A Potential Soot Mass Determination Method from Resistivity Measurement of Thermophoretically Deposited Soot


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Generation of soot particles and thermophoretic deposition on resistivity based soot sensors

Running title: Method development to detect diesel-like soot particles

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Abstract

Miniaturized detection systems for nanometer-sized airborne particles are in demand, as in applications for onboard diagnostics downstream particulate filters in modern diesel engines.

A soot sensor based on resistivity measurements was developed and characterized. This involved generation of soot particles with properties similar to diesel engines using a quenched co-flow diffusion flame; depositing the particles onto a sensor substrate using thermophoresis and particle detection using a finger electrode structure, patterned on thermally oxidized silicon substrate.
The generated soot particles were characterized using techniques including Scanning Mobility particle sizer for mobility size distributions, Differential Mobility Analyzer - Aerosol Particle Mass analyzer for the mass-mobility relationship, and transmission electron microscopy for morphology. The generated particles were similar to particles from diesel engines in concentration, mobility size distribution and mass fractal dimension. The primary particle size, effective density and organic mass fraction were slightly lower than values reported for diesel engines. The response measured with the sensors was mainly dependent on particle mass concentration. Response increased with increasing soot aggregate mobility size, likely due to larger aggregates being more chain-like (smaller effective density) resulting in shorter time to build conducting channels between the electrodes. Detection down to concentrations in order of magnitude 1000 µg/m³ and cumulative mass of 20-30mg was demonstrated. The detection limit can likely be improved by using a more sensitive resistance meter, modified deposition cell, larger flow rates of soot aerosol and modifying the sensor surface.

1. Introduction

Diesel engines are major contributors to emissions of particulate matter (PM) and nitrogen oxides (NOₓ) (Kittelson et al., 1998; Maricq et al., 2007). PM is a complex mixture of small airborne particles and liquid droplets typically consisting of agglomerates of primary particles (with 20-35 nm diameter) and smaller nucleation mode particles mostly in liquid phase. The primary particles in agglomerates are composed of soot (elemental carbon coated with traces of metallic ash) and onto those agglomerates, the heavier organic compounds and sulphuric acid are condensed. The nucleation mode particles on the other hand are dominated by condensed hydrocarbons and sulphuric acid (Maricq et al., 2007; Schneider et al., 2005). In
this investigation, the term “soot particle” refers to the whole agglomerate complex of primary particles and condensed compounds.

Particles, typically of a size less than 10 or 2.5 µm (PM10 and PM2.5) are of growing concern as they contribute to a variety of health and environmental problems (Dockery, 2009; Hansen & Nazarenko, 2004). Fine particles also cause reduction in visibility (Eidels-Dubovoi, 2002; Bond & Bergstrom, 2006), make lakes and streams acidic, deplete the nutrients in soil, and affect the diversity of ecosystems when settling on ground or water. Moreover, particles have both a direct and indirect effect on the earth’s climate by either scattering or absorbing solar radiation and by acting as cloud condensation nuclei (Jacob, 1999).

Considerable efforts have been made to reduce emissions including PM from combustion engines. These efforts include engine development, fuel quality enhancement and introduction of after-treatment systems, such as three-way catalysts (TWC), NO\textsubscript{X} traps and diesel particulate filters (DPFs). Other efforts include the investigation and development of new particle sampling methods and characterization techniques (Bergmann, 2009). However, due to increased stringent PM emission regulations, implementation of DPFs is a very strong tool to achieve such strict limits. The DPFs have shown to filter the PM over 90% under steady conditions with the soot aggregate size from 80 nm to 140 nm measured by the Rayleigh-Debye scattering approach depending on the engine operating conditions (Kamimoto, 2007). While in transient state, the removal efficiency of DPF has been found to be more than 99% for accumulation mode particles (Liu, 2005). The DPF has to be regenerated periodically by burning the trapped soot using different techniques in order to prevent high back pressure on the engine as well as causing filter cracks by large pressure drop across DPF due to clogging. In the event of DPF saturated by engine exhaust particulates on the walls, a proper soot detection system is vital to help trigger the regeneration process. Besides soot sampling on filters followed by characterization techniques (Maricq, 2007) and
complex optical detection such as Laser Induced Incandescence (LII), various operating principles have been applied to develop methods of particle quantification from diesel engine exhausts, pyrolysis, combustion processes, smoke, etc. They include photoelectric sensors, digital imaging based color-band pyrometers, photo and diffusion-charging, multi-wavelength optical sensing and photo-acoustic sensor systems (Lu et al., 2009; Polidori, 2008; Haisch, 2003). However, filter sampling is not a time-resolved method and the optical methods are not cost-effective and robust in harsh exhaust environments; hence, new ways to measure the soot particles are needed.

There are other measurement techniques which use the mobility of agglomerate particles subjected to electrical or gravitational field, in order to investigate the size, mass and density of such agglomerates. Examples of such instruments include Scanning mobility particle sizer (SMPS), Aerosol particle mass analyzer (APM), Engine exhaust particle sizer (EEPS), and Electrical low pressure Impacter (ELPI) etc. These instruments are used for combustion aerosols and diesel exhaust soot particles to measure the electrical mobility diameter but require careful interpretation of results due to complex aerodynamic behavior of fractal-like soot agglomerates with the surrounding gas since the performance of such instruments is affected by the fractal-like structure. Also the multiple charging of soot agglomerates (e.g. in SMPS), larger than 1um can affect the performance even when the impacter is placed at entry point which means the measurement range has to be increased or the size distribution has to be corrected for charges on large particles. Those instruments which work on the basis of aerodynamic diameter such as ELPI can give underestimated apparent size of particles due to fractal-like structure, hence overestimating the number concentration. Although fast time-resolution of the ELPI is advantageous as compared to SPMS but its size resolution is lower than that of SMPS. Efforts have been made (Gulijk et al. 2004) to couple aerodynamic and mobility diameter and estimates of fractal dimensions in order to better understand the
complex aerodynamic behavior of soot agglomerates from diesel exhausts. The model developed by Gulijk et al. (2004) is useful to better measure concentrations when fractal dimension of aggregate is larger than 2. Another useful technique which can measure the mass and density independent of morphology of aggregates is the APM. The measured mass of aggregates by the application of centrifugal and electrostatic forces can be related to the equivalent volumes if the density of material is known. Particle morphology, size and orientation play no role in particle classification by APM only. A DMA-APM system can be used to measure the number concentrations of aggregates based on their mass for a selected mobility diameter. The structural properties of mobility classified particles can be used to determine the inherent material density as a function of mobility size can also be inferred from two-dimensional projected properties by visual techniques such as TEM (Park et al. 2004). Measurement of PM size distributions is sensitive to the sampling conditions applied and the results can significantly be influenced by the dilution method, particularly with regard to the formation of nucleation mode particles (Bergmann et al. 2009). In such situation engine exhaust particles sizer spectrometer (EEPS) can be used in transient cycles and can determine quite well the particle distribution. The EEPS spectrometer permits a time resolution of about 1 second with high sampling rate allowing instantaneous measurement of engine emissions. The EEPS determines particles between 6 nm and 560 nm, covering mostly emitted diesel exhaust particles. A detailed comparison of these measurement techniques has been performed by Zervas et al. (2006) and Intra (2007).

The detection of soot particles downstream DPF can be accomplished by application of combination of above mentioned techniques and measuring the electrical conductivity of particles having deposited between two electrodes. By monitoring the drop in resistance due to soot load on the so called soot sensor carrying above mentioned electrodes, the physical characteristics of soot particles emission can be studied (Fleischer et al., 2005; Lutic et al.
2009). Such methodology can also be applied in other areas such as boilers conversion evaluation and emission from thermochemical conversion of biomass (Lillieblad et al. 2004; Wierzbicka et al. 2005).

In this investigation, we tested the feasibility of combining a series of three techniques to build up a suitable and practical method for the detection of soot particles, for a future application in diesel exhaust after-treatment systems. The techniques consisted of: 1. generation of soot particles with characteristics similar to those in the diesel engine, 2. particle deposition using thermophoresis on sensor substrates, 3. monitoring the decrease in electrical resistivity of the sensor by detection of deposited particles.

2. Experimental methods

2.1 Combustion and soot generator

The designed combustion soot generator (Figure 1) consists of three sections: a diffusion flame, flame quenching and particles mixing. Propane as fuel was fed into the inner of two co-axial stainless steel pipes of 7 and 28 mm i.d., respectively. While particle free dry air (PFA) was introduced through the outer pipe as an oxidant. The stability of the flame, and thus the generated soot, is very sensitive to small variations in the flow pattern. Two mass flow controllers (Bronkhorst High-Tech MFCs) were used to regulate the fuel and sheath air flow rates with high precision. Additionally, the sheath air stream was stabilized with a ceramic honeycomb monolith acting as a flow laminarizer to further enhance flame stability. By varying the fuel and air flow rates and hence the equivalence ratio, soot particles of different concentrations and size distributions was generated. The geometric mean diameters (GMDs) of the generated particles for the equivalence ratios applied are listed in Table 1.
The diffusion flame is quenched horizontally in the quenching zone using particle free dry air at a flow rate of 9 l/min at a height of 55 mm above the flame. There is also a flow laminarizer in the quenching line to prevent excessive flame disturbance. The quenching air dilutes the combustion products from the flame, resulting in a decrease of the soot coagulation process but also causes some additional soot oxidation as opposed to the use of nitrogen as quenching agent. The quenching allows production of high concentrations of size-controlled soot particles and hence it plays an important role in defining the chemical and physical properties of the soot particles produced.

The soot leaving the quenching section is further diluted and completely mixed in the mixing zone using particle free air with a flow rate of 45 l/min. This ensures a uniform soot distribution out from the burner with no need of any further mixing and achieves a controlled soot concentration during the process as well.

2.2 Particles collection efficiency and thermophoretic deposition on sensor

Figure 2a shows a cross sectional view of the thermophoretic soot sampler that was designed and used for the deposition of generated soot particles on the sensor. The sampler was manufactured based on a plate-to-plate thermal precipitator design (Messerer, 2003; Tsai & Lu, 1995). In the sampler, the soot deposition is driven by thermophoretic forces. When a given size distribution of generated soot particles passes through the deposition channel, the particles will be subjected to a force gradient towards the cold surface containing the sensor inducing a thermophoretic velocity, \( U_{th} \). This process is independent of particle size while directly proportional to the temperature gradient in the free molecular regime. In the free
molecular regime (d<λ), the thermophoretic velocity can be described by equation 1 (Hinds, 1999):

\[ v_{th} = -0.55 \frac{\mu_g \nabla T}{\rho_g T_p} \]  

(1)

Where \( \nabla T \) is the temperature gradient in the deposition channel, \( T_p \) is the particle’s average temperature assumed to be same as the gas mean temperature, \( \mu_g \), for the gas dynamic viscosity and \( \rho_g \) for the gas density.

The upper part of the sampler is a circular stainless steel plate (44 mm diameter and 9 mm thickness) heated externally with a heating gun (Model PHG 600-3, Bosch GmbH). A rectangular-shaped deposition channel was grooved into the middle of the upper stainless steel plate with the dimensions L36xW15xH0.5 mm. The lower part consists of two circular aluminum plates (for better heat conductivity) with a diameter of 44 mm and thickness of 1.5 and 2.0 mm for each plate, respectively. The 1.5 mm plate works as a cold surface and hosts the circular sensor surface in the center, while the other 2.0 mm plate is designed to hold the sensor from the bottom. The two plates are joined in a way that the sensor surface is on the same level as the lower cold-plate surface.

The lower part was cooled using a pressurized air jet and the cold-plate surface temperature (\( T_c \)) was adjusted to 110 °C at a fixed air jet flow rate. The temperature for the hot-plate surface (\( T_h \)) was regulated by adjusting the height of the heating gun from the top of the upper part so that a fixed temperature of 180 °C was maintained. Temperatures were measured using two K-type thermocouples placed in the radial center of the sampler at a distance of ~0.5 mm from the inner surface of the hot and cold-plate surface, respectively. The measured temperatures are expected to be the same as the gas temperatures at the hot and cold-plate surfaces inside the deposition channel, producing a temperature gradient of \( dT/dy = 1.4 \times 10^5 \) (°C/m) across the deposition channel.
For a constant flow rate of 300 ml/min used in all deposition experiments the Reynolds number (Re = 23) indicates a laminar flow. However, as the inlet flow enters the deposition channel perpendicularly, a turbulent flow is expected initially and requires a certain length (hydrodynamic length) to become laminar. The hydrodynamic length can be calculated by following equation (Messerer, 2003)

\[ L_h = 0.04 \cdot \text{Re} \cdot D_h \]  

(2)

Where characteristics length for Reynolds number has been taken equal to \( D_h \) which stands for the hydrodynamic diameter of the flow channel calculated by equation (3)

\[ D_h = \frac{2W \cdot H}{W+H}. \]  

(3)

Accordingly for \( W=15\text{mm}, H=5\text{mm} \) and \( D_h=1\text{mm} \), the \( L_h = 0.9 \text{ mm} \) ensures a laminar flow over the sensor. It has been shown in the literature that thermophoretic deposition can be achieved under both laminar and turbulent flow conditions (Munoz-Bueno et al., 2005; Montassier et al., 1991). Moreover, Tsai and Lu (1995) showed that the thermophoretic deposition efficiency is only slightly decreased under turbulent conditions compared to laminar for Re values of 6580 and 1340, respectively.

The particle collection efficiency of thermophoretic soot sampler has been calculated based on the following relation:

Collection Efficiency, % = \( 100\times(\#\text{particles In} - \#\text{Particles out}) / \#\text{particles In} \)

The efficiency represents the number of particles deposited in the sampler due to thermophoresis. The collection efficiency has been estimated based on numbers of particle before and after the sampler assuming the density wouldn’t change due to thermophoresis. The conditions during deposition have been mentioned in table 2
The collection efficiency for monodisperse particles has been shown in figure 3, which shows the overall collection efficiency of particles of about 22-23% with negligible effect of particle size. This data agrees to the finding in the literature (Messerer et. al., 2003) that showed the deposition efficiency of agglomerated soot particles in a thermophoretic plate-to-plate deposition cell was within 5%, independent of particle size over the range of 30-300 nm (the size range relevant for this study). The theoretical thermophoretic velocity for \( d_p < \lambda \) was found to be 0.52 cm/s and that for \( d_p > \lambda \) 0.38 cm/s. The theoretical efficiency of particle collection in the deposition cell was calculated to be 46.4% and 35% cm/s for \( d < \lambda \) and \( d > \lambda \) respectively (Hinds, 1999) which is much higher than actual efficiency shown in figure 3. For our setup…………?????

2.3 Electrical resistivity soot sensor

A novel technique based on measuring the electrical conductivity of soot particles has not yet been fully exploited. It promises to provide a very robust and small sized system for characterizing the soot emitted from engine exhaust. To our knowledge, there is not much information available on such a system, whereas there is a strong need for miniaturized systems in the automobile industry ahead of strict regulations to control emissions. The resistive soot sensor must allow deposition of soot while in collection mode and allow regeneration (soot removal) at exhaust gas conditions. Figure 2b illustrates a standard 16-pin holder at which such a soot sensor substrate (Figure 2c) was glued at the center and gold wire contacts were bonded to the pins of the holder. The soot sensor substrate consisted of a finger electrode structure, patterned on a thermally oxidized silicon substrate and Ti and Au were
sputter deposited to yield an Si/SiO2 (100nm)/Ti (5nm)/Au (200nm) structure. The
interdigitated electrodes obtained using lift-off technology had a width-spacing of 40
micrometers and covered an area of 1mm x 1mm. Silicon pieces were glued to the holder base
upstream of the sensor in order to improve the laminar flow characteristics of the gas flow.
The resistance change between electrodes of the sensor during soot deposition was measured
using a digital multimeter device (TTI 1604 Thurlby Thandar Instruments, UK) capable of
measuring the resistance in the range of 1 kOhm to 40 MOhms.

2.4 Particle characterization set-up

A scanning mobility particle sizer (SMPS 3934 form TSI Inc., USA) was used to
characterize the number size distribution of the generated soot. It consists of a differential
mobility analyzer (DMA 3071) and a condensation particle counter (CPC 3010) operating at a
sample flow rate of 1.0 l/min and a sheath air flow rate of 6.0 l/min allowing a measurement
range of 10-450 nm. Before the generated soot was analyzed with the SMPS system, it was
diluted using an ejector diluter with a modified inlet nozzle (DI-1000 Dekati Diluter, Finland)
to a ratio of 1:13 in order not to exceed the measurable range for the SMPS. After SMPS
verification of a stable size distribution of the generated soot particles, a flow of 300 ml/min
was established from the outlet of the burner through the thermophoretic using a critical
orifice at the thermophoretic sampler outlet (see Figure 4).

Figure 4 here

2.5 OC/EC and TEM analysis

The organic and elemental carbon analysis (OC/EC) of the particles was performed
by collecting samples on pre-baked quartz fiber filters (Tissue quartz, SKC Inc.) and
subsequently analyzed according to the standard thermal method (VDI 2465/2) by a Thermal
Carbon Analyzer (Model 2001, Desert Research Instruments Inc.). The set-up for the soot
collection involved sampling soot directly from the burner outlet into two parallel lines at the same flow rates. In one line only a quartz filter was used, while in the other line a Teflon filter (Zeflour, SKC Inc.) was followed by another quartz filter (Blando & Turpin, 2000). This configuration allows correction for possible gas phase organic vapors absorbed onto the quartz filter.

The morphology of the generated soot particles was investigated by a 60 KeV PHILIPS CM10 Transmission Electron Microscopy (TEM) using an electrostatic precipitator (NAS Model 3089, TSI Inc.) whereas the samples were collected on a carbon-coated copper grid of diameter 3 mm.

2.6 The Aerosol Particle Mass Analyzer (APM)

The APM coupled in series with a DMA (DMA-APM), was used for online mass determination of mobility classified particles (Figure 5). The system can be used for the determination of the particle effective density and mass-mobility relationship (Park et al., 2003). The APM consists of an outer \(r_2\) and an inner \(r_1\) cylinder rotating at the same rotational speed \(\omega\). The aerosol is introduced in the annual gap between the cylinders and a potential \(V_{APM}\) applied to the inner cylinder while keeping the outer cylinder grounded. Thus, the force keeping the charged particles in orbit is the electrical force, balanced by the centrifugal force. Since the centrifugal force is mass dependent, the particle mass can be determined according to equation 4.

\[
m = \frac{qE}{r_2 \omega^2} = \frac{qV_{APM}}{r_2^2 \omega^2 \ln(r_2 / r_1)} \tag{4}
\]
where \( r \) is the average radial distance to the gap between the cylinders from the axis of rotation \(((r_2 - r_1)/2)\), \( q \) the particle charge and \( E \) the electrical field. The APM is described in more detail by Ehara et al. (1996).

Figure 5 here

In the system, a DMA and an APM are coupled in series where the DMA selects particles of one mobility diameter at a time and the mass distribution of the selected particles is determined by stepping the APM voltage. The mobility diameter \( (d_{me}) \) and the particle mass are, in the transition regime, related as:

\[
\begin{align*}
    m &= \frac{\rho}{\chi^3} \cdot \left( \frac{C(d_{me})}{C(d_{ve})} \right)^3 \cdot \left( \frac{\pi}{6} \right) \cdot d_{me}^3 \\
    \rho_{\text{eff}} &= \frac{m}{d_{me}^3} \cdot \frac{6}{\pi}
\end{align*}
\]

Where \( \rho_{\text{eff}} \) is the density of the pure compounds, \( C \) the Cunningham correction factor, \( \chi \) the dynamic shape factor and \( d_{me} \) the volume equivalent diameter. \( \rho_{\text{eff}} \) is the effective density defined as:

\[
\rho_{\text{eff}} = \frac{m}{d_{me}^3} \cdot \frac{6}{\pi}
\]

3. Results and discussion

3.1 Soot generation – stability and characterization

One of the aims of this investigation was to produce a set of soot particle size distributions and concentrations with high stability. Average particle size distributions used for the deposition experiments are shown in Figure 6. All distributions are unimodal, with slight deviations from lognormal distributions. The GMDs based on number concentration were 55, 85 and 110 nm and the geometrical standard deviations (GSDs) were 1.77, 1.80 and
1.81 respectively for the three cases. The GMD of these cases considered to be similar to typical soot size distributions from a heavy duty diesel engine of 60-100nm (Burtscher, 2005).

Diffusion flame burners have been used to generate combustion soot particles in different investigations. Often the stability of soot production has not been discussed (Jing, 1998; Samson et al., 1987; Cleary et al., 1992). Stipe and co-workers (Stipe et al., 2005) have designed an inverted diffusion flame burner to produce soot particles with mobility diameters and number concentrations of 50-200 nm and $4.7 \cdot 10^4 - 10^7$ particles/cm$^3$, respectively. They mentioned the importance of stability in soot generation in terms of mean diameter, number concentration and volume concentration and reported the standard deviations for these parameters to be below 4% during 6h operation. Our designed combustion soot generator also shows a reasonably high stability represented in terms of GMD, GSD and total number concentration. Table 3 shows the GMD and total number and mass concentrations (using the effective densities reported below in Figure 6) for the three cases. The stability in particle size is clearly shown by the small relative standard deviation (RSD). In our study, the recorded GMD varied by maximum 1.7%, the total number concentration varied by max by 5.2% max, and the total mass concentration by up to 7.4%.

Figure 6 here

3.2 Particle composition, effective density and morphology

To establish the organic and elemental carbon contents, particles were collected on filters and analyzed for OC and EC as explained in Section 2.5. The OC/EC analysis for generated soot particles from a slightly smaller but similar burner clearly indicated the presence of very small amounts of organic material (<3%) condensed onto the elemental carbon particles when tested for 103nm and 115nm particles modes.
The effective density was measured using the DMA-APM technique (Park et al., 2003). The effective densities for a given size varied by less than 10\% for three different equivalence ratios. The effective density decreased with increasing particle size from ~0.8 g/cm\(^3\) for 50 nm particles down to below 0.2 g/cm\(^3\) for 400 nm particles. The results are presented in Table 4 and Figure 6. All APM scans showed effective densities (including scans generated with the three different equivalence ratios) within ±10\%. Within each equivalence ratio setting all scans showed effective densities at each specific \(d_{\text{me}}\) within ±3\%, and a standard deviation 0.01 or less. For the smallest sizes measured (50 and 100 nm particles) a trend with lower densities with increasing equivalence ratios was observed, see Figure 6. However, it cannot be ruled out that this is an effect of doubly charged larger particles interfering with the mass spectra of singly charged particles in the APM (Pagels et al. 2009). This will be investigated further. Since the effect of this on the mass size distribution is small, for each size the average effective density over all three cases was used. The mass fractal dimension was determined to be ~2.3.

The mass fractal dimension of 2.3 is almost identical to that found from diesel engines (Park et al., 2003; Maricq & Ning, 2004). The effective densities found here were slightly lower than those found in the literature for diesel engines, typically ranging from ~1-1.2 for 50 nm particles down to ~0.3 for ~300 nm particles (Park et al., 2003). However, our effective densities are higher than those found for a Santoro type diffusion flame (Pagels et al., 2009).

The mass concentration (table 3) was calculated from the SMPS number size distributions data using the measured effective densities. Applying uniform density over size would result in a significant bias, shifting the mass size distribution towards larger sizes, and lead to an overestimation of the mass of the largest particles. Assuming the soot bulk density (~1.8 g/cm\(^3\)) to be constant over size would lead to an overestimation of the total mass concentration by 2-3 times.
The morphology of the soot agglomerates produced by our soot generator was investigated with a TEM analysis. The analysis (using ImageJ 1.41 software) shows a mean primary particle diameter of 15±2 nm for all three cases (see Figure 7) with no significant difference seen between the cases tested.

Figure 7 here

Lee et al. (2002), Mustafi and Raine (2009) and Park et al. (2004) investigated the structural properties of diesel soot and mentioned that the mean primary particle diameter ranged from 28 to 35 nm. However, Maricq (2007) and Burtscher (2005) showed that the engine design, operating conditions and lube oil influence the properties of PM emissions. In general, a somewhat larger primary particle size range was found from different diesel engines, compared to diffusion flame generators. For soot agglomerates produced by a flame in the laboratory, Koylu et al. (1995) showed that the soot structure varies with fuel type for a set of gases, including propane, and the liquid fuels they tested. In addition, they showed that the mean primary particle diameters were 30-51 nm (30 nm for propane) and typically followed a normal distribution. However, the design of the soot generator (diffusion flame in still air) described by Koylu et al. (1995) differs compared to our soot generator which may explain why a larger mean primary particle diameter was observed. Moreover, a simple image analysis of a TEM picture by Zahoransky et al. (2003) for soot agglomerates generated by the commercial CAST burner (close in design to our generator) shows more proximity in the mean primary particle diameter of about 20 nm. To conclude, our designed soot generator shows a high stability in producing three different soot size distributions able to resemble real diesel exhaust soot emissions.

3.3 Deposition by thermophoresis and resistivity measurements
The next step in this study was to investigate the capability of using thermophoresis as a method to deposit soot particles on the soot sensor and determine the key parameters within deposition and detection steps.

As the soot particles, which contain conducting elemental carbon (Burtscher, 2005), deposit on the sensor surface they will start building a network of disordered bridges in the gaps between the metallic fingers until the first conductive layer is established. This process will take a certain time (referred to as on-set time) where no resistance decrease is recorded. There will also be a certain time before the resistivity decreases enough to fall into the measureable range of our system.

Figure 8 shows the electrical resistance over time when depositing soot generated with equivalence ratio 1 (55 nm), 2 (85 nm) and 3 (110 nm) on new sensors continuously for 2h. It also shows a significant difference in on-set time between the three different soot size distributions. The on-set times of 27.0, 7.0 and 1.6 minutes were observed when exposed to soot using three different cases of equivalence ratios 1, 2 and 3 (GMD = 55, 85 and 110 nm), respectively. The on-set time characterizes the time period required to build an electric connection between two electrodes due to certain amount of soot deposited between them. After that time, the resistance started to decrease as indicated by the multimeter. Different exposed soot size distributions did not only show a difference in the on-set time but also in the resistance levels during later part of exposure time, which went on decreasing slowly. For equivalence ratios 2 and 3, the resistance profile seems to be similar, starting with a relatively fast decrease for the first 20 min and then beginning to almost level off, reaching a final resistance of 34 and 8 kOhm for set exposure time, respectively. For the equivalence ratio 1 case, the resistance profile follows a smoother decline ending up at a considerably higher resistance of 1.4 Mohm.

Figure 8 here
The difference in resistivity and on-set time can largely be explained by different mass exposures per minute for the three different cases. After normalization of the resistivity with cumulative mass-exposure, the three curves appeared more similar (Figure 9). Still, there was a difference in resistivity between the cases: The case with the largest agglomerate mobility size (110 nm) showed the fastest decrease in resistivity. There are several possible reasons for this: The particles in the size distribution with GMD = 55 nm are more compact as shown by the higher effective density compared to 85 nm and 110 nm. Depositing a larger number of more compact agglomerates, compared to fewer larger agglomerates with more open structures but with the same total deposited mass will require a longer on-set time as it will take longer to create an electrically conducting bridge between the electrodes. One can expect that the fractal-like conducting branches between two electrodes are being longer for the cases of larger agglomerates as an effect of the decreased effective density. However, it is interesting to note that the relative difference between the three cases increases with time.

The effects are also possibly explained by a poorer conductivity between the primary particles of different agglomerates deposited adjacent to each other than that between primary particles belonging to the same large agglomerate. For example there seem to be some necking (partial sintering) between the primary particles of the agglomerates used in this study which may lead to an increased conductivity between primary particles. Such an interpretation is consistent with the finding that charge carriers tunnel between graphitic conductive islands in soot (Dunne et al., 1997). Finally, as our measurements extend into the transition regime, there might be a slight size dependence of the thermophoretic deposition velocity as discussed in section 2.2. However this is expected to be on the 10-15% level rather than the ratios of up to a factor of two found experimentally between the different cases.

Figure 9 here

3.4 Role of Soot film microstructure and morphology in sensor response
3.5 Resistivity measurements – reproducibility

Since detecting soot by means of electrical resistance change is a process of combining three different techniques (i.e., soot generation, deposition and resistance measurements) where minor parameter changes can take place and influence the results, it is of vital importance to determine the reproducibility of the sensor response to soot detection. Thus, experiments for resistance change over time for case eq. ratio 2 were repeated three times, and for eq. ratios 1 and 3, twice as shown in Figure 10. Repetition of eq. ratios 2 and 3 soot sensing experiments showed a high reproducibility for on-set time, resistance profile and final resistance level. However, for the repeated eq. ratio 1 soot detection experiment, the on-set time was almost the same while a similar profile with lower detection, and thus resistance decrease, was monitored. This, in fact, can most likely be attributed to some parameter that has influenced the deposition and detection process such as differences in sensor surface construction or possible changes in the temperature gradient along the deposition channel.

Figure 10 here

4. Conclusion

It has been demonstrated that a potential combination method to generate, deposit and detect soot particles using electrical resistivity sensors works well and provides the basis for further development of soot sensors to be used in engine exhausts. The soot sampler containing sensor was found to be 22% efficient under thermophoresis generally independent of the particle size. It has also been demonstrated that the detection down to concentrations of about 1000 µg/m3 and cumulative exposed mass of 20-30mg of particles on the sensor is possible. The detection limit can likely be improved by using a more local temperature gradient and modifying the sensor surface together with resistivity meter employed. The
results obtained from this work can be used to further investigate the role of soot morphology, film microstructure and agglomerates which helping to enhance the sensitivity and accuracy of such sensor systems

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Table 1: Flow rates of fuel and sheath air and geometric mean diameter (GMD) of particles produced.

<table>
<thead>
<tr>
<th>Case</th>
<th>Equivalence ratio</th>
<th>Fuel / air flow rates</th>
<th>Soot particles generated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \phi )</td>
<td>(L/min) / (L/min)</td>
<td>GMD, nm</td>
</tr>
<tr>
<td>Equivalence ratio 1</td>
<td>0.632</td>
<td>0.085 / 3.2</td>
<td>55</td>
</tr>
<tr>
<td>Equivalence ratio 2</td>
<td>0.653</td>
<td>0.085 / 3.1</td>
<td>85</td>
</tr>
<tr>
<td>Equivalence ratio 3</td>
<td>0.675</td>
<td>0.085 / 3.0</td>
<td>110</td>
</tr>
</tbody>
</table>

Table 2: Conditions applied during thermophoretic sampling of soot particles.

<table>
<thead>
<tr>
<th>Polydisperse particles mobility diameter, nm</th>
<th>Monodisperse particles diameter, nm</th>
<th>Test time for each particle size</th>
<th>( dT/dy ), ( ^\circ\text{C}/\text{m}^2) (( T_h=180^\circ\text{C}))</th>
<th>Particles flowrate, ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>50, 80, 120</td>
<td>50, 100, 150</td>
<td>5 min</td>
<td>1400</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 3: GMD and GSD for the number size distribution and the mass size distribution as well as total number and mass concentration for the three equivalence ratios tested. Values in parentheses correspond to the relative standard deviation (RSD) (average/1s.d).

<table>
<thead>
<tr>
<th></th>
<th>Eq. ratio 1</th>
<th>Eq. ratio 2</th>
<th>Eq. ratio 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number distribution</td>
<td>GMD (nm)</td>
<td>55 (1.7%)</td>
<td>85 (1.5%)</td>
</tr>
<tr>
<td></td>
<td>GSD</td>
<td>1.80 (1.2%)</td>
<td>1.81 (0.7%)</td>
</tr>
<tr>
<td>Mass distribution</td>
<td>GMD (nm)</td>
<td>GSD</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>---------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>Total number conc.</td>
<td>1.3*10^7 (3.3 %)</td>
<td>2.0*10^7 (5.2 %)</td>
<td>2.4*10^7 (5.0 %)</td>
</tr>
<tr>
<td>before 2nd dil.</td>
<td>103 (2.8 %)</td>
<td>147 (1.8 %)</td>
<td>185 (1.4 %)</td>
</tr>
<tr>
<td></td>
<td>1.55 (1.3 %)</td>
<td>1.53 (1.0 %)</td>
<td>1.52 (0.4 %)</td>
</tr>
<tr>
<td>Total mass conc.</td>
<td>1.7*10^3 (6.4 %)</td>
<td>6.9*10^3 (7.4 %)</td>
<td>1.5*10^4 (5.8 %)</td>
</tr>
<tr>
<td>(µg/m^3)</td>
<td>before 2nd dil.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Average effective densities of the generated soot particles

<table>
<thead>
<tr>
<th>D_p (nm)</th>
<th>Density (g/cm^3)</th>
<th>1 standard dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.76</td>
<td>0.04</td>
</tr>
<tr>
<td>100</td>
<td>0.51</td>
<td>0.04</td>
</tr>
<tr>
<td>250</td>
<td>0.27</td>
<td>0.02</td>
</tr>
<tr>
<td>400</td>
<td>0.19</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Figure 1: Sketch of the soot generator.

Figure 2: A three-dimensional cross section view of the soot sampler (a) and sensor holder (b) including design of the finger electrode sensor structure (c).
Figure 3: Sampler collection efficiency for monodisperse particles due to thermophoresis

Figure 4: Schematic diagram of the experimental set-up.

Figure 5: System configuration of DMA-APM
Figure 6: SMPS number size distributions (a), mass size distributions and effective density (b) of the three settings tested. In b) the average effective density determined by the APM used to calculate the mass size distribution is also shown. The dashed line is the average value for all three equivalence ratios (coinciding with the average for equivalence ratio 2) and the upper and lower lines correspond to the average for equivalence ratios 3 and 1, respectively. Note that these distributions are after the 2\textsuperscript{nd} dilution (1:13), see Figure 4.
Figure 7: TEM images of produced soot agglomerates with GMD 55 nm (A), 85 nm (B), and 110 nm (C).
Figure 8: Examples of a single measurement showing the resistance change over time for sensors exposed for 2h to generated soot particle modes with GMDs of 55, 85 and 110 nm, respectively.
Figure 9: Experiments showing the cumulative mass of soot exposed and the resultant change in resistance for sensors for 2h test by particles with GMDs of 55, 85 and 110 nm. The vertical dashed lines indicate the least cumulative mass of smaller particles (left, 20mg) and large particles (right, 30mg) respectively, that can be distinguishably detected by the resistivity sensor.
Figure 10: Repeated measurements of the resistance change as a result of the cumulative exposed mass for new sensors.