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

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1. INTRODUCTION

Diesel engines are major contributors to urban emissions of particulate matter (PM) and nitrogen oxides (NOx) (Kittelson et al. 1998; Maricq et al. 2007). Fine particles cause reduction in visibility (Eidels-Dubovoi 2002; Bond and 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 (IPCC 2007). 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 and Nazarenko 2004).

Diesel PM is a complex mixture of small airborne particles typically consisting of solid agglomerates of primary particles (with 20–35 nm diameter) and smaller mostly liquid nucleation mode particles. 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 2007; Schneider et al. 2005). In this investigation, the term “soot particle” refers to the whole agglomerate complex of primary particles and condensed compounds.

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), NOX traps and diesel particulate filters (DPFs). However, due to increased stringent PM emission regulations, implementation of DPFs is a very strong tool to achieve such strict limits. The DPFs have been shown to have an efficiency of over 90% for PM under steady state conditions measured by the
Rayleigh-Debye scattering approach depending on the engine operating conditions (Kamimoto et al. 2007). While in transient state, the removal efficiency of the DPF has been found to be more than 99% for accumulation mode particles (Liu et al. 2005). To be in continuous operation, 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 the DPF being saturated by particulates, a proper soot detection system is vital to help trigger the regeneration process.

On-line techniques to carefully characterize the soot from diesel engines or soot generators include: Scanning mobility particle sizer (SMPS) and Engine exhaust particle sizer (EEPS) for mobility size distributions, and the Electrical low pressure Impactor (ELPI) for aerodynamic size distribution. Efforts have been made (Gulijk et al. 2004; Park et al. 2004) to couple aerodynamic and mobility diameter and mass to estimate mass fractal dimensions in order to better understand the complex aerodynamic behavior of soot agglomerates from diesel exhausts. By first selecting particles based on mobility diameter (Park et al. 2008) and then determining the particle mass a DMA-APM system can be used to measure the mass and effective density for a selected mobility diameter, independent of morphology (McMurry et al. 2002).

Other efforts include the investigation and development of simplified and down-scaled new particle sampling methods and characterization techniques (Bergmann et al. 2009). Various operating principles have been applied to develop quantification methods for particles from diesel engine exhausts, pyrolysis, combustion processes, smoke, and so on. They include photoelectric sensors, photo and diffusion-charging, and photoacoustic sensor systems (Lu et al. 2009; Polidori et al. 2008; Haisch et al. 2003). However, up to date, the described methods are not cost-effective and robust in harsh exhaust environments; hence, new ways to measure soot particles are needed.

As a simple, rugged, and cost-effective solution for the detection of soot particles downstream DPF, the electrical conductivity of particles deposited between two electrodes can be monitored to characterize properties of soot particles emitted (Fleischer et al. 2005; Lutic et al. 2010). Such methodology can also be applied in other areas such as emissions from thermochemical conversion of biomass (Lillieblad et al. 2004; Wierzbicka et al. 2005).

PM from diesel engines is likely to introduce variations during measurements and is not easy to control, reproduce, and obtain stable size and mass concentrations as desirable when developing a new soot sensor. Soot produced from flame reactors on the other hand can be made stable and reproducible in terms of size distribution and concentrations (Jing 1998) which is crucial to evaluate the size- and concentration-dependence when developing a soot sensor.

In this work the feasibility of combining a series of three techniques to build up a suitable and practical method for the detection of soot particles has been tested 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 exhaust, (2) particle deposition using thermophoresis on sensor substrates, (3) monitoring the change in electrical resistivity of the sensor occurring from the deposited particles. In this article we investigate the effect of varying the agglomerate size for a constant primary particle size for a deeper understanding of the response characteristics of the sensor.

2. EXPERIMENTAL METHODS

2.1. Combustion 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 dry particle free 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 (ER), soot particles of different concentrations and size distributions were generated. The geometric mean diameters (GMDs) of the generated particles for the ERs applied are listed in Table 1.

The diffusion flame is quenched horizontally in the quenching zone using dry PFA at a flow rate of 9 l/min at a height of 55 mm above the flame. This is a similar procedure to that used in the commercial CAST flame soot generator used for
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 φ</th>
<th>Fuel/air flow rates (L/min)/(L/min)</th>
<th>Soot particles generated GMD, nm</th>
</tr>
</thead>
<tbody>
<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>

Different applications (Zahoransky et al. 2003). 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, additionally it causes oxidation of soot as opposed to the use of nitrogen as quenching agent. The quenching allows generation of high concentrations of soot particles of well-defined mobility size and hence it plays an important role in defining the chemical and physical properties of the soot particles generated.

The soot leaving the quenching section is further diluted and completely mixed in the mixing zone using PFA with a flow rate of 45 l/min. This ensures a uniform, fully mixed soot distribution exiting the soot generator.

2.2. Particles Collection Efficiency and Thermophoretic Deposition on Sensor

Figure 2a shows a cross section 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 et al. 2003; Tsai and Lu 1995). In the sampler, the soot deposition is driven by thermophoresis. When a soot particle passes through the deposition channel, it will be subjected to a thermal force gradient towards the colder substrate surface of the sensor. The induced thermophoretic velocity, \( v_{th} \), is independent of particle size and directly proportional to the temperature gradient in the free molecular regime (\( d < \lambda \)) described by Equation (1) (Hinds 1999):

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

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 mean gas temperature in the channel, \( \mu_g \), 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. A rectangular-shaped deposition channel was grooved into the middle of the upper stainless steel plate with the dimensions L36 x W15 x H0.5 mm. The lower part consists of two circular aluminum plates 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 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.

FIG. 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).
The lower part was cooled using a pressurized air jet and the cold-plate surface temperature ($T_m$) 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 surfaces of the hot and cold plates. The measured temperatures are expected to be similar to the gas temperatures at the hot and cold plate surfaces inside the deposition channel, producing a temperature gradient of $\nabla T = 1.4 \times 10^5$ (°C/m) across the deposition channel.

For the 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 hydrodynamic length to become laminar. The hydrodynamic length can be calculated by the following equation (Messerer et al. 2003)

$$L_h = 0.04 \text{ Re } D_h$$

[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)

$$D_h = 2W \cdot H/(W + H)$$

[3]

Accordingly, for $W = 15$ mm, $H = 5$ mm, and $D_h = 1$ mm, the $L_h = 0.9$ 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 fraction of particles deposited in the sampler. The collection efficiency has been estimated based on the number concentration of particles before and after the sampler. The polydisperse soot particle distribution of geometric mean diameter of 50 nm, 80 nm, and 120 nm were generated from the soot generator and passed through the DMA to select monodisperse particles of 50 nm, 100 nm, and 150 nm before they were passed through the thermophoretic sampler. Each collection test was carried for 300 s under the temperature gradient of $1.4 \times 10^5$°C/m at $T_h = 185°C$.

2.3. Electrical Resistivity Soot Sensor

For application purposes the resistivity soot sensor must allow deposition of soot while in collection mode and 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 a Si/SiO2 (100 nm)/Ti (5 nm)/Au (200 nm) structure. The interdigitated electrodes obtained using lift-off technology had a width/spacing of 40 micrometers and covered an area of $1 \text{ mm} \times 1 \text{ mm}$. 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 kΩ to 40 MΩ.

2.4. Soot Particle Characterization

A scanning mobility particle sizer (SMPS 3934, 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. 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 sampler using a critical orifice at the sampler outlet (Figure 3).

2.5. OC/EC and TEM Analysis

The organic and elemental carbon analysis (OC/EC) of the soot particles was determined 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 and 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...
FIG. 3. Schematic diagram of the experimental set-up consisting of soot generation, deposition, and characterization systems.

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 4). 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 gap between the cylinders and a voltage \( (V_{APM}) \) 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).

\[
m = \frac{qE}{r^2\omega^2} = \frac{qV_{APM}}{r^2\omega^2 \ln(r_2/r_1)} \tag{4}
\]

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).

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:

\[
m = \frac{\rho}{\chi^3} \cdot \frac{C(d_{me})}{C(d_{ve})} \cdot \left(\frac{\pi}{6}\right) \cdot d_{me}^3 \tag{5}
\]

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

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

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 Figures 5a and b. 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 is considered to be similar to typical soot size distributions from a heavy duty diesel engine of 60–100 nm (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 $4.7 \times 10^4$–$10^7$ 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 6 h operation. Our designed combustion soot generator also shows a reasonably high stability represented in terms of GMD, GSD, and total number concentration. Table 2 shows the GMD and total number and mass concentrations (using the effective densities mentioned in Figures 5a and b) for the three cases. 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%.

### 3.2. Particle Composition, Effective Density, and Morphology

To establish the organic and elemental carbon contents (OC/EC), 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 size distributions with GMD of 100–120 nm.

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 ERs. The effective density decreased with increasing particle size from $\sim 0.8$ 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 3 and Figure 5c. All APM scans showed effective densities (including scans generated with the three different ERs) within ±10%. Within each ER setting all scans showed effective densities at each specific $d_{me}$ 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 ERs was observed, (Figure 5c). 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 $\sim 2.3$, which is almost identical to that found for diesel engines (Park et al. 2003; Maricq and Ning 2004). The effective densities found here were slightly lower than those found in the literature for diesel engines, typically ranging from $\sim 1$–1.2 for 50 nm particles down to $\sim 0.3$ for $\sim 300$ 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 2) 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 leading to an overestimation of the mass of the largest particles. Assuming the soot bulk density ($\sim 1.8$ g/cm$^3$) to be constant over size would lead to an overestimation of the total mass concentration by 3–4 times.

The morphology of the soot agglomerates produced by the soot generator was investigated with TEM analysis. The analysis (using ImageJ 1.41 software) shows a mean primary particle diameter of $15 \pm 2$ nm for all three cases (Figure 6) with no significant difference was seen between the cases tested. The fact that both effective density (at each mobility size) and primary particles size is similar for the three cases suggests also that the morphology at a given mobility diameter is similar between the three cases.

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. 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 ours) 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 sensor using the soot sampler and determine the key parameters within deposition and detection steps. The collection efficiency of thermophoretic soot sampler for monodisperse particles is shown in Figure 7, which shows the overall collection efficiency of about 22–23% with negligible effect of particle size (4–5% SD), with diffusion and other loss mechanisms for particles being negligible at such conditions. 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 34–300 nm and temperature gradient of $1.5 \times 10^5$°C/m for channel gap $H = 0.45$ mm.

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 resistance decreases enough to fall into the measureable range of our system (40 MOhm).

Figure 8 shows the electrical resistance over time when depositing soot generated with ER1 (55 nm), ER2 (85 nm), and

### TABLE 2

<table>
<thead>
<tr>
<th></th>
<th>ER1</th>
<th>ER2</th>
<th>ER3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number distribution GMD (nm)</td>
<td>55 (1.7)</td>
<td>85 (1.5)</td>
<td>110 (1.1)</td>
</tr>
<tr>
<td>GSD</td>
<td>1.80 (1.2)</td>
<td>1.81 (0.7)</td>
<td>1.77 (0.8)</td>
</tr>
<tr>
<td>Total number conc. (#/cm$^3$) before 2nd dil.</td>
<td>$1.3 \times 10^7$ (3.3)</td>
<td>$2.0 \times 10^7$ (5.2)</td>
<td>$2.4 \times 10^7$ (5.0)</td>
</tr>
<tr>
<td>Mass distribution GMD (nm)</td>
<td>103 (2.8)</td>
<td>147 (1.8)</td>
<td>185 (1.4)</td>
</tr>
<tr>
<td>GSD</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. (µg/m$^3$) before 2nd dil.</td>
<td>$1.7 \times 10^3$ (6.4)</td>
<td>$6.9 \times 10^3$ (7.4)</td>
<td>$1.5 \times 10^4$ (5.8)</td>
</tr>
</tbody>
</table>

### TABLE 3

<table>
<thead>
<tr>
<th>$D_p$ (nm)</th>
<th>Effective density (g/cm$^3$)</th>
<th>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>
ER3 (110 nm) on new sensors continuously for 2 h. 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 ERs (GMD = 55, 85, and 110 nm, respectively). After the on-set time, resistance started to decrease as indicated by the multimeter. Sensors exposed to different 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 ER2 and ER3, 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 ER1 case, the resistance profile follows a smoother decline ending up at a considerably higher resistance of 1.4 MOhm. The number concentration varied by less than a factor of two between the three cases, suggesting that number concentration is a poor determinant of the sensor response.

The difference in resistivity and on-set time can largely be explained by different mass exposures per minute for the three cases. After normalization of the resistance 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 (GMD 110 nm) showed the fastest decrease in resistance. 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 smaller 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.

To get a deeper understanding of the relation between agglomerate size and the soot sensor response, knowledge of the properties of the porous films that are being formed upon soot
deposition is required. Higher film porosity for a given deposited mass would intuitively lead to an increased electrical resistance. Mädl er et al. (2006) described a model to calculate the film thickness as a function of particle properties and the properties in the thermophoretic deposition cell. Our deposition cell operates at a Peclet number of 0.03–0.1 ($Pe = \frac{\nu_{th}D}{D}$), a dimensionless number accounting for agglomerate diffusivity D and thermophoretic velocity, $\nu_{th}$ dependent on particle size, suggesting that the deposition mainly takes place in the transition regime between the ballistic and diffusion dominated regimes, with the larger agglomerates shifted towards the ballistic regime. Mädl er et al. (2006) showed that the film porosity typically increases with increasing agglomerate size and number of primary particles in the agglomerate, but also that the porosity is higher in the diffusion regime than in the ballistic regime. The simulations by Mädl er et al. (2006) were only performed for relatively small agglomerates ($N_p < 20$). We calculated the number of primary particles per agglomerate for the three cases in our study using the Lall-Friedlander theory (Lall et al. 2006) of fully transparent agglomerates, and found that $N_p$ increases from about 60 to 250 as the mobility diameter was increased from 103 to 185 nm (the mass based GMDs), thus our agglomerates are significantly larger than those used by Mädl er et al. (2006). Therefore no quantitative estimates of the film porosities were made and it is difficult to say whether the porosity increases or decreases with agglomerates size. This might be the case when two opposing factors of Brownian diffusion and thermophoresis affect the building of microstructure and resulting deposition properties (Tassopoulos et al. 1989). One such property is porosity, that can influence the thermal and electrical conductance across the particle film, which is sensitive function of mean free path and in case of its larger value; the deposition properties may behave like in ballistic regime resulting in compact deposits. On the other hand the polydispersity of particles may also result in “tree-like” structures owing to different structural properties than compact films which in turn may be enhanced by increased thermophoretic gradient (Kulkarni and Biswas 2004).

The increased resistance of films from smaller agglomerates may possibly be 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 seems to be some necking (partially sintered hard agglomerates) between the primary particles of the agglomerates used in this study which may lead to an increased conductivity between primary

![Resistence over time](image.png)

**FIG. 8.** Examples of a single measurement showing the resistance change over time for sensors exposed for 2 h to generated soot particle modes with GMDs of 55, 85, and 110 nm, respectively.
particles within the airborne agglomerates. Such an interpretation is consistent with the finding that charge carriers tunnel between graphitic conductive islands in soot (Dunne et al. 1997). In case of soot contaminated by ash, moisture, and corrosion gases (e.g., real diesel engine exhaust) the electrical conductivity of the film might not be affected due to the presence of such elements as long as the structural features are similar. The heteroatoms are of significance for surface interaction with adsorbed gases and not the bulk physical properties such as the conductivity (Dunne et al. 1997).

Finally, as the collection efficiency of the sampler is independent of particle size so there is no expected influence of this parameter on the difference in resistivity. ER1 had the lowest mass concentration (1.7 mg/m$^3$) in the study as shown in Table 2 and a detectable sensor response obtained after 30 minutes. This corresponds to cumulative mass of 20–30 µg as seen from Figure 9. This present lower detection limit can be significantly improved by designing a thermophoretic sampler with more localized deposition on the sensor, higher flow rates or higher temperature gradient, smaller spacing between the electrodes on the substrate or a resistance meter with higher precision.

3.4. 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 ER2 were repeated three times, and for ER1 and ER3, twice as shown in Figure 10. Repetition of ER2 and ER3 in soot sensing experiments showed a relatively high reproducibility for on-set time, resistance profile, and final resistance level. However, for the repeated ER1 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.

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 diesel engine exhausts. The collection efficiency of the thermophoretic sampler was found to be independent of the particle size in the size range tested. It has also been demonstrated that the detection down to 20–30 µg of cumulative exposed mass of particles on the sensor is possible. The sensitivity of the sensor can be improved by using a more local temperature gradient and modifying the sensor surface and finger electrode together with a more sensitive resistivity meter. The results obtained from this work can be used to further investigate the role of soot morphology, film microstructure and agglomerates on the sensor response, which will help to enhance the sensitivity and accuracy of such sensor systems.

REFERENCES


