

18th ETH Conference on Combustion Generated Particles

Zurich, June 22nd – 25th, 2014

Book of Abstracts Poster

Status: 12nd June 2014

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Estimation of the Mean Particle Size by Sampling in Parallel with Two Pegasor Particle Sensors

The Pegasor Particle Sensor (PPS) is a novel aerosol instrument designed to measure particle concentrations directly in undiluted (raw) exhaust conditions. Its operation is based on the electrical charging of exhaust aerosol and determination of particle concentration by measuring the charge accumulated on the particles. An 'ion trap' is utilized downstream of the charging area to prevent measurement of free ions. This is essentially an electrostatic precipitator that collects all ions while allows charged particles of lower electrical mobility to exit the sensor.

The PPS was calibrated with diesel engine exhaust so as to convert the measured current to particle mass and number concentration according to its inlet flowrate [1]. The instrument has been successfully tested so far with light duty diesel, heavy duty diesel, and gasoline direct injection emissions, both in the laboratory and on-board the vehicle [1, 2].

The sensor response to particle size is rather linear with respect to particle diameter, lying between the response to particle number (d_p^0) and mass (d_p^{DF}). This feature allows precise measurements of the number and mass of particles only when the target particle size distribution is similar to the calibration one (i.e. CMD=50nm, $\sigma_g=1.7$). Although this is indeed the case with a range of vehicle and engine technologies today, the measurement becomes less precise the more that the target distribution deviates from the calibrated one.

In this study we present a method to minimize the size-dependency of the PPS by estimating the second-by-second mean particle size in order to correct the original mass and number calibration formulas. The method is based on sampling simultaneously with two sensors in parallel, while operating each sensor with a different ion trap voltage (800V and the default 400V) and hence by capturing a different fraction of the size distribution in each case. The ratio between the output currents of the two sensors can be correlated to the mean size of the particle distribution, assuming a constant geometric standard deviation (Figure 1). The response of the PPS at the different trap voltages - which is required for this correlation - was obtained through calibration with monodisperse laboratory aerosol.

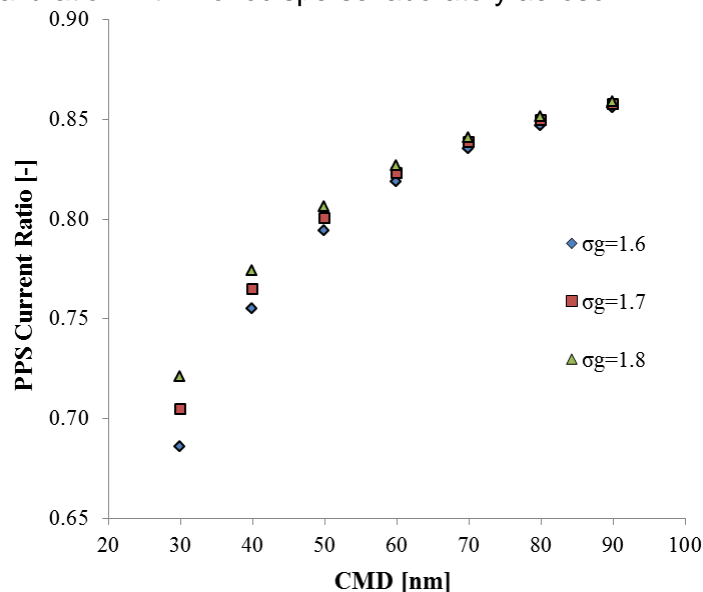


Figure 1: Ratio of the PPS current operating at 800V and 400V ion trap voltage as a function of the size distribution count median diameter (CMD) and standard deviation (σ_g).

In order to evaluate the improved accuracy of the sensor, we have conducted tests with real exhaust of a light duty diesel engine. Two PPS sensors were sampling in parallel along with reference instruments for particle mass and number concentration as well as size distribution. An excellent correlation was observed between the two PPS sensors when operating at the same trap voltage setting during a transient test.

Then, the performance of the new method was explored at various steady state tests points with different particle size distributions. The results showed a reasonably good agreement between the measured and estimated particle size, which can improve the accuracy of the original calibration by up to 50%.

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Assessment of particulate matter emission from Diesel vehicles equipped with DPF and from gasoline direct injection (GDI) vehicles using sampling by TEM grid filtration

Epidemiological studies have linked exposure to particles matter less than 2.5 microns in diameter (PM_{2.5}) with adverse health effects as cardiovascular or pulmonary diseases that cause premature death. The contribution of the transportation sector to the average total emission of PM_{2.5} in the ambient air is 12% [1]. This latter value is likely higher in areas near emission sources (i.e. urban area). Since 2011, all Diesel cars are equipped with a Diesel Particulate Filter (DPF) and respect European standards (Euro 6) for particulate matter emissions which combine a limit number (PN: 6.0×10^{11} particulates/km) with a limit mass (PM: 4.5 mg/km). For gasoline direct injection (GDI) light vehicles, there is a limit number of 6.0×10^{12} part/km (Euro 6b) until 2017. Beyond, PN will be limited to 6×10^{11} part/km (Euro 6c) as Diesel vehicles with the introduction of the WLTC cycle, designed to be as close as possible to the real driving conditions.

In this study, which is part of CAPPNOR project (supported by ADEME), we used a new particle collection technique, a MSP (Mini-Particles Sampler) [2], based on filtration through one class of TEM-dedicated supports, namely TEM porous grids, to directly collect and characterize particles emitted from Euro5 vehicles: two Diesel vehicles equipped with two DPF technologies (a DPF regenerated with a Fuel Borne Catalyst (FBC) and a Catalytic Diesel Particulate Filter (CDPF)) and one Gasoline Direct Injection (GDI) vehicle. Collections were carried out during various engine operations and three driving cycles (NEDC, WLTP and ARTEMIS). Characterizations were performed with TEM coupled with EDX analysis and were focused on the physical size distribution, the morphology, the mass and the chemical compositions of particles emitted during cold and hot start and also during DPF regenerations for Diesel vehicles.

Diesel engines equipped with DPF mainly emit particles during cold start and DPF regenerations. During cold start particles emitted are mainly carbon soot. During the DPF regenerations, PM size distributions are classified as bimodal, mainly consisting of the nucleation and accumulation modes. Typically, these particles are composed of a complex mixture of soot and droplet like particles. The increase of engine speeds during cycles resulted in increase of fractions of metal contents (Ni, Fe, Cr, Mn...) in particulate matters.

GDI engines can emit significantly high PN concentration, mainly carbon soot, depending on the engine operating conditions. GDI will need additional improvements to reach the threshold of Euro 6c, whether by engine calibration and/or by implementing a particulate filter.

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Determination of Airborne Nanoparticle Mass Concentration from Number Concentration using their Effective Density - Application to ELPI Data

Nanoparticles are increasingly used in a wide variety of industries and generated by numerous industrial processes like arc welding, thermal metal spraying (Bémer et al. 2010), metal arc cutting, and combustions. As yet, their health effects are incompletely characterized. Effective density is among the key characteristics of airborne nanoparticles due to its role in particle deposition in the human respiratory tract and in the conversion of number distributions to mass distributions (Mc Murry et al., 2002). Because it cannot be measured directly, different methods have been developed to accede to this parameter. Two main methods are actually proposed: measurement of particle aerodynamic and electrical mobility diameters with DMA – ELPI in series (e.g. Van Gulijk et al., 2005), and measurement of the mass of the particle of a given electrical mobility diameter with DMA – APM in series (Shapiro et al., 2012). The approach chosen in this study is based on the tandem measurement of airborne nanoparticles electrical mobility and mass (tandem DMA/APM). The methodology was first applied to spherical model particles to validate the associated data treatment and protocol. The method was afterwards applied to an aerosol of ultrafine metal particles produced by an electric arc spraying process. The effective density (ρ_e) is determined from the mass of the aggregated particle given by the APM and its volume calculated from the mobility diameter selected by the DMA. From this essential parameter it is then possible to establish the relationships between the three particle diameters d_{ae} (aerodynamic diameter), d_v (volume diameter) and d_m (electrical mobility diameter). As shown on the schematic diagram (Fig.1), these three diameters allow the conversion of the ELPI currents (I) into particle number (N) and then into particle mass (M) concentrations.

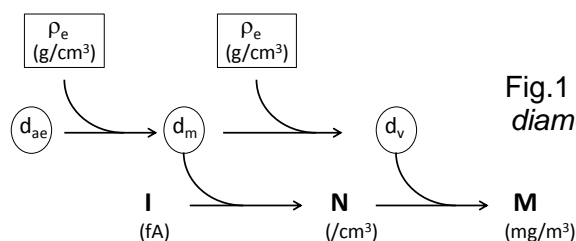


Fig.1 Relationship between the different particle diameters based on the particle effective density.

An aerosol of ultrafine particles was produced from an electric arc gun (Margarido M25) supplied with a 2 mm diameter wire of Zn/Al alloy (85/15 %). The aerosol is sampled after a cyclone, used to remove the micronic fraction of the particles, and diluted by a factor 1000 using dilutors 10 and 100 in series (Palas, VKL 10 and VKL 100). A flow splitter (TSI) is then used to connect the three measuring instruments i.e. an ELPI impactor (Dekati), a SMPS (Grimm, 5.400) and a TEOM microbalance (R&P, 1400A). The initial concentration of the aerosol (before dilution) is about $10^8/\text{cm}^3$ in number and 70 mg/m^3 in mass. The number mean d_m is about 80 nm (SMPS data).

Results show a good agreement between particle number and mass concentrations determined from the different instruments, corrected from the diameters established from the effective density. The most significant divergences were found for the mass concentration determined from ELPI data. This can be explained by the error propagation during the two calculation steps of the mass (Fig.1) required in the case of ELPI. The agreement is particularly good in the case of the particle number concentration determined from ELPI and SMPS.

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Numerical Investigation of Radiation and Gravity Effect on Soot Formation in a Methane Air Diffusion Flame

All hydrocarbon fuels, on combustion, generate a number of pollutants, amongst which soot is a major one, known for its carcinogenic nature. Therefore, control of its emission under stringent pollution control norm, is a major challenge nowadays. The study of diffusion flame under reduced gravity conditions is particularly important in space research. In the present work, a confined axi-symmetric laminar methane air diffusion flame has been simulated numerically under normal gravity (1.0 G), and reduced gravity levels of 0.5 G and 0.10 G. The mathematical model considers the conservation equations of mass, radial and axial momentum, species concentration and energy written in cylindrical co-ordinates. A semi empirical soot model and an optically thin radiation model have also been incorporated. The governing equations are solved with a finite difference technique with appropriate boundary conditions. The thermodynamic and transport properties as well as other parameters involved in the mathematical model have been taken from various correlations available in the literature. A variable size and adaptive grid structure of size 85×45 has been used after grid independence test. The solutions yield various flame parameters at the grid nodes. For understanding the effects of radiation, one set of data has been generated with the consideration of radiation in the mathematical model while another set generated where radiation effect is disregarded. It is observed that the flame height is little more than 12 cm at normal gravity level and finally goes down to around 10 cm for gravity level of 0.10 G with a near spherical shape, when the radiation effect is not considered. When radiation effect is considered, the flame configuration remains almost the same, but the bulge in the flame of 0.10 G is seen to be little more pronounced. Soot volume fraction increases with the reduction of gravity levels, when radiation effect is not considered. In fact, the maximum soot volume fraction increases from a value of 53×10^{-8} at normal gravity to 36×10^{-6} at 0.1 G, an increase by an order of magnitude of 2. Also, the area of the soot laden zone increases with the reduction of gravity levels indicating more soot production. When radiation effect is considered, soot volume fraction increases, not so rapidly though, with the reduction of gravity levels. The corresponding values are 22×10^{-8} and 90×10^{-8} . The area of the major soot forming zone increases with the zone shifting outward along radial direction. Soot number density increases with reduction of gravity levels when radiation effect is not considered, but the increase is not as much as that of soot volume fraction. With radiation too, reduction of gravity causes an increase in values, small though. It is seen, in general, that with the decrease of gravity level, the soot volume fraction as well as number density increase whether or not radiation effect is considered. However, radiation causes a decrease in soot formation at all gravity levels both in volume and number

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Exploring the correlation between soot number density and combustion duration in a GDI engine at part-load conditions

Compared to traditional port-fuel injection engines, Direct Injection Spark Ignition (DISI) engines are more efficient. Nevertheless, even in their latest generation, they produce large numbers of ultra-fine soot particles. An improved understanding of the soot formation processes is required to enable further optimisation of the DISI technology. Most researchers agree that soot formation in these engines is triggered by incomplete air-fuel mixture preparation. In spite of that, the relevant literature shows no overarching agreement about the relationship between soot formation and combustion characteristics. The present work explores this correlation in a modern wall-guided DISI engine at part-load operating conditions.

The test-engine was operated under steady-state, fully-warm conditions, in stoichiometric mode, with early fuel injections to enable theoretically homogenous combustion. The fuel used was a single batch of 95 RON gasoline. The engine speed was varied between 1600 and 3700 rpm, at each of two values of dynamometer torque, 60 and 120 Nm, respectively. A piezo-electric, spark-plug mounted pressure transducer was used to acquire in-cylinder pressure in one cylinder. Ensemble-averaged pressure traces were calculated to analyse combustion evolution in terms of Mass Fraction Burned (MFB). Parallel measurements of size-resolved soot number density distributions were performed using a Differential Mobility Spectrometer, DMS-500 from Cambustion. At each operating point, the engine-out exhaust gas was sampled for 10 continuous minutes. Number density levels as a function of 22 particle size bins were time-averaged and analysed. All tests were repeated three times and showed consistency and repeatability.

Engine-out soot number densities between 1.0×10^6 and 1.0×10^7 particles per cc were recorded. The experimental geometrical mean diameter was between 35 and 55 nm. Due to the short time available between injection and spark timing, air-fuel gas-phase mixing remains always incomplete. Soot is formed in pockets of rich mixture, conceivably as these are entrained into the turbulent flame front. Another source may be wall-wetting and consequent pool-fire. Experimental data suggest it is during the so-called rapid combustion stage, when the flame-front reaches the periphery of the chamber, that most soot particles would be nucleated. A longer rapid burning duration would leave more time for mixture preparation, reducing soot formation. In case of longer duration, lower unburned gas temperature during expansion would reduce the formation of soot via a second mechanism. At the lower engine load investigated, a linear correlation is found between soot number density and combustion duration RBP_{max} (crank angle interval between 10% MFB and the location of peak pressure). On average, a five-fold increase in number concentration between 1.0 and 5.0×10^6 particle/cc, arises from shortening the rapid duration of 3 crank angle degrees. Figure 1 shows how these two quantities vary as a function of engine speed. At the higher load, the linear correlation starts fading for engine speed in excess of 3000 rev/min. The experimental data suggest the detrimental influence of spray-wall impingement supersedes the beneficial effects of greater in-cylinder turbulence, lengthened combustion duration and comparatively lower combustion temperatures. Further work is being carried out to deepen the understanding of these correlations.

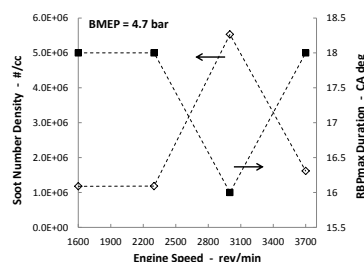


Figure 1

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Fuel Borne Catalysts and Aerosol Emissions Generated by Sinter Metal Filtration DPF System

A series of laboratory tests were conducted in order to characterize aerosols and criteria gases emitted by a diesel engine equipped with the HJS/SMF-AR[®] sintered metal diesel particulate filter (DPF) system. The emissions were assessed for neat ultralow sulfur diesel (ULSD) and ULSD treated with two types of additives containing iron-based fuel borne catalysts (FBCs). The experimental work was executed at the diesel laboratory of the National Institute for Occupational Safety and Health (NIOSH) where the system was evaluated using a naturally-aspirated mechanically-controlled Isuzu C240 engine dynamometer-operated at four steady-state engine operating conditions and over one transient cycle. The DPF system was evaluated while operated in the passive regeneration mode. The effects of the system on emissions were determined using the results of the measurements and analysis obtained from the ports located upstream and downstream of the DPF system. The aerosol measurements and samplings were performed in exhaust diluted in a partial flow dilution system. Number concentrations and size distribution of aerosols in the diluted exhaust were continuously measured using a fast mobility particle sizer spectrometer. The concentrations of elemental and total carbons were assessed using the results of thermal optical analysis performed on samples collected on quartz fiber filters. The mass concentrations of iron were assessed using the results of inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis performed on the samples collected on cellulose filters. Electron microscopy/energy dispersive spectroscopy (EM/EDS) was used to study the presence of iron in emitted aerosols.

In all test cases, the DPF system filtered more than 99% of total carbon (TC) and elemental carbon (EC) mass. The effects of fuel additives on engine-out TC and EC emissions were much less clear. In the cases of I50, I100, and TR tests, the engine-out TC and EC concentrations were substantially lower when fuels treated with ULSD+DT8i and ULSD+DT9 were used in place of neat ULSD. In the cases of R50 and R100, the engine-out TC and EC concentrations were lower when ULSD+DT8i, but not when ULSD+DT9 fuel was used in place of neat ULSD. The tests showed that the evaluated DPF system reduced the total number concentrations of aerosol emitted by the test engine for all test conditions by more than 99 percent. When added at the recommended concentrations, the tested additives had minor impact on the concentration and size distribution of aerosols emitted by the engine and emitted out of the DPF system. The findings from this study should help the mining industry to better understand the benefits and challenges of using the evaluated DPF system to control the exposure of underground miners to diesel aerosols.

Corbin J.C. / ETHZ Switzerland

**Mass Spectrometry of Wood-Combustion Soot:
Positive Matrix Factorization and Refractory Oxygenated Species**

Household wood combustion provides energy for heating and cooking in both rural and industrialized countries. Combustion invariably produces significant amounts of particulate matter (PM) pollution, which varies drastically in composition based on fuel type, combustion conditions, dilution, and post-emission chemistry. For example, with increasing combustion efficiency, wood-smoke PM may be dominated by organic particulate matter (OM), refractory black carbon (rBC), or the inorganic residues known as fly ash (e.g. Torvela et al., 2014). These species are physicochemically diverse, and will consequently play different roles in the health and climate effects of PM following emission. The initial composition of emitted PM will further evolve in the atmosphere as gas-phase compounds condense following oxidation, or as particles coagulate.

The Aerodyne Aerosol Mass Spectrometer (AMS) has been used to study the non-refractory PM (NR-PM) components of wood smoke in detail (including the present sample, Corbin et al. 2014) but does not detect the rBC or fly ash components mentioned above. However, the AMS has recently been extended with a “Soot-Particle” laser (SP-AMS), which can vaporize 1064-nm-light-absorbing refractory PM (LR-PM) via radiative heating. The SP-AMS can thereby quantify the rBC in wood-smoke soot particles. Although neither OM nor fly ash are expected to consist of LR-PM, these species may be conductively vaporized in the SP-AMS if they are internally mixed with rBC.

The fact that soot particles are internal mixtures of OM with rBC complicates the interpretation of carbonaceous ions in the SP-AMS. In particular, the three ions C₁⁺, CO⁺, and CO₂⁺ are all formed in significant amounts from both OM and rBC (Corbin et al., 2013). The mass spectral overlap of these ions must be resolved in order to speciate rBC and OM by SP-AMS.

Here, we use Positive Matrix Factorization (PMF, Zhang et al., 2011) to separate the rBC and OM components of fresh and photooxidized wood-combustion soot. In both cases, PMF shows an rBC factor containing C₁⁺, C₂⁺, C₃⁺, CO⁺, and CO₂⁺. The rBC factor contains negligible amounts of other carbonaceous (organic) ions, suggesting that the oxidized carbonaceous species (CO_x⁺) are rBC components and not refractory OM (Corbin et al., 2013). We discuss and compare this rBC (= C_x⁺ + rCO_x⁺) PMF factor for emissions from two small (9 kW) combustion installations, a modern wood stove and a more-efficient pellet stove. We compare fresh emissions with those following photooxidation in a continuous-flow reactor (Keller and Burtscher, 2012; Corbin et al., 2014). Finally, using specific marker ions, we demonstrate the ability of the SP-AMS to distinguish between diesel and wood-combustion soot in a mixed atmospheric sample.

Czerwinski J. / AFHB Switzerland

Nanoparticle Research on four Gasoline Cars

In the project GasOMeP (Gasoline Organic & Metal Particulates) metal-nanoparticles (including sub 20nm) from gasoline cars are investigated for different engine technologies.

In the present paper some results of investigations of nanoparticles from four gasoline cars – an older one with MPI and three newer with DI – are represented. The measurements were performed at vehicle tailpipe and in CVS-tunnel.

The results show that the older vehicle with MPI emits high particle count concentrations. The size distributions of this vehicle are decisively bimodal with high numbers in nuclei mode.

The emissions of the newer vehicles with DI show sometimes no typical uniform shape of particle size distributions and are at lower level, than for the older vehicle. There is no visible nuclei mode and the ultrafine particle concentrations below 10nm are insignificant.

A size-selective analysis of the composition of NP's in NEDC revealed an increased amount of Na, Mg, Ca & Zn in the lowest size range, below 100nm.

Some of the newer, low-emitting vehicles show at constant speed operation a periodical fluctuation of the NP-emissions.

Increased NP-emissions at cold start were confirmed.

Durdina L. / EMPA Switzerland

Improved Determination of Soot PM Emissions from Aircraft Turbine Engines Using Effective Density

The soot particulate matter (PM) directly emitted by commercial airliners can negatively impact the environment on local to global scale. Accurate quantifications of local air quality and climate impacts of aviation need more accurate PM emissions data. These can be provided by a better determination of PM mass using effective density.

Effective density and mass-mobility exponents (fractal-like dimensions) of soot PM emitted by a modern turbofan engine CFM56-7B26/3 (Boeing 737 family) were determined over the entire operation range from ground idle to take-off. Emissions from this engine were measured using a standardized sampling and measurement system installed in the engine test cell at SR Technics, Zurich airport. To determine effective density, particles were classified by electrical mobility by a Differential Mobility Analyzer and then by their mass-to-charge ratio using a Centrifugal Particle Mass Analyzer. The individual effective density data points were averaged for each particle size and fitted with a power law, describing the mass-mobility relationship of fractal-like agglomerates.

Three effective density distributions with mass-mobility exponents of 2.37, 2.50, and 2.64 accounted for the increase of effective density with engine power. These were then utilized to compute total PM mass concentrations from particle size distributions and to correct the measured non-volatile PM mass concentrations for sampling system losses. A closure was achieved between the computed total PM mass concentrations and the measured non-volatile PM mass concentrations. The determined line loss correction factor for non-volatile PM mass ranged from 2.75 at engine idle to 1.4 at take-off. We also show here that the established method for calculation of non-volatile PM emissions from certification smoke number data may overestimate the emissions at low thrust as much as an order of magnitude as well as underestimate the emissions at high thrust. In general, the tandem particle size and mass measurements could further improve PM mass emission data at low power conditions and could be a useful tool for approximating the PM mass emissions at the engine exit.

This work is supported by the Swiss Federal Office of Civil Aviation (FOCA).

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How the Humidity of a DPF Effects the Microwave Based Soot Load Determination

Background

In today's exhaust gas after-treatment systems, diesel particulate filters (DPF) are an essential element to meet the stringent limits concerning emissions of soot-particles. To know the actual trapped soot mass is important for an efficient regeneration and engine control strategy. One novel approach for measuring the soot inside DPF is a contactless microwave-based method. With stub antennas, electro-magnetic waves are emitted inside the canning, and their reflection and transmission through the filter monolith is measured. Different measurands can be extracted of the reflection- and transmission spectra over frequency, like resonance frequencies, f_{res} , or an averaged transmission factor. Accumulating soot changes the electric properties of the filter and therefore the resonance-spectra also change. In principle, the basic functionality of this system for soot load detection has been proven in laboratory and dynamometer tests [1, 2]. In this study, influencing parameters, like the humidity of the filter and ambient atmosphere shall be examined.

Measurements

An uncoated aluminum titanate wall flow filter, 6" x 5.66", was soot loaded on a dynamometer test bench (3l TDI engine) under constant speed and load. Soot load was measured gravimetrically and the microwave signals were recorded continuously. Afterwards the DPF was exposed to air of different temperature and relative humidity, *r.h.*, (15-80 °C / 15-80 %) in a climatic chamber, while the microwave spectra were measured. This climatic exposure test has been conducted with the soot-loaded as well as a soot-free DPF and the empty canning.

Results and conclusions

During soot loading, resonance frequency (TE112-Mode) and the averaged transmission parameter shifted linearly towards lower values, as expected from literature and own measurements [1, 2].

As can be seen in fig. 1, exemplarily for a soot-free DPF, both, increasing temperature and humidity lead to decreasing microwave signals due to a higher conductivity. Thereby, the higher the temperature is, the larger is the influence of humidity. It has to be emphasized, that signal shifts are quite small compared to the shift during soot loading.

This can be seen in fig. 2. Relative signal shifts are shown for a soot accumulation of $1 \text{ g}_{\text{soot}}/\text{l}_{\text{DPF}}$ and an increase of humidity from 15 to 50 % at 80 °C. In case of a soot-free DPF or empty canning there is almost no influence of humidity, but for a soot-loaded DPF, ambient conditions need to be considered in real-world applications. Fig. 2, however, evidences that the averaged transmission factor is by far less affected by noise factor than the resonance frequency.

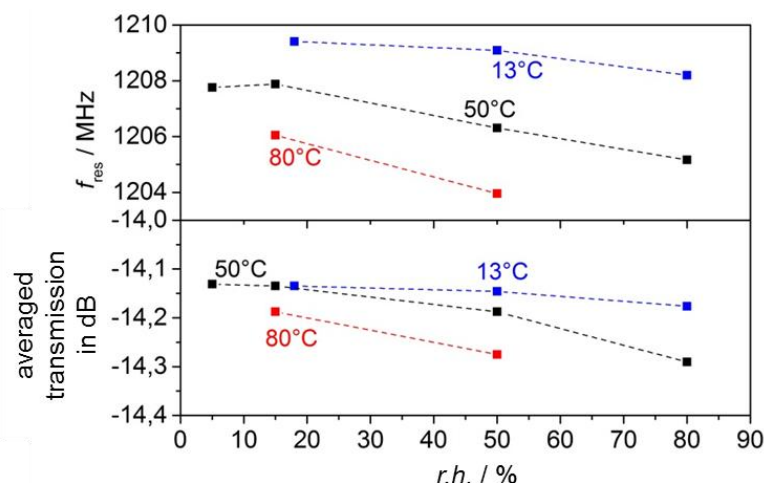


Fig. 1: f_{res} and averaged transmission factor over humidity at different temperatures for a soot-free DPF

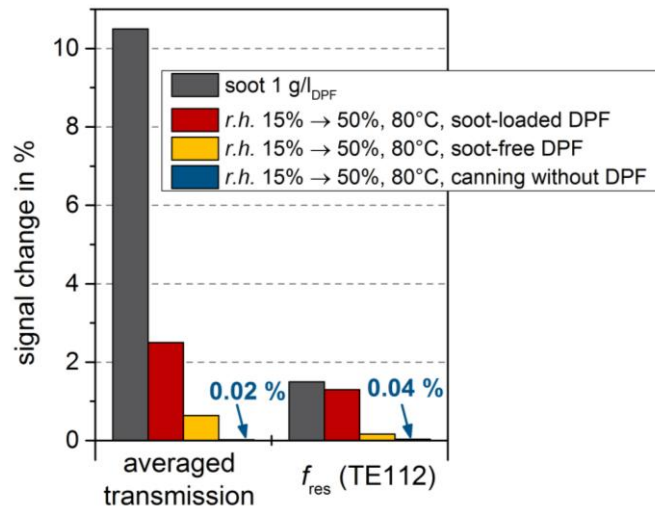


Fig. 2: Change of f_{res} and averaged transmission factor caused by soot accumulation (1 g/l) and a change of humidity

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Frenzel I. / TU Bergakademie Freiberg, Germany

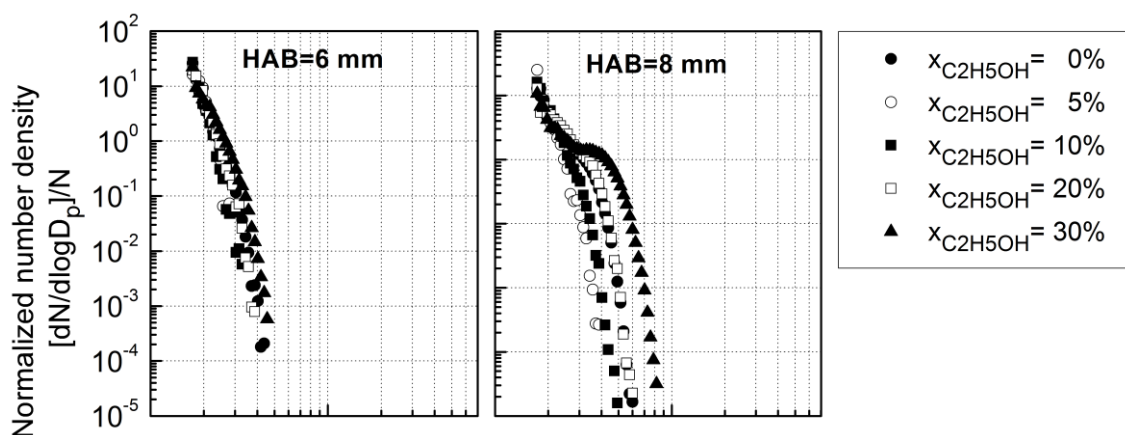
Study on the Influence of Ethanol on the Soot Formation in Premixed Ethylene Flames

Since the use of biofuels has increased rapidly over the last decades due to the ability of the reduction of gaseous and particle emissions in e.g. internal combustion engines, the understanding of the combustion process of hydrocarbon and oxygenate mixtures is still of great importance. Therefore the emphasis of this work is to study the influence of ethanol on the soot formation in selected fuel-rich atmospheric pressure laminar premixed ethylene/oxygen/argon- flames. The ethanol added to the ethylene flames was varied in the range from 0% to 50% of the total carbon fed and two series of measurements were investigated: In the first series the soot formation in three different reference ethylene flames with equivalence ratios of $\phi = 2.2/2.3/2.4$ were studied. With adding ethanol to the fuel and keeping the equivalence ratio constant, the C/O ratio, an important parameter related to soot formation in combustion processes, is changing. Therefore, in the second test series, the C/O ratio was held constant at 0.7. In both series the cold gas velocity was fixed at 8 cm/s (at 273 K and 1 bar) and the fuel/oxidizer mixture was preheated at 323 K.

Soot particle size distributions (SPSDs) are measured at different heights above the burner (HAB) following the evolution of the nanoparticles formed in the flame. The utilized experimental setup consists of a McKenna burner [1] with in situ probe sampling and a suitable gas conditioning system (similar to [2]) for online analysis with a scanning mobility particle sizer (SMPS TSI Model 3936).

The results of the first series of tests with constant equivalence ratio showed that the total soot volume fraction is reduced when ethanol was added. Comparing the soot particle size distributions of the pure ethylene flame with the ethanol doped flames at different HAB with the same particle number density showed that they are quite similar. Comparable results were also observed by others, e.g. [3, 4] and they indicate that the ethanol affects mostly the particle inception.

The SPSPDs of the second series of experiments with constant C/O ratio are presented in Figure 1 exemplarily for four different HAB. In general, with higher amounts of ethanol the equivalence ratio is increasing and therefore soot formation increases. However, the SPSPDs of the pure ethylene flame ($\phi=2.1$) and the flame with 20% ethanol ($\phi=2.26$) are quite similar although the C/O ratio is constant and the flame temperature is just slightly different. This leads to the assumption that the equivalence ratio plays a minor role and just the properties, e.g. the chemical structure, of the fuels are important for the soot formation.



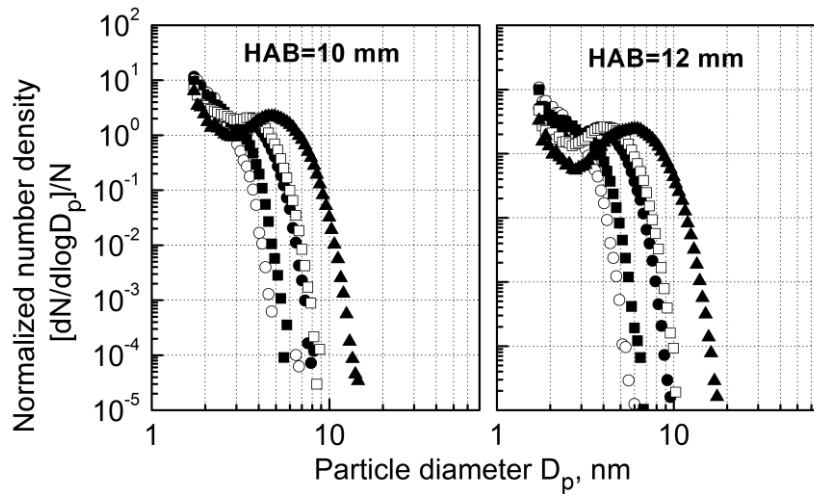


Figure 1: Normalized SPSP of ethylene/ethanol/oxygen/argon- flames with C/O= 0.7 for four heights above the burner (HAB).

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Modeling of the Environmental Benefits of a Post-Market Dual-Fuel Kit for Light and Heavy Duty Trucks

Background. Air quality is a major concern in developed Countries. Emissions from diesel combustion are considered one of the most important sources of alteration of air quality especially in those regions where goods transport is performed preferentially by heavy and light diesel trucks and in most of highly populated European cities. The North of Italy, and in particular the Po Valley region, is one of the most polluted area in EU (Pira and Piolatto, 2013) although the efforts of the local authorities to reduce particulate matter (PM) and other gaseous pollutants concentrations in the atmosphere, such as nitrogen oxides (NO_x). In Lombardy Region diesel contributions to fine PM (PM_{2.5}) account for the 19% (INEMAR Arpa Lombardia, 2010). These particles are constituted of a prevalence of 10 nm particles, (Zheng et al., 2007) and are one of the most relevant contributors to primary ultrafine particles (UFP). In epidemiological studies these particles are suggested to promote adverse cardio-pulmonary effects (Bérubé et al., 2007). As a consequence actions aiming at the reduction of primary emissions from diesel engines, and especially from trucks Euro 4, and earlier Euro, are of primary interest.

Methods and Results. In this work a commercial diesel Euro 3 heavy duty truck was equipped with a post market kit for dual-fuel, diesel-natural gas, propelling. On road experiments were then performed to evaluate preliminary data of the emission levels and fuel consumption of the modified truck.

These data were used in primary approximation to evaluate the maximum technical feasible reduction (MTFR), i.e. the maximal reduction of air pollutants (PM and NO_x). MTFR, considering the application of the kit on all diesel trucks, heavy and light duty, circulating in Italy, was evaluated considering the time horizon at 2020 running the model GAINS-Italy. The maximal reduction of emissions obtainable was determined by a comparison with the reference scenario considering the estimated evolution of the circulating vehicles and the more recent energy scenario, taking into account the national and EU legislation on climate change and environment.

The results obtained, although preliminary, show an impact of the post-market kit on primary emission of PM while no effects are expected on NO_x. Further experimental tests will be performed in order to strengthen the results obtained with additional data.

In conclusion a post market kit able to transform a diesel engine in a dual-fuel one can contribute to the reduction of primary emissions of air pollutant. A more detailed evaluation of the emissions is however required to define the real possible impact of the proposed kit on the overall air quality.

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Hohl Y. / Liebherr, Switzerland

Evaluation of Fuel Quality on New Coating Technology for Advanced Exhaust Gas Aftertreatment

For emission regulation 97/68 EC stage IV, LIEBHERR developed a SCR-only solution with a SCR catalyst as the only necessary exhaust gas after treatment system. The PM limit (0.02 g/kWh) for stage IV is entirely met with internal engine measures.

In Switzerland, a different legislation is in place that only allows for PN lower than 1E12 #/kWh. In order to also cover that market, Liebherr had to come up with another solution in addition to SCR-only.

The following options were considered:

- Installation of a DPF retrofit solution after the SCR-only system
- Development of a new system solution consisting of DOC + DPF + SCR
- Development of a SCR on Filter system

Liebherr decided to develop the SCR on Filter system, mainly for packaging reasons and also because of the involved system costs.

As the SCR on Filter technology has not been used in off-road applications before and might also be a possible solution for an upcoming stage V in the European Community, various validation processes are required.

One important question that needs to be answered in the validation process is the impact of bio-fuel on the functionality of the SCR on Filter system. In order to investigate this effect, an INTERREG France-Suisse funded project (so called SCR on Filter Opti) was started, together with a university and industrial partners in France and a university in Switzerland.



Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra



The target of the SCR on Filter Opti project is to evaluate the impact of using a fuel with bio fuel content and low thermal oxidation stability.

Bio fuel does indeed have a negative impact on the coating performance stability and on the Engine OUT emissions.

The project started in November 2013. All necessary tests will be performed at the engine testbench from R&D Moteur. These include:

SCR on Filter system characterization at 0 hours included:

- Soot reactivity analysis with different fuel and different cycles. The analysis will be done by the University of Mulhouse
- Engine OUT screening with different types of fuel will be done at R&D Moteur
- PN filtration efficiency with different types of fuel. The PN measurement will be done by the Berner Fachhochschule Biel
- SCR on Filter NOx conversion efficiency with different fuels will be done at R&D Moteur

SCR on Filter system characterization during endurance tests and at the end of the operating life included:

- PN filtration efficiency with different types of fuel. The PN measurement will be done by the Berner Fachhochschule Biel
- SCR on Filter NOx conversion efficiency with different fuels will be done at R&D Moteur

Jordan-Gerkens A. / Physikalisch-Technische Bundesanstalt, Germany

**Evaluation of Measuring Methods for Particle Emission from Modern Diesel Vehicles
in Periodic Emissions Control – Studies and Results**

With the continuously improved emission standards in Europe, particulate emissions in exhaust gas of diesel vehicles have been significantly reduced. However, the periodic vehicle inspection has not been amended to reflect this. That's why there is an increasing debate about the suitability of the currently used opacimeters for the quantification of soot emission from vehicles equipped with diesel particulate filters (DPF) and about their ability to identify DPF malfunctions. It is to consider that future periodic inspection procedures will have to cover not only opacity limits but also emission ranges the particle number emissions from diesel engines (with or without DPF) which vary over more than three orders of magnitude. It is not clear whether it will be feasible for a single instrument to cover this large number concentration range. If the purpose of a periodic inspection check is to identify malfunctions of the emission control devices, particularly cracks in the DPF, different procedures may be appropriate for non-DPF- and DPF-equipped diesel vehicles. Switzerland already initiated an alternative procedure for the particle number related inspection of the DPF performance installed in construction machinery. As part of the "ENV02 PartEmission" project, Work Package 2, lead by PTB, three metrological institutions (PTB, METAS and MIKES) and JRC evaluated soot detection instruments as well as the metrological procedures for the periodic emission inspection of diesel vehicles. A collection and review of the technical requirements was laid down in the European regulation and national regulatory authorities for the calibration of opacimeters, in order to establish a frame of reference for the establishment of the calibration procedures for the novel instrumentation as shown in a previous report. A call of interest to approximately fifty European manufacturers of automotive emission testing instruments and their associations was launched. Finally six manufacturers provided prototypes of their new developed instrument. Various detection principles are covered by the candidate instruments: three light-scattering instruments, a measuring ionization chamber, as well as two diffusion size classifiers. These instruments were assessed via comparative measurements of particle number concentration, particle mass concentration and opacity. The laboratory tests were performed over a range of particle number concentrations from 10^3 to 10^8 cm^{-3} , particle mass concentration from 5 to $2800 \mu\text{g m}^{-3}$ and light extinction coefficients from 0.01 m^{-1} to 3.00 m^{-1} . The test aerosols included soot aerosols generated using the new PTB soot aerosol standard based on a modified HiMass-CAST-generator, a home-built CAST-soot generator at METAS and a diesel-soot generator at MIKES. In subsequent field measurements at JRC the instruments were tested on a vehicle chassis dynamometer under controlled conditions similar to the conditions of type-approval testing. Additionally, the instruments were tested under service conditions at DEKRA (Germany). As a general conclusion of the laboratory tests, there is no instrument which covers the whole range of possible car emissions. The best performing device resulted to be a commercially available instrument with the drawback of its complexity and its high price. Also the ionization chamber, an early stage prototype for a simple and cheap instrument has great potential for being developed into an affordable commercial instrument. Both instruments need a dilution system providing a dilution ratio up to 1:1000 for high soot concentrations as the one found in the exhaust of old vehicles. On the other hand, one of the light scattering instruments showed a good correlation up to high concentration (10^8 cm^{-3}) but was less sensitive for small sub-100nm particles and low concentrations. So the possibility to use a complementary instrument measuring the low emissions of modern vehicles apart from the established opacimeter should be considered. The results of the field tests and a final review will also be presented.

Karjalainen P. / Tampere University, Finland

Performance Evaluation and Calibrations of two Commercial Exhaust Particle Counters During a Long Operation Window

The current regulations in Europe for diesel passenger cars (EURO 5/6) and trucks (EURO VI) involve limitation for particulate number (PN). The measurement system includes two diluters where the first one is heated together with an evaporation tube where semivolatile particle fraction is evaporated. After the conditioning, remaining particles are counted with a condensation particle counter (CPC) where the 50% detection efficiency limit is set to 23 nm. These instruments are used in the development of engines and exhaust aftertreatment systems, and in the validations of vehicles. The CPCs are calibrated occasionally; usually the interval is 1 year. Problems may arise if the functioning of the CPC changes during the use due to e.g. deposition of particles or gases, which can bias the results.

We studied the performance of two commercial engine exhaust CPCs (Airmodus A23 and TSI 3790A) during an eight-month engine test period. The CPCs were calibrated at the start, in the middle and at the end of the test period with soot particles from a miniCAST particle generator. Calibrations were also performed both at the beginning and the end with a SCAR device (Yli-Ojanperä et al., 2011) and with a silver nanoparticle generator.

The engine tests were run with a heavy-duty diesel engine where various aftertreatment systems were in place during the tests. The particle concentrations were measured after a diesel oxidation catalyst (DOC) or after particle filters (DPF or pDPF), see Figure 1. The most suitable concentration levels for the instruments (below 10 000 p/cc) were achieved by controlling the dilution ratio of the dilution system.

Both CPCs counted particles well during the entire test period. There were no significant changes in the counting efficiencies during the engine tests. The 3790A measured larger concentrations than A23 (Figure 1), but this effect was constant throughout the experiments. This difference is due to the fact that 3790A used concentration factor (k-factor) of 1.09, and there was no correction factor in use for the A23. However, there was an observation that at small concentration levels the 3790A showed relatively a little bit higher particle concentration than the typical difference between the two instruments.

Both CPCs had approvable detection efficiency curves as a function of particle size, however, the detection curves depended greatly on the particle material used in the calibration. For instance, the cut off diameter observed in the SCAR calibration was significantly smaller than the cut off diameter in the soot particle calibrations. This result is in line with earlier observation of Wang et al. (2010).

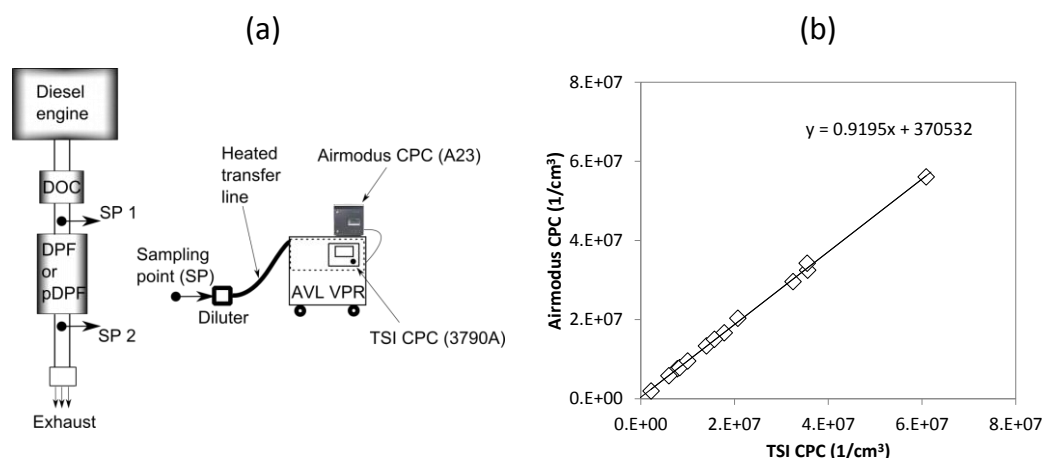


Figure 1. The experimental layout in the engine tests (a) and correlation between the dilution ratio corrected concentrations measured by the instruments during a 13-step stationary test cycle (b).

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Køcks M. / Danish Technological Institute

Shipboard Characterization of a Particle Filter During Operation: Influence on Particle Number Concentration, Particle Size Distribution and Gas Emissions

Ultrafine particles are generally recognized to have an adverse impact on human health and as result, particle emissions from marine engines are under scrutiny. Although regulations on NO_x emission from ships have been implemented and sulphur content in marine fuel is limited to 1.0 % in emission control areas, and further reduced from 2015, emissions from ship traffic is still a much debated subject, especially in harbour cities. Two mitigation strategies are presently being exploited: 1) lowering of the sulphur content in fuel and 2) implementation of emission reducing technologies such as filters and scrubbers.

In this study emission data from a Danish inland ferry with a retrofitted particle filter is presented. All measurements were carried out onboard the Danish inland ferry connecting the island of Ærø with Fyn. The ferry has two main engines (MaK M 20 C, 1020 kW 4-stroke diesel engine) both of them running on marine diesel, in which the sulphur content is limited to 0.1 %.

The emission was characterized at 4 points of engine load: 100%, 85%, 50% and idle. The nanoparticle size distribution and number concentration was measured using a scanning mobility particle sizer (SMPS) (TSI) in connection with a rotating disc dilutor (Matter Engineering) and further connected with a thermal conditioner, heated to 300 °C (ASET15-1), which removes volatiles. Gas emissions (CO₂, CO, HC and NO_x) was measured using standard laboratory gas analyzer equipment.

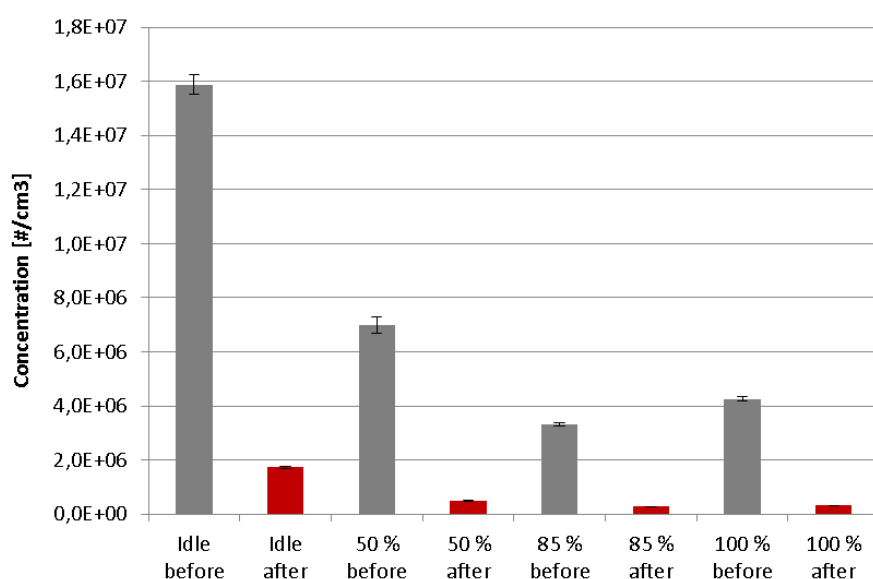


Figure 1: Particle number concentration for engine load: Idle, 50 %, 85 % and 100 %.

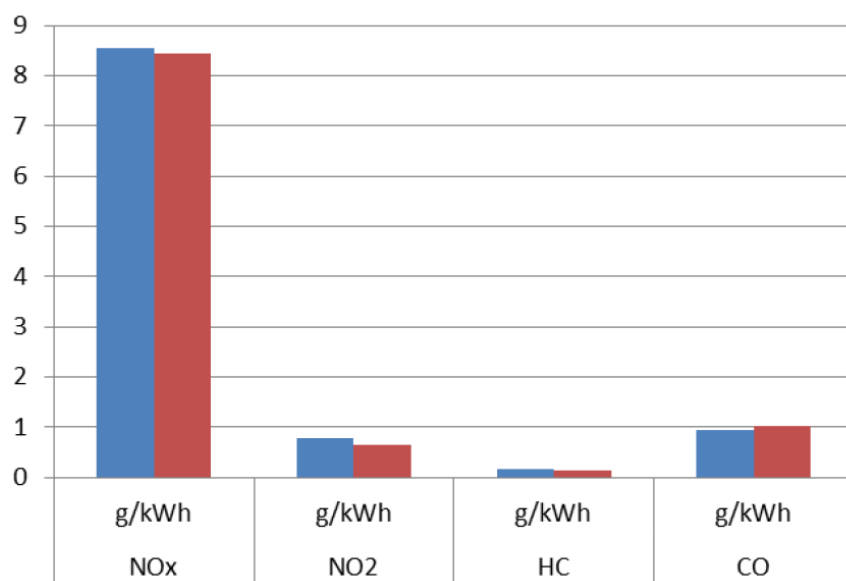


Figure 2: Average gas emissions before (blue) and after the particle filter (red).

The mean particle size depended on engine load, and was below 150 nm during all four engine loads tested. The largest particles were seen with the ferry operating in idle in the harbour during load and unload. Particle number concentration was in average reduced by more than 90 % by the filter. It was expected that the filter would remove more than 99 % of the particles (by number), and the difference observed is very likely, primarily due to leaky by-pass valves.

The gas emission data show NO_x levels comparable to EURO 2 heavy duty diesel engine for vehicles and below the TIER II regulation for ships. CO and HC levels were found to be within the specifications of EURO 5 or 6 for heavy duty engines for vehicles.

In conclusion, the installed particle filter in average reduced the particle emission with more than 90 % by number. The visible smoke from the vessel's funnel, which is typically seen while manoeuvring in the harbour, is also reduced to a minimum.

This work will be followed by installation of a SCR catalyst, work expected to be carried out during 2014

Krishna Kumar Nivedita / PSI Switzerland

Effects of Aging on the Optical Properties of Light-absorbing Carbon from Biomass-burning Emissions

Biomass burning contributes large amounts of black carbon (BC) and particulate organic mass (POM) to the atmosphere, thus impacting the Earth's radiation balance (Bond et al., 2013). The absorption Angstrom exponent (Alpha) of light absorbing aerosols is often employed to parameterize the dependence of light absorption on the wavelength (Lack et al., 2013). Through the use of smog chamber experiments, it has been shown that the Alpha of primary biomass burning emissions is particularly high (ranging between 1.5 and 2.1) in comparison to traffic emissions (ranging between 0.9 and 1.1). However, the effect of aging comparable to the atmospheric lifetime of BC (a few days to weeks) on the optical properties of light absorbing aerosol remains unexplored.

We investigated the effect of extensive aging on the primary emissions of wood burning experiments in a smog chamber. We hypothesize that primary emissions from wood burning (BC with some condensed organics) have an Alpha of about 1.9. With photochemical aging, light absorbing organic compounds form and condense on the primary particles, thus increasing the value of Alpha. With extended aging, the secondary formation rate becomes less than the fragmentation rate of the organic coating and this desorption of organic coating results in a decrease in Alpha (eventually reaching similar or lower values than the original primary aerosol). This is referred to as the bleaching effect.

Experiments were performed at 293 K and 50% relative humidity. Wood burning emissions were injected into a smog chamber and OH chemistry was initiated to form secondary products. Aerosol light absorption was measured using an Aethalometer, and non-refractory aerosol components were measured with an aerosol mass spectrometer (AMS). The primary emissions were around 30 $\mu\text{g}/\text{m}^3$ of BC and 90 $\mu\text{g}/\text{m}^3$ of organics.

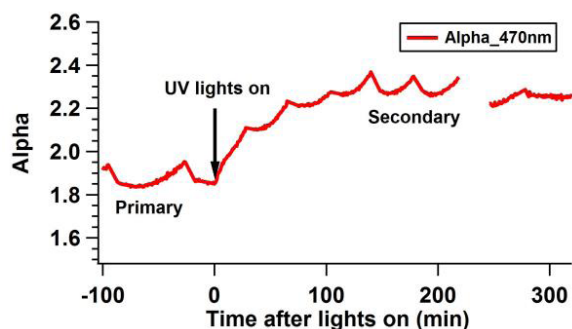


Figure 1. Change in absorption Angstrom exponent (Alpha) in response to secondary aerosol formation/aging over a 5-hour period.

As seen in Figure 1, the Alpha for primary emissions was around 1.9. During aging, a maximum Alpha of 2.3 was observed, after which the Alpha remains constant. A decrease in Alpha was not observed, likely due to insufficient aging in the smog chamber. Experiments performed at lower concentrations and with more aging (resulting in photo-bleaching) will be discussed.

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Kuntze A. / PTB Germany

Characterization of a PTB-Standard for Particle Number Concentration of Soot Particles

Modern engines with high-pressure fuel injection which are equipped with exhaust after-treatment systems emit significantly smaller soot particles and higher number concentration with less mass concentration. These emissions may influence air quality and human health in a serious way. In order to control automotive emissions the European Community adopted the Euro 5b and 6 standards to introduce for the first time a number-based limit.

A basic requirement to ensure those limits is a system for particle number measurements. Therefore engine exhaust condensation particle counter (EECPC) were implemented in PMP conform devices to measure the particle number concentration during the type approval of Euro 5b/6 engines [1]. Currently only commercial instrument manufacturers are providing calibration services for such EECPCs. An independent validation and calibration service without commercial interest is missing. The ISO/dis 27891 provides a calibration routine for particle number concentration and counting efficiency for CPCs taking into account the UN-ECE regulation R49 and R83. [2-3]

At PTB the German National Metrology Institute a set-up for EECPC-calibration is established following the ISO recommendations. The setup is based on a combustion-based soot generator (Mini-CAST) running on propane, which generates soot with diffusion or premixed flames. The infrastructure is intended to generate a highly stable, accurately characterized soot aerosol flow that allows well defined aerosol and particle parameter variations. To setup also includes an aerosol conditioning system, a differential mobility analyzer for ultrafine particles, a high flow/low flow distributor, and a set of particle diagnostic instruments like different condensation particle counters and an aerosol electrometer as reference system. The development of this setup was in part embedded in the ENV02 "PartEmission" project [4] The PTB soot standard 1

generates aerosols with

monodisperse particle number concentrations from 10^1 to 10^6 cm⁻³ and a mean particle number size distribution from 10 to 105 nm with mean width of 1.3 to 1.5. The mid-term goal of this development is to offer a manufacturer independent, traceable calibration for the counting efficiency of EECPCs, electrical and diffusion charging sensors to end users and industry.

[1] Commission Regulation (EC) No 692/2008 of 18 July 2008 implementing and amending Regulation (EC) No 715/2007 of the European Parliament and of the Council on type-approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information.

[2] UN/ECE 2013 Regulation No 49, Offic. J. Eur. Union L:171, 1 (2013).

[3] UN/ECE 2012 Regulation No 83, Offic. J. Eur. Union L:42, 1 (2012).

[4] <http://www.ptb.de/emrp/partemission-home.html>

Kutlar Joss Meltem / Swiss Tropical and Public Health Inst., Switzerland

LUDOK – Documentation Database on Air Pollution and Health Research

Aim

To provide authorities and organizations or interested persons with an easy access to relevant research papers in the field of air pollution and health research.

Methods

The documentation database of LUDOK (Dokumentationsstelle Luft und Gesundheit) selects, categorizes and summarizes relevant research papers on the topic of air pollution and health outcomes for the Swiss Federal Office of the Environment since 1985.

From a monthly systematic search query in ISI Web of Knowledge including PubMed and alerts from important journals the research team selects relevant papers. The focus lies on regulated outdoor air pollutants and candidates for regulation and health outcomes in humans. Population based investigations (epidemiologic research) are most of interest. However, important cell and animal studies are selected as well. The papers are categorized into 8 areas and summarized in German with important key words into a free, publicly accessible database (www.ludok.swisstph.ch). A bi-monthly newsletter highlights new articles.

Results

To date, the database has over 7000 entries increasing by 300 entries every year. The publications on particles have risen constantly over the years. LUDOK contains to date over 3600 articles on particles and over 372 articles that have investigated ultrafine particles and their impact on health. LUDOK has been a valuable source of information for researchers, policy makers and local authorities in Switzerland. The documentation team is frequently consulted for specific questions and has contributed to evidence based policy making e.g. in WHO working groups.

Discussion

The LUDOK database and its surrounding services is a unique source of information regarding air pollution research. By its categorization it enables researchers to search for specific pollutants, outcomes, study designs, study areas, populations and short or long-term effects. Thus researchers can find more specific and relevant publications and studies regarding their interests than with a search in one of the scientific libraries (e.g. PubMed or EMBASE).

It is planned to make the database more accessible to an international audience by enabling a search in in English and French.

La Rocca A. / University of Nottingham

Nanoparticle Characteristics of Exhaust and Soot-in-Oil from Gasoline Direct Injection Automotive Engines

The Direct Injection Spark Ignition (DISI) technology enables improved efficiency but also leads to significantly higher particulate matter emission compared to traditional port-injected gasoline engines. This particulate matter commonly known as soot is typically only a small percentage of a comparable diesel engine but the nanoparticle distribution is shifted towards the smaller sizes. A small proportion of the soot formed in the combustion chamber transfers to the engine oil and contributes its degradation. This is certainly a new challenge for the modern DISI engine as soot-in-oil raises concerns on wear and engine durability.

Exhaust soot generated in internal combustion engines has been widely investigated; soot-in-oil less so due to the challenges introduced by the contamination of the lubricant oil. The morphology, agglomeration and other characteristics of soot-in-oil are of interest as these nanoparticles do not experience the same level of agglomeration as the exhaust soot. Primary particles from used oil samples have the advantage to show structure as it was at the time of adsorption into the engine oil, which prevented further oxidation. To the best of our knowledge, these are the first direct High Resolution Transmission Electron Microscopy observations of GDI soot-in-oil nanostructures and comparison with the exhaust soot.

The soot samples used in the study were collected from a modern wall-guided DISI engine. Solvent extraction and centrifugation have been used to prepare suitable samples for TEM analysis. After preparation, 3 microlitres of the soot suspension in heptane were dispersed onto amorphous carbon or graphene oxide TEM support films obtained commercially from Agar Scientific. Graphene oxide films, which have only recently become commercially available, are particularly advantageous for work of this nature. The reduced contribution to the image from the supporting film makes identification of the structures in the smaller soot primary particles typical of GDI engines more straightforward. Dispersion of samples onto graphene oxide grids was found to give superior imaging of the soot structures in comparison to dispersion onto conventional amorphous carbon film grid.

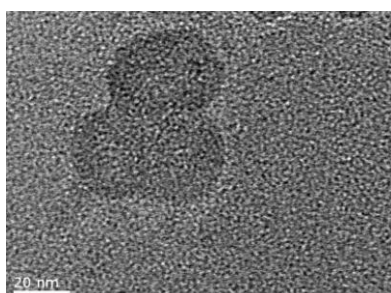


Fig.1 TEM of soot-in-oil agglomerate on conventional amorphous carbon film grid

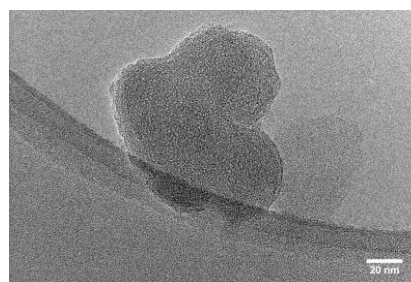


Fig.2 TEM of soot-in-oil agglomerate on graphene oxide film

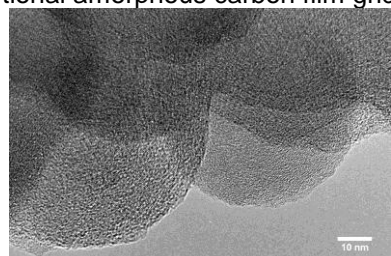


Fig.3 HRTEM soot in oil on graphene oxide film

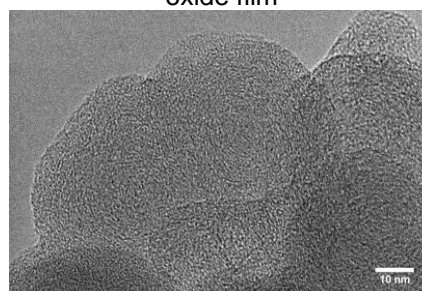


Fig.4 HRTEM exhaust soot on graphene oxide film

Soot primary particles appeared mostly as spheroids with distortions and irregularities assembled into chainlike and small cluster aggregates. Overall, the geometric mean diameters of the primary particles were found in the range 20-70nm. Exhaust soot exhibits a nearly amorphous nanostructure. Conversely, soot-in-oil possesses a radial variation. Typically, a core comprised of short, disorganized segments (nuclei) followed by a layer of fringes viewed edge-on on TEM projections (2-6nm) and in some cases a thin amorphous layer of 2-3nm. Soot-in-oil agglomerate length has a range that spanned

from 40 to 400nm. Differences in nanostructure may reflect a combination of different operating conditions, combustion temperatures and chemical species contributing to particle growth at various stages. A close analysis of the soot-in-oil nanoparticles indicates the presence of volatile structures. From literature it seems that such structures can be formed from the gas phase. This may be more applicable to gasoline derived soot where the hydrocarbons involved are more volatile compared to diesel. Prolonged exposure to the electron beam caused evaporation of these volatile structures.

Leblanc M. / IFP Energies nouvelles, France

Characterization of Unregulated Gaseous and Particulate Emissions During Active Regenerations of Diesel Particulate Filters

The evolution of emission standards related to particles emitted by passenger cars and the recent introduction of a regulation concerning the particle number (Euro6) leads to new challenges regarding the understanding and the description of emission mechanisms. Among these challenges, the Diesel Particulate Filter's (DPF) regeneration process and its contribution to ultrafine particle (UFP) emissions below the 23 nm diameter size currently excluded by the PMP protocol, needs to be addressed. Indeed, active regeneration of DPF leads to undesired particle emissions and to an increase in both particulate mass and number. Therefore, a detailed characterization of their morphology and their composition is required, especially for ultrafine particles, in order to bring further information related to their toxicological effects.

The CAPPNOR project, funded by the French Environment and Energy Management Agency (ADEME), aims to characterize regulated and unregulated gaseous and particulate emissions from three commercially available vehicles complying with the Euro5 regulation: The first one is equipped with a Gasoline Direct Injection (GDI) engine whereas the two other vehicles are Diesel passenger cars equipped with 2 DPF technologies: a DPF regenerated with a Fuel Borne Catalyst (FBC) and a Catalytic Diesel Particulate Filter (CDPF).

The part of the project presented here focuses on the characterization of particles and gaseous emissions related to the regeneration phases of both the FBC and the CDPF, and especially on the active regeneration process.

The vehicles were tested on steady state and transient conditions (NEDC, WLTC, Artemis and urban Artemis cycles) on a roller test bench. The active regenerations have been managed in order to take place after a preliminary loading of the DPFs on the four different driving cycles with an average distance of 800 kilometers, during which the Engine Control Unit (ECU) could trigger an active regeneration if necessary. At the end of the expected loadings, active regenerations were triggered during steady state tests, thanks to a back-pressure sensor's decoy in order to simulate an increased loading of soot particles or ash.

A Fourier Transform Infrared spectrometer (FTIR) allowed the measurement of unregulated gaseous compounds among which sulfur dioxide, nitrous oxide, water and several hydrocarbons or aldehydes, while regulated pollutants were measured with standard dedicated analyzers.

Particles were analyzed with a DMS500 Fast Particle analyzer, two Scanning Mobility Particle Sizers (SPMS) or a Condensation Particle Counter (CPC) (according to the type of tests performed), a multiangle absorption photometer (MAAP) and an Aerosol Mass Spectrometer (AMS). Moreover, particulate matter were sampled on filters with a dedicated dilution tunnel and a Low Pressure Impactor (LPI) in order to analyze and compare Polycyclic Aromatic Hydrocarbons (PAH) adsorbed on sub 30 nm particles from the typical ones of the full range aerosol.

The analysis of gaseous and particulate emissions downstream of the after-treatment systems during the active regeneration phases provides a full description of unregulated emissions coming from the two vehicle technologies and their evolution related to the DPF loading conditions. Moreover, this study highlights the influence of the thermal conditions of after treatment systems during the regeneration on the nucleation process, as well as the effect of the historical background of DPF's loading on its occurrence.

Lee Chun-beom / Korea Automotive Technology Inst.

Multi-Purpose Novel Exhaust Gas Test Rig (High Temperature Exhaust Gas Simulator and Soot/SOF Generator)

To satisfy the enforced exhaust gas regulation nowadays, various exhaust gas treatment systems such as Cooled EGR, DPF, SCR, LNT, DOC, TWC and high temperature sensors to meet the OBD criterion such as O_2 , NO_x , T, ΔP are necessary, due to this situation, cost increase and reliability/durability problem is the hot issue of after-treatment technologies.

To develop these after-treatments systems and to verify the performance of parts, we are using basically real engine and engine dynamometer to test and evaluate the components. But this method requires a lot of time and cost, in addition this engine test method is a difficult method to test and evaluate the characteristics of parts such as the parametric test according to the associated parameters such as temperature, mass flow rate, oxygen contents, toxic gas concentration, soot and SOF

This high temperature exhaust gas simulator can make up for the shortcoming of the engine dynamometer test and this simulator has a capability of characteristic test according to the variables such as precisely and independently controlled temperature and mass flow rate and oxygen concentration and soot/SOF deposition.

Especially this simulator has a capability of fast aging test and reliability test and the simulating test of steady state D-13 mode engine test to verify the required performance of OEM.

This simulator was appraised as an instrument reducing the R&D duration and cost from many Korean parts company and OEM and also proved having a Long life cycle and High speed response, Precise control of Temperature and Mass flow rate and also gives a capability of GUI base Computer controlled test simulating the Engine dynamometer.

For the last 10 years, by using this simulator we developed the EURO-4, EURO-5 and EURO-6 technologies like as ;

- EGR Cooler and EGR Valve:** Pressure drop, effectiveness, thermal shock, reliability, fouling test of soot/SOF

- Catalyst(TWC, DOC, SCR, LNT):** Conversion efficiency, thermal shock, durability, aging effects

- Particulate filter(DPF, GPF, pDPF):** Pressure drop, oxidation rate of PM, regeneration, thermal shock, durability

- High Temperature sensor(O_2 , NO_x , T, ΔP):** Response time, interference, stability, thermal shock, durability, weak point detection and failure scenario check



Air system and Fuel System are located in outside of Facility

Lee Jeonghoon / Korea University of Technology and Education

Black Carbon and Elemental Carbon Concentrations of Spark-generated Carbon Particles

Black carbon concentrations are compared with elemental carbon concentrations for carbon nanoparticles generated using a spark-discharger (DNP 2000, Palas, GmbH). The shape of carbon nanoparticles is usually non-spherical chain-like aggregate, which hinders us from characterizing the optical properties as well as the physical properties. In this situation, we suggest an alternative method for better characterization of non-spherical particles. Our method includes the measurements of electric mobility equivalent size, the number concentration and the mass concentration. The measured black carbon concentrations are converted to light absorption coefficients in order to obtain absorption cross sections, which may be used to estimate index of refraction by curve-fitting the absorption cross sections to that from Mie theory. The size distribution of the carbon nanoparticles, so called, 'Palas carbon' is measured using a differential mobility analyzer (DMA) and a condensation particle counter (CPC). The mobility diameter measured by the DMA allows us to estimate an effective volume for the Palas carbon. The black carbon concentrations are expressed with the unit of a mass concentration. The measurement of number concentration measured by the CPC ensures easy calculation of mass of single black carbon particle. From the effective volume and the mass, we can easily obtain an effective density. Elemental carbon concentrations of spark-discharger are measured by an EC/OC Analyzer (Sunset, USA), which uses a thermal-optical method. In an oxygen-free helium atmosphere, Palas carbon collected onto quartz filter is heated to remove all organic carbon from the carbon. As the organic compounds are vaporized, they are immediately oxidized to CO₂. After the Palas carbon sample on the filter is cooled to a relevant temperature, a 2% oxygen/helium mixture is injected into the sample oven. The sample oven temperature is then increased up to a given temperature, during which the elemental carbon is oxidized to CO₂ due to the presence of oxygen. This CO₂ is then converted to CH₄ and detected by the FID for the quantification of elemental carbon. The black carbon concentration obtained from optical measurement and the elemental carbon concentration obtained from thermal-optical-chemical analysis will enable us to estimate an effective density, which helps to characterize the non-spherical particles.

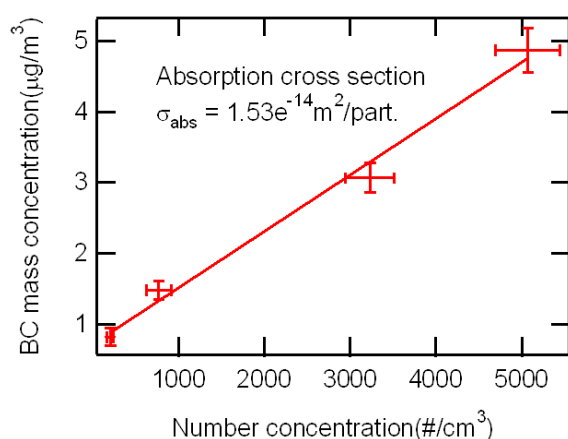


Figure 2 BC concentration vs. number concentration for 100 nm Palas carbon

Link O. / TESTO Germany

The testo 380: New Portable Apparatus for Real-Time Gravimetric Measurement of Particulate Matter in the Sub-Micrometer Range

The adverse effects of particulate matter (PM) on the human health have been widely recognized. In 2013, the world health organization acknowledged PM as a widespread air pollutant and stated, that there is no evidence of a lower exposure level below which no negative health effects occur [1]. Also in 2013 the International Agency for Research on Cancer classified outdoor air pollution as carcinogenic to humans [2].

In accordance with these findings, the German legislation enforced the surveillance of PM emitting sources, one of which is residential heating systems based on solid fuels. To satisfy the demand for new real-time measurements of PM mass concentration the Testo AG developed the testo 380 which was introduced in 2013.

As we have shown with SMPS measurements and has been also reported elsewhere with impactor techniques [3] the majority of the emitted particles under regular burning conditions for these ovens is in the sub-micrometer range.

The testo 380 is based on the well-known impaction technique which has been used for aerosol detection for decades [4]. However, in order to obtain real-time data the impaction plate was replaced by an oscillating quartz crystal which shows a reproducible frequency shift upon mass loading through impaction. Furthermore, the quartz plate is rotated during operation, such that the matter is distributed onto a circle rather than a single point and therefore higher mass loadings can be tolerated [5].

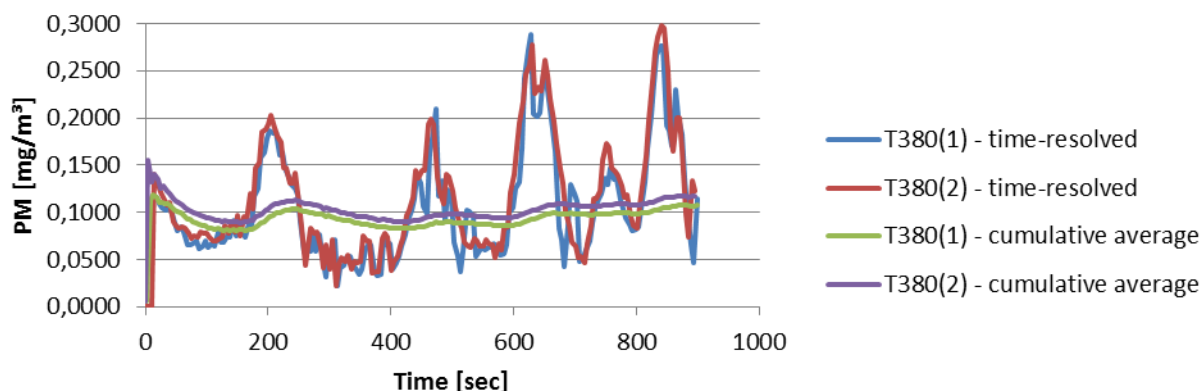
Since the quartz crystal is sensitive to tiny masses in the range of nanograms a dilution system has to be employed in order to reduce typical exposure levels to the sensor significantly. Therefore, a rotating disc diluter, based on the MD19-3E diluter by Matter Aerosol, has been developed and miniaturized [6]. Hemispherical cavities in the rotating disc transport small amounts of exhaust gas to a stream of pre-filtered dilution gas, which then carries the particles to the impactor. By changing the size and number of the cavities and by changing the rotation speed of the disc, dilution factors can easily be adapted. Due to the high dilution ratios the amount of humidity in the diluted gas is significantly reduced such that even without heating of the consequent sampling line no condensation occurs.

By this technology, the PM mass concentration can be evaluated constantly and the final result is delivered right after the measurement. This is a significant benefit over the standard gravimetric filter measurements which require cumbersome and time-consuming pre- and post-processing of filters [7].

As good agreement with the gravimetric filter technique has been shown for a whole series of fuels like wood pellets, wood logs, wood chips, and also for brown and hard coal, the testo 380 could be certified as an official device for surveillance of residential wood burning heaters in Germany [8,9]. Altogether, the testo 380 represents an efficient and cost-saving way of measuring real-time PM emissions with a portable device.

In the figure data of two testo 380 devices during a 15 min measurement of the burning of wood pellets is shown. Nicely, the good accordance of the two devices, revealing in detail the cycles of the burning process is visible, for the time resolved mass-concentration as well as for the cumulative average. In my presentation I will in addition show data on the comparison of testo 380 devices with gravimetric filter measurements on the burning of different solid fuels as well as the evaluation of the performance of an electrostatic precipitator.

Emission from burning wood pellets: Comparison of two T380 devices



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Lonati G. / Politecnico di Milano –DICA, Italy

Ultrafine Particles Generation from Plasma Processing of Graphite

The concern for human exposure to nano- and ultrafine particles at workplaces has been rising during recent past years; however, data are still scarce as well as information on the atmospheric emission from manufacturing plants.

Present work reports fine and ultrafine particle concentrations levels measured at a pilot plant for the production of graphene-based nanomaterials engineered for different applications. These ultrafine nanoplatelets, ranging from 1 to 10 μm of lateral dimensions and 1 to 5 nm of thickness, are obtained by means of plasma thermal expansion, together with both a liquid and a dry state exfoliation.

Data, referring to the indoor open-space, to the closed chamber where production occurs, and to the stream of air extracted from the chamber and released to the atmosphere, were collected before and during production process operation.

Measurements were performed with:

- Portable condensation particle counter for total particle number (TSI P-TRAK 8525, 20 nm-1 μm);
- Ultrafine particle monitor for 6 bins particle size distribution (TSI UFP 3031, 20 nm-1 μm);
- Optical particle counter for 8 bins particle size distribution (Con.Tec P-Dustmonit, 300 nm-10 μm).

Concentration levels in the workplace were around $1.6 \cdot 10^4 \text{ cm}^{-3}$ as a daily average, with no relevant differences with the outside ambient air; however, both in the open space and in the closed chamber an increasing trend was observed during the day, resulting from the superposition of process emissions and workers presence.

During normal operation, concentration levels in the chamber did not show significant discrepancies with the open-space; however, maintenance and process operations (replacement of the exfoliated graphite container) resulted in concentration peaks as high as $5.0 \cdot 10^4 \text{ cm}^{-3}$ or even higher, up to $3.0 \cdot 10^5 \text{ cm}^{-3}$ when the ventilation system in the chamber was switched off.

All particle size distributions measured indoors were dominated by the particles in the smallest size-bin (20-30 nm) with some relevant differences between distributions measured before and during process operation both in the open space and in the closed chamber: namely, process operation resulted in a huge enrichment of the abundance of the finest particles, responsible for the increase in number concentration levels.

Concentration levels in the stream released to the atmosphere were around $1.5 \cdot 10^5 \text{ cm}^{-3}$ (i.e. about 1 order of magnitude higher than indoor values), ranging between $9.7 \cdot 10^4 \text{ cm}^{-3}$ e $2.3 \cdot 10^5 \text{ cm}^{-3}$ and with a size distribution displaying a rather flat mode in the 300-700 nm range, likely as a consequence of particles aggregation in the venting duct out from the chamber.

For indoor environments, these results indicated that the normal process operation has a very limited impact on the concentration levels; conversely, maintenance and process operations can result in high concentration peaks, determined by a sudden increase of the finest particles, followed by a decline pattern lasting 10-15 minutes. Since workers may suffer of high exposure during these events, proper personal protective equipment should be adopted and process automation should be incremented. Conversely, atmospheric emissions do not appear to be of any concern and relevance.

Lu Xingming / University of Brighton, United Kingdom

Understanding the effects of Precursor Loading Factors on the Morphology of Premixed Flame Synthesized nanoparticles

Premixed flame nanoparticles synthesis is emerging a promising method for large scale production of nanoparticle. This paper presents the work undertaken to investigate and establish the effects of precursor loading factors on the morphology of nanoparticles synthesized using premixed flame burner technique. Initially, a brief review of current gas phase flame synthesis techniques have been reviewed and analyzed in this paper. This is done because gas phase methods have been developed for synthesis of a wide variety of nanoparticles, because of the advantages of it being simple, scalable, low-cost and continuous operating mode to give high production yield. It was concluded that premixed flame and the diffusion flame are two main burner types used for synthesis nanoparticles and their merits and demerits presented. Different techniques have been reviewed and presented. In this work, a new premixed flame burner design was undertaken and built for the continuous synthesis of nanoparticles. The, the effects of precursor factors such as feed rate, precursor loading, type, temperature etc were investigated and correlated with flame conditions. Titanium isopropylate (TTIP) was used as precursor and new designed burner system was burned with Butane premixed flame to generator TiO_2 nanoparticles. Nanoparticles collected and analyzed by STEM. The effects of precursor factors on the morphology of end particles have been presented and discussed.

**Mandal Bijan Kumar / Indian Institute of Engineering Science and Technology,
Shibpur, India**

Fuel Dilution and Air-Preheating Effect on Soot Formation in Diffusion Flame

The formation of soot is a common phenomenon during the combustion of hydrocarbon fuels, particularly in diffusion flame. But the detrimental effects of soot on the health and environment are enormous. Sometimes, preheated air is also used for combustion as oxidizer to recover a part of heat energy from flue gases which will be otherwise wasted. Combustion using preheated air changes the flame structure with increase of peak temperature and these results in the enhancement of soot formation in the combustor. Several gases like CO₂, N₂, Ar and He are added to the fuel or air stream to control the emission of soot and other pollutants.

In this work, an attempt has been made to investigate numerically the effect fuel dilution with nitrogen on the soot formation in a laminar axi-symmetric diffusion flame of methane and preheated air. The fuel temperature is kept constant at 300 K whereas the inlet air temperatures are considered as 300 K and 400 K for non-preheated and preheated air respectively. The mass flow rate of methane is kept constant and the inert gas (nitrogen) is added to the fuel in such a way to make it a certain percentage (10%, 20%, 30%, 40%, and 50%) of the total mass flow rate of methane and nitrogen. The governing equations considered here are based on the conservation of overall mass, species concentration, axial momentum, radial momentum and energy equations. Effect of radiation heat exchange has been taken care by incorporating an optically thin radiation model. Finite difference technique based on SOLA algorithm has been used for the numerical solution of the governing equations in cylindrical co-ordinates system. A semi-empirical soot model based on the previous works available in the literature has been modified and adopted here. In the soot formation model, soot volume fraction and soot number density have been considered as the most important variables.

The predictions from the code have been validated with the experimental results available in the literature for the base flame (flame using non-preheated air without any diluent addition). It is observed that although the shape of the flames does not change with dilution of fuel but flame height decreases slightly when fuel is diluted. Temperature is also decreased with higher percentage of nitrogen addition to the fuel as nitrogen absorbs some heat. Soot volume fraction and soot number density reduces with increase in percentage of dilution. The computed results show a large reduction in soot volume fraction and soot number density in between no dilution and 50% dilution of the fuel. The soot volume fraction decreases by an order of magnitude whereas soot number density is reduced by a factor of 3 with 50% by mass nitrogen addition to methane fuel. At the same time, when preheated air is considered, temperature increases (maximum by 100 K) and soot increase substantially. But a combination of preheated air and 30% nitrogen as diluent added to the methane fuel provides reasonably acceptable level of soot emission.

Markowski J. / Poznan University, Poland

Influence of an Oxygen Additive to Jet Fuel on the Particle Emissions from a Small Turbine Engine

The paper presents the results of investigations and analyses related to the potential for use of the JET A-1 with an oxygen additive ($\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$) in small turbine engine. An evaluation has been performed of the influence of different contents of the additive on the particle emission.

Tests of the particle emissions in the exhaust gases were conducted for four fuels with different contents of oxygen additive. During the first phase the distribution of particles diameters was investigated for exhaust fumes from engine fueled with JET A-1 with no additive. The results of the measurements obtained are reference for comparing results of tests carried out with the use of the remaining fuels: JET A-1 with 10, 20 and 30 percentage share of oxygen additive. The additive utilized in the tests is a substance generally used in the chemical industry as a solvent. In accordance with the chemical formula $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$, one molecule of the compound contains 4 oxygen atoms, therefore some changes might be expected in the process of fuel combustion with the participation of such an additive promoting reduction in the number of particles. The test involved measurement of the number of particles and their diameter distribution for 12 points of the engine operation, which have been characterized by the value of thrust within the range from $K_{\min} = 10 \text{ N}$ to $K_{\max} = 120 \text{ N}$.

Analysis of the test results involved particle size distribution in exhaust fumes of engine powered with fuels with different contents of oxygen additive. These are functional dependencies between the relative number of particles from a given range of diameters and the average size of a particle. Distributions have been developed for each test values of thrust and for each type of fuel powering the engine. The selected characteristics of distributions are shown in Figure 1.

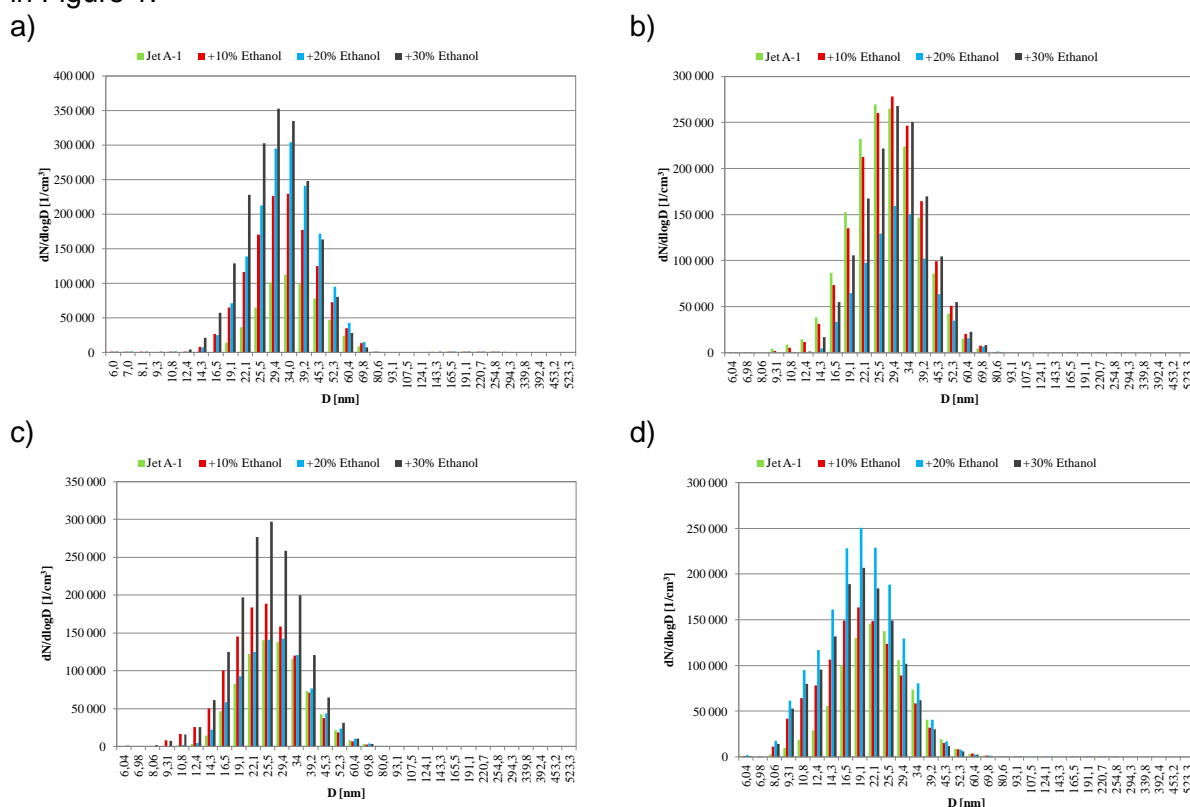


Fig. 1. Size distribution of particles for the tested fuels for thrust of:
a) 10 N, b) 30 N, c) 60 N, d) 120 N

The results obtained indicate the similarity of the particle size distribution for all values of thrust and show changes in the number of particles for individual size distributions. These changes depend on the percentage of additive in the fuel and on the thrust of the engine.

Use of the $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$ additive does not cause changes in the particle size distribution, and only helps to reduce their number in all measuring ranges. These changes result in a reduction in total emissions of particles by about 10%.

Miklánek L. / Czech Technical University

Size Distribution of Particles from a Diesel Direct-Fired Heater

This study offers a preliminary characterization of particle size distribution from a typical production diesel-fired heater (DFH) used in motor vehicles.

With increasing efficiency of combustion engines and deployment of electric drives, less waste heat will be available to heat the passenger compartment, and independent heat sources will become more necessary. Diesel direct-fired heaters (DFHs) are generally used as an independent heat source for any system in which a diesel fuel and a battery power is available. DFHs are also offered as an alternative to idling truck engines to heat the cabin in cold weather.

There are currently no particulate matter emission limits for DFH. Storey and Thomas (Society of Automotive Engineers paper 2003-01-0289) have found the total PM mass from a truck DFH to be 55 mg/h, but little is known about particle size.

The goal of this study was to conduct a preliminary characterization of particulate matter emitted by a typical production DFH during various operating regimes. A sample of conventional DFH for air-heating equipped with low-pressure fuel system was chosen as an object for investigation. A DFH was installed in the laboratory and extensively instrumented with thermocouples, flow meter, a fuel consumption meter, and gas analyzers. A sample of particulate matter from DFH exhaust was diluted by a rotating disc microdiluter (MD-19, Matter Aerosol) and fed into a particle classifier and spectrometer (Engine Exhaust Particle Sizer, TSI). Measurements were taken during start-up, operation at various power levels and switching-off the heater.

Highest concentrations of particles, on the order of 10^7 - 10^8 #/cm³, were found during heating up of the glow plug, start-up (peak around 100 nm), and during switching-off (peak around 10 nm). During operation, particle concentrations generally decreased with increasing power levels (and increasing combustion chamber temperatures and flows), from the order of 10^6 #/cm³ (peak around 34 nm) at the lowest setting to below the detection limit of around 10^5 #/cm³ (peak around 10 nm). Concentrations of 10^6 #/cm³ corresponds to approximately 1 - 2×10^{12} #/kWh of thermal output. The particle concentrations during the start-up were strongly affected by the glow plug, with installation of another type of glow plug yielding lower emissions.

Miller H. / George Washington University USA

Extinction Measurements for Determination of Optical Band Gaps for Soot in Nitrogen-diluted, Ethylene/Air Non-premixed Flames

Visible light extinction was measured in a series of nitrogen-diluted, ethylene/air, non-premixed flames and this data was used to determine the optical band gap, E_{gopt} , as a function of flame position. This work builds on recent Raman and optical band gap (OBG) studies in our lab, which provided experimental support to the model of soot formation where the transition from chemical to physical growth starts with species with molecular masses of only several hundred Daltons. In the current study, light from a SuperContinuum light source is collimated, expanded, and directed into a monochromator. The dispersed light is split into a power metering channel and a channel that is periscoped and focused into the flame. The transmitted light is then recollimated before the detector. After tomographic reconstruction of the radial extinction field, the OBG was derived from the near edge absorption feature using Tauc analysis. This approach was repeated through the full range of heights for four flames of varying dilution levels, from 32%Ethylene/68%Nitrogen to 80%-Ethylene/20%-Nitrogen. An evolution in OBG was observed throughout all flame systems with a consistent range of OBG observed between approximately 1.9eV and 2.3eV. Averaging over all positions the average OBG was approximately 2.09eV for all flame systems. Comparing these results to previously published computational results from our lab relating calculated HOMO-LUMO gaps for a variety of D2h PAH molecules to the number of aromatic rings in the structure, showed that observed optical band gap is consistent with a PAH of about 14 rings or a conjugation length of 0.96nm (Figure (1)). This result agrees with the lower edge of the PAH sizes reported in our recent Raman work that suggest 1.0 – 1.2nm conjugation lengths. These results are consistent with PAH condensation beginning with species about the size of circumpyrene.

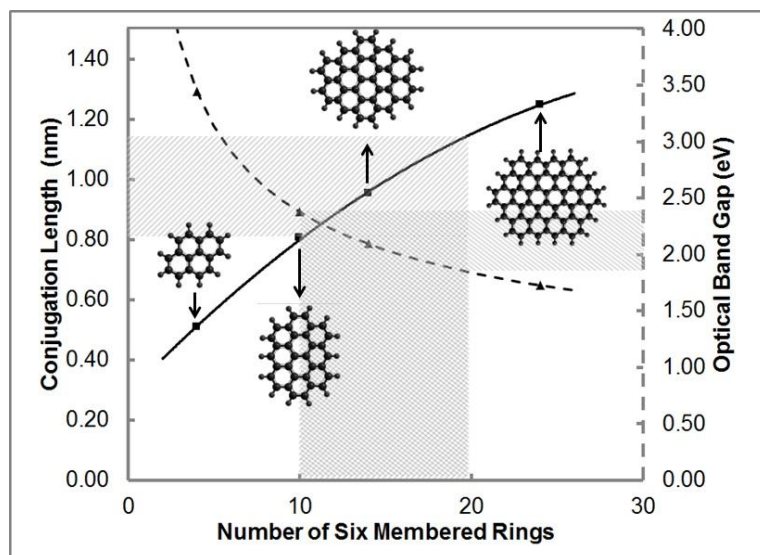


Figure 1. Comparison between calculated HOMO-LUMO energy gaps (OBG) with number of aromatic rings and conjugation length. The dashed line and triangle show the relationship between OBG and number of rings. The solid line and squares show the relationship between conjugation length and number of rings. The grey diagonal lines depict how the range of OBG observed throughout the flame correlate to physical morphology parameters in the 60%-Ethylene/40% Nitrogen flame.

Mühlbauer W. / BERC Bayreuth, Germany

Influence of Different Diesel Fuels under Variation of Injection Pressure and Boost Pressure on Combustion and on PhysicoChemical Properties of Engine-out Soot Emissions

Diesel particulate filters (DPF) are established in modern diesel engines to remove combustion generated soot particles from the exhaust gas. Thus the emission limit values for particulate mass as well as for particulate number could be achieved. The trapped soot in the DPF has to be removed by regeneration, where the soot is oxidized mostly into CO₂ [1, 2]. It is well known from literature that the reactivity of the trapped soot is dependent on the combustion behavior and its morphology. These properties change with engine operating parameters [3–5] and with the used fuel [6, 7].

In the present work, the influence of different diesel fuels at different engine operating conditions on the in-cylinder combustion behavior and on the physicochemical soot properties have been studied. The experiments have been conducted on an optically-accessible single-cylinder diesel engine as well as on a modern light-duty diesel engine (OM 651, Daimler). Injection and boost pressure have been varied with four different diesel fuels (reference diesel fuel without rapeseed methyl ester (B0), diesel fuel according to DIN EN 590:2010 (B7), neat rapeseed methyl ester (B100), Di-n-Butyl Ether (DNBE)). On the optical engine the in-cylinder soot formation and oxidation process have been evaluated by detecting a spectral range of the soot luminescence at 490 nm and the OH radical (OH*) radiation at 308 nm. The soot emissions have been analyzed on both engines by High-Resolution Transmission Electron Microscopy (HR-TEM), by a Scanning Mobility Particle Sizer (SMPS) as well as by a Pegasor Particle Sensor (PPS-M). Furthermore, the soot reactivity of the emitted soot particles has been determined by thermogravimetry under engine-like exhaust conditions (5% oxygen, 95% nitrogen).

The measurements on the optical engine show high differences in the in-cylinder soot formation and oxidation process especially for DNBE. This results in high changes of particulate number emissions. By the study on the light-duty diesel engine significant changes of particulate number and mass as well as of the particulate morphology and structure are observed (Figure 1). This fact entails differences in the reactivity of the soot produced with different diesel fuels under varied injection and boost pressures (Figure 2).

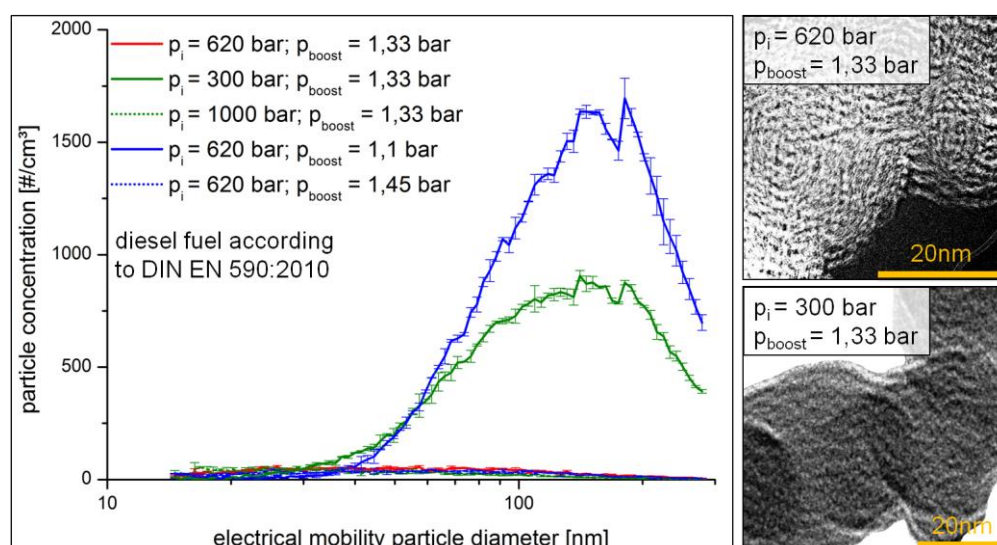


Figure 1: SMPS measurements to analyse the electrical mobility particle diameter (left) and HR-TEM images to get information about primary particle diameter and structure (right)

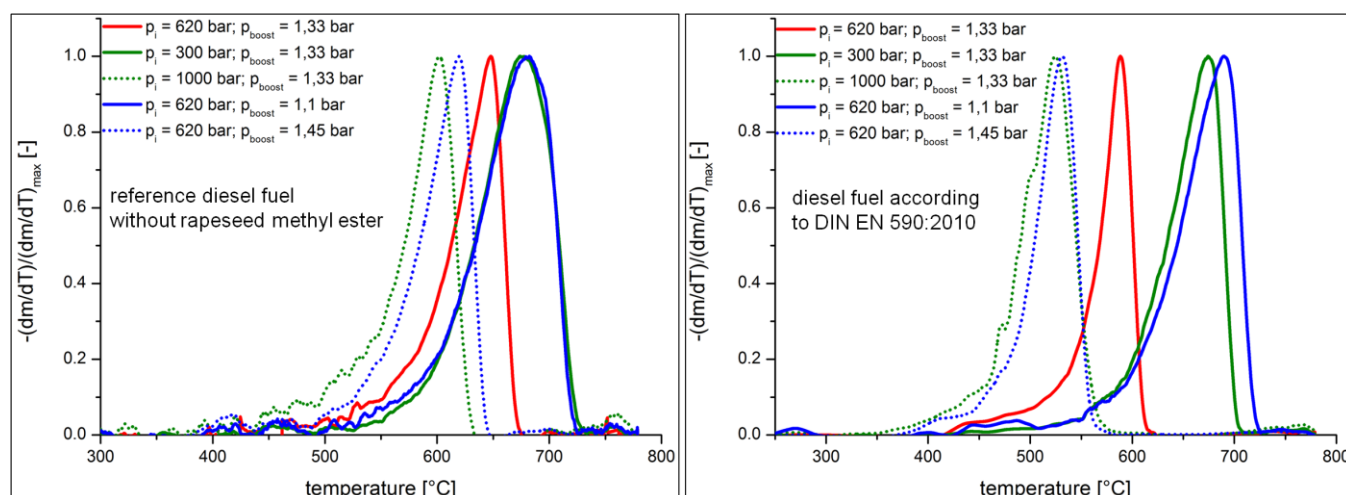


Figure 2: Derivative thermogravimetric analysis (DTG) curves for the reference diesel fuel without rapeseed methyl ester (left) and with diesel fuel according to DIN EN 590:2010 (right) at different injection (p_i) and boost pressures (p_{boost}).

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Multari A. / MAHA, Germany

**OBD vs. Tailpipe Testing - Future Test,
Options for Emission Control Systems of Modern In-Use Vehicles**

A drastic reduction in the emissions of new vehicles has been achieved over the last 20 years, with the introduction of strict worldwide regulations for reduction of all exhaust emissions. In this context also, PTI (Periodic Technical Inspections) schemes have to follow the development of modern vehicle technology. PM as well NO_x as measurement now seems due for a further stage of development.

Both pollutants (PM and NO_x) are reduced by complex exhaust after-treatment systems and engine internal solutions. High vehicle emission rates are often a result of component aging, component failure, or generally poor maintenance. There has also been an increasing in the tampering of emission systems over the last years to avoid high repair costs. PTI emission tests allow a quick and reliable evaluation of the whole emission related systems to determine whether in-service vehicles conform to their design emission levels. PTI emission test requirements and thresholds have not kept pace with development in vehicle technology and type approval procedures (especially for Euro 5 and 6). Updates to the legislation, instruments and procedures are therefore necessary.

Keywords: PM, NO_x, Air Quality, OBD, Vehicle Emission Testing, Diesel and Petrol/Gasoline Emissions, Non-Road Emissions

Nussbaumer Th. / VERENUM Switzerland

Monitoring of Electrostatic Precipitators in Automatic Biomass Combustion Plants

Since biomass combustion is related to PM in the ambient air, strict emission limits were introduced in the Swiss ordinance on air pollution control (OAPC) 2007 with 20 mg/m³ at 13 vol.-% O₂ for 500 kW to 1 MW nominal heat output. Since then, automatic biomass combustion plants larger than 500 kW are commonly equipped with electrostatic precipitators (ESP). Due to the varying heat demand the boilers are often operated in on/off-mode and in part load. Hence optimum control is essential to avoid high PM emissions during periods with ineffective ESP and the project therefore pursues two targets:

1. To monitor ESP availability operated with automatic biomass boilers, to identify potential reasons for increased emissions, and to derive recommendations for control concepts.
2. To develop a monitoring concept enabling authorities to assess the ESP operation and estimate the resulting PM emissions. As a pre-condition for acceptable cost, the concept shall be based on data from the programmable logic controllers (PLC) (hence without continuous particle measurement).

Seven heating plants were therefore equipped with a data acquisition to log PLC data from boiler and ESP. Data on load, temperatures, ventilators, lambda sensor, current and voltage of the ESP were collected during two heating periods with a frequency of 0.5 min⁻¹. Due to differing state definitions between manufacturers and missing standards in data exchange between boiler and ESP, definitions to calculate ESP availability are introduced. In addition to the availability, the total PM emissions during two heating seasons are calculated by assumption of raw gas and clean gas emissions and information on the operation of the boiler and the ESP. To validate this method on PM assessment, on-site measurements were performed to determine the real emissions. Measured and calculated PM emissions are compared during operation modes such as start-up, full load, part load, shut-down and ESP cleaning.

The results on availability and measured PM emissions reveal that the determination of the availability is a valuable concept to monitor PM emissions under real-life operating conditions. In addition, malfunction is found to be the major reason for reduced ESP availability. While four out of seven plants are properly operated with a high ESP availability, three plants exhibit increased emissions. In two cases this is due to long periods of ESP malfunction, whereas in one case too small ESP dimensions are the reason. Therefore a reliable detection of malfunctions and immediate repair are crucial. Without malfunctions, high ESP availability can be achieved if the operating temperature of the ESP is rapidly achieved after start-up and safely maintained during the boiler operation. On the other hand, the analysis also shows that part load and on/off-mode of the boiler do not necessarily lead to increased emissions.

Consequently, the investigation confirms that a monitoring concept based on the availability derived from PLC data is a valuable tool to complement the periodical on-site inspection. Undesired operation and malfunctions of the ESP can be detected which avoids increased PM emissions of automatic biomass combustion plants in practice.

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Acknowledgements

Swiss Federal Office of Energy (BFE)
Federal Office for the Environment (BAFU)
APF GmbH
BETH Filter GmbH
Meisterfilter AG
Scheuch GmbH
Mawera Holzfeuerungsanlagen GmbH
Müller Holzfeuerungen AG
Schmid energy solutions AG

Okuda H. / Shimadzu Corp., Japan

Development of a Novel Electro Mobility Analyzer Based on a New Classifying Principle and Applications for Nanoparticles from Different Types of Vehicles Under Various Conditions

A novel electro mobility analyzer (Nano Aerosol Monitor: NAM) which can classify nanoparticles based on a new principle was developed. It can measure nanoparticle number concentration conveniently on the field where they are generated. The NAM is different from the current differential mobility analyzer (DMA) on the point of that it doesn't have sheath flow. It makes NAM as simpler and compact structure and also high cost efficiency. This instrument has multiple detectors for different elector mobility ranges that are controllable by the operator. And it can measure real-time data. The NAM was evaluated to compare with the UN-ECE particle measurement program (PMP) method. Evaluations were conducted similar to European type approval tests procedure. Three types of vehicles, Euro V complied Diesel engine truck and Euro VI complied Diesel engine truck and Euro 6 complied gasoline DI engine car, were tested under different types of test mode, WLTC and JE05 and JC08, and start conditions, hot start and cold start. Correlations between the NAM and the PMP method were excellent although all vehicle type, test mode, and start conditions were contained. (Correlation coefficient $R^2=0.97$) The NAM was also evaluated by direct exhaust pipe sampling to compare with the PMP method. Euro VI complied Diesel engine truck was tested under JE05 test mode and hot start condition. Correlations between the NAM and the PMP method were excellent. (Correlation coefficient $R^2=0.99$) Since numbers of data were not enough it should be added.

The NAM was tested for on-board measurement. The NAM and the Engine exhaust particle sizer (EEPS) were set on car seats and introduced outside air. Nanoparticle number concentration that came from on-road atmosphere was measured by the NAM and the EEPS simultaneously during freeway driving. Both the NAM and the EEPS measurement diameters range were adjusted as same. The peaks height and the peaks appearance time from the results, which were measured by these two instruments, showed enough correspondence. But the NAM showed overrange in some cases. In conclusion, the NAM and the PMP method showed excellent correlation. And the NAM could adapt for direct exhaust pipe sampling measurement and on-board measurement.

Olin M. / Tampere University, Finland

Sulfur Driven Nucleation in Diesel Exhaust: Simulations of a Laboratory Sampling System

Introduction

Nanoparticles are related to adverse health effects [1,2] and various effects on climate [3]. Diesel vehicles emit nanoparticles, which can be divided to soot and nucleation mode particles. Soot particles are formed during the combustion process, but e.g. nucleation mode particles originated from fuel or lubricant oil sulfur are formed after the exhaust is released from the exhaust pipe due to rapid cooling.

There are currently large uncertainties in modeling the nucleation mode formation in vehicle exhaust. Homogeneous binary water-sulfuric acid nucleation is proposed to be the nucleation mechanism in previous modeling studies [4,5,6]. The nucleation rate of it can be derived from the classical thermodynamics and it is parameterized by Vehkamäki *et al.* [7,8] for computational usage.

Nucleation rate depends on gaseous sulfuric acid concentration with $J \propto [\text{H}_2\text{SO}_4]^n$, where n , i.e. the nucleation slope, depends on the nucleation mechanism. In classical nucleation theory, the slope varies around 6, but in activation [9] or kinetic [10] nucleation mechanisms, the slope is 1 or 2, respectively. Slopes 1 and 2 are found to fit to atmospheric measurement results better than classical nucleation [11]; however, activation and kinetic nucleation mechanisms have not yet been explored in connection with diesel exhaust.

Model

We developed an aerosol model, coupled with a computational fluid dynamics model, which can be applied to study nanoparticle formation and evolution in vehicle exhaust. The model simulates nucleation, condensation, coagulation, and deposition of aerosol. In this version, nucleation is modeled according to the classical nucleation theory.

Simulations

The dilution system of an engine laboratory measurement [12] has been simulated. The simulation domain consists of a porous tube diluter and an aging chamber. Temperature and sulfuric acid concentration of raw exhaust and the particle distribution of diluted exhaust have been measured in the measurements.

The measurement points to be simulated have been chosen to represent conditions in which only the sulfuric acid concentration changed and other variables remained nearly constant in the raw exhaust. This enabled us to examine the nucleation rate dependency on sulfuric acid concentration using the information on the nucleation mode concentration in the diluted exhaust.

Results and discussion

To obtain the measured particle distribution, the nucleation rate from the classical theory had to be adjusted by a correction factor which depended on the sulfuric acid concentration in the raw exhaust. The correction factor varied within five orders of magnitude, even though the sulfuric acid concentrations varied only within one order of magnitude, as shown in Figure 1.

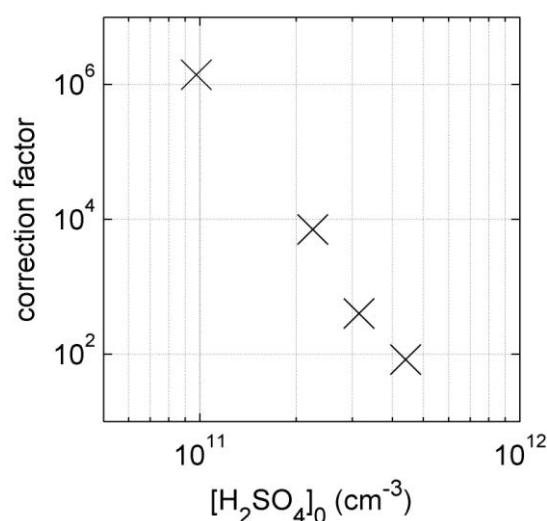


Figure 1. Correction factor versus sulfuric acid concentration in the raw exhaust.

The magnitude and variation of the required correction may indicate that it is impractical to use classical water-sulfuric acid nucleation theory to model the particle formation in vehicle exhaust. Due to the decreasing slope of the correction factor versus sulfuric acid concentration, the classical nucleation theory possibly overestimates n . That indicates that activation or kinetic type nucleation mechanisms could be applied to predict the nucleation rate, or that hydrocarbons or other compounds participate in the nucleation process.

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Otsuki Yoshinori / HORIBA Japan

Performance of Particle Counting System Utilizing a Commercially Available PMP System

The particle number emission (PN) regulation has been implemented since 2011 in Europe. PN measurement procedure defined in the ECE regulation requires detecting solid particles only by eliminating volatile particles, the concentrations of which are highly influenced by dilution conditions, using a volatile particle remover (VPR). To measure particle number concentration after the VPR, a particle number counter (PNC) which has detection threshold at a particle size of 23 nm are adopted, because most of solid particles generated by automotive engines are considered to be larger than 23 nm. On the other hand, several studies have reported the existence of solid and volatile particles smaller than 23 nm in engine exhaust. The applicability of current configuration of the measurement system is still under the discussion in Particle Measurement Programme (PMP). This paper describes investigation into a measurement method for ultrafine PNC with threshold of below 23 nm and evaluation of VPR performance for fine particles. The detection efficiency of an ultrafine PNC was verified by following the ECE regulation procedure. In addition, the possibility of re-nucleation of volatile particles at VPR outlet was evaluated, because the re-nucleated volatile particles which are usually smaller than 23 nm will cause a high bias for solid particle measurements by the ultrafine PNC compared to the standard PNC. We applied a hot catalytic stripper (HCS) in order to effectively remove volatile fractions instead of an evaporation tube (ET). The performance of the modified VPR with HCS was evaluated, and compared with that of the conventional system. The modified VPR showed higher removal efficiency for volatile particle, and also showed higher losses for solid particles smaller than 23 nm, which might affect on the measurement accuracy of fine particles. There were another difficulties in the evaluation of the system performances especially of the calibration particle generators. Overall detection efficiency of the measurement system was estimated by the verified results. Technical challenges against the fine particle measurement were revealed by this investigation, finally.

Patel K.S. / Ravishankar Shukla University, India

Carbons and Persistent Organic Pollutants Distribution in Ambient Air of India

The chemical species i.e. black carbon (BC) carbons, ions, organic compounds, **etc.** are formed as a result of incomplete combustion of the materials. Among them, the BC, persistent organic pollutants (POPs) i.e. **polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), etc.** are considered as elements of health interests [1-3].

A huge amount of coal is burnt in central India for production of metals, cement and energy. Therefore, distribution, variation and sources of the carbons and POP_s in the ambient air associated to the PM of Raipur city, Chhattisgarh, India (21° 23' N, 81° 63' E) are described. The sampling of the particulate matters (PM₁₀ and PM_{2.5}) was carried out for 1 year (February, 2007 – January, 2008). The **most toxic PAHs namely:** phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (Baa), chrysene (Cry), benzo[b]fluoranthene (Bbf), benzo[k]fluoranthene (Bkf), benzo[a]pyrene (Bap), dibenz-[a,h]anthracene (Dbah), benzo[ghi]perylene (Bghi) and indeno[1,2,3-cd]pyrene (Ind) was analyzed.

The concentration of PM₁₀, BC₁₀, OC₁₀ and CC₁₀ (n = 24) in the air was ranged from 116 – 523, 8.8 – 65.5, 7.2 – 55.4 and 6.1 – 58.7 µg m⁻³ with mean value of 283±55, 28.8±6.8, 23.2±5.4, and 22.7±6.8 µg m⁻³, respectively. The concentration of total ΣPAH₁₂ (n = 24) was ranged from 38 – 165 ng m⁻³ with mean value of 93±16 ng m⁻³. The most prominent peaks of higher PAHs (i.e. Bbf, Bap, Bghi and Ind) were seen in the month of December due to the lowest wind speed, ≤1 km². The number of PCBs congeners detected in the air (n = 4) was ranged from 62 – 95 with mean value of 86±16. In all sites, significant concentration of congener 3 was observed. The highest concentration of congeners: 17, 56+60, 82+151, 138+158, 180+193, 201 and 206 was observed in the air. The concentration of the BC, OC and CC in the PM₁₀ (n = 24) was ranged from 7.3 – 13.0, 6.0 – 11.2 and 2.4 – 17.3% with mean value of 9.8±0.7, 8.2±0.6 and 7.8±1.4%, respectively. The concentration of the ΣPAHs in the PM₁₀ was ranged from 238 – 467 mg kg⁻¹ with mean value of 342±19 mg kg⁻¹. The BC, OC and PAHs concentration in the PM was increased as the particulate size decreased.

The concentration of the BC, PAH_s and PCB_s in ambient air of Raipur city was observed to be much higher than the permissible limits. The concentration of BC, ΣPAH_s and ΣPCB_s in the air was found to be higher than other regions of the country and globe.

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On-road Particle Emissions of Passenger Cars Using Portable Emission Measurement System

The paper presents the results of on-road exhaust emission tests of passenger cars fitted with diesel engines. Under such conditions the authors could determine the actual vehicle emissions. The tests were performed on a road portion of a hundred kilometers or so – these tests provide information on the on-road emissions and are a basis for their ecological evaluation. For the measurement of the exhaust emissions the authors used a Portable Exhaust Emissions System. The used data were averaged within individual speed and acceleration ranges thus obtaining the characteristics of the share of operation in individual ranges and the characteristics of the emission matrices of the individual emission components. The above results served for defining of the emission level indicator of the vehicles that can be used for classification of vehicle fleet in terms of their emission level).

The measurement of the on-road exhaust emission was performed under real traffic conditions: urban drive, extra urban, freeway in the province of Wielkopolska. The tests consisted in the measurement of the exhaust components (CO, HC, NO_x and particulate matter for each vehicle) and then with the use of the GPS and OBD data the road emission of each exhaust component was determined.

For the comparison the ranges of engine operation were used that are most frequently utilized under real traffic conditions. They correspond to three areas of operation (Fig. 1): 1 – idle speed, 2 – medium engine speed–medium load, 3 – high engine speed–high engine load. The vehicles were fitted with different powertrains, hence the selected ranges of operation do not overlap (similar areas were compared: as a criterion of similarity the relative engine speed and relative engine load were selected referred to the maximum values).

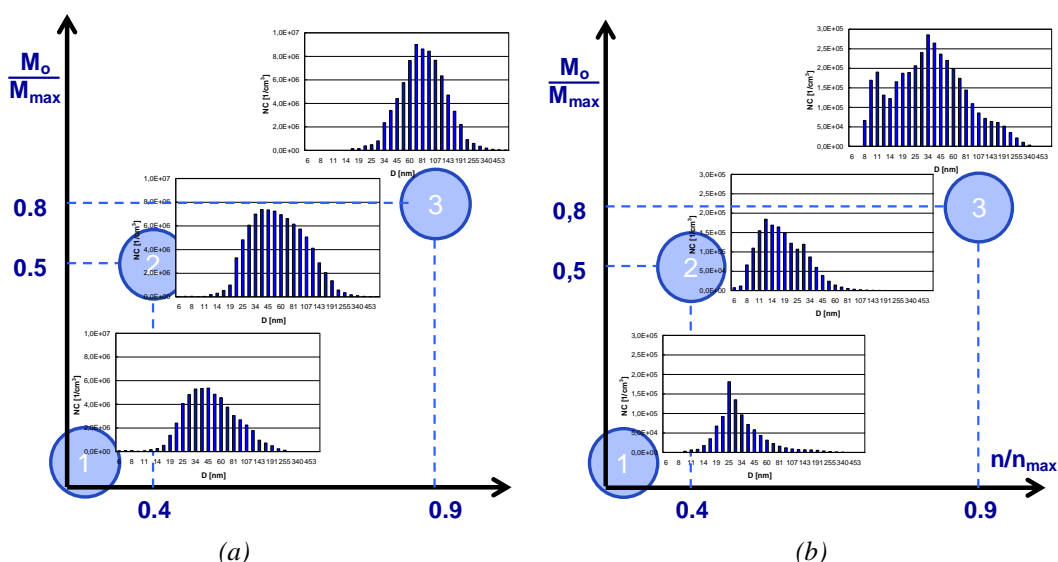


Fig. 1. Engine operating conditions in the coordinates of engine speed – engine load in the on-road tests and particle size distribution: 1 – idle speed, 2 – medium engine speed–medium load, 3 – high engine speed–high load; a) vehicle A, b) vehicle B

From the analysis of the data it results that the normative emission values for the tested SUV vehicles meeting different Euro emission standards and the on-road exhaust emission vary. These differences in the case of some exhaust components under analysis are significant – these are as follows:

- For the Euro 4 vehicle: CO is lower by 80%, HC is lower by 80%, NO_x is higher by 80%, PM is lower by 10%,
- For the Euro 5 vehicle: CO is lower by 90%, HC is lower by 70%, NO_x is four times higher, PM is lower by 30%,

The on-road emission tests indicate that in relation to some of the exhaust components the emission is several times higher. Hence, a trend is seen to legalize and enforce the on-road exhaust emission measurement in Europe.

Ragettli M.S. / University of Montréal

Diesel Exposures in Port Workers in Montreal

Background: Exposure to diesel-emitted particles has been linked to increased cancer risk and cardiopulmonary diseases. In 2012, the International Agency for Research on Cancer (IARC) classified diesel engine exhaust as carcinogenic to humans (group 1). Therefore, accurate characterizations of exposure levels in both occupational and urban environments are necessary to assess the health risk associated to diesel exhaust.

The port of Montreal moves more than one million TEU (twenty-foot equivalent unit) containers each year. Around 2500 container trucks go through the port gates every day and each one has to stop at one of the checkpoints to enter and leave the terminals.

Aims: In this study, the exposure of port workers to various emissions of diesel engines from container trucks was assessed using various measurement devices.

Methods: The exposure to diesel engine emissions was assessed by both personal and stationary measurements at two terminals during five days in 2013. Personal exposure was measured to respirable elemental carbon (EC) (Method NIOSH 5040), oxides of nitrogen (NO_2 and NO) and carbon monoxide (CO) (portable single gas detectors, BW Gaz alert extreme) in the workers' breathing zone. Stationary devices (Dust-Track DRX, P-Track, Engine Exhaust Particle Sizer) were used to monitor particle mass concentration, particle number concentration and particle size distribution, respectively. Stationary devices were placed directly at the terminal's checkpoints. Aerosol samples were collected on microscopy copper-grids (200 mesh) coated with carbon film stuck on polycarbonate filters and were subsequently analyzed for chemical composition by transmission electron microscopy (TEM) coupled with an energy dispersive X-ray spectroscopy (EDX). Furthermore, two urine samples for six workers were collected for the determination of 1-hydroxypyrene (1-OHP). The first sample was collected Monday morning before the work and the second on Friday afternoon at the end of the workweek.

Results: The average daily concentrations of fine and ultrafine particles were between 16,000 and 67,000 particles·cm⁻³. Wind speed and the number of trucks explained 73% of the total variance of the number concentration. Peak particle number concentrations up to 500,000 particles·cm⁻³ were associated with the crossing of container trucks with refrigeration systems and "old" trucks with engine exhaust at the level of the worker. The elementary chemical analyzes showed the presence of spherical aggregate carbon particles associated with various metal such as iron and aluminium. Other chemicals such as calcium are associated to the background. The highest concentration of elemental carbon and the average concentration were 4 µg·m⁻³ and 2 µg·m⁻³, respectively. The maximum concentration of urinary 1-OHP was 0.12 mol/mol creatinine and no 1-OHP concentration increase was observed during the workweek. All the gas concentrations were below the detection limit.

Conclusions: Port workers employed at the checkpoints are exposed to diesel exhaust below the elemental carbon recommendation level of 100 µg·m⁻³. However, precaution could be taken into account since no health-based recommendation has been proposed subsequently to the IARC group 1 classification in 2012.

Rahinov I. / The Open University of Israel

Diagnostics of Combustion Synthesis of Iron Oxide Nanoparticles: from Gas Phase Intermediates to Solid Particulates

Flame-assisted synthesis is a route for scalable production of nanosized metal oxide materials with well-defined properties. Iron oxide nanoparticles are used in diverse applications, including optical magnetic recording, catalysis, gas sensors etc. Their properties are dependent on their characteristics, such as size distribution, phase and morphology. Detailed understanding of the mechanism governing the particle formation in flames is a necessary pre-requisite for flame synthesis of NPs with tailored functionalities.

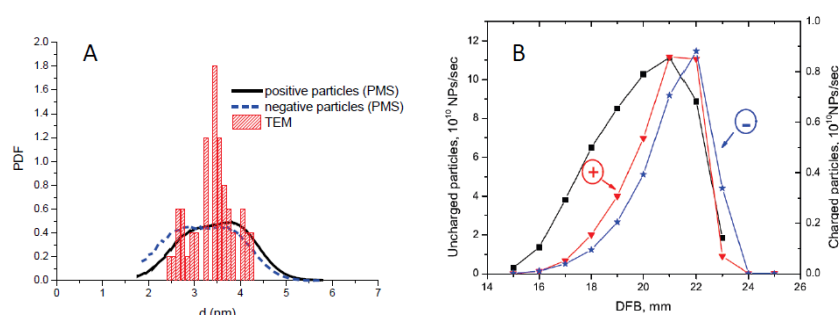


Figure 1: (A) The size distribution derived from PMS measurements (for negative and positive particles) compared to the one derived from transmission electron microscopy analysis. (B) The fluxes (proportional to number concentration) of positive, negative and neutral iron oxide particles measured by PMS-QCM.

Mechanism validation calls for quantitative (and desirably *in-situ*) diagnostics of both gas-phase species (e.g. FeO) and nascent solid iron oxide NPs. Recently we have introduced a combined Particle-Mass-Spectrometry-Quartz Crystal Microbalance (PMS-QCM) analysis technique[1-2]. The analysis protocol incorporates molecular beam sampling of the flame aerosol, sorting the charged particles according to mass/charge ratio (m/z) via electrostatic deflection and detection of neutral particles by monitoring the oscillation frequency of the quartz crystal exposed to the particle-laden molecular beam. This yields the information regarding total mass concentration, probability density distribution of m/z and particle number density (see Figure 1).

Furthermore, we have studied the increase of the resonance frequency of the quartz crystal induced by laser irradiation. The magnitude of the frequency detuning effect is proportional to the amount of energy absorbed on one of the crystal electrodes. When the crystal is covered by flame-generated nanoparticles (deposited by molecular beam sampling), the amount of the laser energy absorbed, and the consequent frequency detuning are reflecting the magnitude of the absorption coefficient of the NP layer (see Figure 2).

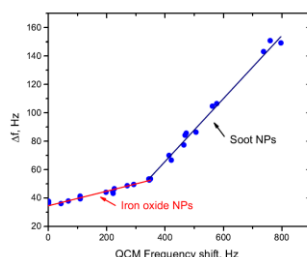


Figure 2: He-Ne laser-induced quartz crystal detuning measured during particle deposition. When iron oxide nanoparticles generating flame was replaced by sooting acetylene flame, steeper dependence of the detuning on the amount of deposited nanoparticles is observed, reflecting larger absorption coefficient of soot nanoparticles compared to iron oxide.

The chemistry of iron-containing gas-phase intermediates (e.g. FeO) is also critical in establishing the final characteristics of the synthesized iron oxide nanoparticles. However, their monitoring in particle-laden environment with standard methods, such as laser induced fluorescence, is hampered due to light scattering from solid particulates and luminosity of

particle-generating flames. In this work these interferences were circumvented by deploying Intracavity Laser Absorption Spectroscopy (ICLAS). While the sensitivity to narrowband absorption of the gas-phase FeO is largely enhanced, ICLAS is not sensitive to the broadband absorption by the NPs, allowing to monitor FeO in particle-laden environment –see Figure 3.

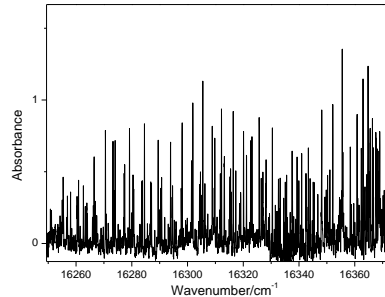


Figure 3: Spectrum of the 611nm-band of the FeO orange system recorded by ICLAS in particle-laden rich methane/air flame.

These methods of diagnostics allow to follow the iron oxide synthesis in flames and to make comparisons to the existing models of nanoparticle formation.

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Comparison between Particulate Matter Mass, Number of Particles, Ultrafine Particle and Black Carbon Emissions by Electronic and Normal Cigarettes in Real-Life Conditions

Aims. An electronic cigarette is a battery-powered device that produces an aerosol containing a mixture of nicotine, propylene glycol and flavoring, depending on the different commercial brands. E-cigarettes pose a regulatory challenge to the medical community, as they may reduce the harm of cigarette smoke but at the same time reinforce addictive smoking behavior. Uncertainties also exist as to whether they do promote a clinically relevant cessation rate in smokers who use e-cigarettes to quit smoking. Furthermore, e-cigarettes are supposed to emit much fewer pollutants in both particulate matter (PM), fine particles (FP), ultrafine particles (UFP) and black carbon(BC).

The aim of the present study was to investigate the emission of PM generated by e-cigarettes and normal cigarettes under real-life conditions.

Methods. Real-time measurement and comparison of electronic cigarettes with and without nicotine and normal cigarettes in a 48 m³ normal office of an Italian comprehensive cancer Institute with no air conditioning and 0.8 air exchange rate (ACH) of PM mass using pre-calibrated model Aerocet 531 of Metone Instruments Inc. as PM₁, PM_{2.5}, PM₇, PM₁₀ and TSP in µg/m³, FP number of particles on 8 sizes from 0.3 to 10.0 µmeters using model 212-2 of Metone Instruments Inc., UFP in number of particles per cubic centimeter from 10 to 1,000 nanometers using model TSI3007 of TSI and BC using model AE31 of Magee Scientific Inc. were measured. Outdoor concentrations were measured contemporaneously to compensate for urban background changes and all data are expressed in difference over the background.

Results. PM mass in µg/m³ (SD) as PM_{1.0} PM_{2.5} PM_{7.0} PM_{10.0} TSP: e-cig without nic 3.5±7.3 7.2±9.6 8.7±9.9 9.9±10.3 11.6±15.5 e-cig with nic 0.0±0.3 0.5±1.1 -0.3±3.1 -0.6±4.4 1.2±10.1; normal cig 76±18 139±32 155±36 158±37 160±37 respectively. $p < 0.005$. FP as number of particles c/c (SD) from 0.3, 0.4, 0.5, 0.6, 1.0, 2.5, 5.0, 10.0 µm, e-cig (mean with & without nicotine): 434(3635), 581(953), 406(420), 240(169), 63(44), 9(16), 2(5), 0(2). Normal cigarettes: 790,907(99,093), 213,960(50,598), 78,081(21,906), 18,666(6,071), 1,077(450), 2(14), 1(5), 3(2) respectively. UFP in particles per c/c: e-cig with nicotine: 566(190), e-cig without nicotine: 641(185), normal cigarettes: 179,010(9,137). BC: e-cig with and without nicotine didn't show any statistical difference over the background, but normal cig at 370, 470, 520, 590, 660, 880 and 950 nm in nanograms per m³(SD): 49,018(21,816), 18,891(7,696), 10,554(3,728), 7,409(2,360), 5,490(1,644), 3,171(824), 2,671(866) respectively

Conclusion. our investigation proved that e-cigarettes produce less PM than conventional cigarettes and no black carbon and therefore may be less hazardous in terms of secondhand exposure. This finding can be of interest to physicians and policy makers, but further studies are necessary to investigate acute and chronic effects of secondhand exposure to e-cigarette smoke in order to rule out any possible issues of health concern

Silvis W. / AVL List, Austria

Aircraft Gas Turbine Non-Volatile Particle Mass and Number Emissions Measured with an AIR 6241 Compliant System

Aircraft Emissions of PM have been regulated to date using the smoke number (SN) metric under global standards and recommended practices described in ICAO Annex 16 Volume II. In 2013, the SAE E-31 committee published an information report, AIR 6241, describing a standardized measurement system and appropriate instrumentation to provide alternative non-volatile PM mass and number metrics in order to more properly characterize these emissions. Prototype systems conforming to these recommended practices had been developed by FOCA, the Swiss Federal Office of Aviation, Cardiff University, and the Missouri University of Science and Technology. A commercial version is now available from AVL.

We'll review the technical rationale and specifications common to these systems and present some recent measurement results. These provide information on the relationship between these new metrics and the smoke number measurement, on the relationship between mass and number for different engine thrust levels, and on the levels at which PM mass and number are being emitted by commercial high bypass aircraft and an older low bypass turbine. Comparison of measurements from the FOCA developed system and the AVL system performed at the SR Technics Laboratory in Zurich as well as data collected from a J-85 engine at the University of Tennessee Space Institute will be presented.

The ability to characterized particulate with a concentration metric or emissions index instead of a smoke number permits PM to be treated similarly to the mass metrics for gaseous pollutants, which use a weighting over a Landing & Take Off (LTO) cycle and some implications of this will be discussed.

Similar measurement experience collected by engine manufacturers in the near future is expected to result in refinements to the procedures, and to guide the determination of permissible levels for future regulation. More importantly, the ability to make these more scientifically useful measurements will help us understand and potentially reduce the contribution to the atmosphere of nanoparticle pollution from this source.

Smallwood G. / NRC Canada

Calibration of Black Carbon Real-Time Mass Instruments: Development and Status

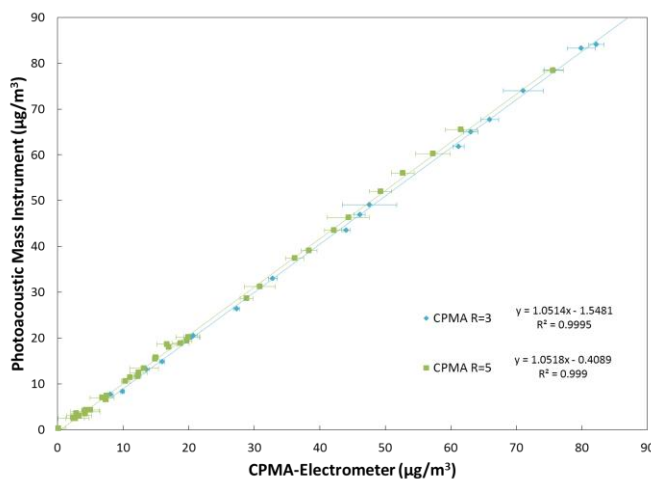
Black Carbon (BC) is a known health hazard and a critical climate forcer. Recent studies implicate BC as the second-most important climate-forcing agent after carbon dioxide. As such, reliable measurement of BC emissions from sources and in the environment is required. Real-time mass concentration measurement instruments, including those based on photo-acoustic principles or laser-induced incandescence principles, have been demonstrated many times to have excellent linearity and correlation with BC concentration. These instruments often demonstrate biases when engaged in comparisons, likely due to differences between the initial calibration and the instrument response to BC. There is a potential benefit in terms of improved measurement accuracy when instruments are calibrated against an absolute reference for black carbon.

Two approaches for the calibration of real-time BC mass concentration instruments are presented. In both cases, the source is a stable black carbon aerosol source, an inverted flame burner producing a soot aerosol with over 95% elemental carbon (EC). The output of this BC source is sampled, passed through a one micron cyclone to remove particles shed from the walls, and split into multiple streams.

In the first calibration method one stream is directed to the real-time measurement instruments while another stream is sampled with quartz filter collection. The quartz filter is then analyzed using a thermal/optical method to assess the EC and organic carbon (OC) masses. The results from the real-time mass instrument measurements are compared to the mass of elemental carbon (EC) determined from the thermal/optical analysis of the filter. This is performed over a range of concentrations.

The second calibration method involves the use of a centrifugal particle mass analyzer (CPMA) in conjunction with an aerosol electrometer to measure the mass concentration of a charged aerosol in real time. The CPMA selects the aerosol by mass-to-charge ratio and the electrometer measures the charge concentration. During calibration, the sample BC aerosol is charged using a unipolar charger and a target mass-to-charge ratio is selected by the CPMA before the sample is split and measured by the real-time mass instrument and the aerosol electrometer. The electrometer measurement and CPMA setting allows a direct measure of the charged particle mass concentration which can be compared to the real-time instrument reading. Uncertainties associated with the two methods are discussed.

Fig. 1 Calibration result for the CPMA Electrometer approach, illustrating the effect of CPMA resolution on the result.



Soylu S. / Sakarya University, Turkey

Examination of the Effects of Basic Vehicle and Engine Operating Parameters on Particle Number Emissions of a City Bus

The effects of basic vehicle and engine operating parameters on the particle emissions of a city bus were examined under real-world urban driving conditions. To perform the examinations, real time data for the parameters and solid Particle Number (PN) emissions were collected synchronously from the city bus on the routes of the Sakarya Municipality. The real-world driving conditions were especially preferred, because laboratory tests may have not represented the real-world use of the busses. The PN measurement system was preferred, because it provided very high sensitivity to the engine transients and background emissions especially at the low particle emission levels typically found in modern diesel engines. It was observed that the engine transient conditions, which commonly observed during the city bus accelerations, were the most favorable conditions for the particle emissions. During the acceleration periods, while the fuel rate, boost pressure, engine speed and engine power increase to their maximum, the lambda steeply decreases to its minimum due to the turbo-lag phenomenon. In this period, the locally rich fuel-air mixture may have been the reason for the dramatic increase of the PN. Once the engine operation is stabilized, the lambda rises up and the PN concentration decreases sharply. The results indicated that the PN formation is dependent strongly on the fuel-air mixture enrichment rather than the engine speed, torque and power. Therefore, there is no linear relationship between the PN concentration and the engine operating parameters. The correlations between the PN concentrations and the vehicle operating parameters, such as speed, acceleration and vehicle specific power, were less than satisfactory, also.

Spielvogel J. / Palas Germany

New Certified Optical System for Continuous Ambient Aerosol Monitoring

Presented is the Fidas[®] fine dust monitoring system. It has just passed the requirements of EN 15267-1 & -2 for use as equivalent test method for regulatory monitoring of PM-2.5 and PM-10 in Europe. It has therefore been tested according to EN 12341, EN 14907, and the equivalency guideline at four locations over all seasons. In the course of 14 months 285 comparison data points with reference gravimetric samplers were collected and evaluated following the strict guidelines of the aforementioned standards. Data from this comparison will be presented and discussed.

In the second part the technology and unique points will be presented in detail. While the technological basis stems from instrument development in 2000, five years of specific development regarding continuous ambient air quality monitoring preceded the equivalence and aptitude test. The Fidas[®] sensor technology makes use of the approved measurement technology of optical light scattering on single particles and is equipped with a LED polychromatic light source with stable output. The scattered light intensity is detected under 90° through a patented aperture technology, thus preventing border-zone error and enabling coincidence detection. This particular approach also enables in field calibration and verification of instrument performance.

The Fidas[®] system operates with a volume flow of 5 l/min and is equipped with a Sigma-2 sampling head that allows representative sampling even at strong winds. It further uses an intelligent aerosol drying system (IADS) to prevent erroneous particle size classification due to moisture. Its modular design facilitates the use in measurement stations.

It's important to point out that simultaneously multiple PM-fractions (e.g. PM-1, PM-2.5, PM-4, PM-10, TSP) as well as particle number and concentration can be reported. The latter are valuable information when examining possible health implications due to inhaling aerosol particles.

Stettler M.E.J. /University of Cambridge, UK

Aircraft non-volatile Particle Emissions: Estimating Number from Mass

This paper presents a method to estimate non-volatile particle number emissions from measurement of non-volatile particle mass and size distribution. The method utilises Sorensen's [1] description of the mobility of fractal aggregates and uses the geometric mean diameter (GMD), geometric standard deviation (GSD), mass-mobility exponent (D_m), primary particle diameter (d_{pp}) and material density (ρ_0) to relate the number concentration (N) to the total mass concentration (M) of fractal aggregates. This method extends existing methods that estimate aircraft non-volatile mass emissions for the legacy aircraft fleet [2].

Sorensen [1] showed that for aggregates in the free molecular flow regime ($Kn \gg 1$) formed via diffusion limited cluster aggregation, the mobility diameter of fractal aggregates, d_m , can be related to the number, N_{pp} , and size of the constituent spherical primary particles, d_{pp} , by,

$$d_m = d_{pp} N_{pp}^{\frac{1}{D_m}} \Rightarrow N_{pp} = \frac{d_m^{D_m}}{d_{pp}^{D_m}},$$

It follows that if the particle size distribution is assumed to be lognormal and mono-modal, the total mass of aggregates is the D_m -th moment of the lognormal distribution,

$$M = \rho_0 \left(\frac{\pi}{6}\right) d_{pp}^{(3-D_m)} N(\text{GMD})^{D_m} \exp\left(\frac{D_m^2 \log(\text{GSD})^2}{2}\right).$$

This equation can be re-arranged and M and N can be substituted for mass (EI_m) and number (EI_n) emissions indices, emissions normalised by fuel burn,

$$\text{EI}_n = \frac{\text{EI}_m}{\rho_0 \left(\frac{\pi}{6}\right) d_{pp}^{(3-D_m)} N_0(\text{GMD})^{D_m} \exp\left(\frac{D_m^2 \log(\text{GSD})^2}{2}\right)}.$$

Particle losses occur during transport of gas turbine particle emissions from the engine exit to instruments; Timko et al. [3] estimated particle number losses in their sampling system to be up to 80% for particles of 20 nm mobility diameter, which corresponds to the geometric mean of the non-volatile gas turbine particle size distribution, measured to be 20-30 nm [4].

Figure 1 shows a comparison between measurements and estimates of particle number emissions indices for 16 different engines at different engine thrust settings after correcting measurements for line losses. At cruise altitude, particle number emissions determine the concentration of ice nuclei that can lead to contrail formation, with significant and highly uncertainty climate impacts [5,6]. Further results compare estimates of PM mass and number using the methods developed in this study to existing measurements of emissions from aircraft at altitude. Sensitivity analysis shows that the GMD contributes to the greatest variability in particle number estimates. We will use this method to update estimates, including associated uncertainty, of global aircraft particle number emissions for future application in climate impact studies.

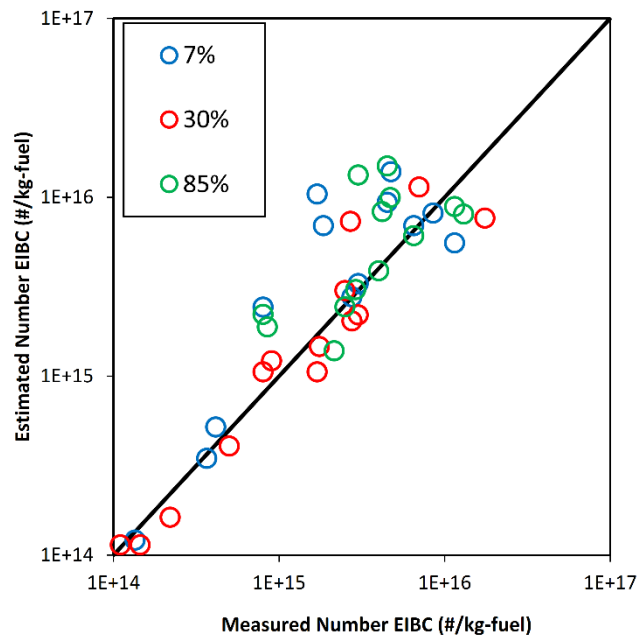


Figure 3: Comparison between measurements of particle number emissions corrected for line losses and estimates at different engine thrust settings (7, 30 and 85%).

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Stolcpartova J./ Czech Technical University

Locating Urban Hot-Spots with mobile On-line Size-resolved Nanoparticle Measurement

This work investigates the spatial distribution of particulate matter in Spořilov, a Prague residential neighborhood completely surrounded by three freeways, two of which are major heavy truck thoroughfares.

Internal combustion engines are often the prime source of air pollution, which is responsible, both in EU and in CZ, for ~10x more premature deaths than traffic accidents. Of highest concern are very small particles which efficiently deposit in human lung alveoli, penetrate cell membranes, and cause or contribute to a variety of ailments. The emissions of PM are not distributed uniformly; a small fraction of high emitting vehicles account for a large share of fleet PM, and for a given vehicle, PM emissions tend to be concentrated into short high-emissions episodes, such as accelerations, hard transitions, or high load following a period of extended idling. Neither it is expected that particles in ambient air are distributed evenly along the roadways, but that disproportionately more particles could be in places such as intersections or freeway entrances.

To discern from general ambient dust, woodburning stoves, and most other non-engine related sources producing larger particles, size-resolved measurements of particles in the 5-500 nm range were taken with an online particle classifier (Engine Exhaust Particle SizerTM) mounted, along with batteries, GPS and other accessories, on a hand cart and pushed around the neighborhood on five separate days, making one-minute or longer stops at various places of interest. Meteorological data from a nearby observatory and ambient air quality data from the national monitoring network were used to corroborate the data.

The average concentrations of particles in the 5-100 nm size range ranged from under or around 10^4 #/cm³ on quiet residential streets to $2-8 \times 10^4$ #/cm³ on streets next or close to a freeway to $1-2 \times 10^5$ #/cm³ on walkways over and near the freeway, with peak concentrations over 10^6 #/cm³. Total particle counts from the size distributions and measured by a condensation counter (P-trak) correlated reasonably well. Locations with discernible effects of passages of individual vehicles were characterized by high ratio of mean-to-median concentration over the measuring interval.

The measured concentrations near the freeways were much higher than elsewhere in Prague, where total average urban background concentration was 7×10^3 #/cm³, with 4×10^3 #/cm³ on clean days, 2×10^4 #/cm³ on "polluted" days, 1.4×10^4 #/cm³ at an intersection, and $3-4 \times 10^4$ #/cm³ next to a freeway (Rimnacova et al. 2011, Atmospheric Research, 101, 539-552). Low concentrations of nanoparticles in the inner neighborhood and general absence of a significant accumulation mode throughout the area suggest that woodstoves, leaf burning, and other combustion sources were not likely a major contribution to the concentrations measured near the roadways.

While there is no ready explanation for the rather high PM concentrations encountered, a combination of elevated emissions from truck engines encountering congestion enroute to the area, poor technical condition of many trucks, extremely high traffic volumes, and complex spatial shape of the hilly neighborhood are among suspects under investigation.

Supported by EU LIFE+ program, project MEDETOX (LIFE10 ENV/CZ/651), www.medetox.cz

Tarik M. / PSI Villigen Switzerland

Online Determination of Size Distribution and Elemental Composition of Nanoparticle Aerosols by a scanning Mobility Particle Sizer coupled to an Inductively Coupled Plasma Mass Spectrometry (SMPS-ICPMS)

The chemical and physical characterization of particles from micrometer down to the nanometer range is of prime importance in many fields including air quality control, combustion processes and production of engineered nanoparticles. All nowadays used techniques are either offline methods and/or cannot provide simultaneously chemical and physical information. SMPS (scanning mobility particle sizer) is a widely used technique to determine the size distribution and the concentration of particles in aerosols such as in emission control of combustion processes. The chemical composition analysis is commonly carried out in offline fashion by sampling the particles prior to analysis. Inductively coupled plasma mass spectrometry (ICPMS) is one of the most powerful techniques in elemental chemical analysis. Using offline analytical methods either for size or composition characterization, contamination and/or morphology alteration of the particles can occur during the sampling steps. To overcome these drawbacks and in order to perform online analysis allowing simultaneous information about chemical composition and the size distribution of particles in an aerosol stream, a SMPS instrument was coupled to an ICPMS system. Owing to a rotating disk diluter (RDD) the flow of the aerosol introduced into the SMPS can be well predefined and fixed independently from the flow of the primary aerosol to be measured. Model aerosols were generated by nebulizing and drying water-based nanoparticle suspensions into air atmosphere. The resulting dry nanoparticle aerosol was subsequently diluted and introduced into the SMPS-ICPMS. The ICPMS transient signal was found to correlate to the particle volume concentration rather than to the number concentration measured by SMPS. The volume weighted particle size distribution of the measured aerosol was calculated from the number based SMPS signal assuming spherical particles. Furthermore, gold and silver nanoparticle suspensions with nominal diameter of 20 nm and 80 nm, respectively, were blended and measured by the combined setup and it was able to resolve clearly the two types of particles.

Tartakovsky L. / Technion Israel

Effects of Cabin Filter on Ultrafine Particle Concentrations inside Passenger Cars

This work presents results of particle mass, number and size measurements inside passenger cars (PCs). Effects of the built-in and the retrofit in-cabin air purifiers on particle concentrations and average size inside a vehicle are studied. The measurements are made with various vehicles of different makers, under different ventilation conditions and different starting particle concentrations in the vehicle cabin. Particle number concentrations (PNC) in the cabin of vehicles without an adequate air filter, with a genuine OEM-made filter of different types and a non-original air filter are studied. Influence of a retrofit high efficiency cabin air filter was investigated too.

Various parameters are known as influencing the ultrafine particles concentration inside a vehicle: ventilation mode, fan speed, cabin air filter, outside particle concentrations, driving speed, vehicle age, etc. The time required to reduce the in-cabin particle levels to the value of 4000 cm^{-3} , typical for a clean office is found to be at least 6 minutes. An old car couldn't reach this PNC value. Genuine filters are proved to be more efficient as compared with the non-genuine ones. The lowest values of particle concentrations inside a PC without air purifier are registered under the recirculation ventilation mode, but the issue of CO_2 accumulation limits the use of this mode to very short driving events. The results of our measurements suggest that in case of using the recirculation ventilation mode, acceptable CO_2 concentrations inside a car are exceeded after approximately 6-7 min of driving. We studied particle concentration values that may be achieved inside a vehicle's cabin after 7 min of driving in the recirculation ventilation mode at different initial particle concentrations. It was found that PNC decreased after 7 min to values $2500 - 22000 \text{ cm}^{-3}$ for the initial in-cabin particle concentrations of $45000 - 428000 \text{ cm}^{-3}$, respectively. Increasing the speed of the ventilation fan reduces the time required to reach the clean-office PNC, as shown in Fig.1.

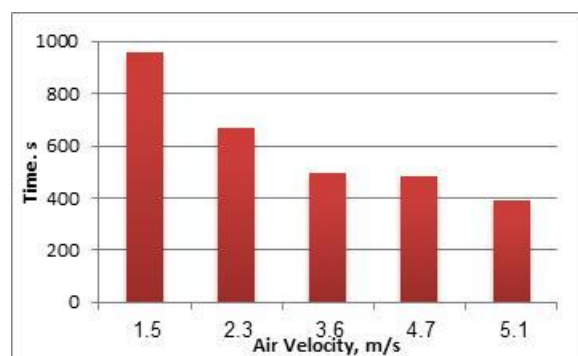


Figure 1: Time to reach the clean-office values of PNC from a starting level of 90000 cm^{-3} for various speeds of the air exiting the ventilation channel

Use of the retrofit high efficiency air purifier leads to a dramatic reduction, by 95 - 99%, in the measured ultrafine particles number concentration inside a vehicle compared with outside readings – Fig.2.

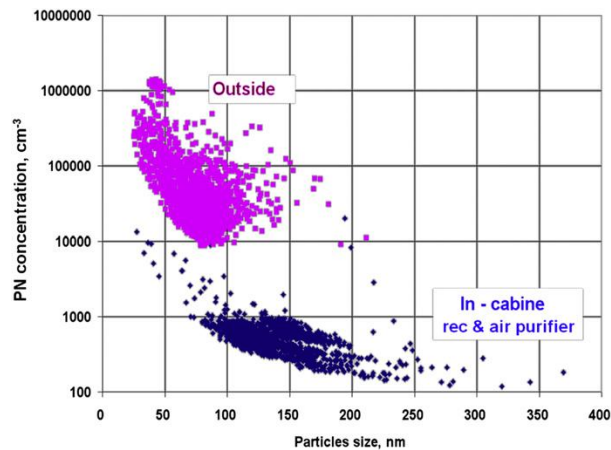


Figure 2: Particle size and number concentration measured outside and inside a vehicle with the retrofitted high efficiency air purifier

This air purifier allows achieving extremely low particle concentrations without a danger of vehicle occupants' exposure to elevated CO₂ levels. Smoking inside a car leads to a dramatic increase, by approximately 90 times, in PM_{2.5} concentrations

Taylor M. / EMINOX, UK

**SCRT® Technology and Application. First Experiences with 3rd Generation
SCRT® Systems**

SCRT® is a well-established after treatment technology that has maintained prominence in both the OE and retrofit markets through regular technical advancements. With the EURO VI standard becoming mandatory for new vehicles from 2014, SCRT technology has become an integral part of the original configuration of heavy-duty diesel powered vehicles. Especially for buses in service for public transport, SCRT®-retrofitting enables pre-EURO VI buses to serve in pollution hot-spots with a very high emission reduction performance

The new generation 3rd SCRT® system of Eminox does not only achieve excellent reduction figures for Nox, NOx, PM and other secondary emissions; the system is much smaller and makes the systems easier to apply to a greater number of applications within the existing envelope space. Millbrook tests with a Scania L94 bus retrofitted with a 3rd generation SCRT® system revealed – among others - the following figures: NOx reduction: 95%; NO2 reduction: 96.7%; Peak NH3: 0.5ppm; CO2 eq (N2O): 0.75%.

The paper presents a history of the development of SCRT® systems with the respective emission reduction figures from 1st and 2nd generation systems. The 3rd generation SCRT® system of Eminox with its newly developed SCR catalyst by Johnson Matthey exceeds previous performance. These systems offer excellent performance of regulated and secondary emissions in real world environments. They are smaller in size than previous generation of SCRT, making it possible to apply them to difficult applications. This new technology provides Eminox/JM the technical solution to combat local air quality requirements reliably and safely.

Topinka J. / University in Prague, Czech Republic

Toxicity of Size Segregated Aerosol in the Ambient from Heavily Polluted City of Ostrava, Czech Republic

Exposure to air pollutants significantly contributes to morbidity and mortality of inhabitants living in affected regions. Ostrava, one of the most industrialized cities in the Czech Republic, suffers from serious air pollution problems especially during winter seasons.

The aim of our study was to analyze toxicity of extractable organic matter (EOM) from particulate matter (PM) of four different size fractions ($< 0.17 \mu\text{m}$ - ultrafine; $0.17 - 0.5 \mu\text{m}$ - lower accumulation mode; $0.5 - 1 \mu\text{m}$ - upper accumulation mode; $1 - 10 \mu\text{m}$ - coarse fraction). PM samples were collected during winter 2012 (January 26 – February 20, 2012) using a high volume cascade impactor (BGI 900, USA) on polyurethane foam (PUF) with an integrating time of 23 h. PUFs were extracted with dichlormethane and chemical analysis of polycyclic aromatic hydrocarbons (PAHs) was performed using HPLC with electrochemical detection. The whole sampling period (24 days) was divided in 2 major parts: 1. Cold weather with frequent inversion episodes, 11 days (1a) and periods between inversion episodes, 7 days (1b); 2. Windy and warm weather (temperature was $15-20^{\circ}\text{C}$ higher than in the rest of sampling period, 6 days (2). Toxicity studies were conducted using A549 cells, a model human lung epithelial cell line (A549). The studies included analysis of cytotoxicity, bulky DNA adducts detection, measurement of oxidative damage to lipids and proteins.

Very high PM concentrations were found during inversions ($\text{PM}_{10} \sim 130 \mu\text{g}/\text{m}^3$). Upper accumulation mode ($0.5-1 \mu\text{m}$) is the most abundant PM fraction for all sampling periods representing 33-40% of total PM mass. PM levels were ~ 3 -fold higher during inversion period compared to warm and windy period. Concentrations of B[a]P are extraordinary high. Total B[a]P levels in PM_{10} varied between $7-18 \text{ ng}/\text{m}^3$ while limit recommended by WHO is $1 \text{ ng}/\text{m}^3$. The PM size fraction $0.5-1 \mu\text{m}$ was the main carrier of B[a]P and PAHs. Accordingly, the results suggest highest bulky DNA adduct levels after cell treatment with extracts (EOMs) from particle size fraction $0.5 - 1 \mu\text{m}$ in all three pooled groups. Highest DNA adduct levels were also found after treatment of cells with EOM samples collected during inversion period. These samples exhibit approximately 5-fold higher genotoxicity compared to windy and warm period. The results of oxidative damage to biomolecules did not indicate clear effects of EOMs; however, there was a trend of decrease of levels of oxidative stress markers, particularly peroxidized lipids. In contrast to genotoxicity (DNA adducts), ultrafine PM fraction ($< 0.17 \mu\text{m}$) is the most efficient oxidant of biomolecules.

Supported by the Czech Science Foundation (Grant #P503-12-G147) and by EU LIFE+ program, project MEDETOX (LIFE10 ENV/CZ/651), www.medetox.cz

Tregrossi A. / CNR Naples

Analysis of Large PAH as Components and Precursors of Nano/Ultrafine Carbon Particulate Matter

Adverse health effects of ultrafine and nanoparticle air pollution are considered greater than the health effects associated with coarse (PM₁₀) and fine particulate matter (PM_{2.5}) in consideration of their high contribution to the particle number as opposed to their very low contribution to the total PM mass. New air quality standards and testing methods are thus going to be established based on the measurement of airborne particle number down to the very small size featuring nano/ultrafine particles. The predominant contribution of organic carbon, to the nano-ultrafine particles, mainly coming from combustion sources, has been established (1-2), however the chemical complexity of organic carbon, mostly constituted of aromatic species, requires sophisticated techniques for detecting and identifying their chemical composition, and eventually testing their biological activity. Large polycyclic aromatic hydrocarbons (L-PAH), defined as aromatic species with aromatic core of at least 24 carbon atoms (3), are the common thread linking small volatile PAH and carbon nanoparticles formation occurring during some phases of the combustion process or in the case of failure of the combustion system. Indeed, L-PAH constitute a class of species which can be separated from the carbon particulate matter through extraction/chromatography and are also individuated as main structural moieties linked each other by single bond and bridging rings in the bulk of carbon particles. This suggests their possible role as precursors of nano/ultrafine particles formation. In previous work structural insights on the L-PAH fraction of carbon particulate matter have been obtained by size exclusion chromatography (SEC) coupled with UV-Visible absorption. Specifically, the optical band gap and the UV peak position of L-PAH components have been evaluated by means of a spectral reconstruction procedure (4). In this work the characteristics of L-PAH produced from fuel-rich combustion, namely sooting premixed flames, have been studied by their preliminary SEC separation from the particulate matter and detailed analysis with other diagnostic, mainly spectroscopic, tools. The study of the properties of L-PAH formed in sooting premixed flames has been made easy from referring to pitch samples, almost totally composed of L-PAH in a quite similar mass range. Structural analysis of L-PAH constituting the pitch and isolated from the flame-formed PM has been focused on the carbon network structure in terms of sp² and sp³ sites and size and stacking of the aromatic units. The L-PAH structure and composition have been inferred by looking at specific absorption and emission spectral features measured in the UV-visible range as the optical band gap and the position of the maximum absorption and fluorescence.

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Ubogu Emamode A. / University of Sheffield, UK

Evaluating The Effects of Effective Density Measurements on Particle Mass Emissions from a Gas Turbine

Questions have been raised about the suitability of the gravimetric technique for the measurement of low PM emissions - characteristic of gas turbines. Sampling times of the order of several hours are required to obtain sufficiently high sample sizes with minimum errors to quantify low particle mass emissions. Low particle mass emissions pushes the gravimetric method nearer its sensitivity and reproducibility limits. However, the use of real time instruments has also posed different challenges in measuring particle concentrations from combustion sources.

The preference of the particle mass concentration for quantifying particle emissions from combustion sources, makes it inevitable in converting measurements made using a number-size distribution instrument. The conversion of gas turbine particulate emissions size distribution to particle mass concentration is known to be challenging due to assumptions of particle effective density. Particle effective density relates the particle mobility size and aerodynamic size and it is also the basic requirement for the conversion of particle size distributions to mass distributions. Usually, the particles are assumed to be spherical and a unit density applied during the conversion (Lobo et al, 2012). Preliminary experiments on a gas turbine (Durdina et al, 2013) has shown the size dependence of effective density, but haven't quantified the error reduction it introduced when used to evaluate the particle mass.

This poster evaluates the reduction in error by comparing mass concentration estimates between a uniform density and size dependant effective densities. Using automotive diesel fuel, particulate emissions from a small scale gas turbine at three different operating conditions, idle – condition 1 (C1), and a variation of the air/fuel ratio for condition 2 (C2) and condition 3 (C3) was tested. Sampling at the test conditions was conducted over a six minute experimental window once the turbine stabilized. Using a particle sizing instrument and a smoke meter the exhaust particle samples were analysed, while gaseous analyzers were deployed to monitor the gaseous emissions. Similar trends were observed between the particle number/size distribution and the smoke meter reading across the three conditions with the particle sizes ranging between 10 and 120 nanometres. A significant difference was observed between the mass concentration evaluations using a uniform particle density and effective densities ranging from 0.5 and 1.65 g/cm³ for particles between 250 and 6nm respectively.

Uhrner U. / Graz University, Austria

Inter-regional Air Quality Assessment – bridging the Gap between Regional and Kerbside PM

Many areas located in southern alpine valleys and basins face in particular during winter time unusual high PM concentrations. Due to the complex terrain and related complicated atmospheric processes, air quality and exposure assessment is a difficult task. Although municipalities like Leibnitz (SE-Austria, pop. 9000), Maribor (NE-Slovenia pop. 95000) and Klagenfurt (S-Austria, pop. 90000) have quite low population and no big industries, the national and EU air quality standards have been exceeded frequently and significantly within the last years. Source-receptor modelling identified PM from traffic and residential heating as main sources. However, the impact of transport and the impact of secondary aerosols remained still unclear and form one of the major objectives of the study presented here.

A new multi-scale model approach was developed simulating air chemistry and aerosols from European level at coarse resolution (25 km) down to resolutions allowing for a representation of valley and basins located sources and subsequent air chemistry and transport processes (1 km). In a further step, the pronounced gradients from strong localized sources, such as road traffic or residential heating, were resolved by micro-scale modelling within the local core domains Leibnitz, Maribor and Klagenfurt. In order to make the best use of both model systems, emissions were processed on 1 km resolution for S-Austria/Slovenia and for the micro-scale simulations (order of 10 m accuracy).

A good agreement with various measurements located in the core domains was obtained for simulated total PM₁₀ (see Fig. 1). Comparisons with filter analysis and aethalometer measurements, sampled at 6 characteristic sites, indicate that the modelled PM₁₀ composition is realistic. The inorganic secondary PM₁₀ turned out to be the major PM component on the regional level. PM attributable to residential heating revealed to be the second most abundant PM component, which is strongly influenced by local emissions using wood. Even at the kerbside Völkermarkter Straße (VM) in Klagenfurt, PM traffic exhaust (carbonaceous and predominantly UFP) components are significantly smaller than domestic heating contributions. Traffic exhaust and non-exhaust related PM is only at main arterial roads a major component.

Traffic and agriculture are major precursor sources for ammonium nitrate formation. As secondary formed aerosols contribute strongly to the PM₁₀/PM_{2.5} burden in the concerned regions, the interaction of NO_x from traffic and NH₃ from agriculture is highlighted. The analysis of the regional emission reduction scenarios shows that region-wide NH₃ measures are more effective in total PM reductions than measures on NO_x (e.g. speed limits on major roads and highways).

The holistic air quality assessment, which comprised the creation of the PM_{inter} emission data base and the combination of two model systems, enables the replacement of the “unspecified PM background” usually applied in dispersion simulations for environmental assessment and a better chemical or source related specification of PM components. The approach can be used for holistic environmental assessment and more specified health assessment studies. The chosen approach demonstrated that the combined use of the WRF-Chem and the GRAL model can represent realistically concentration patterns ranging from urban background to kerbside locations.

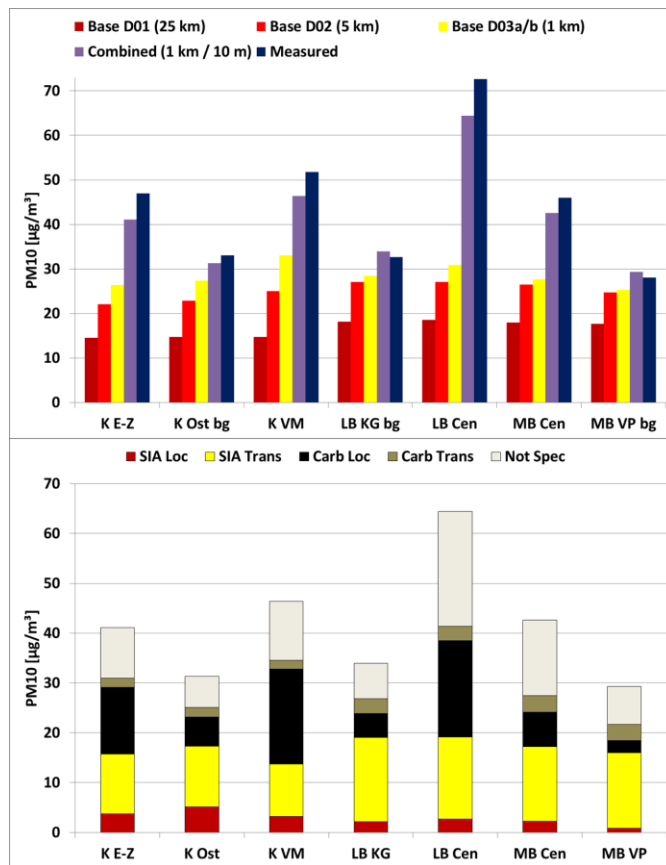


Fig. 1: January mean PM10 computed with WRF-Chem and measured at characteristic PMinter monitoring stations using different horizontal resolutions and the combined WRF-Chem/GRAL (left), simulated regional & local contributions for secondary inorganic (SIA) and carbonaceous (Carb) PM10 components WRF-chem/GRAL simulations (right). “Trans” refers to emission/formation outside the 3 core areas and transport to the core areas; “Loc” to emission/formation inside the 3 core areas. Carbonaceous PM10 is health relevant PM originating mainly from traffic & domestic heating.

Väkevä M. / Airmodus, Finland

1-3 nm Particles in Urban Air

Atmospheric particle nucleation has been proven to take place also in polluted urban environments [1]. In addition to the secondary particle formation there are other sources of nano-sized particles in urban air. E.g. vehicle emissions contain not only numerous ultrafine particles, but also small aerosol particles of the order of possibly just a few nanometers in diameter. This has been discussed e.g. by the researchers of the University of Tampere, Finland [2,3]. Sub 10 nm and even sub 3 nm particles are likely detectable in the vicinity of other ambient combustion sources as well. The composition and formation mechanisms of the nucleation mode particles are still under debate and require further studies. We anticipate that studying the diurnal behavior and the growth of the nano-sized particles may tell something about their sources.

We have developed, together with the University of Helsinki, a nano Condensation Nucleus Counter (nCNC) system for the measurement of the number size distribution of 1-3 nm particles [4,5,6]. The nCNC system was originally developed for ambient nucleation studies, and it has been used for field studies in different environments. It has also been used for laboratory studies of molecules, molecular clusters and aerosol particles of known composition, which has been confirmed using an API-TOF mass spectrometer. We will present an overview of some of the findings so far and discuss the application of the system in urban environments. We will present data measured in an urban background site. We have also observed sub-3 nm particles at a clean remote forest measurement site, when industrial vehicles were operating in the vicinity of the measurement location.

In addition, we will discuss the best practices of nano-particle measurement. For example the losses of 1-3 nm particles are remarkable, and without proper care, the sampling methods will affect the measurements.

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Wahl C. / DLR-VT, Germany

Engine Emission Ground-Tests with Jet A-1 / Farnesane Blends

The use of renewable fuels like **Farnesane**, as a drop in fuel to conventional kerosene (Jet A-1) can help to reduce the CO₂ footprint of the aviation industry. Farnesane (2,6,10-trimethyldodecane - C₁₅H₃₂) is produced by Amyris and Total from biomass through a combination of fermentation and hydroprocessing steps. These engine ground tests evaluated the impact of the farnesane aviation grade produced from sugarcane on the engine performances.

Engine ground tests were performed at the Lufthansa Technik test rig in Hamburg in order to evaluate the impact of alternative fuel blends on engine performance and emissions. The engine used was a **CFM56-5C4**, normally in service on an Airbus A340. The engine was scheduled to undergo heavy maintenance after the test runs. Before the planned tests, Lufthansa performed a routine engine test to ensure there were no issue which could disturb the farnesane blend test results.

The fossil Jet A-1 fuel used in the tests came from the Leuna refinery in Saxony-Anhalt, Germany. Fuel from this refinery was selected because its physical properties were in the middle of the range of typical kerosene used in Germany.

A total of three test runs were performed; first the Leuna Jet A-1 as reference fuel, then with the blends of this Jet A-1 containing 10% and 20% of Farnesane by volume. At the beginning of each test, the engine was initially run at cruise power in order to burn the fuel in the piping from previous tests, and to bring the engine to the nominal operating temperature. After this preconditioning, the test starts with the following ICAO power settings:

- 10 minutes at IDLE, 7 % power
- 5 minutes at FLIGHT IDLE (APPROACH), 30 % power
- 5 minutes at CRUISE (no ICAO point), 65 % power
- 3 minutes at CLIMB, 85 % power
- 1 minute at TAKE OFF, 100 % power
- a few minutes at IDLE for engine cool down

The total fuel consumption for each of the test runs was approximately 2,000 liters, including cool down and preconditioning.

Exhaust emissions were measured via a probe inserted into the exhaust tunnel of the test rig. The distance from engine exhaust nozzle to the probe was about 16 m. This arrangement causes an immediate dilution with ambient air and a cool down of the exhaust gases. The advantage of this setup is that particle agglomeration as well as thermophoresis is suppressed. In the experimental setup the sampling probe was followed by a heated 20m stainless steel sampling line. Gas emissions were detected using a FT-IR spectrophotometer. In the particle line was a Dekati diluter followed by an TSI Engine Exhaust Particle Sizer. Due to simultaneously measured CO₂ concentrations, emission indices (EI's) could be calculated for all detected compounds.

The study concluded that in emission terms the farnesane blends perform similar to or better than the reference kerosene. Especially in particle mass there is a clear reduction at all test points by increasing farnesane content. In performance terms, the farnesane blends perform similar to the reference kerosene.

Wang Xiaoliang / Desert Research Institute, USA

A New Inversion Matrix to Improve Engine Exhaust Particle Sizer (EEPS) for Vehicle Emission Measurement

The TSI Engine Exhaust Particle Sizer Spectrometer (EEPS) measures particle size distributions in the diameter range of 5.6–560 nm 10 times a second (Johnson et al., 2004). Its high temporal resolution makes the EEPS superior for measuring fast-changing size distributions in many applications, such as engine and vehicle emission characterization under transient conditions, traffic emission measurements on-board vehicles, at roadside stations and in roadway tunnels, characterization of diesel particulate filter (DPF) performance, and study of particle size distributions in other combustion processes, such as biomass burning.

The EEPS works on the principles of unipolar charging, electrical mobility classification, and charge detection using a parallel arrangement of electrometers. The charging and mobility classification characteristics define the EEPS inversion matrix, which is used to invert the measured electrometer currents to particle size distributions. The default inversion matrix currently implemented in the EEPS was initially developed based on spherical or near-spherical particles. It is known that the charging characteristics of engine exhaust particles, specifically fractal carbonaceous agglomerates, differ from spherical particles because agglomerates uptake more charge than spheres at a given mobility diameter (Maricq, 2008; Xiao et al., 2012). As a result, it has been observed that currently the EEPS underestimate sizes and concentrations of engine exhaust particles, particularly for those >150 nm as shown in Figure 1. A different inversion matrix is needed for engine exhaust particles.

This paper reports on efforts to improve the EEPS performance for engine exhaust measurements. First, the EEPS firmware was modified so that the raw electrometer currents are stored together with inverted size distributions during measurement. This allowed the raw data to be re-analyzed with different instrument matrices. Next, an EEPS was placed in parallel with a scanning mobility particle sizer (SMPS) to measure polydisperse and mobility classified monodisperse particles from the diluted exhaust of a John Deere 4045H diesel engine operating under steady-state conditions. The performance of the EEPS with the default inversion matrix was characterized. Then a new inversion matrix was developed and used to recalculate size distributions. Finally, the EEPS was compared with SMPS for size distributions of particles from a diesel engine and a vehicle with gasoline direct injection (GDI) engine under different steady-state conditions. As shown in Figure 1 as an example, the EEPS with the new matrix showed significantly better agreement with the SMPS in most test cases compared to the default matrix.

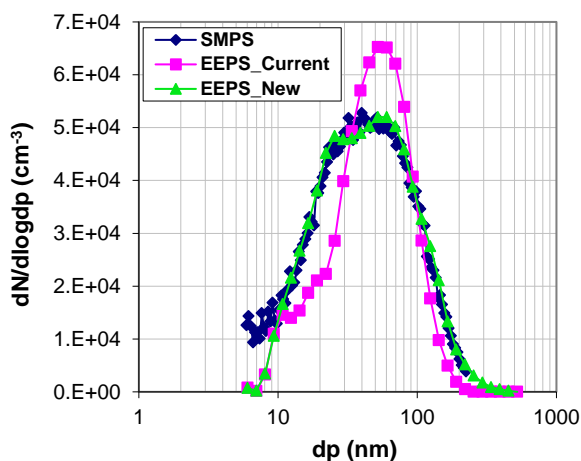


Figure 1. A comparison of diesel engine exhaust particle size distributions measured by a SMPS and an EEPS with the current and new inversion matrices.

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On-line Measurement of Organic Compounds Adsorbed on Diesel Exhaust Particles by PTR-TOFMS

PTR-TOFMS (Proton Transfer Reaction – Time of Flight Mass Spectrometer) is able to analyze gaseous organic compounds (i.e. volatile organic compounds) on-line in real time with high sensitivity of lower than ppb. For now, PTR-TOFMS is mainly used for measurement of volatile organic compounds (VOCs) in gaseous phase for atmospheric research.

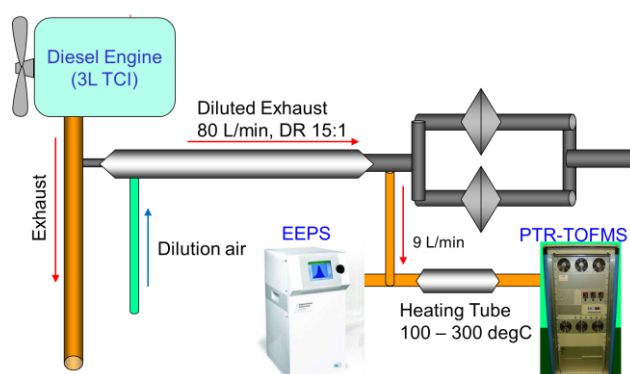
Diesel emissions consist of a large number of organic compounds in gaseous- and particle-phase. Particle emission from modern diesel engines has become very low by installing particle filters. For measurement of gaseous organic compounds, PTR-TOFMS was used to analyze DPF regeneration. The results of the previous paper clearly showed that speciated VOC emissions during active regeneration were not correlated to high particle emission.

PTR-TOFMS is capable of measurement of organic compounds with higher molecular weight. So it is desirable to measure particle-phase organic compounds using PTR-TOFMS. To analyze particle-phase organic compounds by PTR-TOFMS, sampled exhaust was passed through a heating tube to evaporate adsorbed organic compounds, which were then introduced to PTR-TOFMS.

To determine the concentrations of particle-phase compounds, 2 experiments were conducted. At the first experiment, the heating tube was kept at lower temperature (ca. 100 degC) to measure the concentrations of gaseous organic compounds. At the second experiment, the heating tube was heated at higher temperature (ca. 300 degC) to measure the total concentrations of both gaseous and particle-phase organic compounds. The concentrations of particle-phase compounds were determined from the difference between the two measured values.

In this work, analysis of particle-phase organic compounds by PTR-TOFMS was conducted using a modern HD diesel engine (displacement 3L with turbo-intercooler) for small trucks. Exhaust was sampled from an exhaust pipe to a partial flow dilution system. In the dilution system the sampled exhaust was mixed with dilution air at a constant dilution ratio. The diluted exhaust was measured by PTR-TOFMS for organic compounds analysis and EEPS (Engine Exhaust Particle Sizer) for particle sizing.

This paper shows results of emissions of particle-phase organic compounds during a ramped steady-state operation of the engine. The results of particle-phase compounds with higher m/z and particle size distribution are also discussed.



Reference: N. Yanagisawa et al., "Transient Behavior of VOCs Emission and Particle Size Distribution during Active Regeneration of Diesel Particulate Filter Equipped Diesel Engine", SAE 2011-01-2087

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Investigation of Potential Impacts on the Environment During Combustion of Nanomaterial Containing Waste

Nanomaterials are used in various fields of consumer products such as textiles, cosmetics or packaging. As a result, it must be assumed that nanomaterial-containing products are reaching in an increasing extent the domestic waste and hence the waste incineration. So far there is little-known how engineered nanomaterials behave during combustion and whether exposures are expected in the environment through the increased use of nanomaterials.

Until now this outstanding issue requires a systematic investigation due to the increased possibility of exposure. Potential danger needs to be identified at an early stage to take the appropriate countermeasures if necessary. In particular, the release of engineered nanosized particles into the air might pose health risks. Fraunhofer UMSICHT examines this issue in research commissioned by the German Federal Environment Agency. Through experiments in small combustion units and measurements in one waste incineration plant the behaviour of nanomaterial-containing waste during the combustion is investigated. The entire route from the waste via incineration, flue gas treatment to a possible release to the environment is considered. Finally the experiments should identify and as far as is feasible quantify the distribution paths of the studied nanomaterials in slag and fly ash, as well as in the flue gas.

First nanomaterials were burned in a pilot plant in order to understand the behaviour of nanomaterials during combustion. The experiments in the pilot plant of UMSICHT were carried out in a grate furnace (modelled after a waste incineration plant fixed bed combustion) with 100 kW thermal capacity. As model substance nanoparticulate titanium dioxide (primary particle size of about 10 nm) was chosen. Reasons for the choice are the high usage in consumer products and thus increasing amount in waste incineration plants at the end of the life cycle.

In the experiments cascade impactor measurements were performed in order to classify the distribution of the particle size according to the particle mass. Titanium content of the flue gas and fuel were analyzed by inductively coupled plasma with mass spectrometry – furthermore selected dust and ash samples were analyzed by scanning electron microscope and associated energy dispersive X-ray spectroscopy.

Bringing the nanomaterial into the fuel three different variants were investigated in pilot scale - the application of nano titanium dioxide as an aqueous titanium dioxide suspension on wood pellets, titanium dioxide fixed in pellets as well as the mixture of wood pellets and plastic masterbatch containing titanium dioxide.

From the experiments it can be seen, that the fixing of the nanomaterial in and on the fuel has a limited influence on the release during the combustion process. Because of the easy handling the surface application of the nanomaterial on the fuel is favoured for further experiments.

Furthermore the pilot-scale results have shown that titanium dioxide, with a primary particle size of 10 nanometers were mainly detected in the flue gas samples fraction with a particle sizes over 300 nanometers. This indicates that the added nano titanium dioxide is agglomerated or aggregated.

Currently the data from the experiments in the waste incineration plant are validated.

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Influence of engine operating parameters on PM size, structure and reactivity

The removal of soot from diesel exhaust is necessary due to protection of the environment and human health (Betha and Balasubramanian, 2011; Nel, 2005; Jacobson, 2001). The introduction of diesel particulate filters proved to be the most promising means, removing emitted particulate matter (PM) from diesel exhaust. In order to avoid high filter back pressure as well as high fuel consumption and loss of engine power, the filter must be regenerated periodically by oxidation which is determined by a variety of parameters. Different engine operating conditions and the resulting changes in size and structure of soot are one of them. Raman spectroscopy is a useful tool for the analytical investigation of structural properties and changes of carbonaceous materials. The correlation between the different Raman spectra and the reactivity of diesel soot is subject of numerous scientific papers (Knauer et al., 2009; Ivleva et al., 2007). Raman spectra of carbon based particulates produce two distinct bands of excitation (D band at 1350 cm^{-1} , G band at 1580 cm^{-1}). The intensities (I_D/I_G) and the full width at half maximum (FWHM) of the bands reflect the structural changes of soot. Among other things, the size of the PM has a decisive influence on the oxidation behavior (Liati et al., 2012; Su et al., 2004).

In the present work, the influence of different engine operating parameters on diesel PM distribution, structure and reactivity was analyzed. The engine, used for the generation of PM samples is a modern 4-cylinder diesel engine with common-rail direct injection and open interface for ECU. The fuel used is standard B7 diesel fuel. The effect of different engine operating conditions was examined while the speed and the pedal position have been kept constant (1000 rpm, 25 %). The injection pressure and the boost pressure were varied (Table 1). The Particle Size distribution was measured with a Scanning Mobility Particle Sizer (Figure 1). Particle mass was analyzed with the Pegasor PPS-M Particle Sensor. In addition PM samples, collected from the exhaust after diesel oxidation catalyst on tissuquartz filters, were used for Thermo-Gravimetric Analysis (TGA) and Raman spectroscopy. TGA was employed to examine the oxidation behavior of the different types of soot. Different soot structures that emerge from different operating conditions should be pointed out by Raman spectroscopic analysis.

Table 1: Different engine operating conditions

Sample	Operating Condition
Basic application	$p_{inj} = 630 \text{ bar}$, $p_{boost} = 1,33 \text{ bar}$
low_inj	$p_{inj} = 300 \text{ bar}$, $p_{boost} = 1,33 \text{ bar}$
high_inj	$p_{inj} = 1000 \text{ bar}$, $p_{boost} = 1,33 \text{ bar}$
low_boost	$p_{inj} = 630 \text{ bar}$, $p_{boost} = 1,1 \text{ bar}$
high_boost	$p_{inj} = 630 \text{ bar}$, $p_{boost} = 1,45 \text{ bar}$

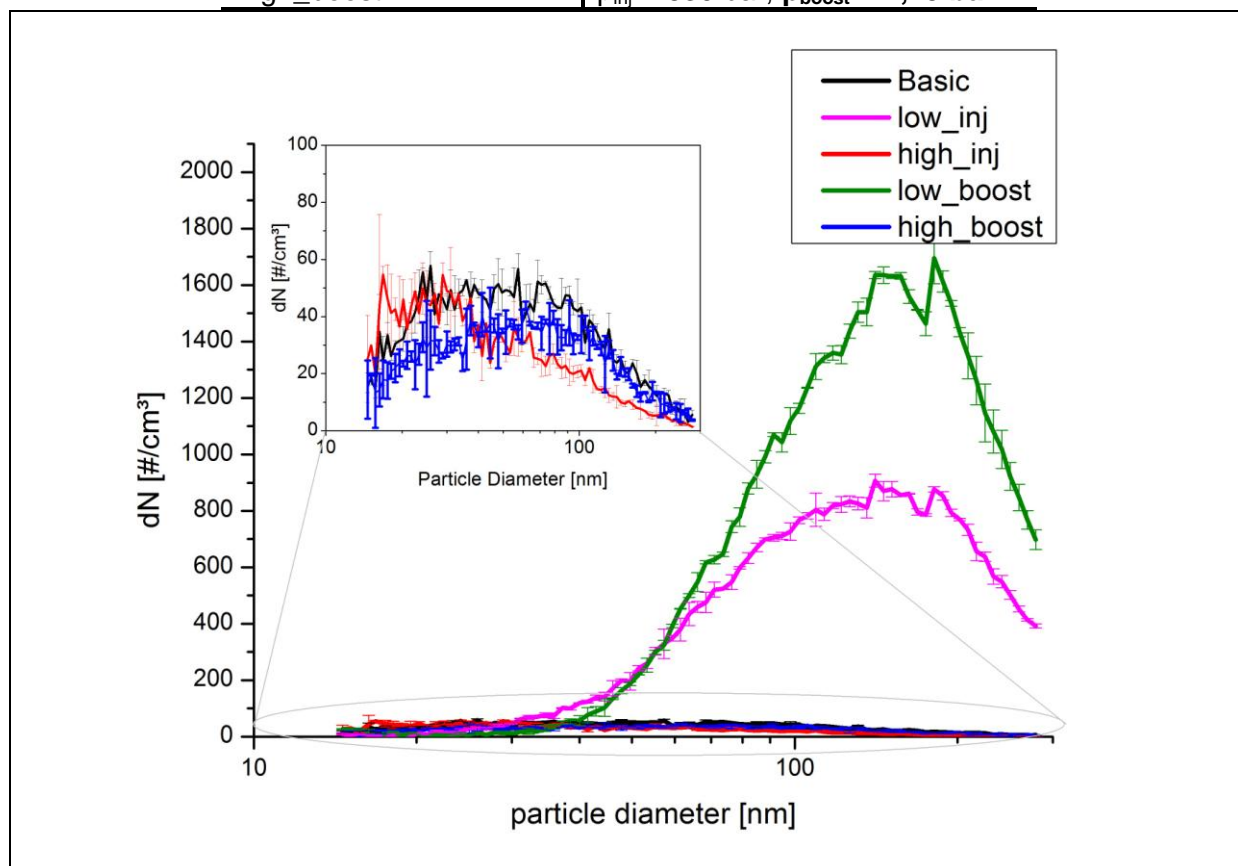


Figure 4: Particle size distribution under different engine operating conditions