Evaluation of novel soot sensors for periodic emission control of vehicles

1. Background

Currently opacimeters are used for measuring exhaust particle emissions during periodic emission control of vehicles. Due to increasingly stringent emission standards (e.g. EURO 5 and 6), particulate emissions from modern vehicles has reduced considerably. Also, the emitted mean particle size has shifted to smaller sizes. As a result, currently used opacimeters are not sensitive enough for measuring these particle emissions. Therefore, alternative measuring instruments are needed.

In co-operation between the EMRP project ENV02 PartEmission and CLEEN MMEA 4.5.1, a metrological validation and a comparison of novel measuring instruments was performed in order to asses the suitability of candidate instruments for particle measurements during vehicle inspection. Instruments with different operating principle (e.g. light scattering, diffusion charging, ionization chamber) was evaluated in laboratory conditions.

The aim of this measurement campaign was to compare candidate instruments performance using a laboratory generated diesel soot aerosol. Instrument performances were evaluated with respect to accuracy, linearity, sensitivity, response time and cross-interference, to mention but a few. Similar test has already been performed at other participating laboratories PTB (Germany) and METAS (Switzerland). PTB performed measurement using only large particles 100 – 200 nm and high concentrations $2 – 10 \cdot 10^7$ cm^{-3} with particle number (CPC), particle mass (gravimetric) and opacity (German reference opacimeter) as reference. METAS performed measurement in a wide particle size range 23 – 200 nm at concentrations of $4 \cdot 10^4 – 1.5 \cdot 10^6$ cm^{-3} using particle number (CPC) as reference. In this campaign, measurements were performed in the size and concentration range relevant for modern diesel vehicles. Some of the measuring points were the same as for the other participants in order to allow for cross-validation. In our campaign both number concentration (CPC) and mass concentration (gravimetry) was used as references.

2. Measuring instruments

The measuring instruments studied in the comparison campaign are listed in table 1. All instruments, except for the ionization chamber[1], are commercial instruments some of which are still in the prototype stage. Instruments were selected for the campaign bearing in mind the intended application of emission control during periodic vehicle inspection. Therefore, the chosen instruments had to be affordable, easy to use and robust. Moreover, the instruments must have a short response time as the emission tests during vehicle inspection are transient measurements (full acceleration test). Also, the instruments must be able to measure raw exhaust directly from the tailpipe, and therefore the instruments were equipped with auxiliary heating lines and dilution where necessary. The instruments are based different operating principles, which gave us an opportunity to compare different sensing techniques with each other. Particle mass concentration readings from the light scattering instruments and particle number concentration readings from the electrical sensors and ionization chamber were used for comparison with reference instruments

[1] The ionization chamber is designed and constructed by Michal Vojtisek at the Technical University of Liberece (TUL)

(CPC: number, gravimetric: mass). The ionization chamber measures particle length and therefore a conversion to particle number was made. The conversion was performed as described by Litton et. al. [1] by assuming a mean particle diameter of 80 nm and a particle size distribution with GSD 1.8. Results from the Bosch instruments are not shown because the results were found invalid due to incorrect usage of the device.

Table 1. Measuring instruments studied in the comparison

Instrument	Operating principle	Sample flow
Pegasor PPS-M	Electrical charging and sensing	3,0 L/min
Bosch BEA080	Light scattering	3.8 L/min
MAHA Met 6.2	Light scattering	2.6 L/min
AVL Smoke 2000	Light scattering	3.3 L/min
Matter NanoMet3	Electrical charging and sensing	4.6 L/min
Ionization chamber	Electrical charging and sensing	10.1 L/min
CPC (number ref.)	Condensational growth and optical detection	1.5 L/min
Gravimetric (mass ref.)	Weighing of filter and flow measurement	10 L/min
		Total: 38.9 L/min

3. Measurement setup

The test aerosol was generated with a self-made diesel soot generator. The generator comprises a modified commercial vehicle cabin heater followed by dilution, mixing and a thermodenuder. The vehicle heater is modified in such a way that the air to fuel ratio can be controlled. This enables one to adjust the generated particle size distribution by changing the air to fuel ratio. In these experiments the mode size of the particle size distribution was adjusted by changing only the air flow to the burner. The mixing chamber allows the aerosol to age and thus stabilizes the generated particle size distribution. A thermodenuder (Dekati) was used for removing volatile species. This is important for the gravimetric measurements as the filters might adsorb gas phase material and thus lead to false determination of particle mass concentration [2]. Using this soot generator configuration it is possible to generate a diesel soot particle size distribution with GMD 27 –164 nm and GSD 1.7 – 2.0 [2].

The soot generator output flow rate of 7 L/min was further diluted and mixed with either dry or humidified compressed air in an ejector diluter (Dekati). The ejector ensures proper mixing of the aerosol. The particle concentration of the generated test aerosol was reduced and adjusted using a dilution bridge. A scanning mobility particle sizer (SMPS) was used for measuring the generated particle size distribution. The aerosol was divided to the instrument using a TSI 4-port flow splitter preceded with a static mixer which ensures homogenous particle concentration before the splitter. As there were 8 instruments, the flow at each branch was further divided using a y-shaped branch. The instruments at the end of each y-branch were paired so that the flow rates were as equal as possible in order avoid uneven flow splitting. Furthermore, the sampling tube lengths to the instruments were matched according to mutual flow ratios so that the residence time in the tubing was equal and therefore also the particle losses.

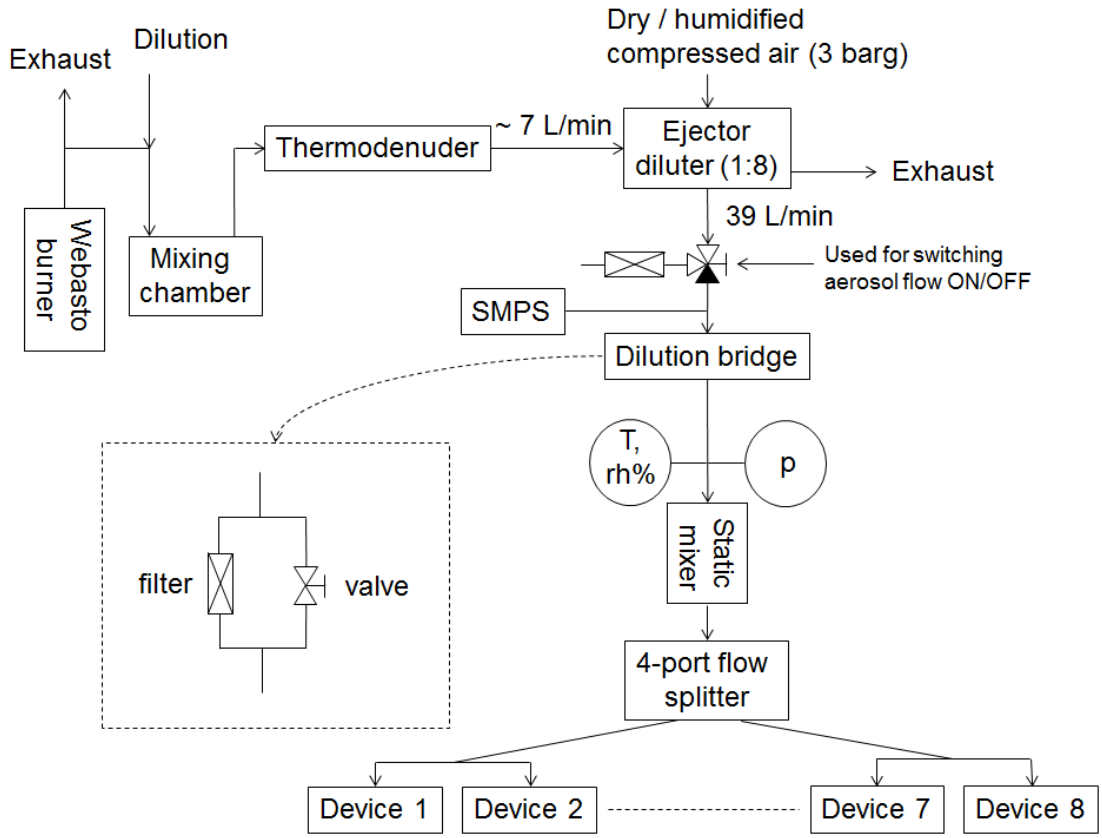

Figure 1. Experimental setup used for evaluating performance of particle measuring instruments.

4. Measurements

The measurement instruments were evaluated in a broad particle size range from 30 nm to 150 nm at particle number concentrations from 6 $\cdot 10^3$ cm^{-3} to 1 $\cdot 10^6$ cm^{-3}. The measurement points are summarized in table 2. An important aspect of the instruments performance is linearity. Therefore, linearity was studied at four different particle sizes namely 40 nm, 60 nm, 100 nm, 150 nm. Particle number concentration measured with the CPC was used as a reference also for instruments measuring only particle mass concentration (light scattering instruments). This is, however, sufficient for assessing their linearity as the particle size distribution remained unchanged while changing the particle concentration of the test aerosol. At concentrations above $4 \cdot 10^4$ cm^{-3}, the CPC input was diluted in order to decrease the input concentration to a range were the CPC calibration is valid. The dilution ratio of the Dekati ejector dilutor was measured in a separate experiment using a CO_2 analyzer and it was found to be 1:8.4.

Table 2. Measurement points during the campaign

Nominal particle size (nm)	Nominal particle concentration (cm^{-3})							
	0	$6 \cdot 10^3$	$1 \cdot 10^4$	$4 \cdot 10^4$	$1 \cdot 10^5$	$2 \cdot 10^5$	$4 \cdot 10^5$	$1 \cdot 10^6$
30				x				
40	x	x	x	x		x		
60	x	x	x	x	x	x	x[b]	
100	x	x	x	x[b]	x	x	x[b]	
150	x		x	x	x	x	x[b]	x

[a]Effect of humidity on the instrument response was studied at this point
[b]Gravimetric measurements were performed at these points

Accuracy of instruments is another important parameter to evaluate. Accuracy is defined as the interrelation between the particle concentration (cm^{-3} or mg/cm^3) displayed by the instrument and the particle concentration of the reference instrument (number: CPC, mass: gravimetry). The accuracy of the instruments was studied by measuring the particle size dependant response at two nominal particle concentrations $4 \cdot 10^4$ cm^{-3} and $4 \cdot 10^5$ cm^{-3}. At particle number concentration of $4 \cdot 10^4$ cm^{-3} the size response was studied at 30 nm, 40 nm, 60 nm, 100 nm and 150 nm particle sizes. In these measurements only particle number concentration was used as a reference because the mass sampled on filters would not have been sufficient for accurate gravimetric measurements. Because of this, the particle size response was studied also at higher particle concentrations ($4 \cdot 10^5$ cm^{-3}) where gravimetric measurements could be performed. These measurements were made using 60 nm, 100 nm and 150 nm particles.

Real vehicle exhaust contains besides particles also other substances, such as CO_x, NO_x, hydrocarbons and water vapour. Water vapour content of the aerosol is known to affect the charging of particles. Therefore, it is possible that measuring instruments based on particle charging, such as the Pegasor, Matter and ionization instruments, might experience cross-interference due to water vapour. The effect of aerosol relative humidity (water vapour content) was studied by changing the aerosol humidity content while keeping the particle concentration and particle size constant at $4 \cdot 10^4$ cm^{-3} cm^{-3} and 100 nm, respectively. The humidity content of the aerosol was adjusted by humidifying the dilution air in the measurement setup. The humidification was done using a bubbler saturator and two metering valves in such a way that a fraction of the flow entered the bubbler were it reached water vapour saturation state (rh=100%) and mixed at the output with the dry air flow that bypassed the saturator.

The response time of the instruments was studied by alternately switching the particle flow on and off. A total amount of three cycles of “down to up” and “up to down” concentration step changes were performed. The response time was defined as the time it takes for the instrument to reach 80 % of the total concentration step change after switching the particle flow on/off. Three “down to up” and “up to down” values were averaged to calculate the response time for each instrument. Response time measurements were performed at high particle concentrations of $4.5 \cdot 10^6$ cm^{-3} and 150 nm particle size. Results were compensated for the residence time in the tubing between the valve and the instruments.

All measurements lasted for 1 min except for measurements were gravimetric sampling was performed. In these measurements a sampling time of 10 min was used in order to sample enough mass onto the filters. The result for each instrument was calculated as the mean particle concentration during the measurement period.

5. Results

5.1. Linearity measurements

Results from the linearity tests performed with 40 nm soot particles are shown in figure 2 and 3. The light scattering instruments appear insensitive towards 40 nm particles as the instruments response to this particle size is similar to their response to particle free air (zero concentration). The Pegasor sensor shows a negative correlation towards increasing particle concentrations. Moreover, the measured particle concentration is one order of magnitude higher than the CPC readings. This odd behaviour might be caused by malfunction of the instrument. It is possible that the sensor might have got contaminated during earlier laboratory measurements in another campaign performed

using high particle concentrations. The ionization chamber and the Matter instrument are the only instruments sensitive towards small 40 nm particles. The ionization chamber gives an increasing response for increasing particle concentrations above $4 \cdot 10^4$ cm^{-3}. For concentrations below this, the signal is dominated by noise such that the response cannot be distinguished from the zero concentration response. The Matter instrument gives increasing response for increasing particle concentrations over the whole studied concentration range $6 \cdot 10^3$ cm^{-3} - $2 \cdot 10^5$ cm^{-3} (figure 3). However, the response is nonlinear especially at concentrations below 10^4 cm^{-3}.

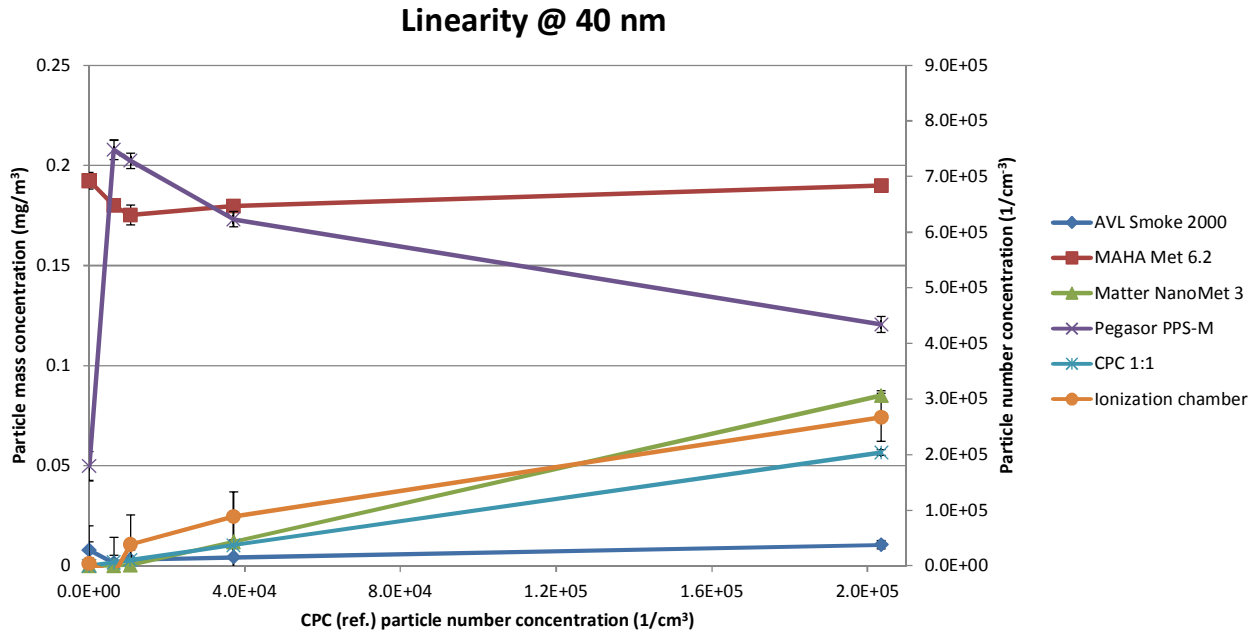

Figure 2. Linearity of measurement instruments for 40 nm soot particles. Light scattering instruments (AVL and MAHA) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (Matter, Pegasor and ionization chamber) are plotted against the right y-axis. Standard deviation shown as error bars.

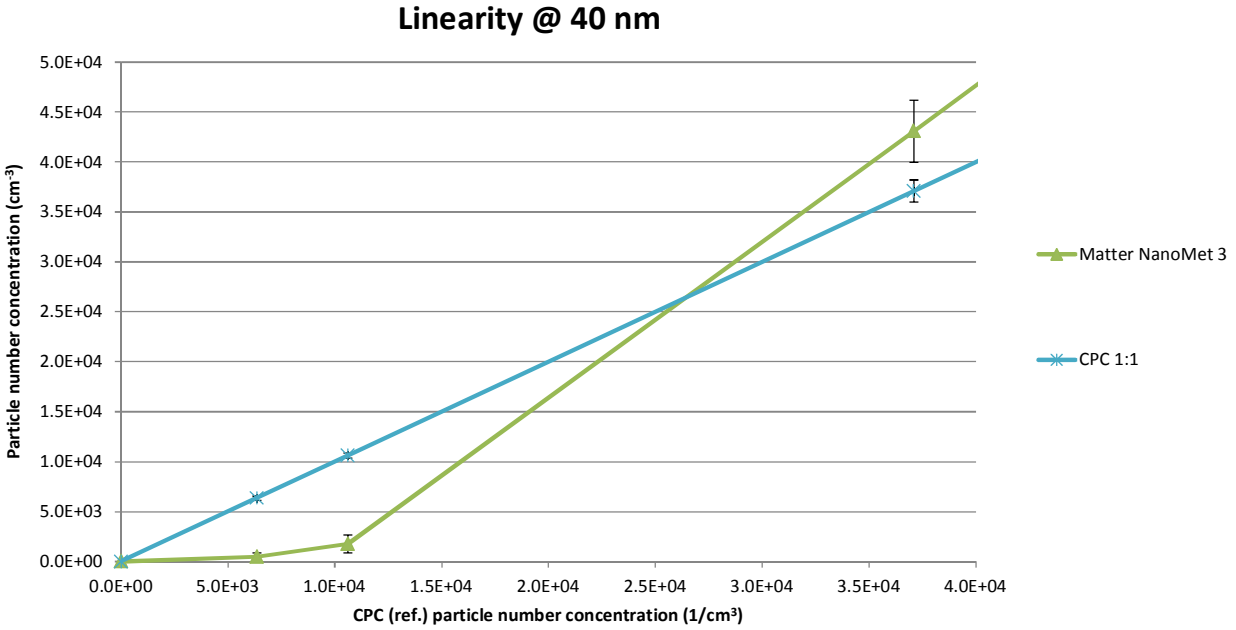

Figure 3. Linearity of Matter instrument for 40 nm soot particles and concentrations below $4 \cdot 10^4$ cm^{-3}. Standard deviation shown as error bars.

Linearity measurements performed at 60 nm are shown in figure 4 and 5. The MAHA instrument doesn't respond to particles of this size and the AVL starts to detect particles at concentrations $2 \cdot 10^5$ cm^{-3}. As with the 40 nm particles, the Pegasor sensors response is inconsistent. This suggests that there is some sort of instrument failure. For the instruments showing a response to this particle size (figure 5), the Matter instrument is the only one showing good linearity ($R^2 = 0{,}9893$) and an ability to measure particles at concentrations down to $6 \cdot 10^3$ cm^{-3}. The ionization chamber response at concentrations of $4 \cdot 10^4$ cm^{-3} and below is dominated by noise and thus the response cannot be distinguished from the zero concentration response.

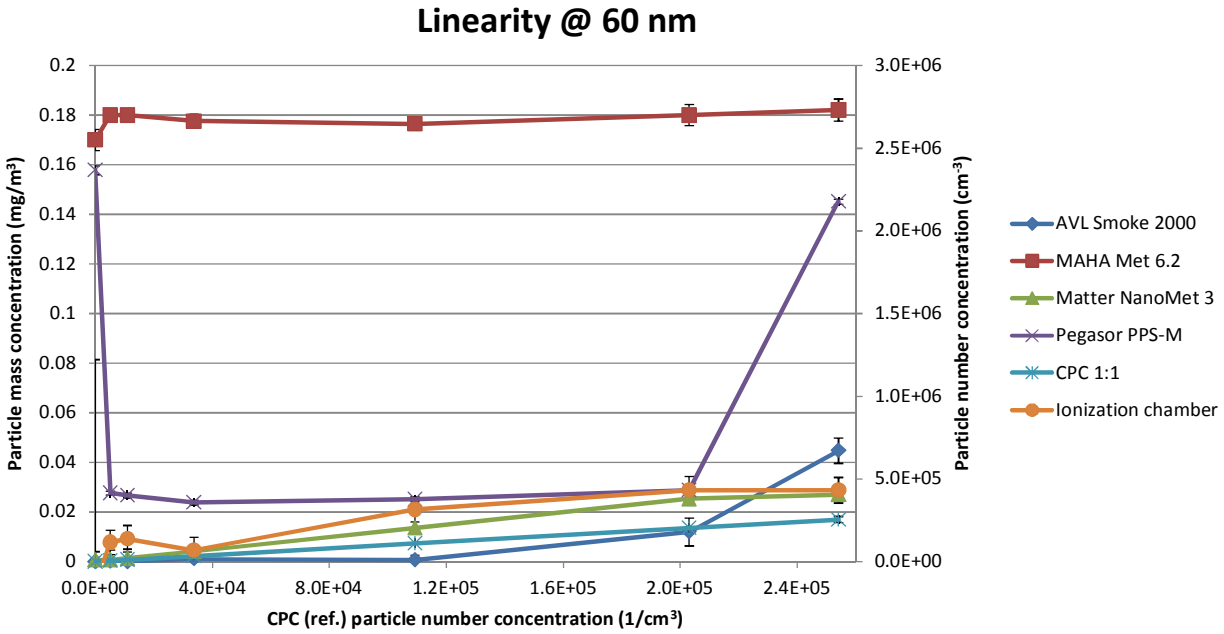

Figure 4. Linearity of measurement instruments for 60 nm soot particles. Light scattering instruments (AVL and MAHA) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (Matter and Pegasor) are plotted against the right y-axis. Standard deviation shown as error bars.

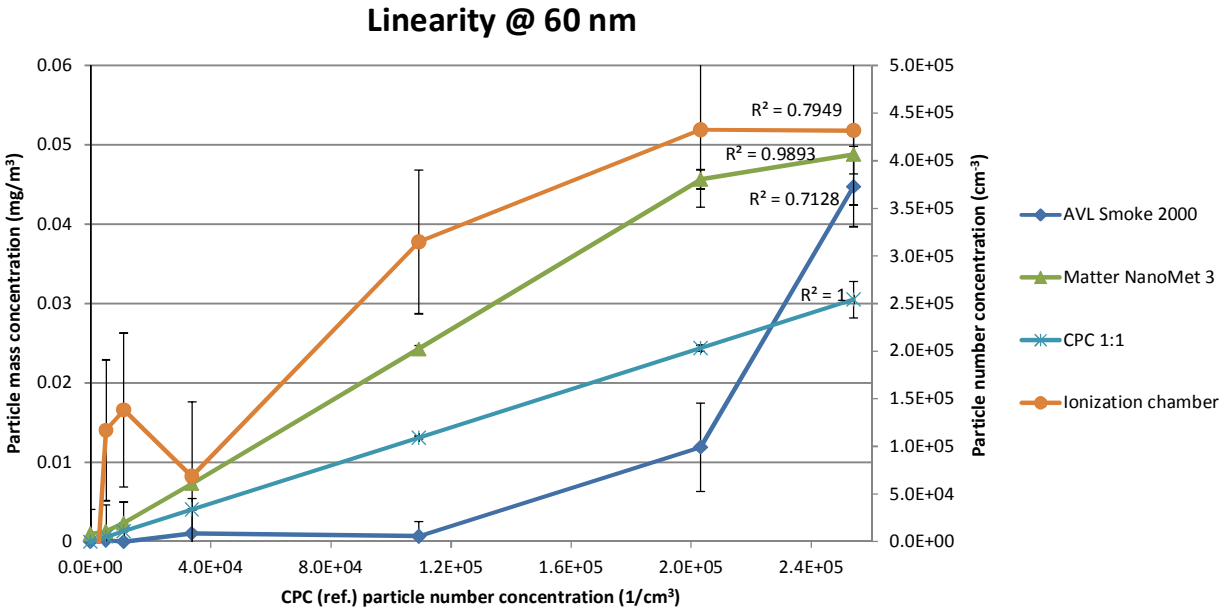

Figure 5. Linearity of measurement instruments responding to 60 nm soot particles. AVL mass concentration is plotted against the left y-axis and the Matter and ionization chamber number concentrations are plotted against the right y-axis. The goodness of linear fit is shown as R^2. Standard deviation shown as error bars.

Similar measurement performed with 100 nm particles show that light scattering instruments are able to detect particles at these particle sizes (figures 6 and 7). Again the MAHA instrument is less sensitive than the AVL instrument. At particle concentrations of 10^5 cm^{-3} and below, the response of the MAHA instrument is nonlinear. The AVL instrument on the other hand shows good linearity (R^2 = 0,998) down to concentration of $4 \cdot 10^4$ cm^{-3}. At concentrations below this, the AVL response cannot be distinguished from the zero concentration response. The Pegasor sensor shows a similar negative correlation towards increasing particle concentrations as seen for 40 nm particles. The Matter instrument performed best. It had the best linearity (R^2 = 0,9993) and it was able to reliably measure particles at low concentrations of $6 \cdot 10^3$ cm^{-3} (figure 7). However, at these low concentrations the response was nonlinear similarly to the linearity measurements at 40 nm and 60 nm particle size. The ionization chamber was also very linear (R^2 = 0,9982), but the noise became significant at concentrations of 10^4 cm^{-3} limiting the sensitivity at this concentration range.

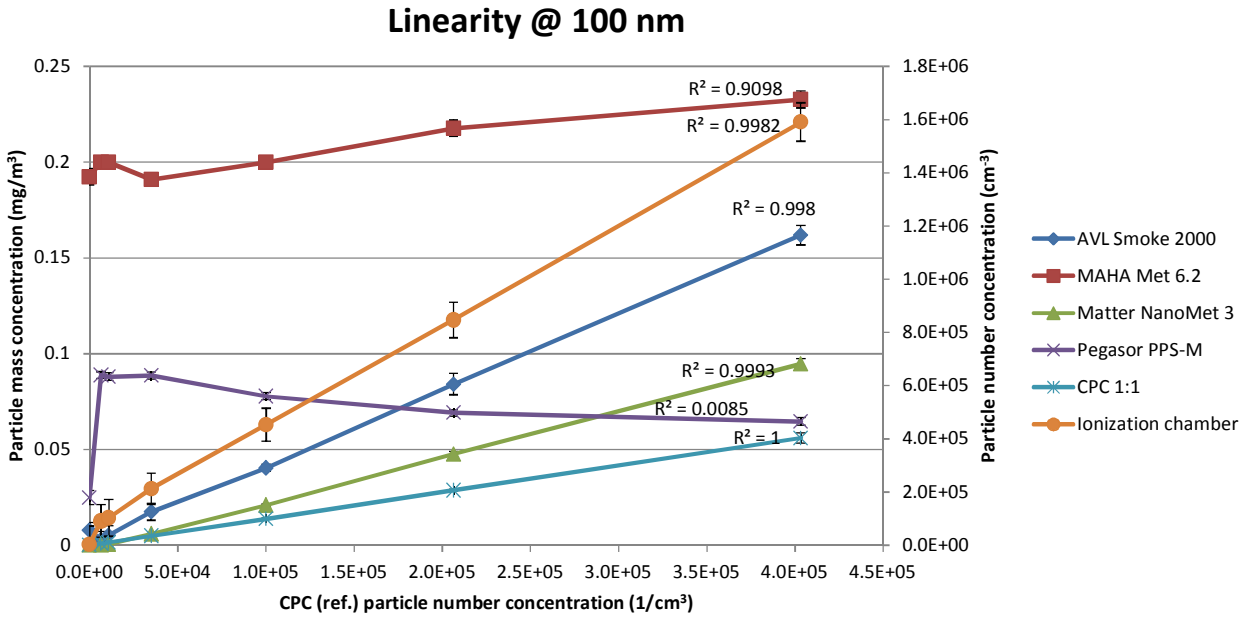

Figure 6. Linearity of measurement instruments for 100 nm soot particles. Light scattering instruments (AVL and MAHA) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (Matter, Pegasor and ionization chamber) are plotted against the right y-axis. Standard deviation shown as error bars. The goodness of linear fit is shown as R^2.

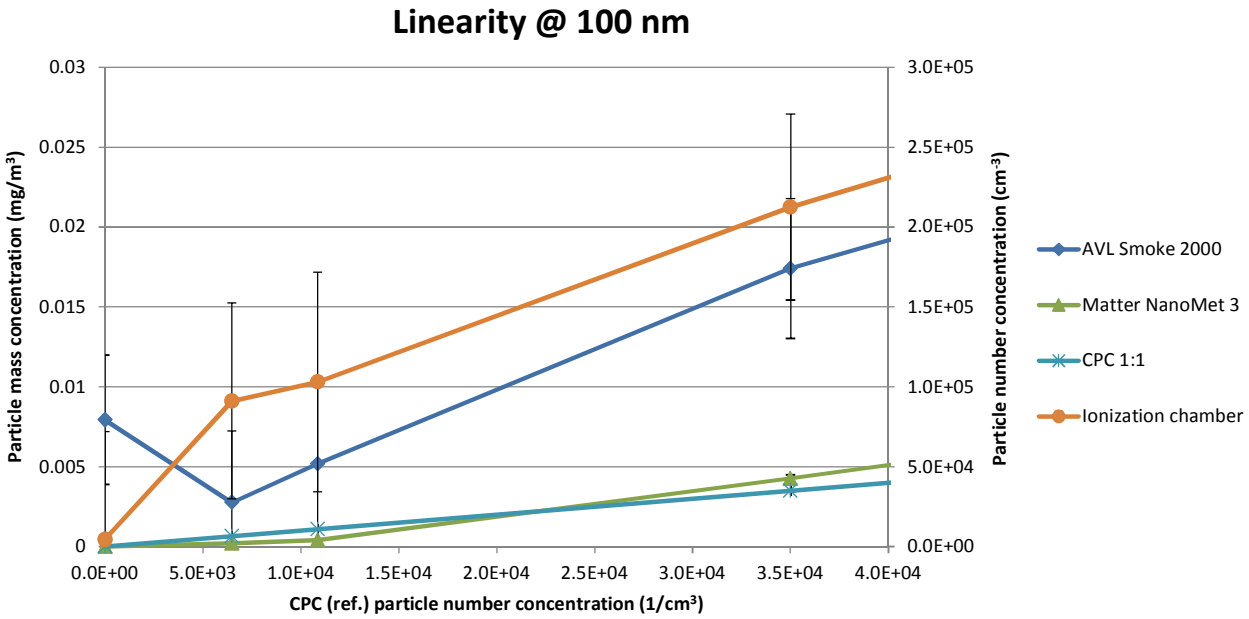

Figure 7. Linearity of measurement instruments responding to 100 nm soot particles with concentrations below $4 \cdot 10^{-4}$ cm^{-3}. AVL mass concentration is plotted against the left y-axis and the Matter and ionization chamber number concentrations are plotted against the right y-axis. Standard deviation shown as error bars.

Linearity measurements were also performed at 150 nm particle size (figure 8 and 9). These results are similar to the results for 100 nm particles. Both the light scattering instruments and the Matter and ionization chamber instrument have a linear response to increasing particle concentrations. As seen also with smaller particles, the AVL instrument is more sensitive to concentration changes than the MAHA instrument. AVL has a linear response for 150 nm particles down to 10^4 cm^{-3} while the MAHA is linear only down to $4 \cdot 10^4$ cm^{-3} (figure 9). Moreover, the slope is steeper for the AVL instrument. Again the Matter instrument showed the best linearity (R^2 = 0,9968) over the whole studied particle concentration range from 10^4 cm^{-3} to $1.4 \cdot 10^6$ cm^{-3}. The ionization chamber was also found very linear (R^2 = 0,996), but the response at small concentrations of 10^4 cm^{-3} was noisy which was also seen in previous linearity measurements.

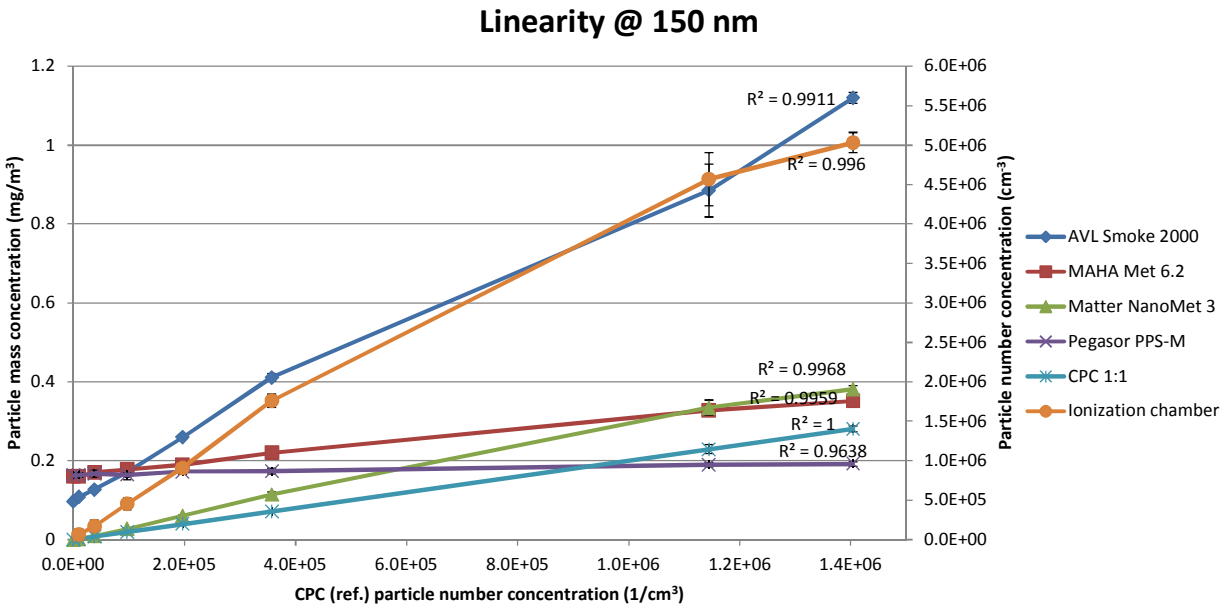

Figure 8. Linearity of measurement instruments for 150 nm soot particles. Light scattering instruments (AVL and MAHA) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (Matter, Pegasor and ionization chamber) are plotted against the right y-axis. The goodness of linear fit is shown as R^2. Standard deviation shown as error bars.

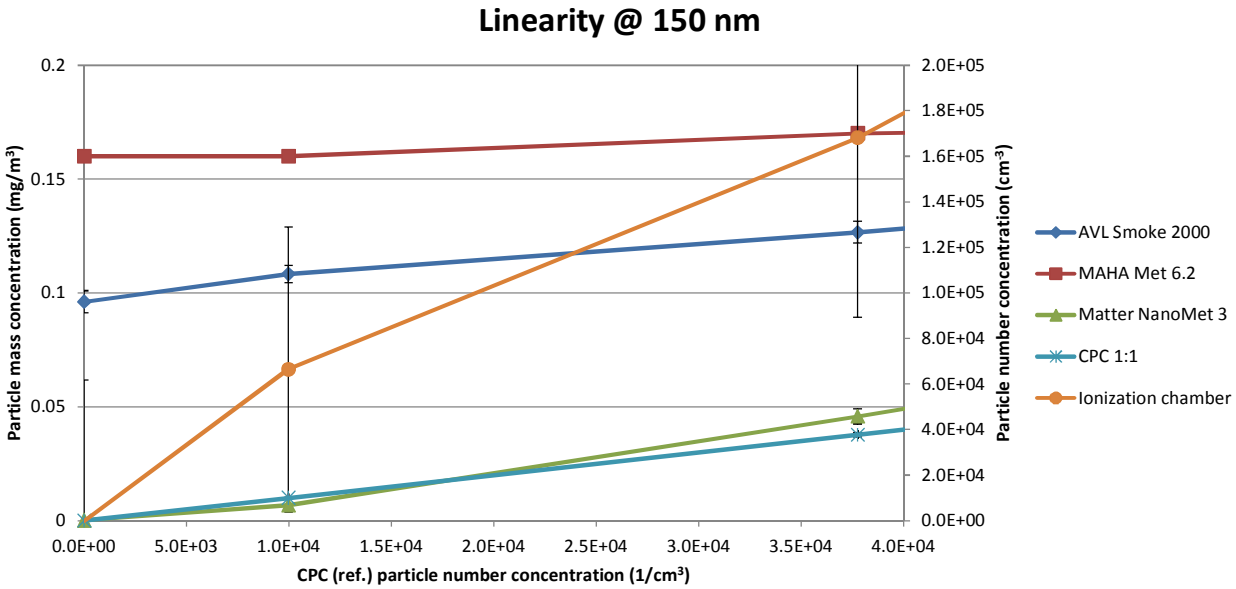

Figure 9. Linearity of measuring instrument responding to 40 nm soot particles and concentrations below $4 \cdot 10^4$ cm^{-3}. Light scattering instruments (AVL and MAHA) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (Matter, Pegasor and ionization chamber) are plotted against the right y-axis. Standard deviation shown as error bars.

5.2. Size dependant response

Results from measurements of the instruments size dependant response at particle concentrations of $4 \cdot 10^5$ cm^{-3} is shown in figure 10. The light scattering instruments measuring mass concentration are expected to correlate with the gravimetric results. As the particle concentration was kept constant at the studied particle sizes, the mass concentration was expected to increase towards larger particle sizes. This was seen for the gravimetric method which was used as a reference. The AVL results correlates with the gravimetric results and its response was found to be 23% – 29% lower than the gravimetric results. This offset was independent of particle size. The MAHA instrument on the other hand showed a size dependant response when compared to the gravimetric results. The MAHA results seem to correlate better with the particle number concentration determined with the CPC, although it should be measuring particle mass concentration. The Matter response was 40% – 50% higher than the reference value (CPC value). This offset did not however depend on particle size. Results of the ionization chamber correlate better with mass than number concentration. This is expected as the ionization chamber measures particle length concentration, which changes when the particle size distribution changes.

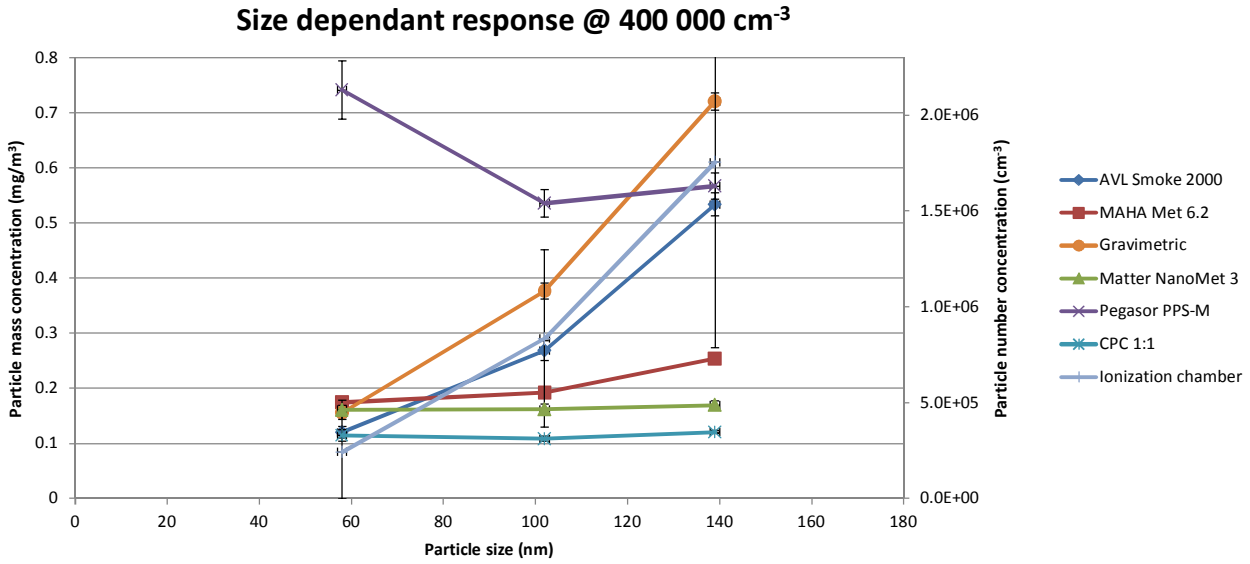

Figure 10. Particle size dependant response at particle concentrations of $4 \cdot 10^5$ cm^{-3}. Light scattering instruments (AVL and MAHA) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (Matter, Pegasor and ionization chamber) are plotted against the right y-axis. Standard deviation shown as error bars.

The size dependant response was also measured at particle concentrations of $4 \cdot 10^4$ cm^{-3} (figure 11). At this low particle concentration gravimetric measurements could not be performed accurately because the sampled mass would have been too small for accurate weighing. The MAHA results are not reliable as it has been shown that the MAHA instrument is not sensitive towards particle concentrations of $4 \cdot 10^4$ cm^{-3}. Also the AVL instrument lacks sensitivity for detecting these low concentrations. Only at 150 nm, the instrument gives a measurable response. The Ionization chamber shows similar behaviour as for the size dependant measurements at high concentrations, i.e. the particle number response increases towards larger particle sizes. At low concentrations of $4 \cdot 10^4$ cm^{-3} the Matter instrument performs well at particle sizes above 100 nm and response is 20% higher than the CPC value. At sub 100 nm particle sizes the response was found size dependant.

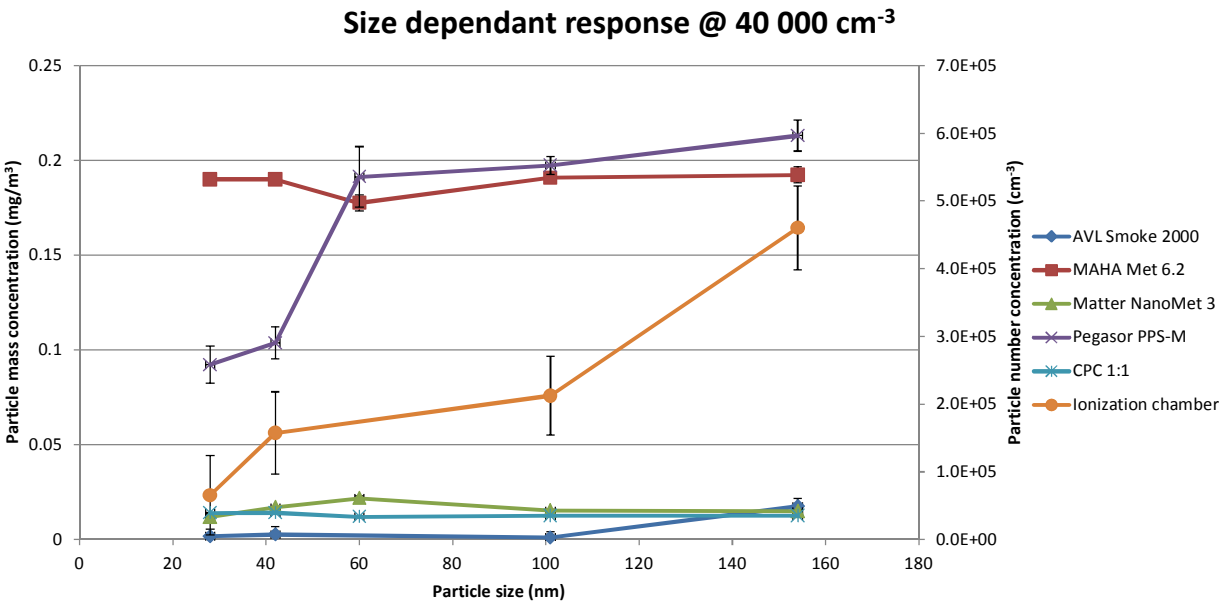

Figure 11. Particle size dependant response at particle concentrations of $4 \cdot 10^4$ cm^{-3}. Light scattering instruments (AVL and MAHA) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (Matter, Pegasor and ionization chamber) are plotted against the right y-axis. Standard deviation shown as error bars.

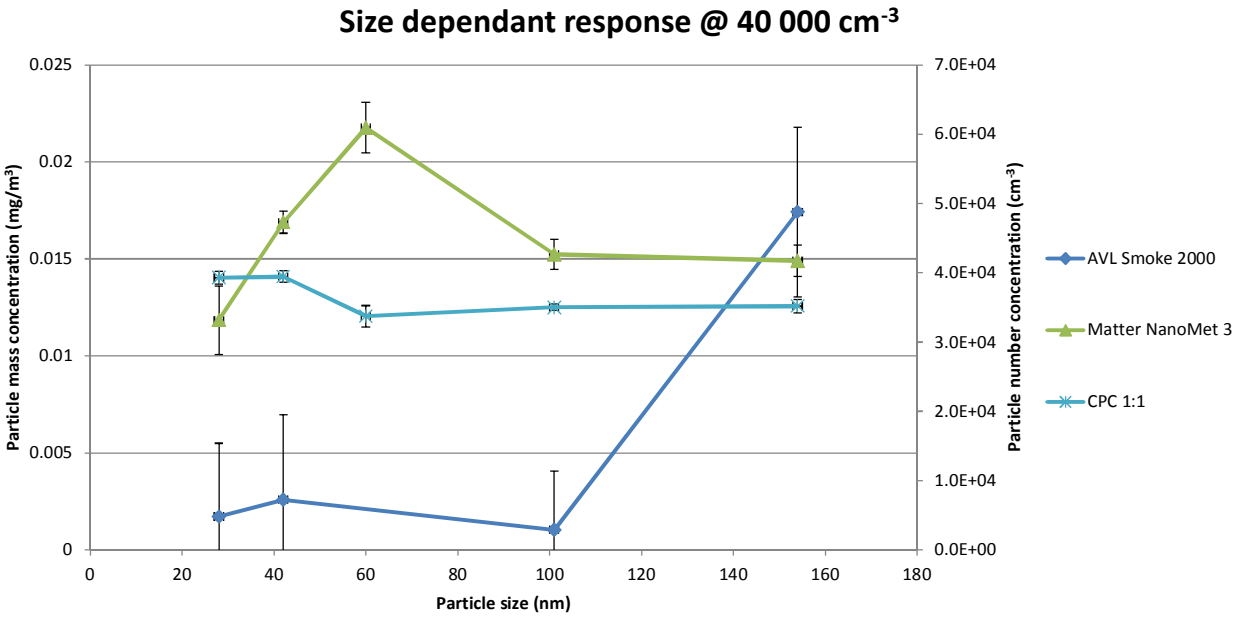

Figure 12. Particle size dependant response at particle concentrations of $4 \cdot 10^4$ cm^{-3}. AVL instrument measuring mass concentration is plotted against the left y-axis and the Matter instrument is plotted against the right y-axis. Standard deviation shown as error bars.

5.3. Effects of aerosol relative humidity

Results of measurements at different relative humidities (figure 13), indicate that the relative humidity of the aerosol doesn't have clear effect on the instruments response. The Matter instrument response is almost identical in shape to the CPC response indicating that water vapour content of the aerosol doesn't affect the relative difference between the two instruments. For the AVL and ionization chamber instruments it might seem that lowering the relative humidity from 33 %rh to 10 %rh would affect the response. This is, however, probably only an artefact of the measurement, as a change in particle size during the measurement would result in a similar effect for instruments sensitive towards particle mass (AVL and ionization chamber). However, this could not be verified as the size distribution was only measured before the experiments. The Matter instrument doesn't suffer from the change in particle size, as it also measures particle size and takes it into account in the conversion algorithm.

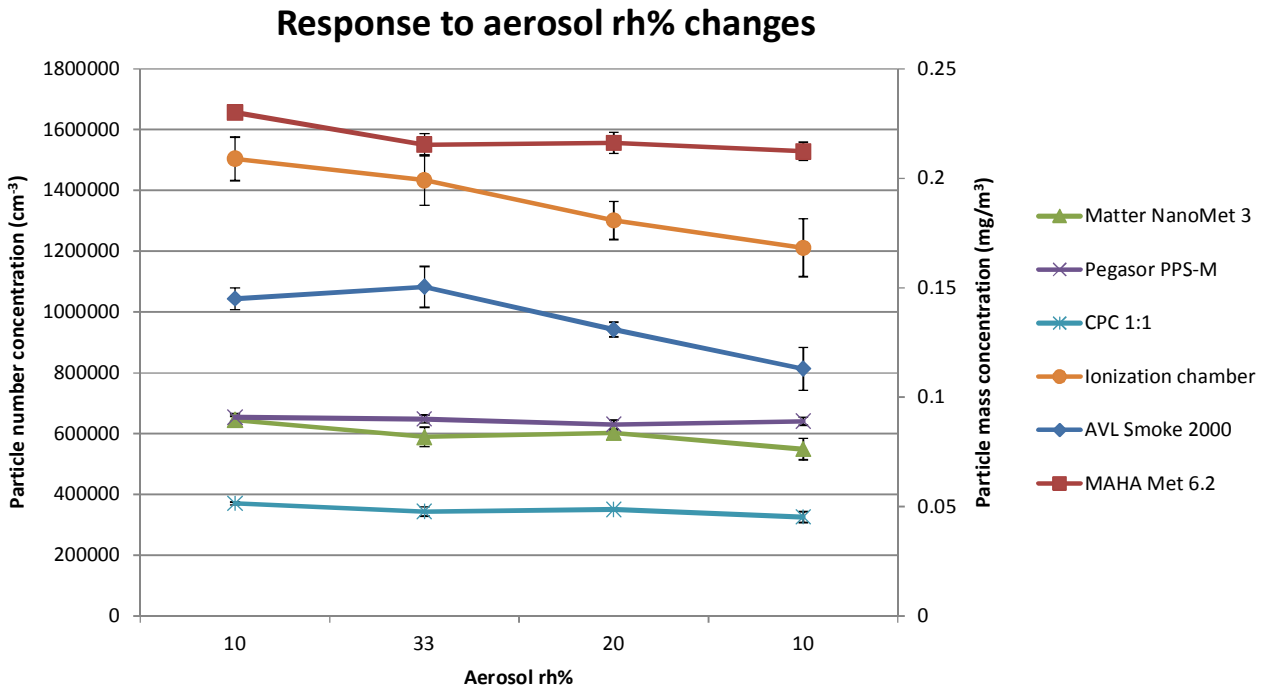

Figure 13. Effect of aerosol relative humidity measured at a particle concentration of $4 \cdot 10^5$ and particle size 100 nm. Light scattering instruments (AVL and MAHA) measuring only mass concentration are plotted against the right y-axis and the electrical sensors (Matter, Pegasor and ionization chamber) are plotted against the left y-axis. Standard deviation shown as error bars.

5.3. Response time measurements

The response times of the instruments is shown in table 2. The Matter instrument had the shortest response time of 1.3 s. This was a surprising result because the matter instrument is equipped with a dilution unit (rotating disc) and therefore it was expected to have some excess delay. Short response times between 4 s and 7 s was measured for the CPC, Pegasor, MAHA and Ionization chamber instruments. For the AVL instrument a huge delay of 39 s was measured. This result doesn't seem meaningful as the instruments operating principle is similar to the MAHA. MAHA, Pegasor and AVL was connected to the same measurement computer, so an error in the synchronization of the computer clocks cannot explain the observed delay.

Table 2. Measuring instrument response times

Instrument	Response time (s)	Standard deviation (s)
Pegasor PPS-M	4.2	0.7
Bosch BEA080	NA	NA
MAHA Met 6.2	7	0
AVL Smoke 2000	39	0.4
Matter NanoMet3	1.3	0.7
Ionization chamber	6	2.1
CPC (number ref.)	4.2	0.7
Gravimetric (mass ref.)	NA	NA

6. Conclusions

The only instrument capable of measuring sub 100 nm particles reliably at particle concentrations down to 10^4 cm^{-3} is the Matter NanoMet 3 instrument. The light scattering instruments are able to measure particles larger than 100 nm. The AVL light scattering instrument was found more sensitive than the MAHA instrument, and it was able to measure linearly down to particle concentrations of $4 \cdot 10^4$ cm^{-3}. Results from the Bosch instrument were invalid due to misuse of the instrument. The Pegasor instrument gave inconsistent results. It was expected that the sensor might have got contaminated during previous measurement campaigns performed using high particle concentrations. The ionization chamber, although not a commercial instrument, was found to outperform the light scattering instruments. It was able to measure particles in the whole studied particle size range from 30 nm to 150 nm. The sensitivity was limited by noise of the instrument and reliable results were achieved for particle concentrations above 10^5 cm^{-3}. As a conclusion, the Matter NanoMet 3 and the ionization chamber may both be considered suitable for measuring exhaust particles from modern diesel vehicles, i.e. sub100 nm particles. Matter NanoMet 3 is the best choice at the moment as it is commercially available. The apparent drawback of this instrument is, however, the complexity and thus the high price. The ionization chamber is a simple and cheap instrument based on a house-hold smoke alarm, and therefore it has great potential for being developed into an affordable commercial instrument.

References

[1] Litton, Charles D., et al. "Combined optical and ionization measurement techniques for inexpensive characterization of micrometer and submicrometer aerosols." Aerosol Science and Technology 38.11 (2004): 1054-1062.

[2] Högström, Richard, et al. "Study of the PM Gas-Phase Filter Artifact Using a Setup for Mixing Diesel-Like Soot and Hydrocarbons." Aerosol Science and Technology 46.9 (2012): 1045-1052.