for wood stoves should include limits for indoor air pollution. People should change to electric fireplaces to avoid health-hazardous air pollution.

**Acknowledgement:** These results could not have been presented without financial support of COWIfonden & Birdlife Europe.

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## **Physical and chemical characterization of indoor particle sources**

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The hazardousness of indoor particle sources is widely known. Indeed, the human exposure in indoor environments characterized by indoor sources with high emission rates can lead to the occurrence of cancer. The carcinogenic effect is due to the transportation of chemical compounds (e.g., heavy metals or polycyclic aromatic hydrocarbons) in different aerosol metrics [1]. To date, the lack of studies that contextually characterize the physical and chemical composition of indoor particle aerosol sources and, especially, in the sub-metric range, suggests investigating this field.

In this work, a physical and chemical characterization for different indoor sources (e.g., candles) was conducted. Number concentrations and particle number size distributions were measured with condensation particle counter (CPC) and scanning mobility particle sizer (SMPS), respectively, to evaluate the emission number rates. Chemical fraction size-segregated were obtained collecting polycarbonate substrates through a low-pressure cascade impactor (ELPI+™) in the range of 6 nm – 10 µm. The subsequent analysis adopted were inductively coupled plasma mass spectrometry (ICP-MS) and gas chromatography coupled mass spectrometry (GC-MS). The results show the presence of heavy metals and polycyclic aromatic hydrocarbons especially in the sub-metric range and in different size ranges, including ultrafine particles.

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## **xEV Fuel Economy Policy for Republic of Korea**

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Global primary energy supply has increased in line with global economic growth, reaching 14.3 billion TOE in 2018. Oil accounts for 39% of this supply, with transportation using 32.4% of it. South Korea is the world's eighth-largest energy consumer, with the transport sector accounting for 17.7% of its consumption in 2020, 80% of which is spent on roads. To improve energy efficiency in the road sector, the Republic of Korea is promoting three major policies managed by the Ministry of Trade, Industry, and Energy, with the Korea Energy Agency in charge of the system.

The first policy is the Corporate Average Fuel Economy (CAFE) for vehicles, requiring automakers to comply with government-set standards for average fuel economy and average greenhouse gas emissions of vehicles sold in South Korea. It applies to light-duty vehicles and has been in effect since 2006. By 2023, passenger cars and vans (with 10 people or less) will need to achieve 24.4 km/L, while vans (with 11-15 people) and small trucks will need to achieve 15.4 km/L.

The second policy is the fuel economy label, which is an indirect regulation that helps consumers choose vehicles with good fuel economy. It has been required for light-duty vehicles since 1988 and displays urban, highway, and combined fuel economy. Cars using internal combustion engines (ICEVs) and hybrid electric vehicles (HEVs) are given 1 to 5 efficiency grades depending on their fuel economy.

The third policy is the high-efficiency eco-friendly vehicle support system, exempting consumers from paying taxes when purchasing high-efficiency vehicles, including HEVs, PHEVs, BEVs, and FCEVs, with up to 6.6 million won (\$6,000) reduction.

The system for improving vehicle energy efficiency is managed through vehicle fuel economy data. Fuel economy of vehicles is measured through testing by an authorized testing agency or manufacturer's testing facility approved by the government. Tests involve running the Federal Test Procedure (FTP) and the Highway Fuel Economy Test (HWFET) cycles on the chassis dynamometer. ICEVs use the Carbon Balance method, analyzing vehicle emissions and calculating fuel consumption inversely. HEVs and PHEVs use the Carbon Balance method, considering battery Net Energy Change. BEVs' fuel economy is calculated by measuring the charge/discharge energy of the battery.

South Korea is preparing to implement a heavy-duty vehicle fuel economy system to manage energy efficiency blind spots in the transportation sector. Heavy-duty vehicles use a lot of energy due to their long mileage and low fuel economy. Evaluating heavy-duty vehicle fuel economy includes simulation and chassis dynamometer testing, with the latter providing accurate fuel economy information to consumers.



## **2D-hexagonal boron nitride and lung exposure: Exploring cellular interaction and potential health effects in bronchial and alveolar airway epithelial cell models**

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Inhalation is one of the most pertinent routes of exposure to nanoscale materials in occupational settings. Hexagonal boron nitride (hBN) is an emerging 2D material attracting significant attention due to its superior electrical, chemical and therapeutic properties. For a successful commercial application of 2D-hBN, it is of key importance to understand its safety in occupational settings. However, biological interactions of 2D-hBN and its behavior at the cellular level has not been studied well. Here, an investigation of how 2D-hBN (obtained from the Graphene Flagship consortium) interacts with bronchial (Calu-3) and alveolar (A549) epithelial cells under air-liquid interface-based exposure was conducted. Our results revealed that 2D-hBN was readily taken up by the cells, but did not trigger cytotoxic effects (e.g., damage of epithelial barrier integrity or cell membrane) at tested dose ranges (1, 5 and 10  $\mu\text{g}/\text{cm}^2$ ) for 24 h. To understand cellular interactions, sub-cellular distribution and co-localization of 2D-hBN at organelles, the particles were labeled with green fluorescent (FITC)- bovine serum albumin (BSA) and tracked intracellularly over time using confocal microscopy and flow cytometry. In addition, the cellular interaction of 2D-hBN was further validated by applying label-free detection methods such as transmission electron microscopy (TEM) and confocal-RAMAN microscopy. The result showed intracellular deposition of hBN in the endosomes and lysosomes after 24 h. We also observed an enhanced accumulation of lipid droplets, which later triggered lipophagy. Overall, our data indicate a potential effect of 2D-hBN exposure on cellular lipid metabolism in airway epithelial cells.

**Keywords:** 2D material, Pulmonary exposure, Lung *in vitro* model, Label-free detection, Lipophagy

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## Potential ecotoxicity of biomass combustion-derived fine and ultrafine particles

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**Introduction & Background:** Air pollution is the greatest environmental health risk in the 21st century [1]. One of the significant sources of air pollution worldwide is biomass burning. Despite the undeniable benefits of biofuels as a green energy source, the pollutants released during the combustion process must not be forgotten. Besides gaseous pollutants (CO, C<sub>x</sub>H<sub>y</sub> and NO<sub>x</sub>), a great number of particulate matter (PM) is produced [2]. PM pollution has been shown to have not only adverse effects on human health but as well as the environment. For the reasons given above, the authors of this study focused on the possible ecotoxicity of PM produced during the domestic combustion process. Ecotoxicity was assessed using zooplanktonic *Daphnia magna* acute toxicity immobility assay. According to the authors' knowledge, this is the first case study of the use of immobility assay for contribution of aerosol pollution to the environmental impact.

**Methodology:** The combustion tests were carried out on a manual log feed stove from the Czech manufacturer ABX, model Grönland, specially adapted for experimental purposes. The fuel used is barkless beech wood beams (80×80×250 mm) with a moisture content of around 6.1 %, and ash content was 0.3 % of raw biomass. It was fed in cycles with an interval of 40 - 45 minutes and the weight of the fuel added per cycle was 2 kg. The PM sampling was carried out according to ČSN EN 13284-1; quartz filter (porosity 0.3 μm). Another type of sample was a liquid condensate of particles after cooling the flue gas below its dew point. The *Daphnia magna* assay was performed according to OECD 202. The composition of the samples was determined by ICP spectrometer ARCOS (Spectro) and GS/MC method under standard conditions on a GCMS-QP2010 Ultra (Shimadzu).

**Results & Conclusion:** PM condensate was tested with and without particles. In both cases the mortality after 24 hours was 100 %. This means that it is the dissolved components that strongly contribute to the toxic effect. The 24hEC50 value was 37 % and the 48hEC50 value was determined to be 16 %. The toxicity of PM on the filters was investigated using aqueous leachate and a contact test. The mortality in the case of aqueous leachate was 0 %. The results of the contact test (PM captured on filter and PM transferred to the dilution solution) were the same, where the mortality percentage after 48 hours of exposure was 60% in all cases, and the samples were therefore assessed as toxic. Comparing the results of these tests, it can be stated, that the presence of PM plays a key role in the toxic effects on the organism. The composition of PM was similar to the condensate particles. The main difference was in soluble and insoluble ions. The concentration of water-soluble ions is lower than in condensate. The presence of Cu, Fe, Sr and Pb indicates a possible harmful effect of these particles. A high amount of organic compounds, mainly PAHs were identified in the samples. The sixteen-priority compound from US EPA has been found among the PAHs. The emitted PM from biomass combustion can lead to a toxic effect. Heavy elements and PAHs might be key toxic components of PM. Oxidative stress is suggested as the mechanism of toxicity. To understand the impact on human health and the environment, there is a need to investigate further.

**Acknowledgement:** This paper has been supported by projects TJ04000415 (TAČR) and FSI-S-23-8223 (BUT).

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## **Development and Inter-Comparison of Aerosol Particle Loss Measurement Methodologies for Aircraft Gas Turbine Combustion Engine nvPM**

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In recent years, there has been a growing concern of the effects of aviation gas turbine combustion engine emissions, with an estimated 16,000 premature deaths per year <sup>[1]</sup>. In addition, combustion generated nvPM aviation emissions are thought to be the main source of anthropogenic particulates in the upper atmosphere <sup>[2]</sup>. Due to these concerns, the ICAO has recently introduced a global nvPM emissions reporting standard <sup>[3]</sup>.

Aircraft gas turbine combustion emissions comprise of a complex mix of gases, semi-volatile, and non-volatile solid particles (nvPM). For modern engines, the solid particles are usually below 100 nm in diameter, and consist of solid carbonaceous factual aggregates <sup>[4]</sup>.

Due to the harsh environment at the aircraft engine exit, long sampling tubing are used to transport the exhaust sample to the measurement systems. As has previously been investigated, there are numerous mechanisms that cause the loss of nvPM to the walls of the sampling tubing (Hinds, 1998). The quantification and reduction of the nvPM loss through the sampling tubes is particularly important to determine the real nvPM emissions at the aircraft engine exit <sup>[3]</sup>. Previous studies use several methodologies to determine the nvPM loss through representative sampling tubes <sup>[5]</sup> and existing aircraft engine emissions regulation measurement sampling tubes <sup>[6]</sup>.

This study looks to compare current methodologies to measure nvPM loss through sampling tubes against newly proposed methodologies. Six methods were compared: SMPS full scans, SMPS size selecting pre-CPC measurements, CPC measurements with SMPS size selecting pre sampling tube - with these three methods using both dual CPC system and one CPC system upstream and downstream. The study was conducted using silver nanoparticles (7.5 – 20 nm) as a proxy to freshly emitted aviation gas turbine combustion engine nvPM, as such; a brief comparison of the silver nanoparticles against nvPM will also be included.

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**Upcoming standardization for charge conditioners used in particle characterization and for the generation of calibration and test aerosols - ISO 19996**

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Charge conditioning of aerosol particles by attachment of generated airborne ions is the key process to establish a known size-dependent charge distribution in an aerosol. For some time now charge conditioners other than the traditional radioactive sources or corona chargers exist and may show different performances. To address this a new standard [1] is currently finalized that provides guidance on performance characterization, test and calibration of charge conditioners when used for particle size classification or for generation of sub micrometer test aerosols. For a given particle size, the particles' electrical mobility is proportional to the net number of elementary charges on the particle. Therefore, the knowledge of the particle charge distribution is an essential requirement for particle size classification with differential electrical mobility analyzing systems (DMAS) [2,3].

This standard provides an overview of the main ionization sources, such as radioisotopes, soft-X-ray sources and corona discharge devices and details their different charging performances along with several influencing factors, such as for example particle size and surface area and carrier gas characteristics. The standard provides several quantitative metrics for the performance of charge conditioners along with relatively fast performance procedures with test aerosols and more elaborate test methods, e. g. with ambient aerosols. It may be used to specify the performance of charge conditioners and for adequate quality control of DMAS. The standard also contains recommendations for the documentation of test results.

Furthermore, operational parameters are defined that should be specified in accompanying documentation. This includes for example the maximum particle number concentration, the flow rate range, the allowed type of carrier gas, and the recommended particle size range.

[1] ISO 19996 "Charge conditioning of aerosol particles for particle characterization and the generation of calibration and test aerosols", in preparation

[2] ISO 15900 "Determination of particle size distribution — Differential electrical mobility analysis for aerosol particles"

[3] ISO 27891 "Aerosol particle number concentration — Calibration of condensation particle counters"

## Carbon Black vs Black Carbon - Application-oriented Analysis of Nanomaterials

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The production of carbon black (18 mio ton/a) greatly exceeds the global anthropogenic emissions of black carbon (7 mio ton/a). Despite their similarities, both materials are usually characterized by different communities, with different aims and with different techniques. We adopt measurement techniques developed for exhaust particle emissions for the application-oriented analysis of engineered nanomaterials (ENMs), such as carbon black.

The newly developed Mass & Mobility Aerosol Spectrometer (M2AS) is capable of simultaneously measuring the particle mass and the mobility diameter throughout the whole particle distribution within 5 to 15 minutes. In combination with a high-intensity powder-deagglomeration setup, the relevant structural level of an ENM (e.g., carbon black aggregates) can be analysed directly. The knowledge of particle number distribution with respect to size and mass allows for deriving key performance indicators relevant for the respective material.

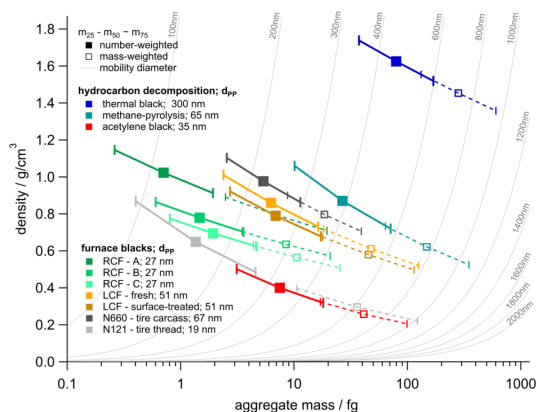
We present such data for carbon blacks produced for the usage in tires, rubber goods, inks and paints and compare results with TEM-images and other application-oriented metrics such as the oil-absorption number (OAN). For comparison, we present data on diesel engine soot.

By plotting the effective density as a function of the carbon black aggregate mass at the size-distribution median values (Figure 1 right), information on the “openness” of the structure, the aggregation level and other information can be gained. Moreover, single values such as the number of aggregates per gram or a theoretical single aggregate layer can be calculated.

For three black pigments (Regular Colour Furnace Blacks - RCF, green symbols), TEM images are shown (Figure 1 left) and are compared with the oil-absorption number (OAN), a metric for the aggregate pore volume. As can be seen, these RCF's have identical primary particle diameters of 27nm. From RCF-A to RCF-B the aggregation level and pore volume increase. These differences can be equally well, but much faster detected by an increase in the median aggregate mass and diameter and a decrease in the effective aggregate density.

### Aggregation level - regular colour furnace black

TEM-imaging + oil absorption number	number of aggregates/gram	single layer of aggregates
RCF-A; OAN: 0.68 cm <sup>3</sup> /g d <sub>pp</sub> : 27 nm	4.6 · 10 <sup>14</sup> /g	11.2 m <sup>2</sup> /g mass = 2.30 · 10 <sup>-6</sup> · dia <sup>2.692</sup>
RCF-B; OAN: 1.08 cm <sup>3</sup> /g d <sub>pp</sub> : 27 nm	2.8 · 10 <sup>14</sup> /g	9.7 m <sup>2</sup> /g mass = 1.97 · 10 <sup>-6</sup> · dia <sup>2.688</sup>
RCF-C; OAN: 1.28 cm <sup>3</sup> /g d <sub>pp</sub> : 27 nm	2.2 · 10 <sup>14</sup> /g	9.1 m <sup>2</sup> /g mass = 1.99 · 10 <sup>-6</sup> · dia <sup>2.671</sup>



## Assessing the potential to improve polarimetric aerosol property retrievals for black carbon aerosol

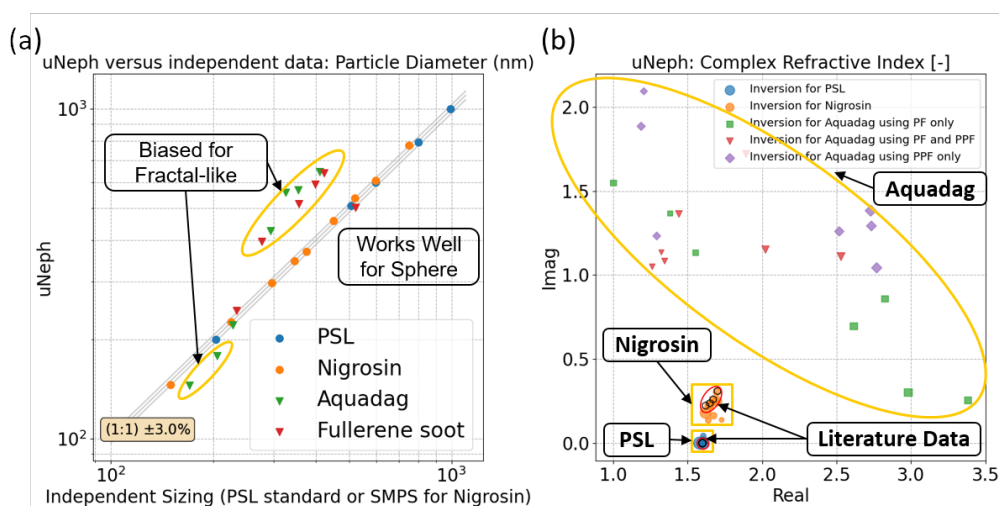
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Angular distribution and polarization dependence of light scattered by aerosols allow the retrieval of their microphysical properties using inversion algorithms. However, systematic bias in retrieved properties is known for light-absorbing aerosol (e.g., black carbon, BC) owing to simplified aerosol representation. Therefore, evaluating if using an aerosol model tailored towards combustion aerosol improves BC retrieval quality is worthwhile.

This study explores this using the uNeph, a new prototype of laser imaging polar nephelometer. The uNeph is designed to perform in situ measurements of the phase and polarized phase functions of aerosols at 532nm. We probed homogeneous spherical (PSL, nigrosin) and non-spherical (fullerene soot, Aquadag) aerosols with different optical properties. An algorithm based on least square minimization and assuming spherical particles, i.e., using Mie theory, was applied to infer the size distribution parameters and the complex refractive index. A good agreement between Mie curves and the uNeph measurement is achieved for PSL spheres and light-absorbing spherical nigrosin particles. The retrieved complex refractive index was independent of probed particle diameter and in agreement with literature data (Fig. 1b). Good agreement was also achieved for aerosol number and volume concentration. By contrast, it is not possible to fit Mie curves that match both phase function and polarized phase function measured by the uNeph for non-spherical Aquadag and fullerene soot samples. Consequently, the retrieved geometric mean diameter is highly biased compared to independent data (Fig. 1a).

Future work will focus on i) measurement of more realistic soot generated under well-constrained conditions, ii) a better forward model that can match uNeph observations hence providing more accurate retrievals. Insights from lab experiments shall later be applied to ambient aerosol to assess the potential for improved retrieval of light absorption from polarimetric data.



## **Standardisation of Black Carbon aerosol metrics for air quality and climate modelling (EPM StanBC Project)**

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Black carbon (BC) contributes to climate forcing and is an air pollutant impacting health. Equivalent Black Carbon (eBC) mass concentrations are typically measured in real time with light absorption photometers. Being very sensitive to changes in emissions, eBC mass concentration might be regulated in the future as a metric for soot-like combustion by-products. However, neither eBC mass nor the related aerosol light absorption measurements have been standardised, traceability is incomplete and uncertainties are not adequately understood.

The new EU project StanBC (2023-2026) will aim at developing new standards for aerosol light absorption coefficient and mass absorption cross-section, whose combination leads to eBC mass concentration. The specific technical objectives are the following:

1. To standardise in-situ reference methods for aerosol light absorption coefficient (extinction minus scattering and photo-thermal interferometry) and develop a robust uncertainty budget estimation as a function of the wavelength and ambient aerosol properties (e.g. single scattering albedo, SSA).
2. To standardise methods for the measurement of the aerosol mass absorption cross-sections (MAC) (i.e. at various wavelengths) based on traceable measurements of light absorption and EC mass.
3. To develop procedures for calibrating filter-based light absorption photometers against the reference methods using a series of well-defined synthetic aerosols generated in the laboratory. The SSA of the synthetic aerosols will span the whole range from
4. To develop a new CEN standard which describes: a) Traceable reference methods for determining aerosol light absorption coefficients and b) Procedures and materials for calibrating filter-based photometers against the reference method(s).

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## Size resolved elemental analysis of bimetallic nanoparticles using SMPS-ICPMS

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Nanoparticles (NPs) size and composition have shown to play a role in different physical and chemical processes, therefore their characteristics must be well defined. [1] The simultaneous analysis of physical and chemical properties of nanoparticles is critical for several applications including air quality control, combustion processes, and production of engineered nanoparticles. Scanning mobility particle sizer (SMPS) in combination with inductively coupled plasma mass spectrometer (ICP-MS) has been demonstrated to give size resolved elemental composition and concentration of metallic aerosol. [2] In this contribution, the capabilities of the hyphenated SMPS-ICP-MS system has been extended to characterize nanoparticle suspensions, and the performance for analyzing bimetallic nanoparticles was evaluated.

Commercially available gold nanoparticles and in-house synthesized copper nanoparticles were used to test the system. Firstly, the aerosols were generated using an ultrasonic nebulizer from the particle suspensions. Then using a rotating disk diluter (RDD), the flow of the aerosol was introduced into the SMPS-ICP-MS system. The RDD system not only dilutes the incoming aerosol, but also acts as a gas exchange device. The SMPS provides information on size distribution and number concentration of the aerosol, while ICPMS allows for determination of elemental composition with excellent detection limits and a wide dynamic measuring range. By coupling these two techniques, we are able to simultaneously obtain size and chemical information on nanoparticles. In order to verify the results, the CuNPs were also analyzed with single-particle inductively coupled plasma mass-spectrometry (sp-ICP-MS) and low-resolution transmission electron microscopy (LR-TEM). The results were in agreement within the three analytical techniques.

Further copper-silver nanoparticles were synthesized and analyzed using the SMPS-ICP-MS setup. Information about the particle size distribution and the relative elemental composition could be determined. Scanning TEM energy-dispersive X-ray spectroscopy analysis was also carried out and the results were in agreement with the hyphenated setup.

In conclusion, this study shows that SMPS-ICP-MS can be used to characterize bimetallic NPs in highly concentrated suspensions, with the promise of being used as a complementary analytical tool for the analysis of nanomaterials.

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## Crystallization of Ag-Au alloyed Nanoparticles by Molecular Dynamics

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Bimetallic nanoparticles possess unique properties resulting from the synergistic effects of their constituent metals.<sup>[1]</sup> The arrangement of crystal domains and surface characteristics of these nanoparticles result in tunable optical and catalytic activity as well as improved oxidation resistance.<sup>[2]</sup> Silver-gold (Ag-Au) alloyed nanoparticles are particularly advantageous in catalytic synthesis and biomedical applications due to their plasmonic properties.<sup>[3]</sup> Adding Au to Ag nanoparticles during their preparation can significantly reduce their surface oxidation and limit leaching of toxic Ag<sup>+</sup> ions, while preserving their most desirable surface reactivity and plasmonic properties.<sup>[4]</sup>

This study employed molecular dynamics with the many-body embedded-atom method (EAM) potential which has been widely used in description of pure Au or Ag sintering and crystallization.<sup>[5]</sup> For example, during cooling, surface Au atoms gradually diffuse into the core of an Ag-Au particle at a decreasing ratio of 3-4 %, until the phase transformation occurs around 800 K (Fig. 1), showing the influence of bulk Au ratio on crystallization and a clear decrease of surface Au (yellow) atoms. The effects of cooling rate and annealing temperature on surface Au ratio are investigated. The crystal sizes are calculated through X-ray diffraction pattern analysis for particles having Au fractions between 20 to 50 % and particle size of 2-8 nm and compared with experimental results.<sup>[4, 5]</sup>

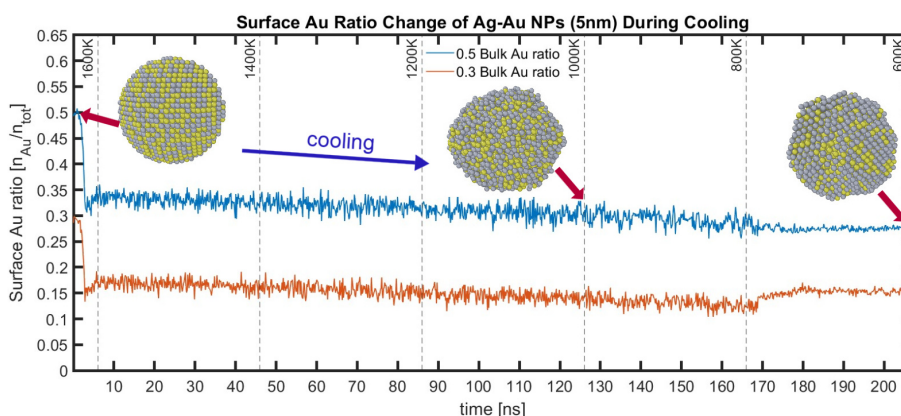


Figure 1. Surface Au ratio during cooling from 1600 K to 600 K by 5 K/ns for 5 nm Au-Ag alloyed NP, with the bulk ratios of Au at 50 % (blue) and 30 % (orange).

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## Crystallization Onset of Aerosol Au Nanoparticles

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Gold nanoparticles have a wide range of applications, including catalysis, sensing, medicine, nanolithography and ion detection [1]. Although the wet-phase (Turkevich) process is commonly used for commercial Au nanoparticle production, gas-phase (flame, plasma, laser, etc.) processes are advantageous for their scalability, unique particle morphology and high purity [2]. The crystal structure of Au nanoparticles influences their performance in plasmonic and photonic applications, making important the understanding of their crystallization and control of the resulting crystal structures.

The melting point for different particle sizes is used to validate our method [1]. The supercooled solidifying temperature ( $T_s$ ) is determined, revealing a metastable region between the liquid and solid phase. The onset of crystallization is revealed by tracking the largest cluster size and its retained atoms fraction (RAF) during crystallization. Initially, the RAF fluctuates around 0 %, a characteristic of subcritical cluster dynamics, followed by a rapid increase up to 90 % (Fig. 1, red line). The largest cluster size also fluctuates before that increase of RAF, eventually encompassing almost the entire nanoparticle. The onset of crystallization is identified when the RAF starts to increase, with the corresponding critical crystal containing, for example,  $4 \pm 1$  atoms at 500 K and  $20 \pm 5$  atoms at 800 K (Fig. 1, green dash line). The 3D-snapshots of crystal composition inside the Au particle at RAF = 10, 20, 50 and 80 % reveals that crystallization takes place by “catastrophic” nucleation and coagulation far below  $T_s$  (Fig. 1a, 500 K), while through nucleation and gradual accretion to a single crystal near  $T_s$  (Fig 1b, 800 K). The crystallization onset is also marked by a sharp drop in potential energy and the amorphous particle fraction during which the subcritical nuclei transform into super-critical crystals. Additionally, crystals are found to grow via both accretion and cluster merging, with crystal domain reorganization after the crystalline transformation is completed, as revealed by the calculated X-ray diffraction (XRD) patterns. The final average crystal size is calculated and compared using both XRD patterns analysis and direct tracing of crystals, showing the influence of crystallization temperature, with the largest crystal size obtained at temperatures near  $T_s$ .

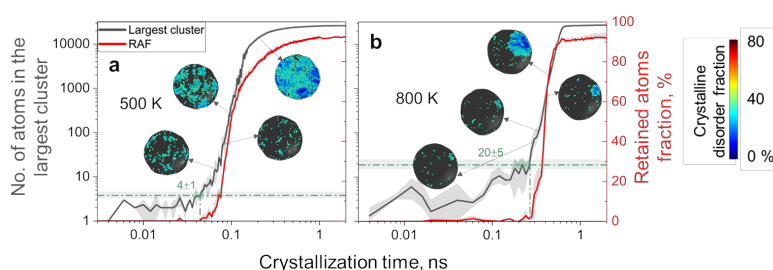


Figure 1. Number of atoms in the largest cluster (black line, left axis) and its retained atoms fraction (RAF, red line, right axis) of a 10 nm Au particle at (a) 500 and (b) 800 K with 3D-snapshots of its cross section (colored by crystalline disorder fraction of each atom).

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