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Laboratory evaluation of novel soot sensors for periodic emission control of modern diesel vehicles

Project: ENV02 PartEmission (EMRP)
WP2: Evaluation of measuring methods for particle emission from modern diesel vehicles in periodic emission control
(Task 2.1, Deliverable 2.1.2)

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Executive Summary

Due to the continuously improved Emission standards in Europe, particulate emission in exhaust gas of diesel vehicles has been reduced over the last years to a degree that the current legal method for periodic emission control reaches its sensitivity level. Consequently, there is a rising need to revise the periodic emission control and to establish more sensitive metrics and measurement techniques that can be used to identify malfunctions in the exhaust after treatment system of diesel vehicles.

Several prototypes based on different physical measurement principles are now available on the market, which are measuring particle mass and particle number concentration of the particulate emission in exhaust gas of diesel vehicles. A call of interest was started in March 2012 at approximately fifty European manufacturers and their associations for automotive emission testing instruments. At first, eight confirmations were obtained, and finally six manufacturers are providing prototypes of their new developed instrument. These instruments were evaluated for their ability of measuring particle emission at three different national metrology institutes - namely Germany (PTB), Switzerland (METAS) and Finland (MIKES). Three instruments of the prototypes determined particle mass as well as light extinction coefficients by traversing the particles through a laser beam and measuring the scattered light in different angles. These instruments were developed for the measurement of exhaust emissions with particle sizes above 80 nm and were more sensitive by a factor of 100 than the established opacimeters. Two other instruments detected the particle mass, number and surface concentration by charging the particles, and subsequently collecting them and measuring the total current. This measuring principle is known as diffusion charging. These two instruments were equipped with a dilution unit. A new approach is using a set of commercial smoke detectors (Ionisation Chamber) to determine the particle mass and number from the total particle length

The analysis for all instruments contains the findings from Mamakos, et al. (2012) leading to the following test ranges: number concentration from 10^4 to 10^8 cm^{-3}, mass concentration from 5 µg m^{-3} to 380 mg m^{-3}, and light extinction coefficients from 0,01 to 3,0 m^{-1} using particle size distributions with a geometric mean diameter from 23 to 240 nm and mean width of the particle size distributions from 1,4 to 2,2. Thereby tested parameters were sensitivity (linearity for combustion particles and diesel particles, size response and response to particles below 100 nm), response times and treatment to volatile particles. Special emphasis was also given to the comparability between the laboratories.

As a general conclusion, there was no instrument which covered the whole range of possible particulate emissions of diesel vehicles in the range of the light extinction coefficients from 0,01 and 3,0 m^{-1}. The measurement principles electrical charging and sensing as well as the ionization chamber can be considered as suitable for measuring of sub 100 nm particles from modern diesel vehicle exhaust. One of the diffusion charging instruments showed the best performance. It measured reliable particles below 100 nm for representative particle mass and number concentrations of modern diesel emissions. Due to its short response time it was very user friendly, and furthermore it was the only instrument owing an evaporation unit to evaporate volatile compounds of the exhaust gas in conformity to the Particle Measurement Program (PMP) of the Transport Devision of the UNECE. The apparent drawback of this instrument is, however, the complexity and thus of the highest price. The ionisation chamber is a simple and cheap instrument based on a house-hold smoke alarm, and therefore it has a great potential for being developed into an affordable commercial instrument. However, its response to CAST particles was not as good and a complex reanalysis is necessary to convert the measured values into evaluated parameters. But both systems need a dilution system for high soot concentrations of old diesel vehicles. On the other hand, one of the light scattering instruments showed a good correlation up to high concentrations and was less sensitive for small particles and low concentration.

Finally, a complementary instrument should be considered apart from the established opacimeter to measure the low emission of modern diesel vehicles.

1 Background

Soot particles emitted from diesel engines have already risen interest to the scientific community, society and policy makers in the last decades of the last century due to their high abundance in highly populated regions (urban regions) and their discussed effects on human health (Lighty, et al., 2000; Wichmann & Peters, 2000). Therefore, the first emission standards for particle mass concentration of diesel vehicles have been introduced in Europe starting with EURO 1 in 1992 (see Table 1). Since then, the emission standards have become more and more stringent (e.g. recently with EURO 5 and 6), leading to considerable reduced particulate emissions from modern diesel vehicles.
A collection and review of the technical requirements lay down in the European regulation and also through national regulatory authorities for the calibration of opacimeters. In order to establish a frame of reference for the establishment of the calibration procedures for the novel instrumentation was shown in the first report of this workpackage 2 of the ENV02 PartEmission. (Mamakos, et al., 2012).

Table 1: European Emission standards for diesel vehicles with particle mass concentration (PM) and particle number concentration emitted per kilometer respectively kilowatt-hour (PN).

Passenger car	Norm	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5a	Euro 5b	Euro 6
	Year of approval test	1992	1996	2000	2005	2009	2011	2014
	PM (mg /km)	180	80/100[a]	50	25	5	4.5	4.5
	PN (1/km)	--	--	--	--	--	$6 \cdot 10^{11}$	$6 \cdot 10^{11}$
Heavy Duty	Norm	Euro I	Euro II	Euro III	Euro IV	Euro V		Euro VI
	Year of approval test	1992	1996/98	2000	2005	2008		2013
	PM (mg/kWh)[b]	612/360	250/150	100/160	20/30	20/30		10
	PN (1/kWh)					$8 \cdot 10^{11}$		$6 \cdot 10^{11}$
	Opacity (m^{-1})			0.8	0.5	0.5		

[a] with direct fuel injection
[b] values are given for different test cycles

Lately, with the introduction of EURO 5b have been additionally introduced the emission standards for particulate number concentration. As these emission requirements can only be achieved by actively post processing the exhaust gas by means of particle filter trapping. The largest particles have been removed from the exhaust. Consequently, volatile particles do no longer condensate on large particles but rather form new small particles. Therefore, the emitted particle mass has reduced significantly and the mode of the diesel exhaust particles has been shifted to particles below 100 nm, even to 80 nm and smaller (Burtscher, 2005). This change in physical properties of the emitted particles by diesel engines needs to be considered when it comes to the periodic emission control of these vehicles. Currently, opacimeters (legal method) are used for measuring exhaust particle emissions during periodic emission control of diesel vehicles. However, the principle of transmission becomes less sensitive the smaller the particles are. Consequently, the current legal method is no longer the appropriate technique for the new generation of modern diesel vehicles (Euro 5b und Euro6).

In order to account for technical progress in the future a successor metric for opacity has to be identified. Alternative measuring instruments are now available as prototypes which are more sensitive to the size range of particles emitted by modern diesel vehicles by either measuring particle mass, surface or number.

With workpackage 2 of the EMRP project ENV02 PartEmission, the national metrology institutes (NMIs) of Germany, Finland and Switzerland including the joint research center (JRC) in ISPRA address the task of the development of a well-based metrological background for the introduction of these prototypes into legal metrology. In a first step, the available prototypes and potential future measurement principles were summarized and aligned with specific requirements concerning

periodic emission control (Mamakos, et al., 2012). In a second step a metrological validation of these novel measuring instruments was performed in the laboratories of three NMIs in order to assess the suitability of candidate instruments for particle measurements during vehicle inspection. Thereafter, these instruments will be tested for periodic emission control in a field test at JRC as well as in practicable usability tests at DEKRA.

Here are presented the results of the second step (which is deliverable 2.1.2 of WP2 of the ENV02 PartEmission). The task was to evaluate candidate instruments with different operating principles (e.g. light scattering, diffusion charging and ionization chamber) in three different laboratories (Germany (PTB), Switzerland (METAS) and Finland (MIKES)) with special regard to their ability for the measurement of particle emissions from modern diesel vehicles within the periodic emission control. The displayed concentrations of the candidate instruments (opacity, particle mass, surface or number concentration) were compared to metrologically traceable instruments owned by the NMIs. Thereby different types of combustion aerosol were used: combustion aerosol with high soot concentration and larger particle sizes from the HiMass-CAST soot generator (L. Jing, Zollikofen, Switzerland) at PTB and CAST-soot in lower concentrations with small particle sizes at METAS and laboratory generated diesel soot aerosol at MIKES. Details on the soot aerosols are summarized in Table 3Table 2. In particular tested parameters were the sensitivity of the instruments (signal to noise level, linearity for different combustion particle concentrations and ability to measure particles below 100 nm), response times of the instruments and treatment of volatile particles. For the comparison between the laboratories an electrical sensor was conducted as round robin device. A malfunction was not displayed during the round robin test due to contamination of the sensor, so that the comparison couldn't be performed as planned.

2 Measuring instruments

The measuring instruments studied in the comparison campaign are listed in Table 2. All instruments, except for the ionization chamber, are commercial instruments. Some of them are still in the prototype stage (L1, L2, L3). The instruments were provided by the manufacturer who configured their instruments according to the measurement ranges defined in Mamakos et al. (2012)[1,2]. 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 garage equipment. The instruments are able to measure raw exhaust directly from the tailpipe, and therefore the DC instruments were equipped with auxiliary heating lines and dilution where necessary. The instruments are based on different operating principles, which gave us an opportunity to compare different sensing techniques with each other. The instruments don’t measure the same physical properties of the test aerosol. While all light scattering instruments recorded particle mass concentration and opacity (converting the light scattering signal in a transmission signal), the electrical charging instruments recorded particle mass and number concentration. The ionization chamber measured particle length and therefore a conversion formula is needed to particle number and mass concentration. The conversion was performed as described by Litton et al. (2004) by assuming a mean particle diameter of 80 nm and a particle size distribution with mean width of 1.8. Moreover, the zero calibration had to be implemented after the measurements as the post processing is not already implemented in the instrument software. The instruments under test were measured against different national references at the different NMIs (Reference opacimeter, AVL 439 at PTB; CPC and SMPS at METAS; CPC and gravimetrical mass at MIKES).

[1] Recommended measurement ranges were particle number concentration 10^5 to 10^8 cm^{-3}; light extinction coefficients 0,01 to 3,0 m^{-1}; polydisperse combustion aerosol with a geometric mean diameter from 50 to 100 nm and mean width for the particle size distribution of 1.6 to 1.9 as typically found for light-duty diesel exhaust (Harris & Maricq, 2001).

[2] Personal communication to manufacturers regarding the configuration of the light scattering instruments: The device configuration comprises a calibration factor and a conversion formulas for the absorption coefficient k in 1/m and the mass concentration C in mg/m^3. The calibration factor allows a linear gain correction in the range from 0,001 to 3 m^{-1}.

Table 2: Soot sensors studied in the comparison. Candidate instruments are presented as well as the used references.

Instrument		Operating principle	Measured parameters		
			Mass	Number	Opacity
Candidate instruments	L1	Light scattering	x		x
	L2	Light scattering	x		x
	L3	Light scattering	x		x
	DC1	Electrical charging & sensing	x	x	
	DC2	Electrical charging & sensing	x	x	
	IC	Ionization chamber	x[d]	x[d]	
References used	Gravimetric [c]	Weighing of filter and flow measurement	Mass concentration reference		
	CPC [b,c]	Condensational growth and optical detection	Number concentration reference		
	Opacimeter [a]	Light attenuation	Opacity reference		
	SMPS [b]	Electrical mobility measurement in an electrical field	Particle size reference		

[a] PTB, [b] METAS, [c] MIKES

[d] Mass and number concentration were not measured directly but derived from particle length according to Litton et al. (2004).

3 Measurement setup and procedure

In order to assess the candidate instruments in the broadest possible aspects, all three involved NMIs used different setups and different combustion aerosol to test the soot sensors. While PTB used mass and opacity as reference, METAS and MIKES used particle number concentration as reference, with three additional measurements using particle mass as a reference at MIKES. Details on the test aerosol are given in *Table 3*. The different measurement setups and procedures conducted at the NMIs are described NMI by NMI in the Section below (3.1 - 3.3).

Table 3: Specification of the aerosol used at the different NMIs.

NMI	Campaign date	Aerosol type	Generator	Size		Number concentration	Mass concentration	Opacity
				GMD[a]	MWSD[b]			
PTB	Jan/Feb 2013	CAST	High mass CAST [c]	50 – 240 nm	1.6 – 2.2	$1.16 \cdot 10^7$ – $1.1 \cdot 10^8$ cm^{-3}	3000 – 380000 µg m^{-3}	0.01 – 2.98 m^{-1}
METAS	June 2013	CAST	Prototype CAST [d]	23 – 200 nm	1.4 – 1.7	$4 \cdot 10^4$ – $1.5 \cdot 10^6$ cm^{-3}	5 – 2800 µg m^{-3}	Not measured
MIKES	Sep 2013	diesel soot	diesel soot generator [e]	30 – 150 nm	1.7 – 2.2	$6 \cdot 10^3$ – $1 \cdot 10^6$ cm^{-3}	[f]156 – 721 µg m^{-3}	Not measured

[a] Geometric mean diameter (GMD) of the size distribution

[b] mean width of size distribution (MWSD)

[c] modified HiMass-CAST (L.Jing, Zollikofen, Switzerland)

[d] homebuilt at METAS

[e] homebuilt at MIKES

[f] Gravimetric measurements only at these mass concentrations

3.1 Measurements at PTB

3.1.1 Measurement setup at PTB

The PTB-setup for the evaluation of instruments included a modified HiMass-CAST (L. Jing, Zollikofen, Switzerland) as soot generator, a dilution system for mixing particle free air under controlled conditions (T and RH), a conditioning unit for stabilizing and a sample flow splitter with 10 sample ports for the reference and monitoring instruments as well as devices under test (see Fig. 1).

The soot aerosol was generated in 19 diffusion flames with controlled propane to air ratio and quenched with a controlled nitrogen flow about high-precision mass flow controller. This generation process allowed a controlled adjustment of particle size and size distribution. The output flow of the soot generator (450 l/min) was diluted in a self-developed diluting system (counter flow mixer), which ensured a proper mixing of the soot aerosol in an adjustable ratio with particle free air under controlled humidity and temperature conditions. The absolute aerosol flow after the dilution was around 900 l/min depending on the mixing ratio. Afterwards, the mixture between dilution air and soot aerosol have to be stabilized in a conditioning unit. With this configuration a soot aerosol with GMD of 50 – 240 nm and MWSD of 1.7 – 2.2 was provided for the instrument evaluation.
The sample flow splitter allowed a simultaneously sampling of 10 different instruments. As reference an opacimeter (AVL 439, Graz, Austria) was used, which is characterized by PTB internal calibration routine[2]. In order to decrease the input concentration a rotation disc thermodiluter was located upstream of a SMPS and EECPC (*Figure 1*) with a dilution factor 1:1000. The SMPS system was used for measuring the particle number size distribution and the CPC (marked as EECPC) for measuring the total number concentration as a PMP compliant device. The gravimetrical mass of the soot aerosol was determined by filter sampling. The following sample flows were used for the instruments: reference opacimeter with 16 l/min and rotation disc and thermodiluter with approximately 2 l/min.

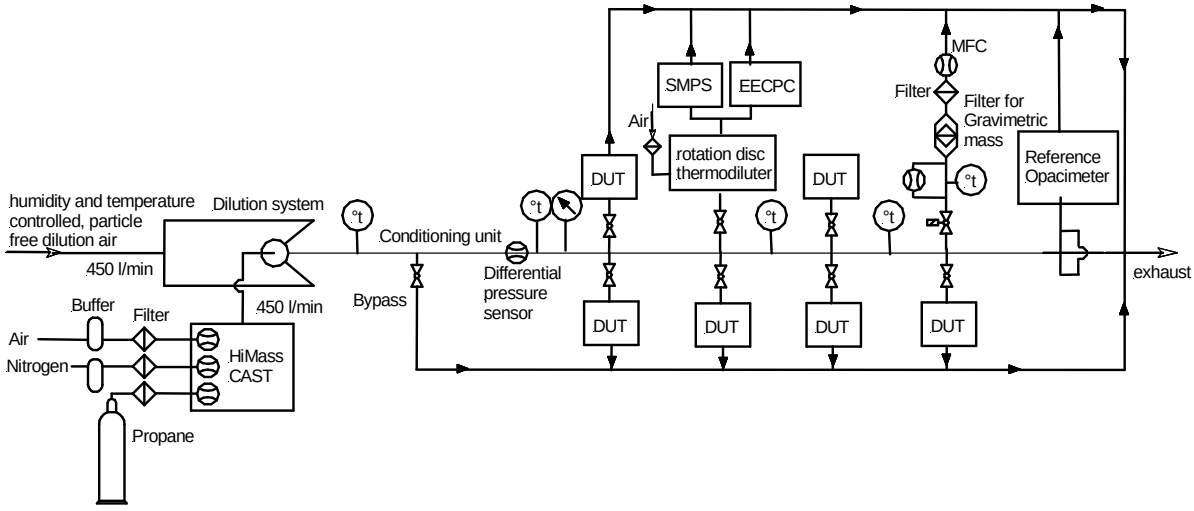

Figure 1: Experimental setup used for evaluating the performance of the candidate instruments at PTB.

3.1.2 Measurement procedure at PTB

At PTB the candidate instruments were evaluated with a soot aerosol of an opacity between 0.01 to 2.98 m^{-1}, mean particle sizes between 50 to 237 nm and particle number concentrations between $1.16 \cdot 10^7$ to $1.1 \cdot 10^8$ cm^{-3}. This corresponds to a particle mass concentration of around 3000 µg/m^3 to 380000 µg/m^3. These parameters were adjusted in parallel to cover a wide range for exhaust conditions of old diesel engines to modern diesel engines. Also, this wide measurement range was chosen by PTB, because this describes the current requirement for an opacimeter in Germany (Eichordnung 18-9). Note, the opacity of modern diesel vehicles is commonly lower than 1 m^{-1}.
The detection efficiency of the light scattering instruments is defined as the interrelation between the opacity displayed by the instrument and the opacity of the reference opacimeter. A linear correlation coefficient was determined between the measured opacity by the devices under test to the measured opacity by the reference opacimeter. Additionally, the gravimetric mass of the soot particles were compared to the measured mass concentration of the devices under test which don't record the opacity (namely DC1, DC2 and IC, see Table 2). The determination of the gravimetrical mass was performed as a monitoring value.

[2] Calibration routine with traceable transmission filters

3.2 Measurements at METAS

At METAS the instruments were tested according to the requirements for nanoparticle measuring instruments which will be used for construction machine periodic emission control in future in Switzerland (SR 941.242). All nanoparticle measurement devices which will be used in Switzerland for periodic emission control of combustion machinery need to pass a national conformity assessment (module B and F) for being introduced to the Swiss market. Those instruments will be tested for particle counting efficiency using CAST aerosol and tetracontane at METAS.

3.2.1 Measurement setup at METAS

The combustion aerosol is produced using the prototype version of the BigCAST generator build in the aerosol and particles laboratory at METAS shown in Figure 2. Particles are generated by burning C_3H_8 using air in the presence of N_2. All flows can be adjusted such that the geometric mean diameter of the size distribution of the generated aerosol can be varied from around 20 nm to 200 nm. Right behind the JingCAST, the generated aerosol passes the PSC (Particle Size Converter, which is basically a coagulation volume to allow particle to coagulate). Two different dilution units (MD 19 and Final diluter) can be introduced right behind the BigCAST and adjusted in various stages enabling a concentration range from $\approx 10^3$ cm^{-3} to 10^6 cm^{-3}. The GSD of the generated aerosol was around 1.6. After the dilution, the test aerosol was split isokinetically and provided to the device under test, the CPC, (Grimm, Aerosol Technik GmbH & Co, Germany) and a SMPS (TSI GmbH, USA). In order to work in the single counting mode of the CPC the test aerosol was diluted using a VKL 100 (Palas GmbH, Germany). Moreover, the flow through the CPC was monitored using a MFM (Red-y, Vögtlin, Switzerland) and due to regular CPC calibration the CPC could be considered as a stable reference for particle number concentration. The SMPS was used for two purposes, first to continuously monitor particle size of the generated aerosol and second to deduce a particle mass from the used aerosol as the concentrations were so low that gravimetric measurements could not be performed. For the SMPS the flow was measured as well. While particle size could be considered to be a traceable reference, the deduced particle mass from the SMPS should be considered as a good estimate rather than a traceable reference as a particle density is used which might vary for different particle sizes (details on the procedure are given in Section 3.2.2).

Tetracontane droplets were generated by heating tetracontane to 161°C in a glass flask. N_2 was saturated by tetracontane by mixing it with the gaseous tetracontane. The tetracontane-N_2 mixture was then cooled down to 15°C leading to the homogenous formation of tretracontane droplets. A number concentration of $2 \cdot 10^5$ cm^{-3} and a geometric mean of 34 nm were reached by dilution. The size distribution was very sharp in comparison to the CAST aerosol with a GSD of 1.4.

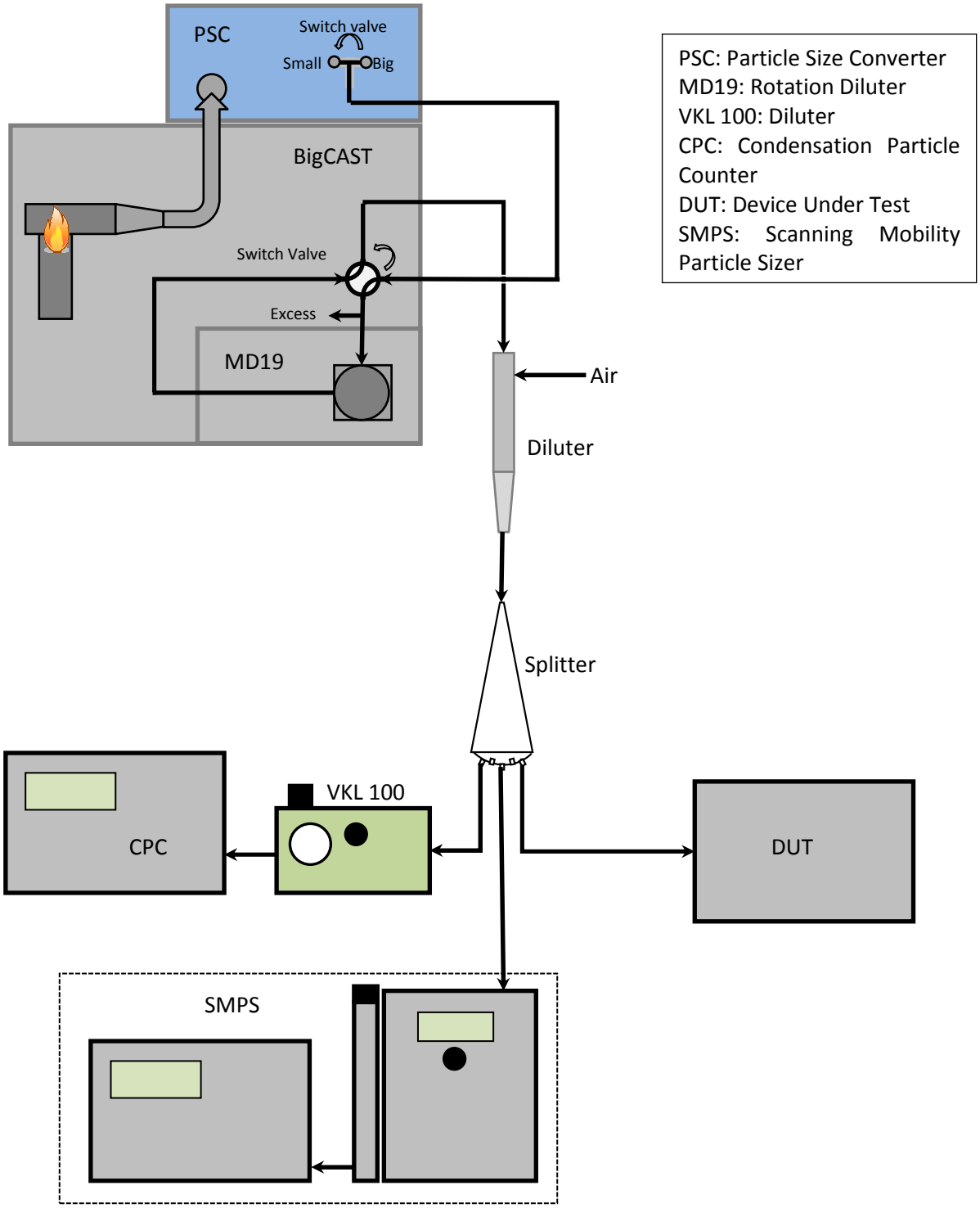

Figure 2: Measurement setup used at METAS. The combustion aerosol is generated using the BigCAST. After passing a coagulation volume (only for larger particle sizes) the aerosol is continuously diluted and then split isokinetically and distributed to a CPC (Reference for number concentration), a SMPS and the device under test.

3.2.2 Measurement procedure at METAS

The soot instruments under test were evaluated following the procedure of module B testing according to SR 941.242. SR 941.242 defines nanoparticles as solid, carbon containing particles in the engine exhaust ranging from 20 nm to 300 nm in particle mobility diameter (according to ISO 15900:2009). The efficiency of the measurement device is defined as the ratio between particle number concentration reading of the instrument and the particle number concentration at the entry of the instrument. The latter is recorded by the METAS national normal for particle number concentration.

The efficiency requirements of SR 941.242 are summarized in Table 4. The required size particle concentration range of those instruments is $5 \cdot 10^4$ cm^{-3} to $5 \cdot 10^6$ cm^{-3}. These requirements led to the measurement procedure summarized in Table 5.

Table 4: Efficiency requirements for nanoparticle measurement instruments according to SR 941.242.

Mobility diameter	Efficiency threshold E
23 nm nanoparticle	E < 50 %
41 nm nanoparticle	50 % < E
80 nm nanoparticle	70 % < E < 130 %
200 nm nanoparticle	E < 200 %
30 nm tetracontane droplets	E < 5 %

Table 5: Measurement procedure for soot instruments under test at METAS. The nominal particle size is the geometric mean diameter (GMD) of the produced size distribution by the BigCAST.

Nominal particle size GMD (nm)	Nominal particle concentration c_n (cm^{-3})	
23	$5 \cdot 10^5$	
41	$5 \cdot 10^5$	
80	$2 \cdot 10^5$	$2 \cdot 10^6$
200	$5 \cdot 10^4$	
Tetracontane droplets 30	$2 \cdot 10^5$	

Only those instruments which had an evaporation unit were tested with tetracontane droplets. Moreover, not all devices under test recorded number concentration (see Table 2 for details). However, the mass concentrations as required by SR 941.242 are too low to allow a traceable gravimetric measurement as measurement uncertainty would be too high. As the aim was to follow the measurement procedure of SR 941.242 for all instruments, we only estimated the particle mass concentration from the size distribution of the test aerosol measured by the SMPS system:
In a first step the mass concentration of the test aerosol was calculated by integrating the size distribution of the SMPS using the density of diesel smoke (ρ = 0.7 mg/cm^3 according to Symonds et al. (2007)):

$$\rho SMPS = \frac{\pi \rho}{6} \int d_n^3 \, C_n(d_n) \, \mathrm{d}d_n \qquad (1)$$

Then the counting efficiency of the SMPS was evaluated by calculating:

$E_{SMPS}=N_{SMPS}/N_{CPC}$. (2)

The best estimate of the mass concentration is then:

$\rho_N= \rho_{SMPS} \cdot E_{SMPS}$. (3)

3.3 Measurements at MIKES

3.3.1 Measurement setup at MIKES

The measurement setup used at MIKES is shown in Figure 3. 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 (Högström, et al., 2012). 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 (Högström, et al., 2012).

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 spatially 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 to 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.

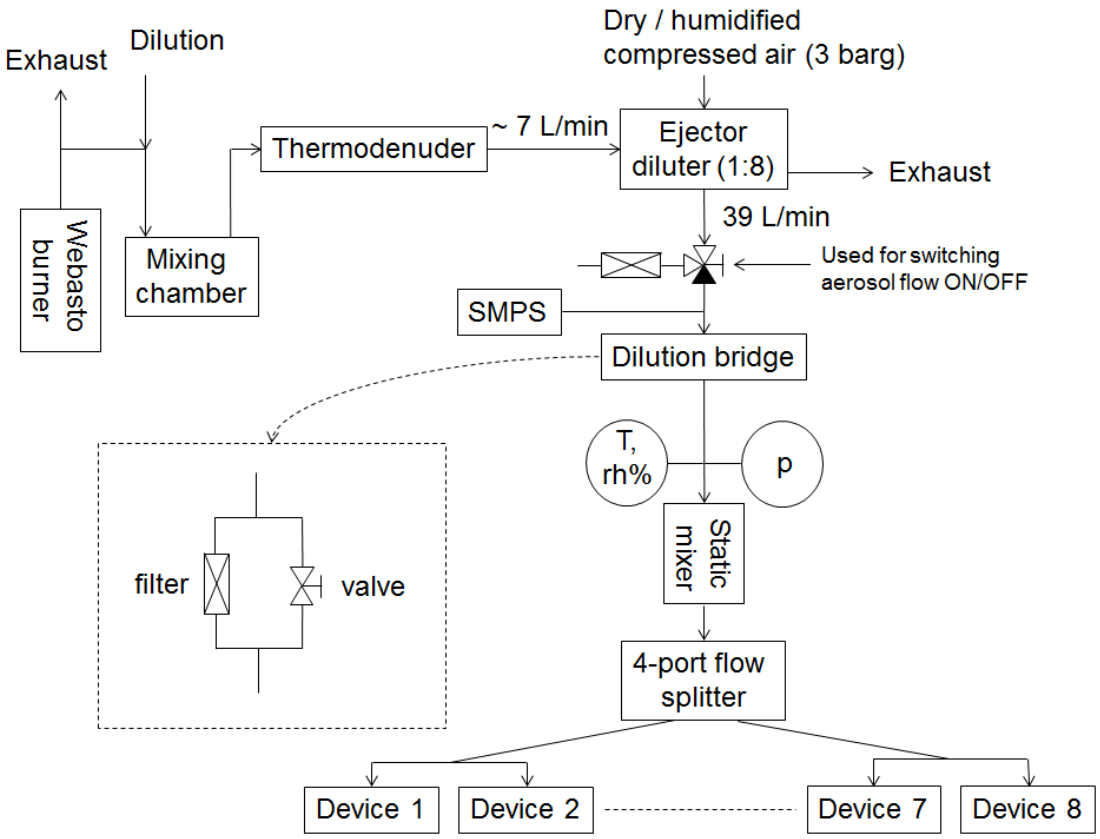

Figure 3: Experimental setup used for evaluating performance of particle measuring instruments at MIKES.

3.3.2 Measurement procedure at MIKES

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 6.

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 and 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 6: Measurement points during the campaign at MIKES.

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[a]	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

Efficiency of instruments is another important parameter to evaluate. Efficiency is defined as the interrelation between the particle concentration (cm^{-3} or $\mu g/cm^{-3}$) displayed by the instrument and the particle concentration of the reference instrument (number: CPC, mass: gravimetry). The efficiency of the instruments was studied by measuring the particle size response of the instruments 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 accurately 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 DC2, DC1 and IC, 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} and 100 nm, respectively. The humidity content of the aerosol was adjusted by humidifying the dilution air. The humidification was done using a bubbler saturator and two metering valves in such a way that the fraction of the flow that entered the bubbler practically reached water vapour saturation state (rh=100%) and was then 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.

Unfortunately, results from the L2 instruments are not shown for data collected at MIKES because the results were found invalid due to incorrect usage of the device.

4 Results

A variety of tests were performed at the three different European NMIs. Therefore the presentation will started with an overview over the measurements sorted by the measurement parameter – opacity, particle mass concentration and particle number concentration (Section 4.1) and then dived into the more detailed properties of the candidate instruments starting with linearity (Section 4.2), followed by the size response (Section 4.3), and the instruments ability to record small particles sizes (Section 4.4). The candidate instruments were also evaluated with regard to their response to volatile particles (Section 4.5) and their response time (Section 4.7). Moreover, the comparability between the laboratories was investigated (Section 4.6).

One task of this deliverable was to evaluate the instruments for periodic emission control. Here, only the results will be presented and discussed corresponding to particle properties in modern diesel exhaust, namely < 10 mg/m^{-3} and < 0.2 m^{-1}. Additional data that were collected are given for the interested reader in the appendix without any discussion.

4.1 Data overview (PTB, METAS, MIKES)

As first parameter has to be analyzed the traditional parameter used for emission control testing: **opacity**.

As already mentioned in the introduction, modern diesel vehicle currently emit very low opacity values. Therefore, only the light scattering instruments are still record this parameter, which is tested by PTB (Figure 4). PTB is the only NMI during the round robin comparison, which is still using a traceable infrastructure for the validation of candidate instruments according to verification ordinance 18-9.

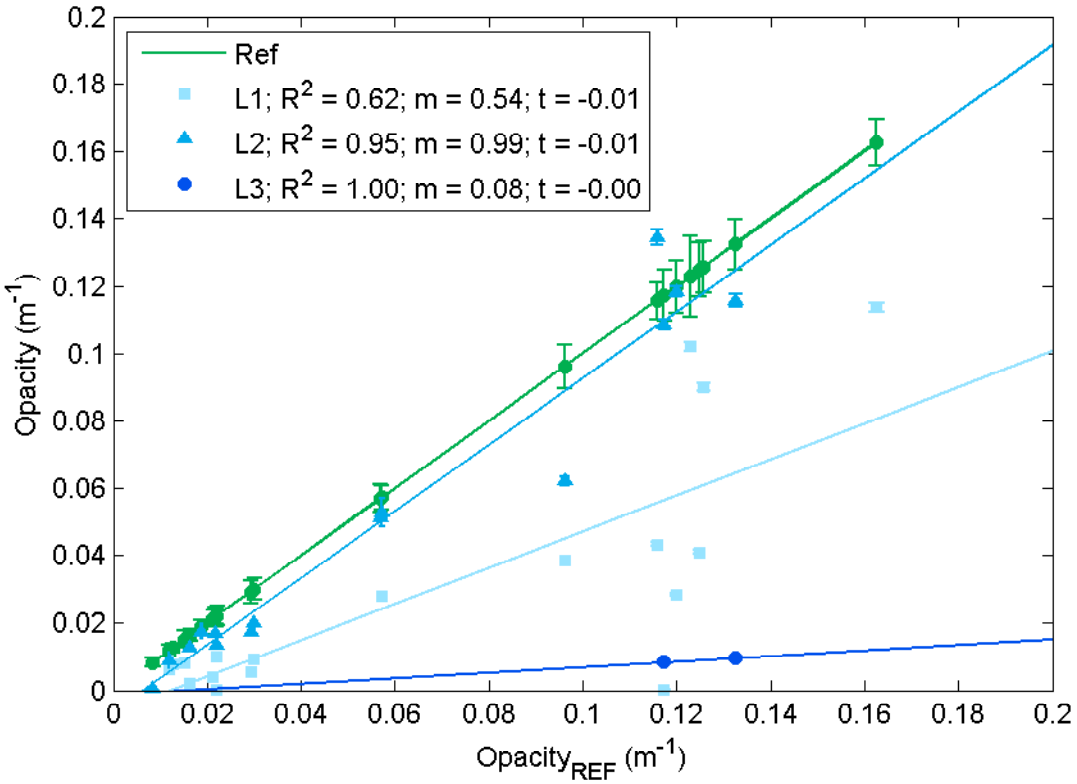

Figure 4: Summary of PTB opacity measurements for the light scattering instruments including a linear fit (y=mx+t) and coefficient of determination for the expected range of exhaust of modern diesel vehicles (k < 0.2 m^{-1}). For the devices under test, the error bars denote the standard deviation.

Only one candidate instrument (L2) was able to reproduce the reference value in this opacity range, however most values were slightly too low. For L1 and L3 the opacity values were considerable too low.

As second parameter the **particle mass concentration** will be discussed here. It is also the only metric which was recorded[3] by all candidate instruments and assessed at PTB (Figure 5), METAS (Figure 6) and MIKES (Figure 7).

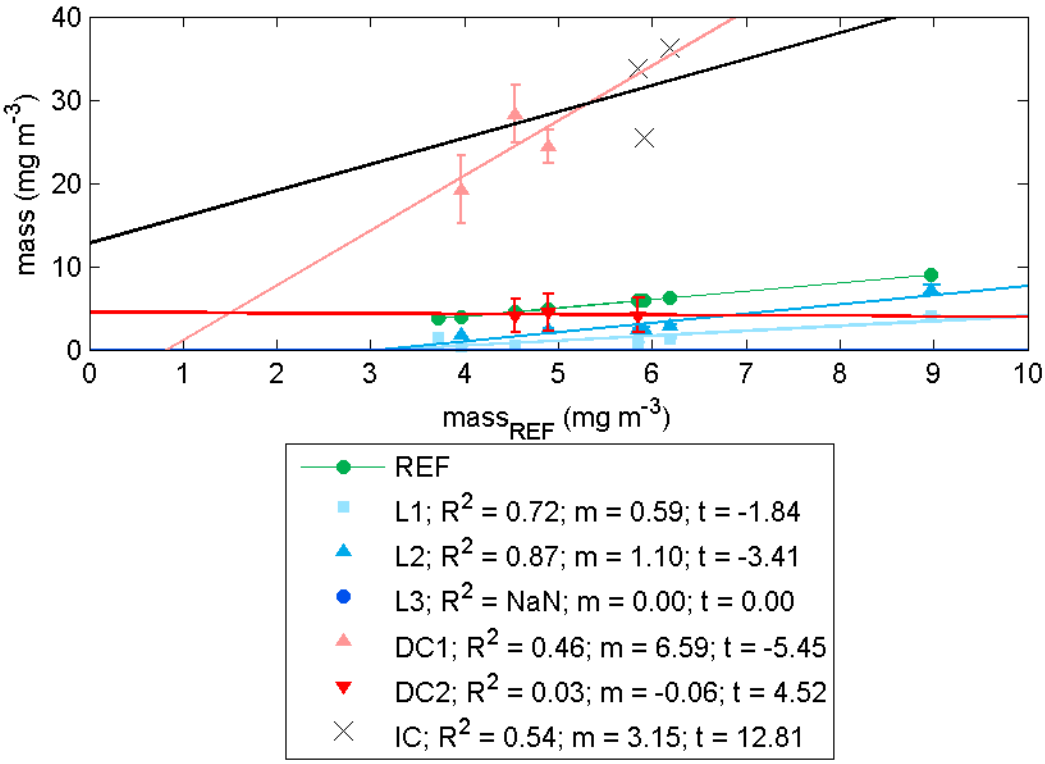

Figure 5: Summary of PTB mass concentration measurements for all candidate instruments only displayed for particle mass concentrations relevant for modern diesel vehicles (< 10 mg/m³). Error bars of the devices under test (except for IC) represent standard deviations. Linear fits (y=mx+t) are displayed as well, together with the coefficient of determination.

The largest mass concentration range was covered by PTB (see Section 3.1.2 and Appendix). However, only the range comparable to modern diesel exhaust emissions will be discussed here. The instrument that reproduced the reference value at PTB in the best way was DC2. While L1 and L2 measured too low values, L3 did not record any data at all. Both IC and DC1 measured too high values. Consequently, it appears that the principle of light scattering reaches its limits at these concentrations, because all instruments differed in the same direction from the reference values. Contrastly, the DC instruments have the potential to reproduce the reference value, because DC2 was realtivley close to the reference values.

While PTB measured in a rather wide mass concentration range (≈4 to 400 mg/m³), METAS and MIKES collected data at lower particle mass concentration (below ≈2 mg/m³). Note that the measurement ranges for PTB did not overlapp with the one from METAS and MIKES (see Table 3).

With only 5 measurement points per instrument, the coefficients of determination for the measurements at METAS are rather high as expected (see Figure 6). While the DC instruments and the IC measured too high values for most of the measurement points in comparison to the reference, L3 measured too low values. This compares partly to the measurements performed at PTB (Figure 5). Although the mass concentrations at METAS were even lower than at PTB, L3 did record some values. So apparently the L3 sensor works at these low mass concentrations but not reliably. The linear regressions for L1 and L2 seems to indicate that the instruments agreed well with the reference. However, a more detailed look at the data as presented in the following sections reveals a

[3] IC did not directly measure particle mass concentration, but particle mass concentration could be determined from total particle length according to Litton et al. (2004). Details are given in Section 2.

different picture. It needs to be mentioned that DC2 aligned very well with the reference below 500 µg/m^3.

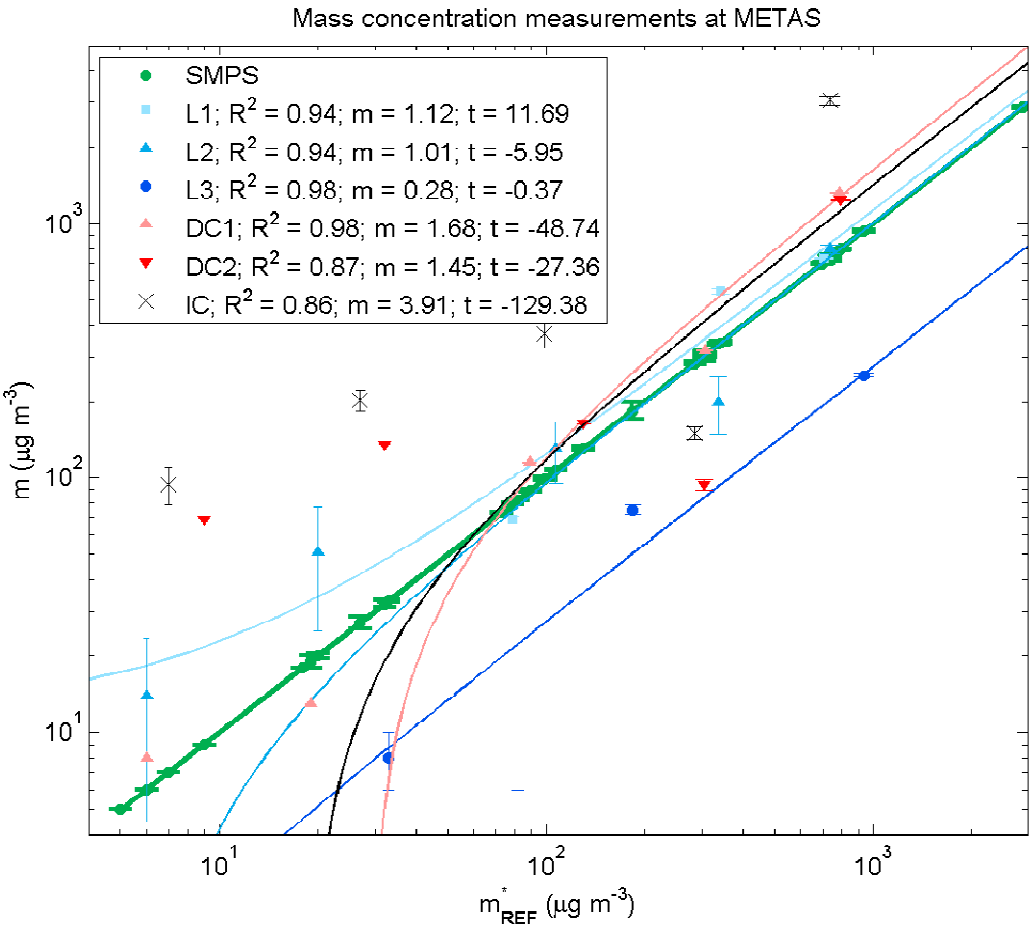

Figure 6: Summary of mass concentration measurements at METAS including coefficient of determination and coefficients for a linear fit (y=mx+t). Note that m_{REF} at METAS was not a gravimetric measurement, mass values were deduced from SMPS measurements (for details on the calculations see Section 3.2.2). Note that values are displayed on a log-log-scale.*

MIKES measured in the same particle mass concentration range as METAS (Figure 6 & Figure 7). However, the chosen reference at MIKES was a gravimetrical one, which is supposed to be more precise. Interestingly, the results from MIKES show a similar picture as at PTB, but at lower particle mass concentrations. L1 measured too low values compared to the reference; the 3 higher values from DC1 were too high and from DC2 too low as compared to the reference. For the smallest measured mass value, this behavior changed for the DC instruments. Moreover, the L3 also got very close to the reference value for the lowest concentration. This is remarkable, as L3 did not record at all the lower values at PTB and was far below the reference at METAS. A more detailed analysis as presented in the following sections is needed to judge their performance.

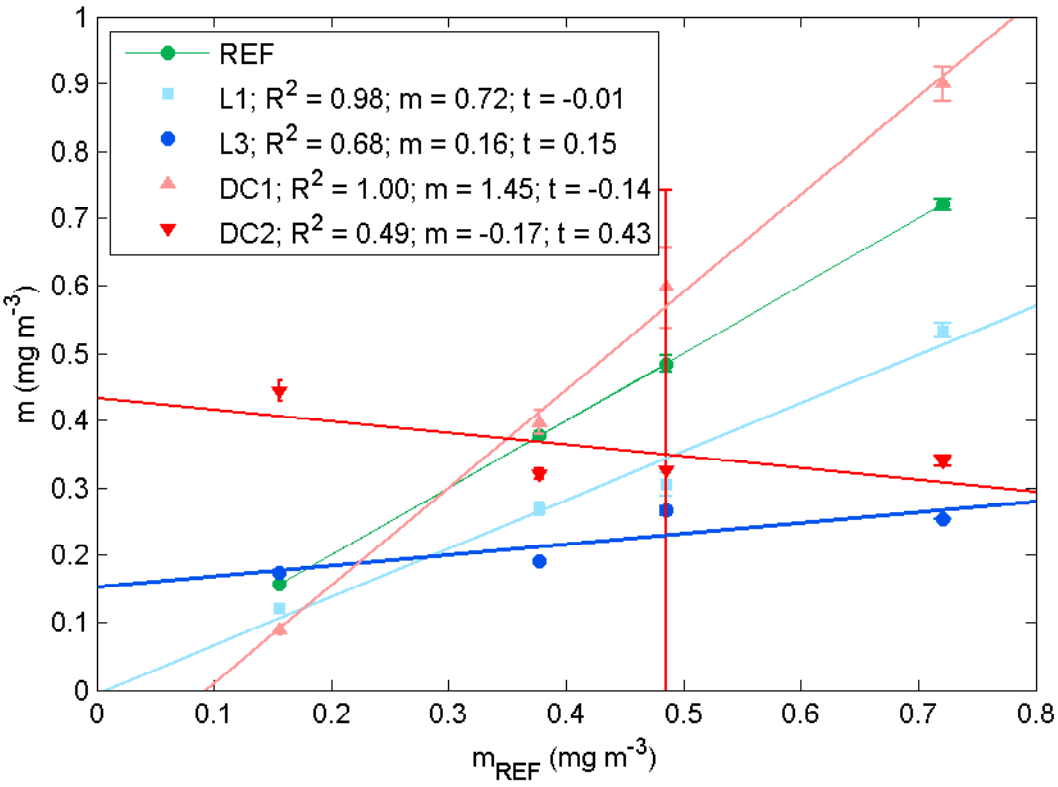

Figure 7: Particle mass concentration measurements performed at MIKES, the error bars denote standard deviations, Linear fits (y=mx+t) and coefficients of determination are given as well. For IC particle mass was not calculated at MIKES.

Particle number concentration is a particle metric which is commonly used in climate science and which has gathered more and more attention both in health studies and in emission studies. It has been introduced as an appropriate emission metric in Euro 5b for diesel vehicles, in Euro 6 for gasoline engines and in Euro VI for trucks and buses. Moreover, this metric has been chosen as the most appropriate one for periodic emission control of building machinery in Switzerland. Both METAS (Figure 8) and MIKES (Figure 9) assessed the particle counting performance of the candidate instruments as this metric is a promising one for future emission control. Both NMIs chose similar particle sizes and concentrations, such that the overall results were comparable. At both NMIs the instrument that was the best comparable to the reference is DC1 with very good values close to $4 \cdot 10^5$ cm^{-3} and slightly higher values for large particle concentrations ($\approx 10^6$ cm^{-3}). DC2 obviously had some problems at MIKES (Figure 9). The recorded values at concentrations around 10^5 cm^{-3} scatter a lot, but were higher compared to the reference. The only value measured at larger concentrations ($\approx 10^6$ cm^{-3}) was smaller than the reference. This differs from the values recorded at METAS (Figure 8), where the value at $\approx 10^6$ cm^{-3} was higher than the reference. While the IC data recorded at METAS scatter a lot, a trend for the IC data gathered at MIKES can be observed. Although the measured values were in summary around 3 times higher than the reference, the coefficient of correlation was

rather high (Figure 9). A detailed analysis of the measured data in the following sections, will help to understand the reasons for the observed features.

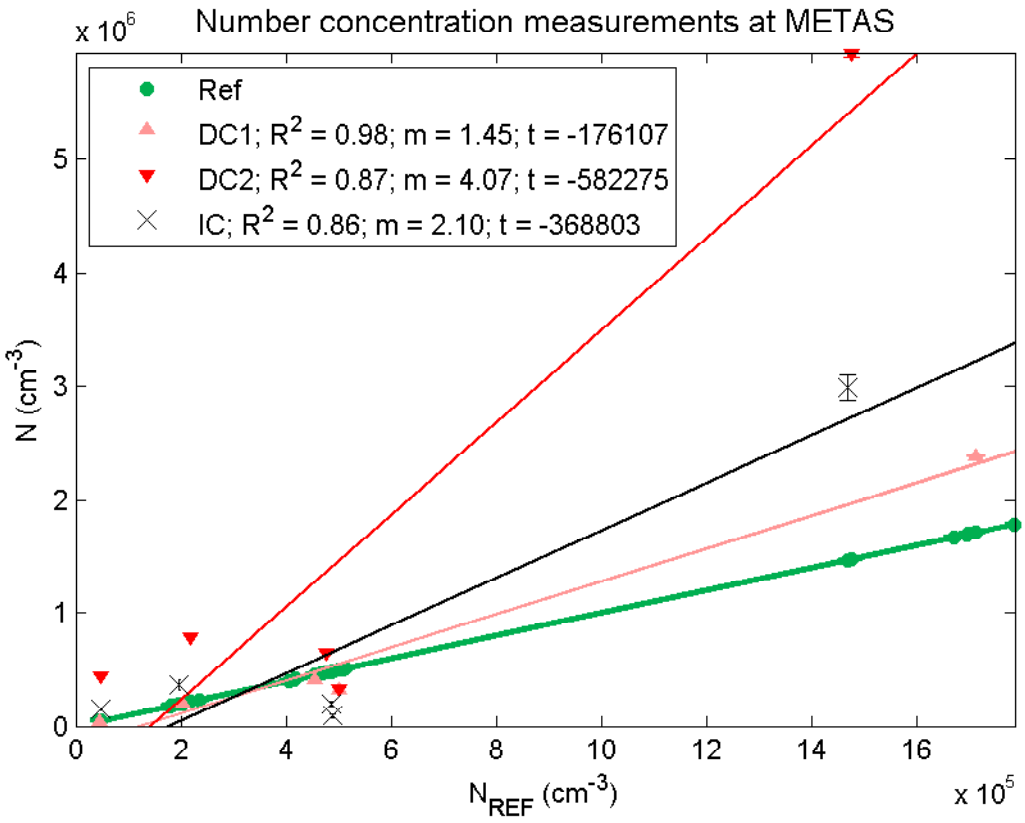

Figure 8: Summary of METAS number concentration measurements for those candidate instruments recording particle number concentration (Table 2) including coefficient of determination and coefficients for a linear fit (y=mx+t).

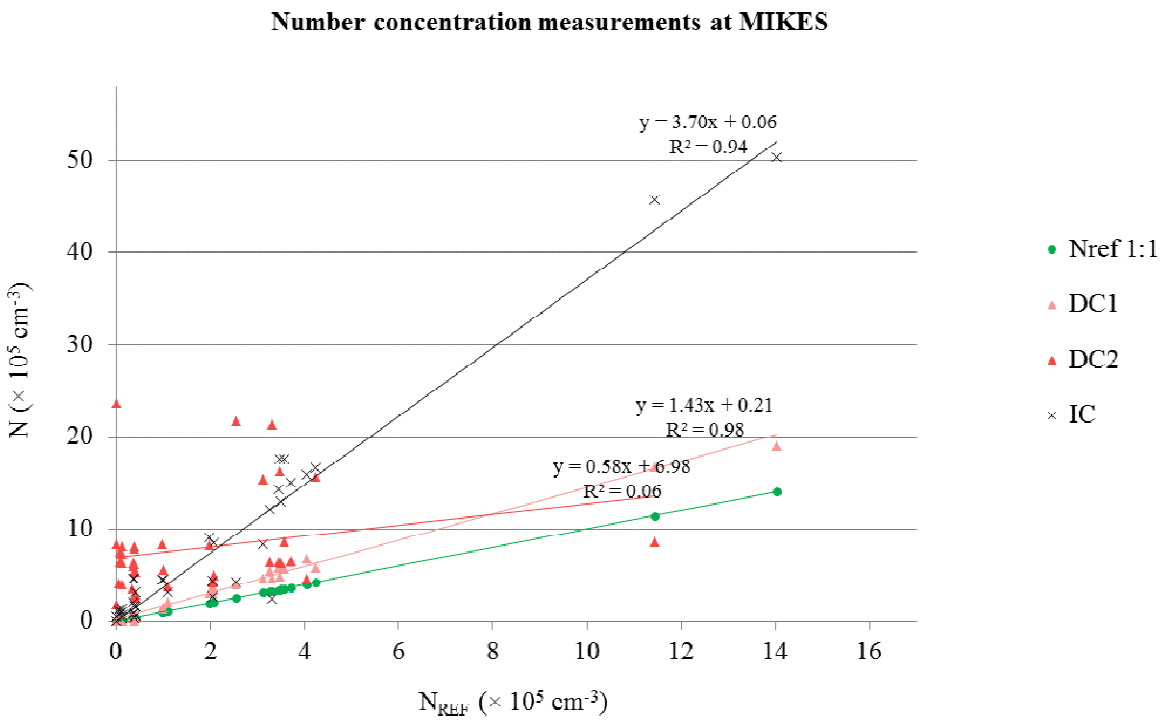

Figure 9: Summary of MIKES number concentration measurements for those candidate instruments recording particle number concentration (Table 2) including coefficient of determination and a linear fit.

4.2 Linearity measurements (PTB, METAS, MIKES)

Linearity over the full measurement range of the instrument is a major need for a reliable measurement device. Linearity for opacity was tested at PTB using CAST aerosol at 160 nm. As the opacity values used for this linearity test are much higher than the ones that can be expected for modern diesel vehicles. These results will be discussed and presented in the Appendix. Moreover, linearity for number concentration was tested using diesel soot at MIKES (Section 4.2.1) for several particle sizes and using CAST aerosol with a mobility diameter of 80 nm at METAS (Section 4.2.2).

4.2.1 Linearity measurements for number concentrations using diesel soot (MIKES)

Results of the linearity tests performed with soot particles at 40 nm are shown in Figure 10 and Figure 11. Both light scattering instruments[4] appeared insensitive towards 40 nm particles as the instruments response to this particle size was similar to their response to particle free air (zero concentration). The DC2 sensor showed a negative correlation towards increasing particle concentrations. Moreover, the measured particle concentration was one order of magnitude higher than the CPC readings. This odd behaviour might be caused by malfunction of the instrument. It might be possible that the sensor got contaminated during earlier laboratory measurements in another campaign. The IC and DC1 instrument were the only instruments sensitive towards small 40 nm particles. The IC gives an increasing response for increasing particle concentrations above $4 \cdot 10^4$ cm^{-3}. For concentrations below this, the signal was dominated by noise that the response can't be distinguished from the zero concentration response. The DC1 instrument gave 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 10). However, the response was nonlinear especially at concentrations below 10^4 cm^{-3} (Figure 11).

[4] As mentioned in section 3.3.2 L2 data could not been evaluated for MIKES as the instrument was not used correctly.

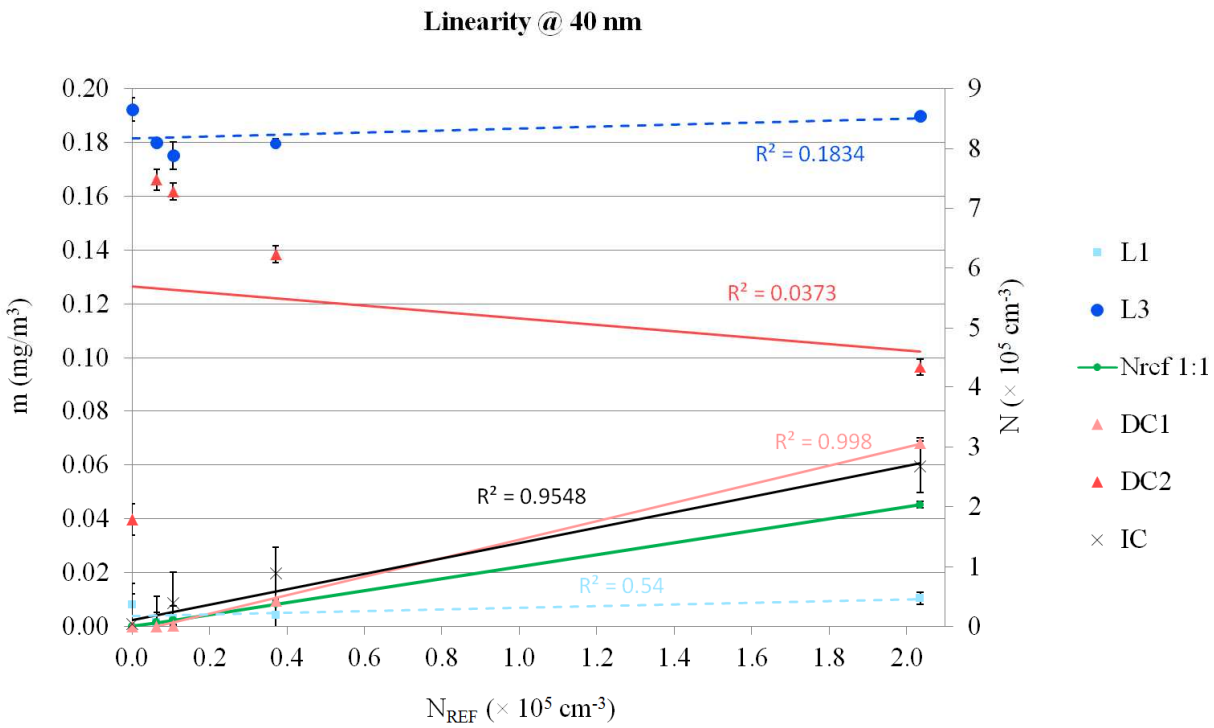

Figure 10: Linearity of candidate instruments for soot particles at 40 nm. Light scattering instruments (L1 and L3) measuring only mass concentration are plotted against the left y-axis (dashed line) and the electrical sensors (DC1, DC2 and ionization chamber) are plotted against the right y axis. Standard deviations are shown as error bars. The goodness of linear fit is shown as R^2.

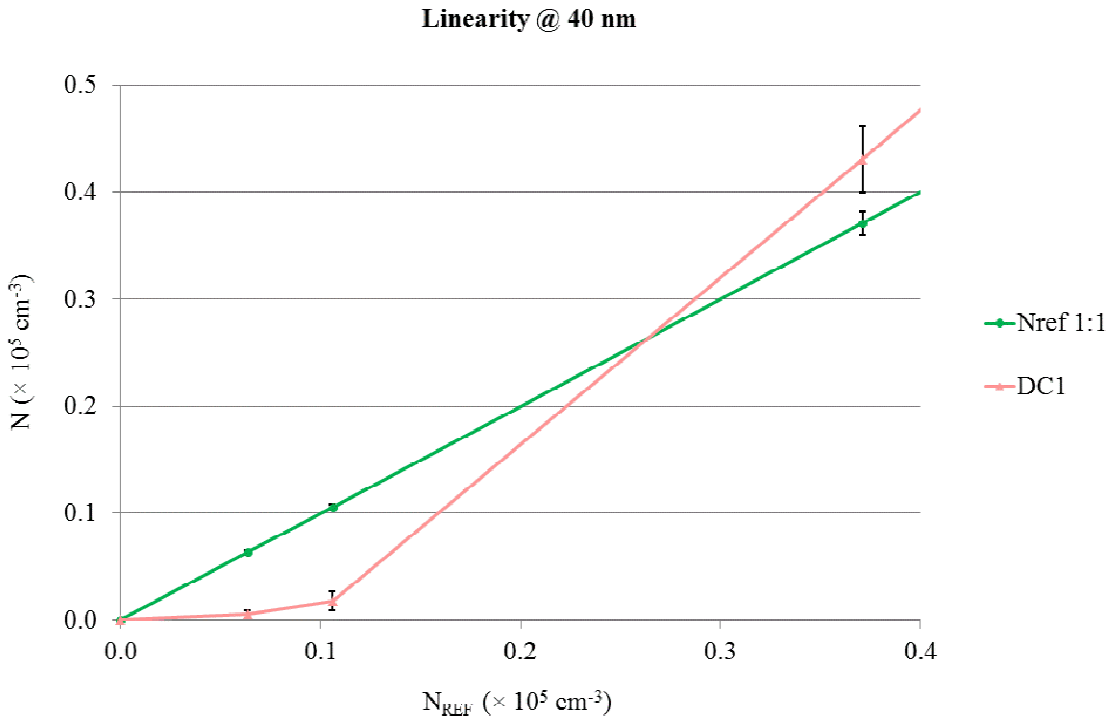

Figure 11: Linearity of DC1 instrument for soot particles at 40 nm and concentrations below $4 \cdot 10^4$ cm^{-3}. Standard deviations are shown as error bars. This figure is a detail of Figure 10.

Linearity measurements performed at 60 nm are shown in Figure 12 and Figure 13. The L3 instrument did not respond to particles of this size similar as for the 40 nm particles as the recorded mass did not differ from the value of particle free air. However, the L1 started to detect particles at concentrations around $2 \cdot 10^5$ cm^{-3}. As with the 40 nm particles, the DC2 sensors response is inconsistent. This suggests that there was some sort of instrument failure at MIKES. For the instruments showing a response to this particle size (Figure 13), the DC1 instrument was the only one showing good linearity (R^2 = 0.99) and an ability to measure particles at concentrations down to $6 \cdot 10^3$

cm^{-3} at 60 nm. The IC response at concentrations of $4 \cdot 10^4$ cm^{-3} and below was dominated by noise and thus cannot be distinguished from the zero concentration response. This is a similar behaviour as observed for particles at 40 nm.

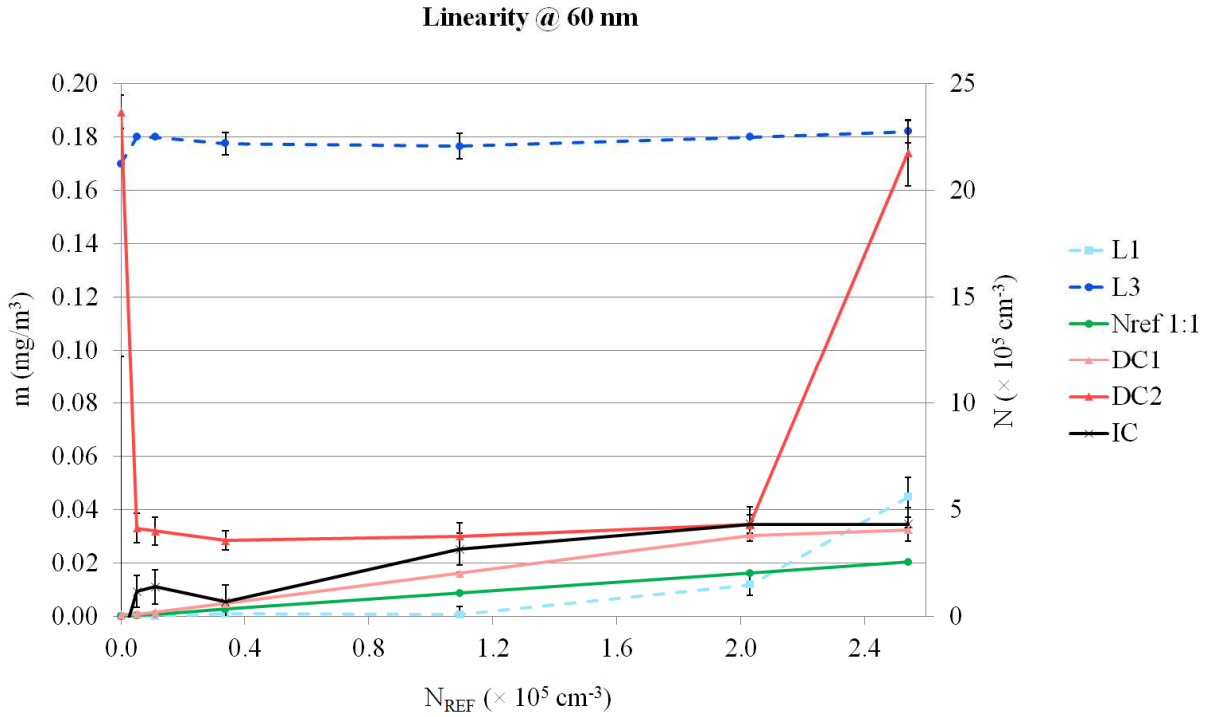

Figure 12: Linearity of candidate instruments for soot particles at 60 nm. Light scattering instruments (L1 and L3, dashed line) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (DC1 and DC2) are plotted against the right y axis. Standard deviations are shown as error bars.

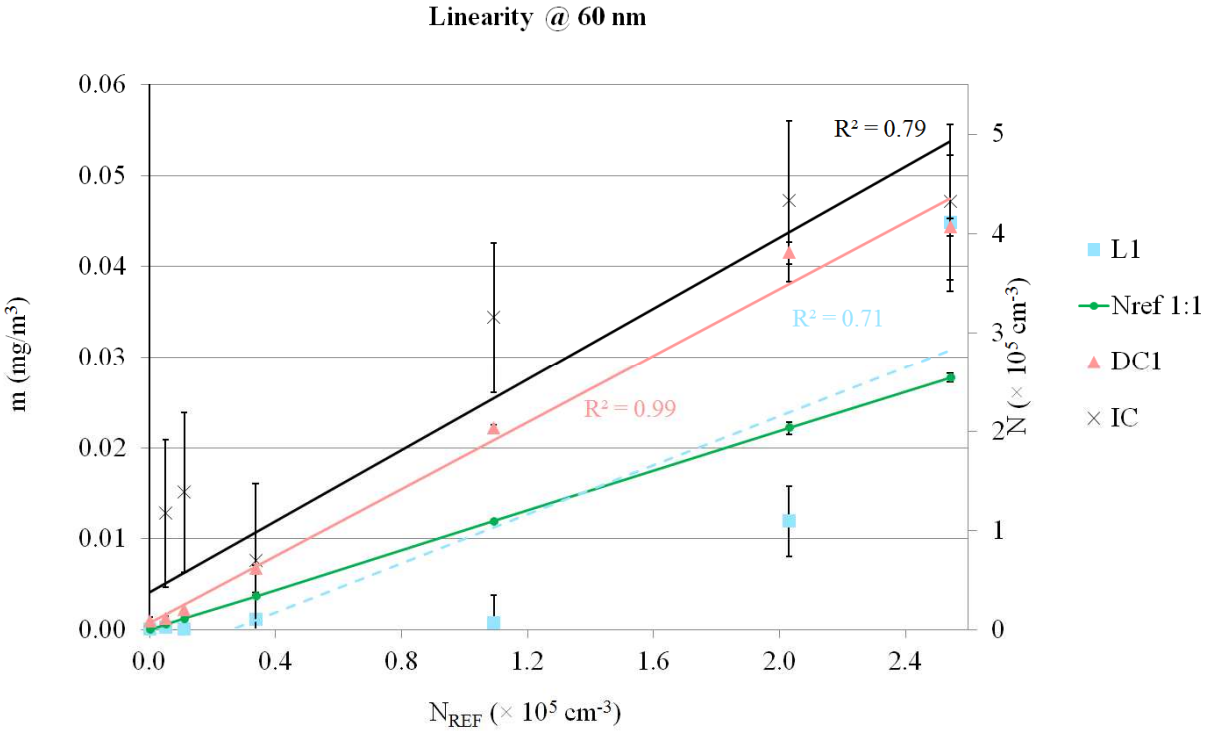

Figure 13: Linearity of candidate instruments responding to soot particles at 60 nm. L1 mass concentration is plotted against the left y-axis (dashed line) and the DC1 and IC number concentrations are plotted against the right y-axis. Standard deviations are shown as error bars. The goodness of linear fit is shown as R^2. This figure is a detail of Figure 12.

Similar measurements performed with particles at 100 nm showed that light scattering instruments were able to detect particles at these particle sizes (Figure 14 and Figure 15). So we assume that the light scattering instruments started to detect particle sizes somewhere between 60 nm and 100 nm. Similar to the 60 nm particles the L3 instrument seemed less sensitive than the L1 instrument due to the smaller slope. However, as no mass reference was measured over the whole size range the exact slope for particle mass is unknown. At particle concentrations of 10^5 cm^{-3} and below, the response of the L3 instrument was nonlinear (Figure 14).

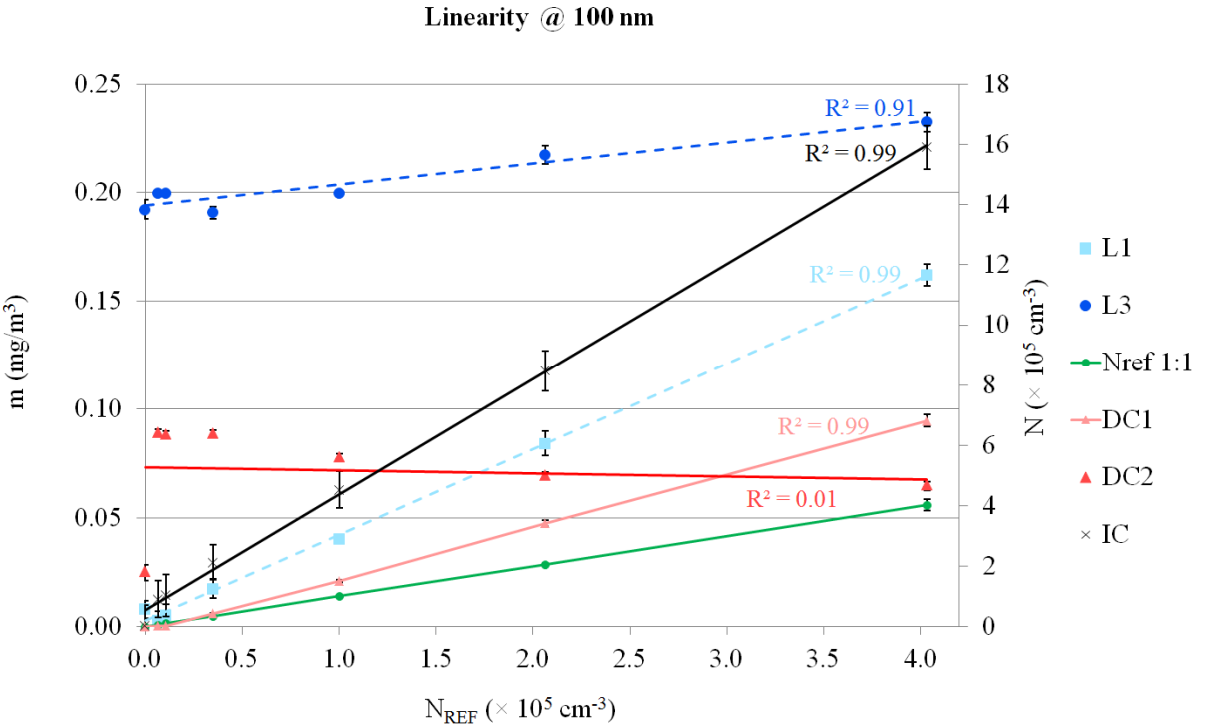

Figure 14: Linearity of candidate instruments for soot particles at 100 nm. Light scattering instruments (L1 and L3 dashed line) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (DC1 and DC2) are plotted against the right y axis. Standard deviations are shown as error bars. The goodness of linear fit is shown as R^2.

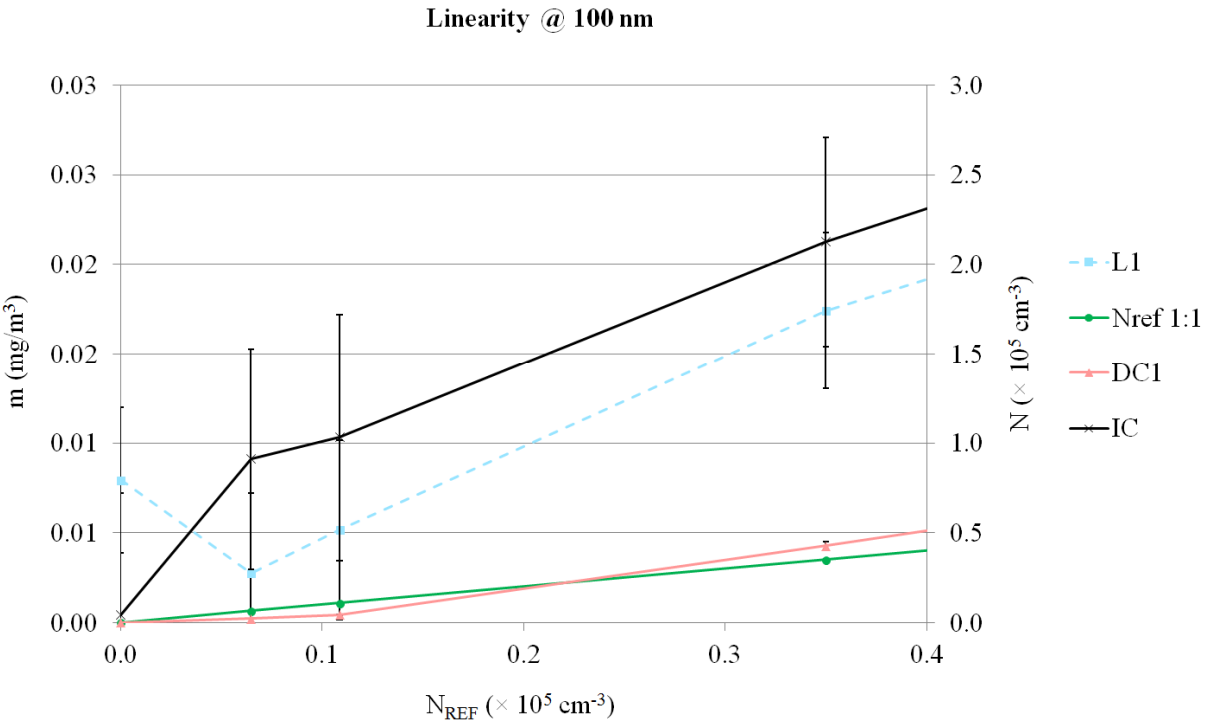

Figure 15: Linearity of candidate instruments responding to soot particles at 100 nm with concentrations below $4{\cdot}10^4$ cm^{-3}. L1 mass concentration is plotted against the left y-axis and the DC1 and IC number concentrations

are plotted against the right y-axis. Standard deviations are shown as error bars. This figure is a detail of Figure 14.

On the other hand, the L1 instrument showed a good linearity (R^2 = 0.99) down to concentration of $4 \cdot 10^4$ cm^{-3}. At concentrations below this, the L1 response could not be distinguished from the zero concentration response (Figure 15). The DC2 sensor showed a similar negative correlation towards increasing particle concentrations as seen for particles at 40 nm. This supports further the hypothesis that something was wrong with the DC2 sensor. The DC1 instrument performed as best. It had the best linearity (R^2 = 0.99) and it was able to measure reliably particles at low concentrations of $6 \cdot 10^3$ cm^{-3} (Figure 15). However, at these low concentrations the response was not linear similarly to the linearity measurements at 40 nm and 60 nm in particle size. The IC was also very linear (R^2 = 0.99), but the noise became more significant at concentrations of 10^4 cm^{-3} limiting the sensitivity at this concentration range.

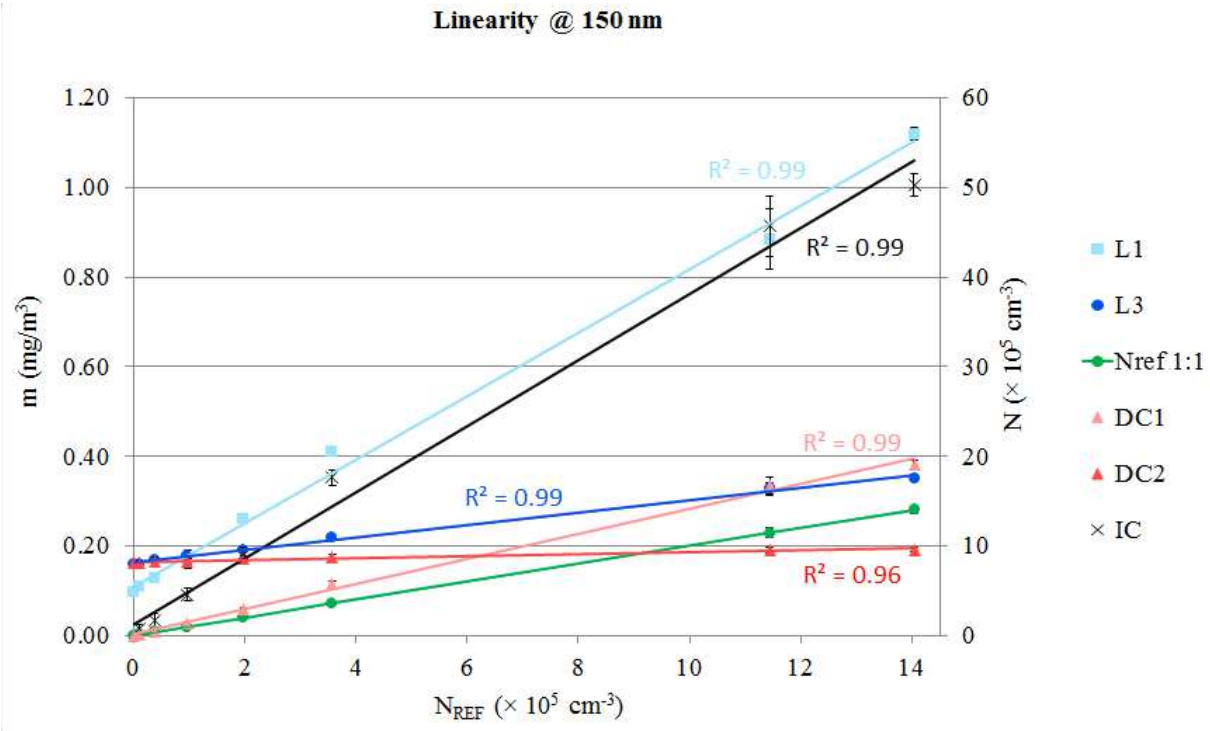

Figure 16: Linearity of candidate instruments for soot particles at 150 nm. Light scattering instruments (L1 and L3 dashed line) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (DC1 and DC2) are plotted against the right y-axis. Standard deviations are shown as error bars. The goodness of linear fit is shown as R^2.

Linearity measurements were also performed at 150 nm particle size (Figure 16 and Figure 17). Both the light scattering instruments and the DC1 and IC instrument had a linear response to increasing particle concentrations. As seen also with smaller particles, the L1 instrument was more sensitive to concentration changes than the L3 instrument. The L1 instrument had a linear response for particles at 150 nm down to concentration at 10^4 cm^{-3} while the L3 was linear only down to concentration of $4 \cdot 10^4$ cm^{-3}. Moreover, the slope was steeper for the L1 instrument. Again the DC1 instrument showed the best linearity (R^2 = 0.99) over the whole studied particle concentration range from 10^4 cm^{-3} to $1.4 \cdot 10^6$ cm^{-3}. Also, was found a very linear coefficient of R^2 = 0.99 for the IC instrument, but the response at small concentrations of 10^4 cm^{-3} was noisy which was also seen in previous linearity measurements.

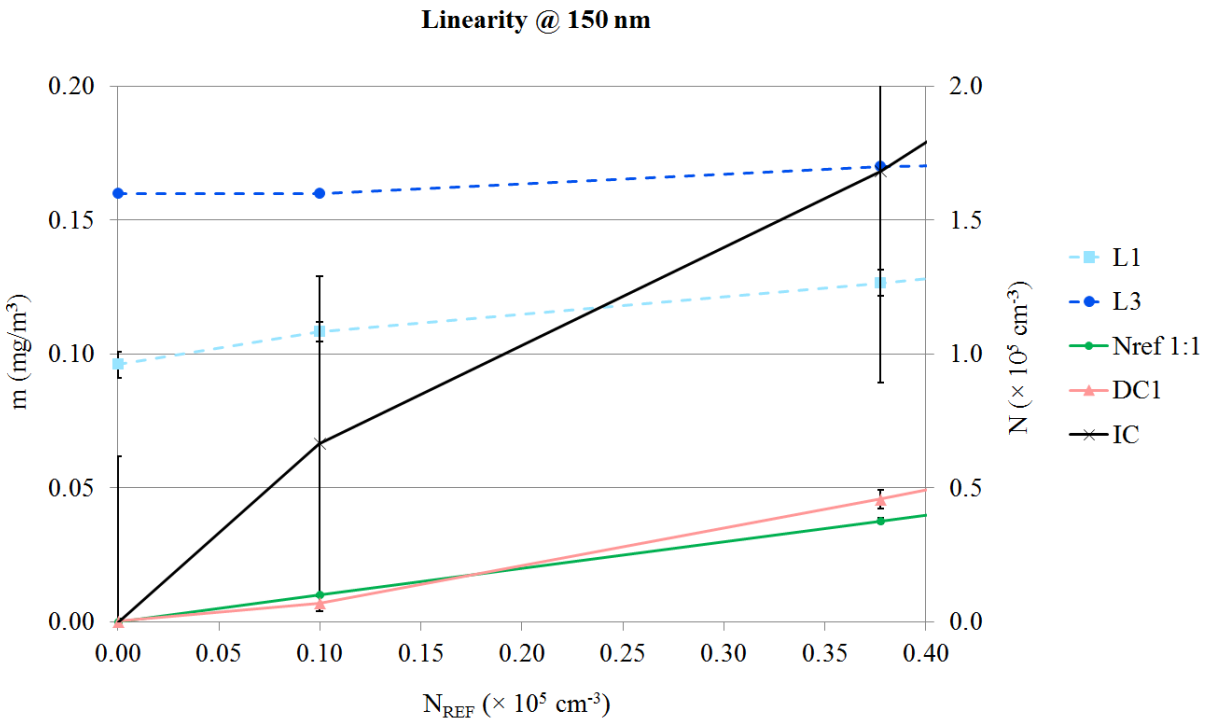

Figure 17: Linearity of candidate instruments responding to soot particles at 150 nm with concentrations below $4 \cdot 10^4$ cm^{-3}. L1 mass concentration is plotted against the left y-axis and the DC1 and IC number concentrations are plotted against the right y-axis. Standard deviations are shown as error bars. This figure is a detail of Figure 16.

4.2.2 Linearity measurements for number concentrations using CAST @ 80 nm (METAS)

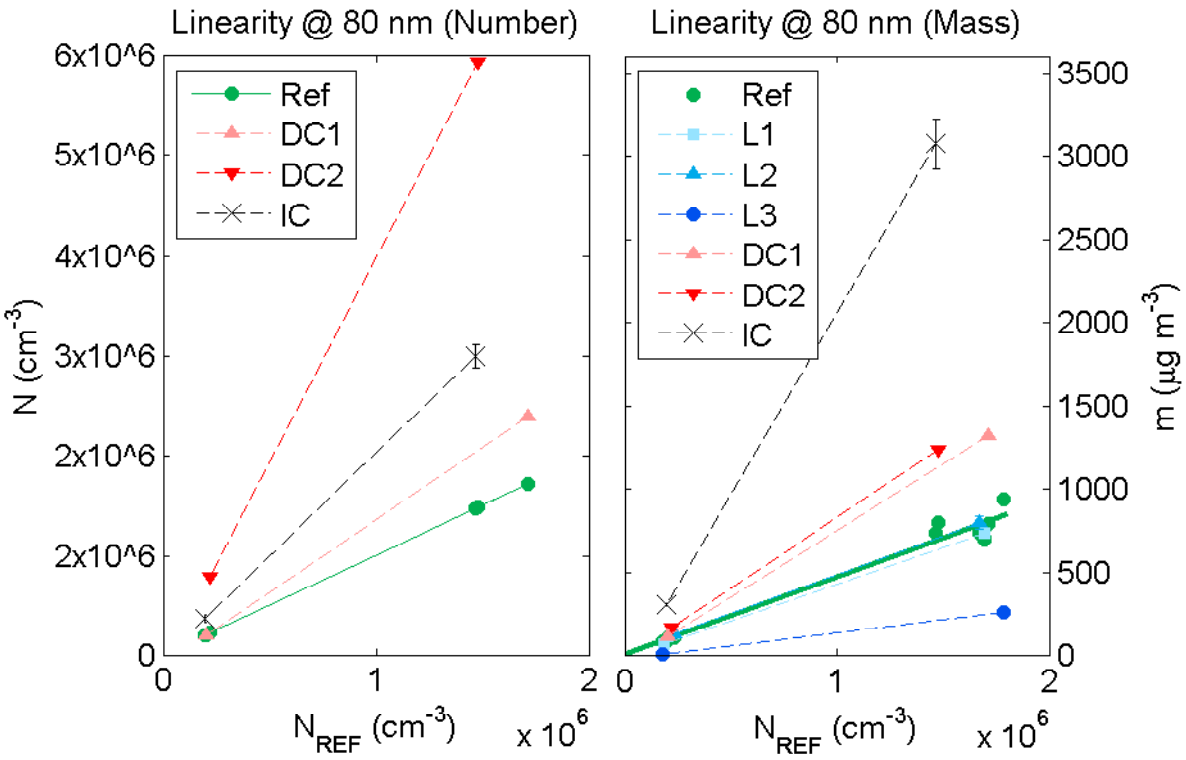

Figure 18: Linearity measurements at 80 nm performed at METAS using CAST aerosol. For the devices under test, standard deviations are shown as error bars. For the reference instrument extended uncertainties are shown for the number concentration and reduced uncertainties for mass concentration.

As the measurements at METAS followed the measurement procedure of the SR 941.242, linearity concerning particle number concentration was only measured at 80 nm. As a reference the CPC was used. Linearity is shown for number concentration for those instruments recording number concentration (Figure 18, left) as well as for mass concentration (Figure 18, right). Both for mass and number concentration, the DC and IC instrument measured higher concentrations than the reference, with DC1 showing a good response at least for the lower concentrations. Moreover, the counting efficiency increased for higher number concentrations, as the slopes increased. Concerning the light scattering instruments, L1 and L2 nearly perfectly aligned with the behaviour of the reference at 80 nm, while the L3 obviously had some problems, as it was the only instrument measuring less than the reference. This is in accordance with the linearity measurements performed at MIKES. So while L1 and L2 seems to be sensitive for particle sizes larger than at least 80 nm and at a particle number concentrations larger than $1 \cdot 10^5$ cm^{-3}, L3 is still insensitive to 80 nm particles and only starts counting at sizes larger than 100 nm.

4.3 Size response (MIKES, METAS)

4.3.1 Size response at constant number concentration using diesel soot (MIKES)

Results from size dependant response of the candidate instruments at particle concentrations of $4 \cdot 10^5$ cm^{-3} are shown in Figure 19.

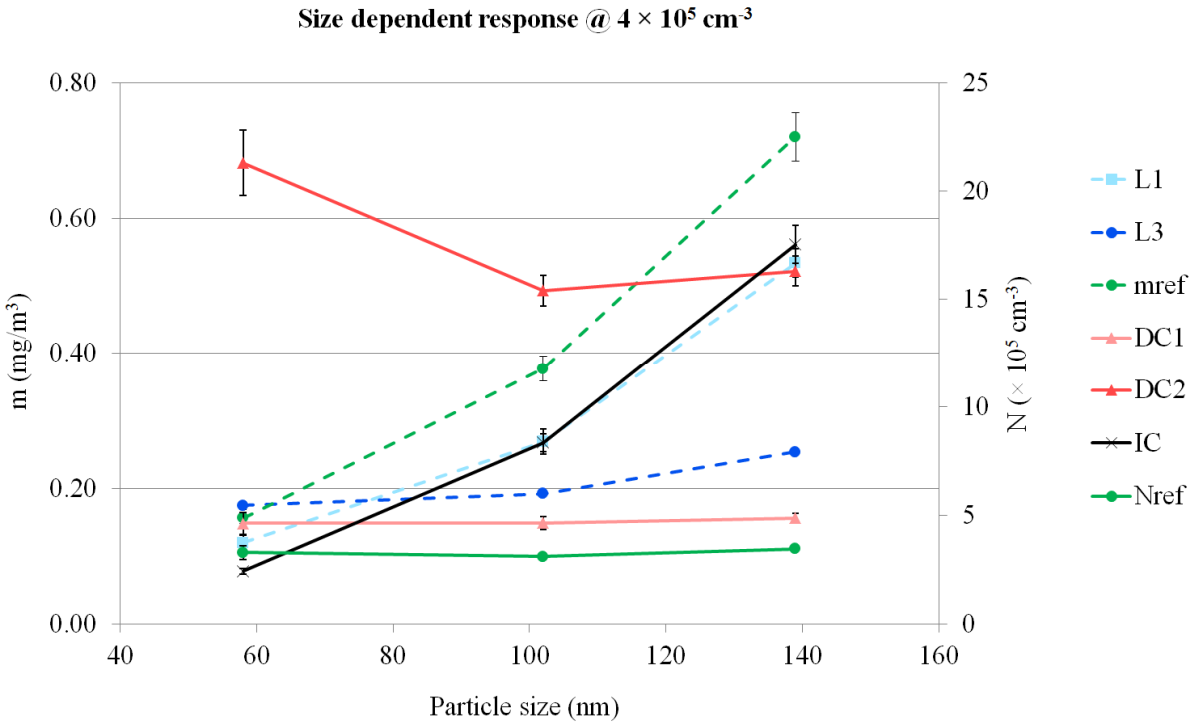

Figure 19: Particle size dependent response at particle concentrations of $4 \cdot 10^5$ cm^{-3} measured at MIKES using diesel soot. Light scattering instruments (L1 and L3) measuring only mass concentration and the gravimetric mass reference m_{ref} are plotted against the left y-axis (depicted as dashed lines). The electrical sensors (DC1 and DC2), IC and particle number reference N_{ref} are plotted against the right y-axis (depicted as solid lines). Standard deviations are shown as error bars.

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 L1 results correlate 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. This trend corresponds as well with the measurements at PTB where L1 was found to measure smaller values than the gravimetric reference (Figure 5). On the other hand the L3 instrument showed a size dependant response when it compared to the gravimetric results. The L3 results seem to correlate better with the particle number concentration determined with the CPC, although it should be measuring the particle mass concentration. The DC1 response was 40% – 50% higher than the reference value (CPC value). However, this offset did not depend on particle size. The results of the IC instrument correlated better with mass than number concentration. This is expected as the IC measures particle length concentration, which changes when the particle size distribution changes and this was the case for these measurements.

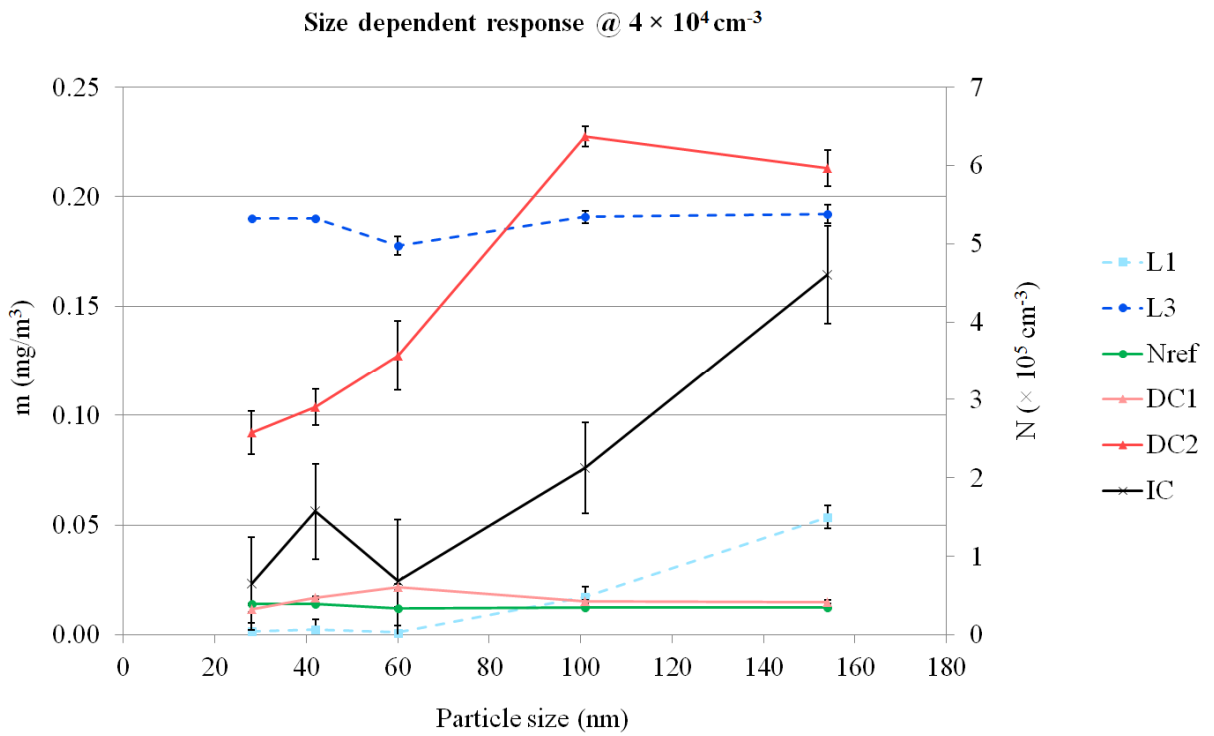

Figure 20: Particle size dependent response at particle concentrations of 4·10^4 cm^{-3}. Light scattering instruments (L1 and L3, dashed lines) measuring only mass concentration are plotted against the left y-axis and the electrical sensors (DC1 and DC2), IC and N_{ref} are plotted against the right y-axis. Standard deviations are shown as error bars.

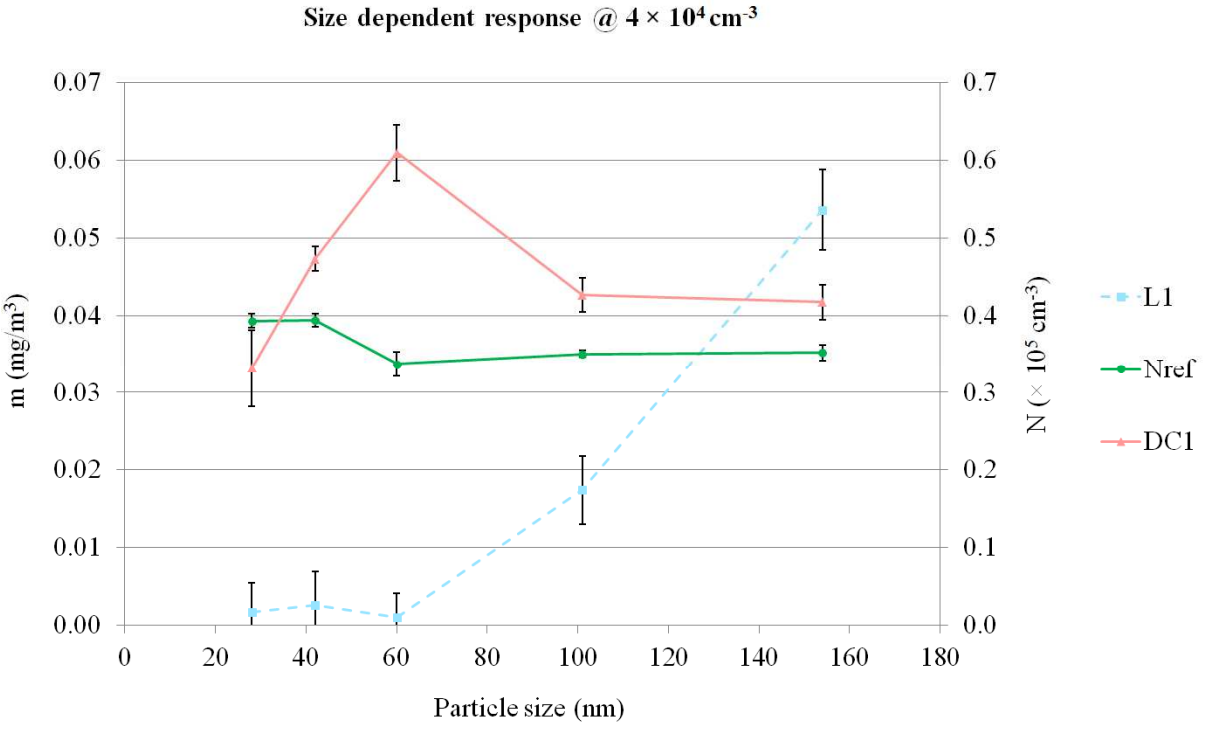

Figure 21: Particle size dependent response at particle concentrations of 4·10^4 cm^{-3}. L1 instrument measuring mass concentration is plotted against the left y-axis and the DC1 instrument and N_{ref} is plotted against the right y-axis. Standard deviations are shown as error bars. This figure is a detail of Figure 20.

The size dependant response was also measured at particle concentrations of 4·10^4 cm^{-3} (Figure 20 and Figure 21). At this low particle concentration the gravimetric measurements could not be performed accurately because the sampled mass would have been too small for accurate weighting. The L3 results were not reliable as it has been shown that the L3 instrument was not sensitive

towards particle concentrations of $4 \cdot 10^4$ cm^{-3} (see Section 4.2 and figures therein). Also the L1 instrument lacks sensitivity for detecting these low concentrations. Only at 150 nm, the instrument gave a measurable response. The IC instrument showed similar behaviour as for the size dependant measurements at high concentrations (Figure 19), i.e. the particle number response increases towards larger particle sizes. At low concentrations of $4 \cdot 10^4$ cm^{-3} the DC1 instrument performed well at particle sizes above 100 nm and the response is 20% higher than the CPC value. At sub 100 nm particle sizes the response was found slightly size dependant.
For both concentrations the DC2 behaviour was odd similar to the linearity measurements. Instrument failure due to pollution might be the reason explaining this behaviour.

4.3.2 Size response using CAST aerosol (METAS)

Due to the measurement setup used at METAS for the production of the CAST aerosol (Figure 2) combustion particles at 200 nm could not be produced at similar high concentrations as the particles below 200 nm ($4 \cdot 10^4$ cm^{-3} instead of 10^5 cm^{-3}). It is therefore difficult to say whether the detection efficiency for 200 nm differs from the smaller particles due to the size or due to the smaller concentration (Figure 22). The results for the small particles (< 100 nm) are discussed in Section 4.4.

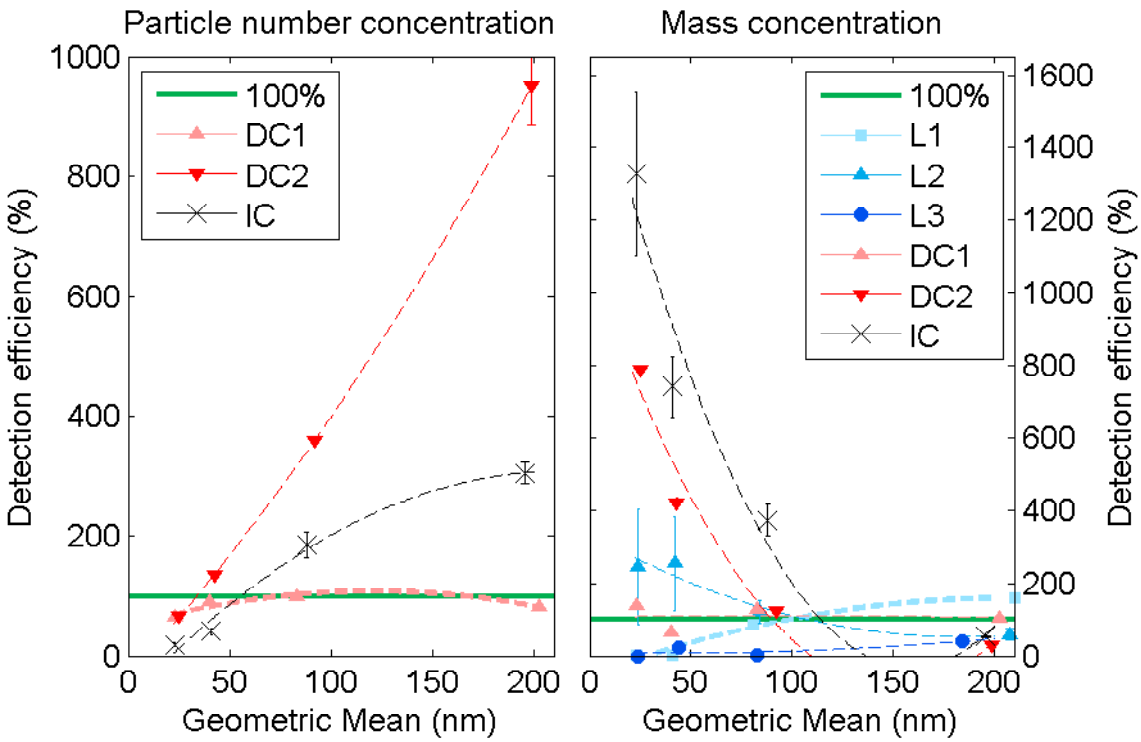

Figure 22: Summary of the detection efficiencies measured for the candidate instruments at METAS at the particle sizes measured at METAS

4.4 Instrument response to small particle sizes (METAS, MIKES)

Special emphasis was given to the response of the candidate instruments to small particle sizes. On the one hand these small particles are considered to be most harmful to human health (Brown, et al., 2001) and on the other hand the number of small particles emitted from diesel vehicles strongly increased with the introduction of particle filters (Burtscher, 2005). Without the presence of Diesel Particulate Filters (DPFs) large particles even grow further by condensation of volatile components. If these particles are removed, small particles form by means of homogenous nucleation. Therefore the geometric mean diameter of the emitted particles found in modern diesel exhaust is typically found to be below 100 nm (Burtscher, 2005; Harris & Maricq, 2001).

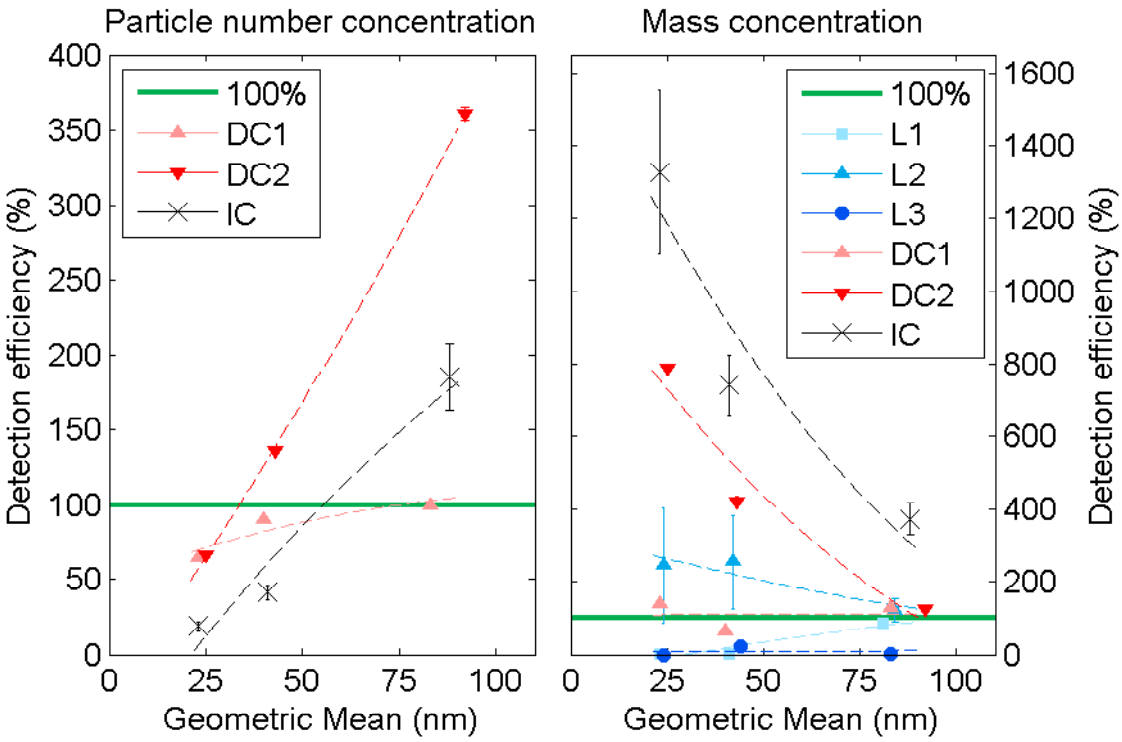

Figure 23: Detection efficiency (value recorded by the instrument under test divided by the reference) of the devices under test for particle sizes smaller than 100 nm at particle number concentrations around $2 \cdot 10^4$ to $5 \cdot 10^4$ cm^{-3} measured at METAS. Error bars show the standard deviation. For those instruments measuring number concentration the detection efficiency is referred to the CPC (left panel) for those instruments measuring mass concentration, the detection efficiency is referred to the deduced mass concentration from the SMPS (see Section 3.2.2 for details).

Concerning particle number concentration measurements with CAST aerosol, non of the candidate instruments showed a constant detection efficiency for particle sizes below 100 nm (Figure 23). While the DC1 instrument would at least pass the requirements for 41 and 80 nm defined in the SR 941.242 (see Table 4 for details on the efficiencies), the counting efficiency of DC1 and IC increased

too steeply. A reason for this steep increase for DC2 could be the increase of probability of multiple charged particles with increasing particle size and that the correction for multiple charges as implemented at the moment is not sufficient. Interestingly, the counting efficiency concerning particle mass decreased with increasing particle size both for DC2 and IC. Moreover, although the counting efficiency of the number concentration of DC2 and IC was below 100% for 23 nm, the counting efficiency of mass concentration was 800 % and higher. We assume that the conversion factor from the measured quantity to mass (IC: assumption 80 nm particle size, see Section 2) is the reason for this huge difference. The best counting efficiency concerning mass concentration for particles smaller 100 nm was achieved by DC1. Although the mass efficiency is not constantly above or below 100%, DC1 was the closest to the detection efficiency of the reference. The detection efficiency of the light scattering instruments clearly shows that they have some problems with smaller particle sizes. While for 80 nm the counting efficiency approaches 100% for L1 and L2, L2 measured a too high mass, and L1 and L3 basically did not measure any particles at 40 nm. Moreover, L3 did basically not react to particles of 80 nm either. This indicates that the light scattering instruments have problems to detect small particles, which was already investigated by the linearity tests at particle sizes of 40 nm and 60 nm at MIKES (see Section 4.3 for details).

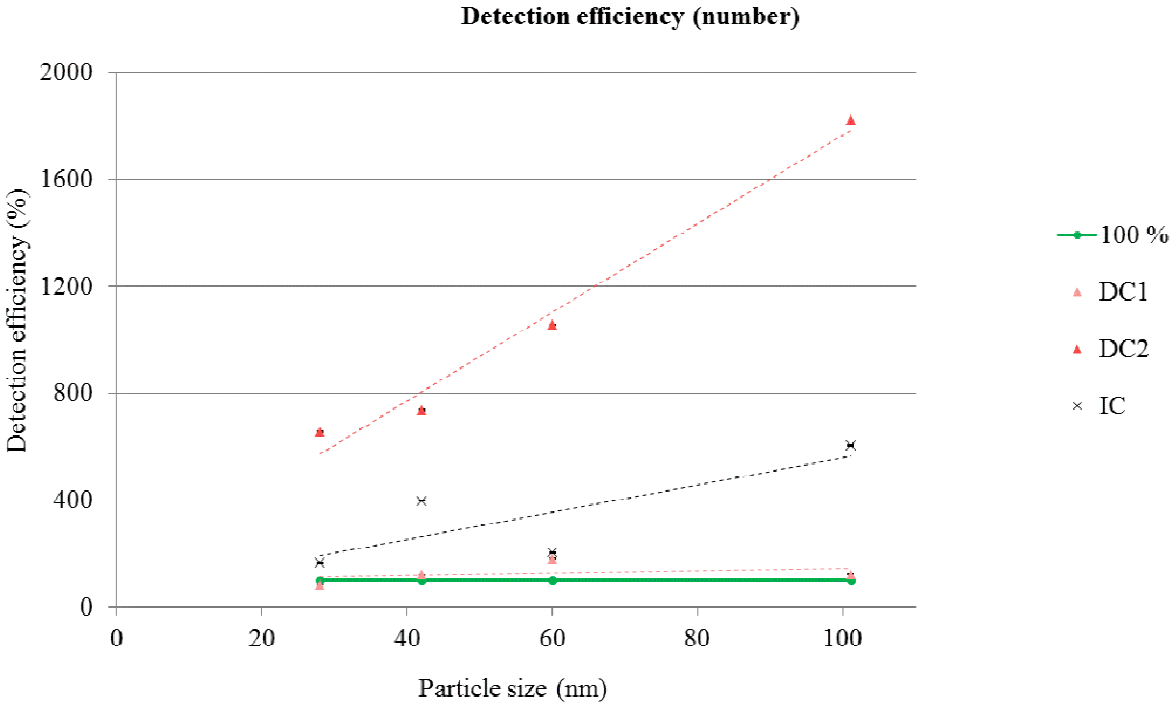

Figure 24: Detection efficiency of instruments measuring particle number concentration (Table 2) measured at MIKES using diesel soot. CPC was used as reference. Measurements were made at a particle concentration of $4 \cdot 10^4$ cm^{-3}.

When changing the aerosol type from CAST to diesel soot, the picture remains qualitatively the same for particle number concentration (Figure 24): the counting efficiency of the DC1 was the closest to 100 % and both DC2 and IC counting efficiency increased with particle size. However, the counting efficiency stayed above 100 % for all particle sizes. The increased counting efficiency in comparison to the measurements at METAS reflects what was already investigated during the linearity tests: DC2 sensor might have worked incorrectly.

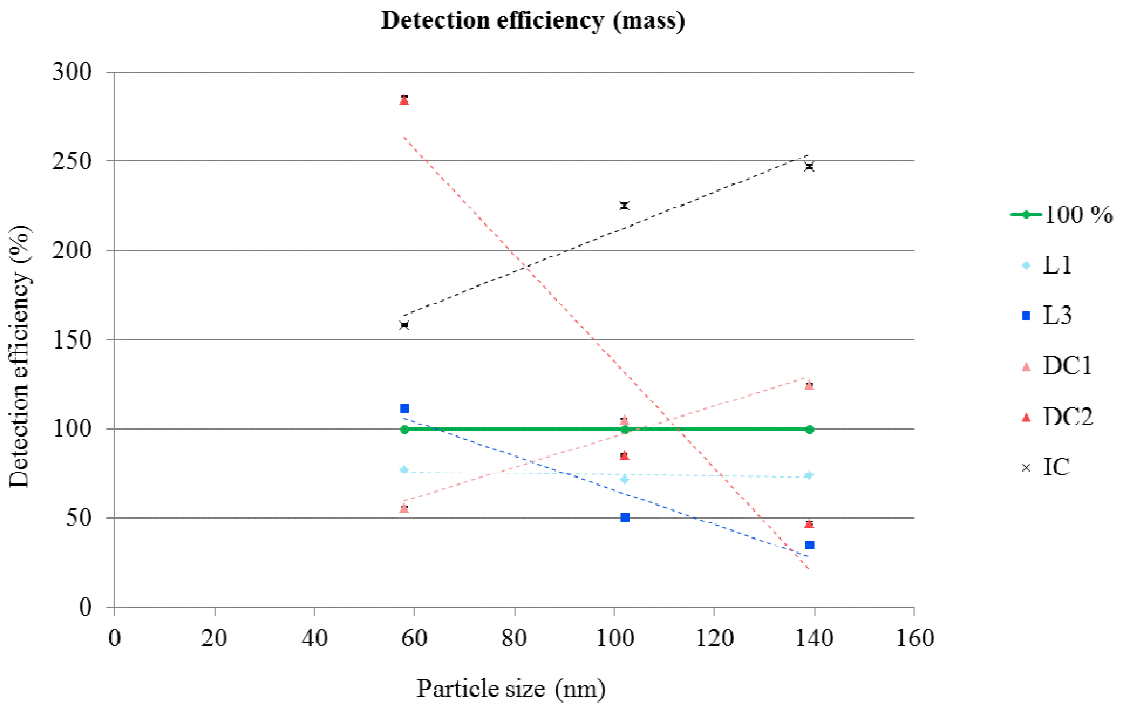

Figure 25: Detection efficiency of instruments capable of measuring particle mass concentration using diesel soot. Gravimetric weighing of filters was used as reference. Measurements were made at a particle concentration of $4 \cdot 10^5$ cm^{-3}.

Gravimetric weighing of filters is a trustable reference if a certain mass can be achieved; this is not the case for particle sizes smaller than 60 nm. Figure 25 therefore shows all measurements performed at MIKES. The light scattering instrument L1 had a detection efficiency of about 75 % which remains constant for particles in the size range from 60 nm to 140 nm. The measurement at METAS at 80 nm fits very well into this trend. Surprisingly, the L3 had a counting efficiency above 100 % for 60 nm and then decreased for larger sizes. This is an odd behaviour as L3 had a counting efficiency far below 100 % at METAS for particles < 80 nm. Both for the DC instruments as well as for the IC instrument the detection efficiency depends on the particle size. Surprisingly, the IC number concentration readings had a better correlation with mass concentration, which can be seen when comparing Figure 25 with Figure 24. The DC1 instrument for particle number concentration response (Figure 24) is less sensitive to particle size than the mass concentration response shown in Figure 25. Overall, the instrument that recorded small particles in the most reliable way was the DC1.

4.5 Response to volatile particles (METAS, MIKES)

4.5.1 Response with respect to relative humidity (MIKES)

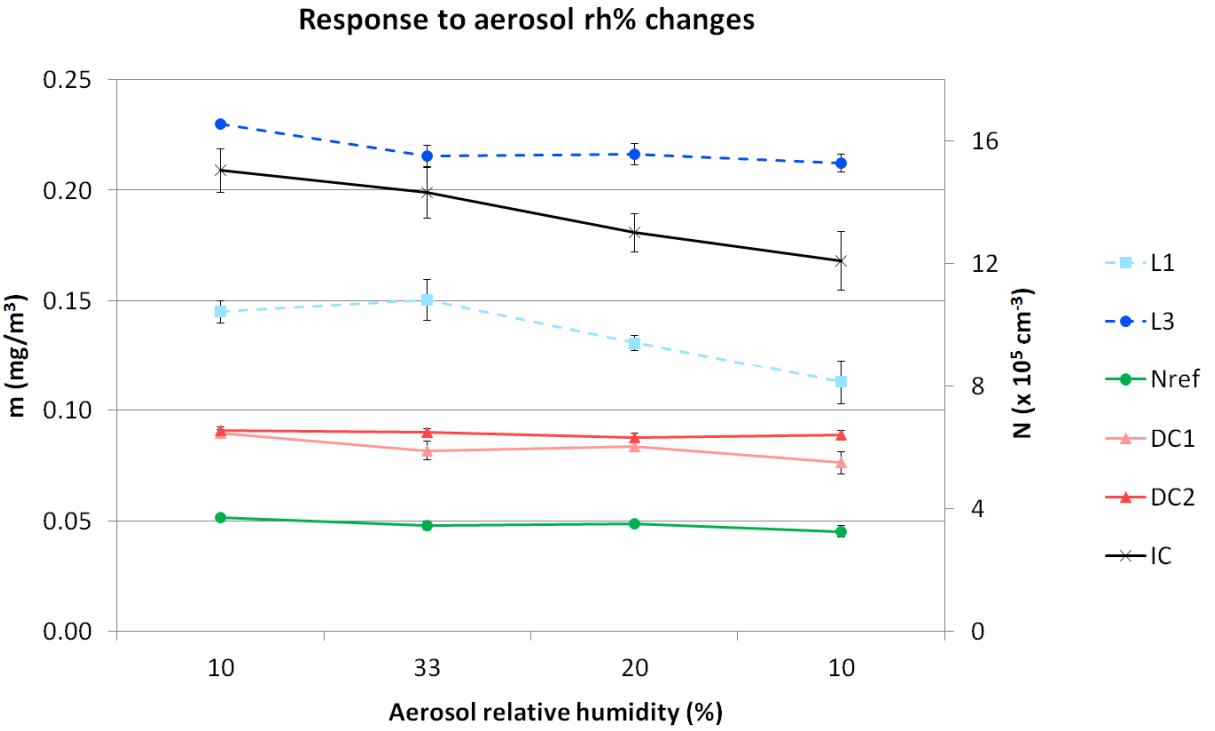

Figure 26: Effect of aerosol relative humidity measured at a particle concentration of $4 \cdot 10^5$ cm^{-3} and particle size of 100 nm. Light scattering instruments (L1 and L3) measuring only mass concentration are plotted against the right y-axis and the electrical sensors (DC1, DC2 and IC) are plotted against the left y-axis. Standard deviations are shown as error bars.

The results of measurements at different relative humidities (Figure 26) indicate that the relative humidity of the aerosol doesn't have a clear effect on the instruments response. This is especially pronounced as only DC2 reproduces the measured value at a relative humidity of 10 %. The difference between the first and the second 10 % measurement is especially pronounced for the light scattering instruments and the IC. This was unexpected as the DC sensors were supposed to react for changes in relative humidity. The DC1 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 L1 and IC 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 (L1 and IC). However, this could not be verified as the particle size distribution was only measured before the experiments. The DC1 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.

4.5.2 Response to tetracontane (METAS)

According to the Swiss legislation for combustion building machines, volatile compounds in the exhaust gas should not change the measurements. Therefore the respective instruments must be capable to evaporate volatile compounds. Tetracontane is considered to be a representative test aerosol for volatile compounds in exhaust gas. As the only candidate instrument owing an exhaust gas preparation, we only tested the DC1 with tetracontane particles at 30 nm. The DC1 was able to nearly fully evaporate the tetracontane particles as the counting efficiency for DC1 was far below 1% (see Table 7).

Table 7: Tetracontane measurements at METAS.

Tetracontane aerosol		Reference (CPC)		Candidate instrument		Counting efficiency
Geo. Mean (nm)	GSD	N (cm^{-3})	Std (cm^{-3})	N (cm^{-3})	Std (cm^{-3})	N_{DC1}/N_{REF}
34	1.41	$2 \cdot 10^5$	$2 \cdot 10^3$	10	3	0.01%

4.6 Comparability (PTB, METAS, MIKES)

Comparability between the laboratories is an important aspect as well, under the point of view of repeatability of the measurements. Unfortunately, none of the measurement points was repeated exactly at the NMIs, such that only comparisons of different concentration ranges can be performed. Nevertheless, a suitable instrument would at least fulfill certain linearity across concentrations and therefore a comparison of different concentration levels is still useful.

A very important aspect is as well whether CAST aerosol is close enough to diesel soot such that it can still be considered as an appropriate calibration aerosol. Therefore were compared CAST versus diesel results at three different sizes for measurements performed at PTB, METAS, and MIKES.

4.6.1 CAST versus diesel @ 40 nm (METAS, MIKES)

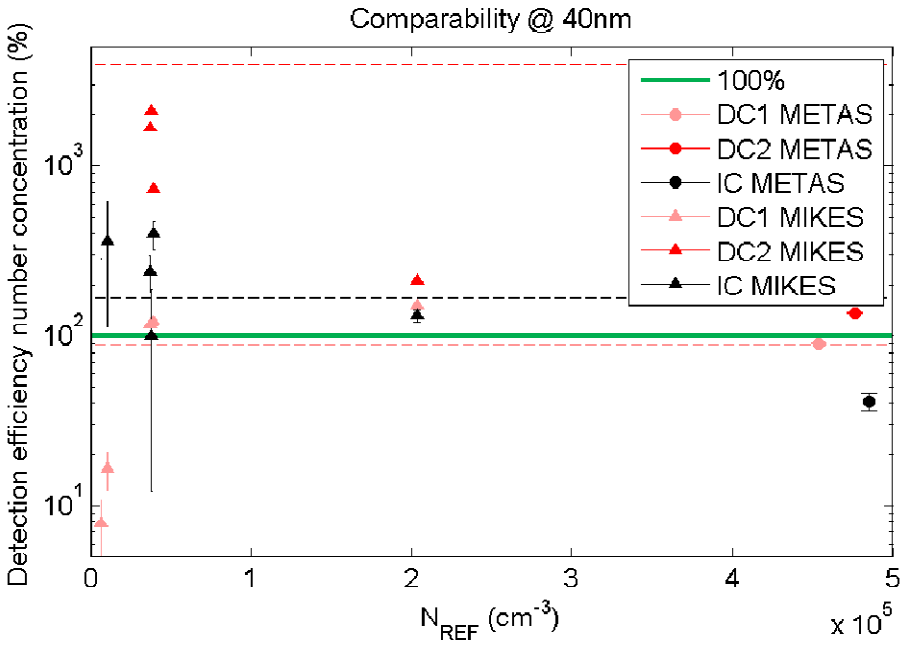

Figure 27: Comparison of the detection efficiency measured at METAS (circles) and MIKES (triangles) @ 40 nm. The green line denotes 100% counting efficiency (ideal instrument). Error bars denote the standard deviations. The mean values for the detection efficiencies measured at MIKES are given as a dashed line. As a reference both NMIs used the CPC.

Particles at 40 nm were only measured at METAS and MIKES. As none of the instruments showed a clear linearity concerning particle number concentration (Figure 10), it is impossible to say whether the difference between the two NMIs was a result of the differences in the used test aerosol or just an effect of linearity. Interestingly, for DC1 the mean value from the values collected at MIKES corresponds to the counting efficiency measured at METAS. Moreover, DC1 was the instrument being the closest to the reference of all instruments. The results at MIKES for DC2 should be

considered with care, as it cannot be ruled out that there was an instrument failure as already indicated above.

4.6.2 CAST versus diesel @ 60 nm (PTB, MIKES)

Although PTB performed a lot of measurements, only few measurements were performed for particle sizes around 60 nm (Figure 28). None of the candidate instruments could reproduce its measurement efficiency determined at PTB or at MIKES. Again the question rises whether this is a problem of linearity of the instruments or the differences in used aerosol. Moreover, a detection efficiency of 100 % was neither reached.

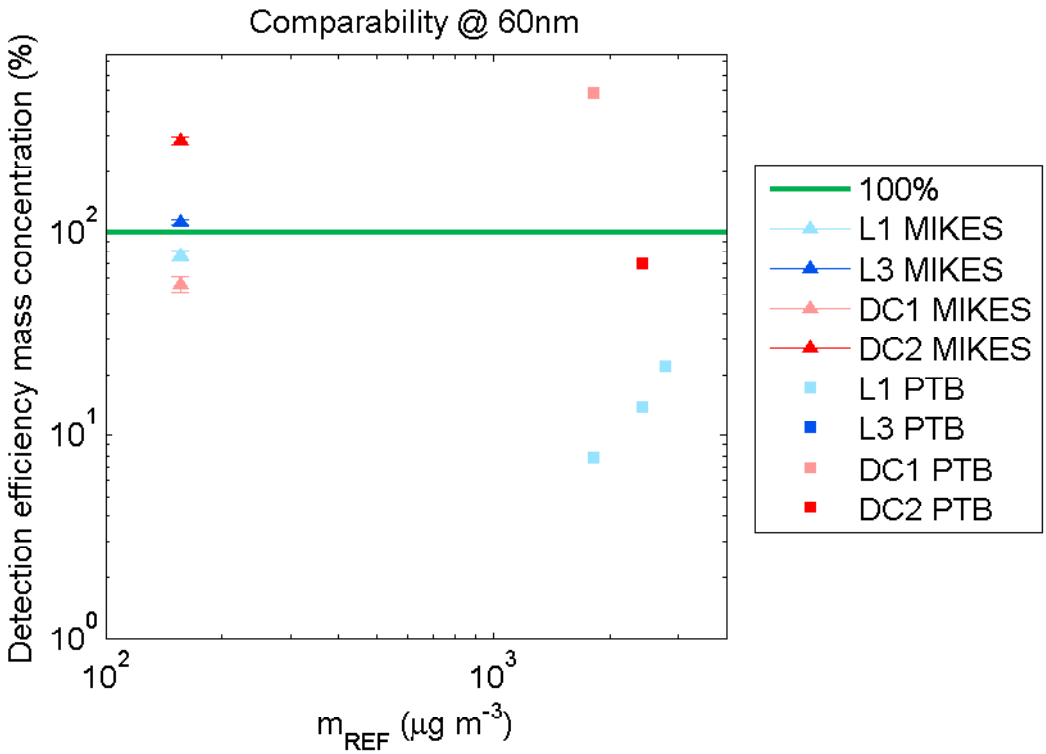

Figure 28: Comparison of the detection efficiency measured at MIKES (triangles) and PTB (squares) @ 60 nm with respect to particle mass concentration (reference: gravimetric measurements). The green line denotes 100% counting efficiency (ideal instrument). Error bars for the triangles denote standard deviations as determined by MIKES.

4.6.3 CAST versus diesel @ 100 nm (PTB, MIKES)

For particle sizes of around 100 nm the mass concentration detection efficiency was a slightly better reproduced at the two different NMIs than for 60 nm: while the detection efficiency of L1, L3 and

DC2 was below 100% the one of DC1 was above. Both DC instruments were close to the counting efficiency of 100 % for the measurements at MIKES.
It needs to be mentioned, that for both comparisons at particle sizes of 60 nm and 100 nm the amount of data that could be compared was very low. At least the detection efficiency of L1 varied a lot (Figure 28 & Figure 29). Furthermore, DC2 was supposed to have some problems at least at MIKES, consequently a comparison is questionable for DC2.

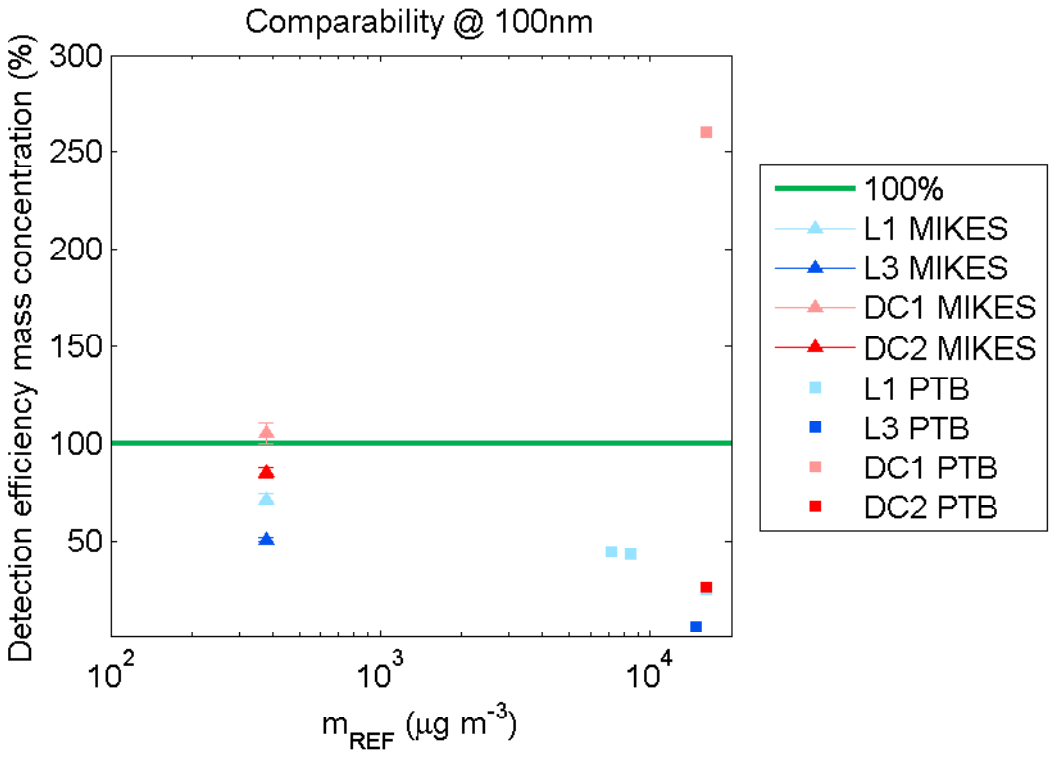

Figure 29: Comparison of the detection efficiency measured at MIKES (triangles) and PTB (squares) @ 100 nm with respect to particle mass concentration (reference: gravimetric measurements). The green line denotes 100% counting efficiency (ideal instrument). Error bars for the triangles denote standard deviations as determined by MIKES.

4.7 Response time measurements (MIKES)

The response times of the instruments is shown in Table 8. The DC1 instrument had the shortest response of all instruments. This was a surprising result because the DC1 instrument is equipped with a dilution unit (rotating disc) and therefore it was expected to have some delay. Short response times between 4 s and 7 s were measured for the CPC, DC2, L3 and IC instruments. For the L1 instrument a huge delay of 39 s was measured. This result doesn't seem meaningful as the instruments operating principle is similar to the L3. The L3, DC2 and L1 were connected to the same

computer, so an error in the synchronization of the computer clocks cannot explain the observed delay.

Table 8: Soot sensor response times.

Instrument	Response time (s)	Standard deviation (s)
DC2	4.2	0.7
L2	NA	NA
L3	7	0
L1	39	0.4
DC1	1.3	0.7
IC	6	2.1
CPC (number ref.)	4.2	0.7
Gravimetric (mass ref.)	NA	NA

5 Conclusions

The instrument that delivered the best measurement results for particle sizes and concentrations relevant for modern diesel exhaust emissions was the DC1. It was the only instrument, which was capable of measuring sub 100 nm diesel particles reliably at particle concentrations down to 10^4 cm^{-3} (MIKES). Moreover, it was the instrument being the closest to the requirements for nanoparticle instruments defined in SR 941.242 (METAS)[5]. However, for particle mass concentrations > 4000 $\mu g/m^3$, it measured too high concentrations (PTB). Additionally, it is the only instrument being able of evaporating volatile compounds such as tetracontane, as an evaporation unit is integrated into the instrument. It is recommended that all instruments should integrate an evaporation system in the future.

The light scattering instruments were able to measure diesel particles larger than 100 nm by detecting their particle mass concentration (MIKES). For diesel particles, the L1 light scattering instrument was found to be more sensitive than the L3 instrument, and it was able to measure linearly down to particle concentrations of $4 \cdot 10^4$ cm^{-3}. Unfortunately, results from the L2 instrument at MIKES were invalid due to misuse of the instrument. However, all light scattering instruments were found less sensitive for particle sizes below 70 nm for the laboratory studies. This was especially confirmed for particle sizes below 50 nm. While L1 and L3 measured too low values for small CAST particles in this size range, L2 measured too high values (METAS). This is in contrast to their response, which were measured for the same particle type (CAST) but higher mass concentrations (above 4000 $\mu g/m^3$ at PTB): L1 and L2 recorded values below the reference. This shows that the prototypes of light scattering instruments reach their limits at small particle sizes and low concentrations. For diesel particles, the ionization chamber, although not a commercial instrument was able to measure diesel particles in the whole studied for 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} (MIKES) after a complex reanalysis based on a conversion algorithm by the operator. However, the detection efficiency for the CAST particles increased with particle size for particle number while it decreased with particle size for particle mass concentration (METAS). For larger particle mass concentrations (> 4000 $\mu g/m^3$) the detection efficiency was comparable to the one of DC1. Overall, even considering that the conversion algorithm based on an assumption of a given particle size and particle size distribution the IC is an instrument has the potential to become a cheap alternative to DC1. The detection efficiency of DC2 for the CAST particles at METAS had the same trends as the one for IC. While DC2 was rather close to 100 % detection efficiency for 23 nm and 41 nm in number concentration, it was far of in mass concentration. Nevertheless particles at 80 nm were recorded rather reliable concerning mass concentration.

After the laboratory tests the manufacturer found a non-soot contamination within the DC2 instrument that wasn't displayed as malfunction at this time. It could be possible that the sensor might have got contaminated during previous measurements. T his would also explain the strange size dependency of the detection efficiency measured at METAS. This hypothesis is further emphasized by the fact that DC2 was the instrument with the closest results to the reference for particle mass measurements at PTB. However, it is a clear drawback that the DC2 instrument did not supply a warning, if pollution might have falsified the results in the described way. Therefore, a further development into a useful and reliable instrument seems to be possible as it is based on the same physical measurement principle than DC1.

As a general conclusion, there is no instrument which covers the whole range of possible diesel car emissions of a opacity between 0,01 and 3 m^{-1}. Both measurement principles, the electrical charging and sensing as well as the ionization chamber principle, can be considered as suitable for measuring sub 100 nm particles from modern diesel vehicle exhaust. The DC1 instrument is the best choice at the moment as it is commercially available and showed the best performance. The apparent

[5] At METAS the 6 different candidate instruments were tested for their suitability according to SR 941.242. The only instrument fulfilling at least partly the requirements as defined in SR 941.242 was DC1. Further development of the DC1 could lead to an instrument fulfilling the requirements of SR 941.242.

drawback of this instrument is, however, the complexity and thus the high price. The IC 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. But both instruments need a dilution system up to a factor of 1:1000 for high soot concentrations from old vehicles. On the other hand, one of the light scattering instruments showed a good correlation up to high concentration and was less sensitive for small particles and low concentration.
Finally, a complementary instrument should be considered apart from the established opacimeter to measure the low emission of modern diesel vehicles.

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Appendix

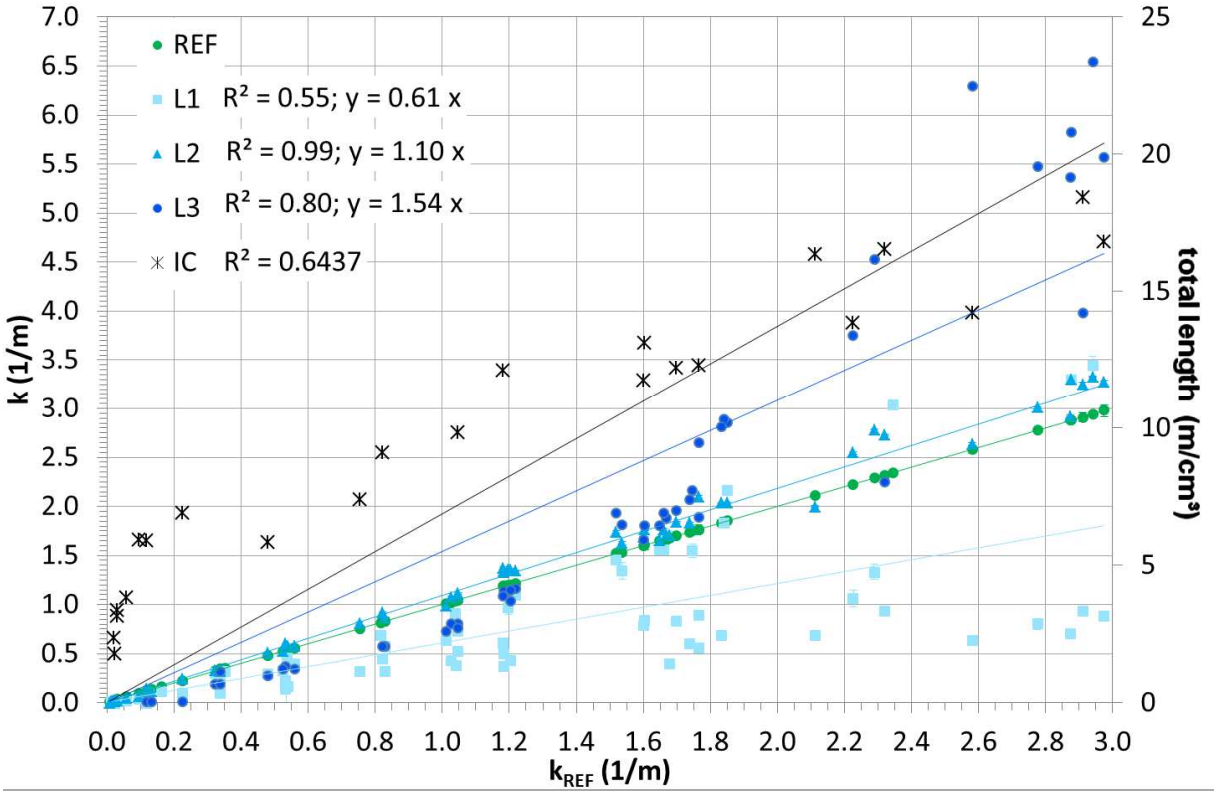

Figure 30. Summary of PTB opacity measurements for the light scattering instruments including a linear fit (k=0.0 to 3.0 m^{-1}, particle size 50 to 237 nm, particle number concentrations from $1.16 \cdot 10^7$ to $1.1 \cdot 10^8$ cm^{-3}). The total length as recorded by the IC instrument is plotted on the right axis. For IC only the coefficient of determination is given. For the devices under test, the error bars denote the standard deviation.

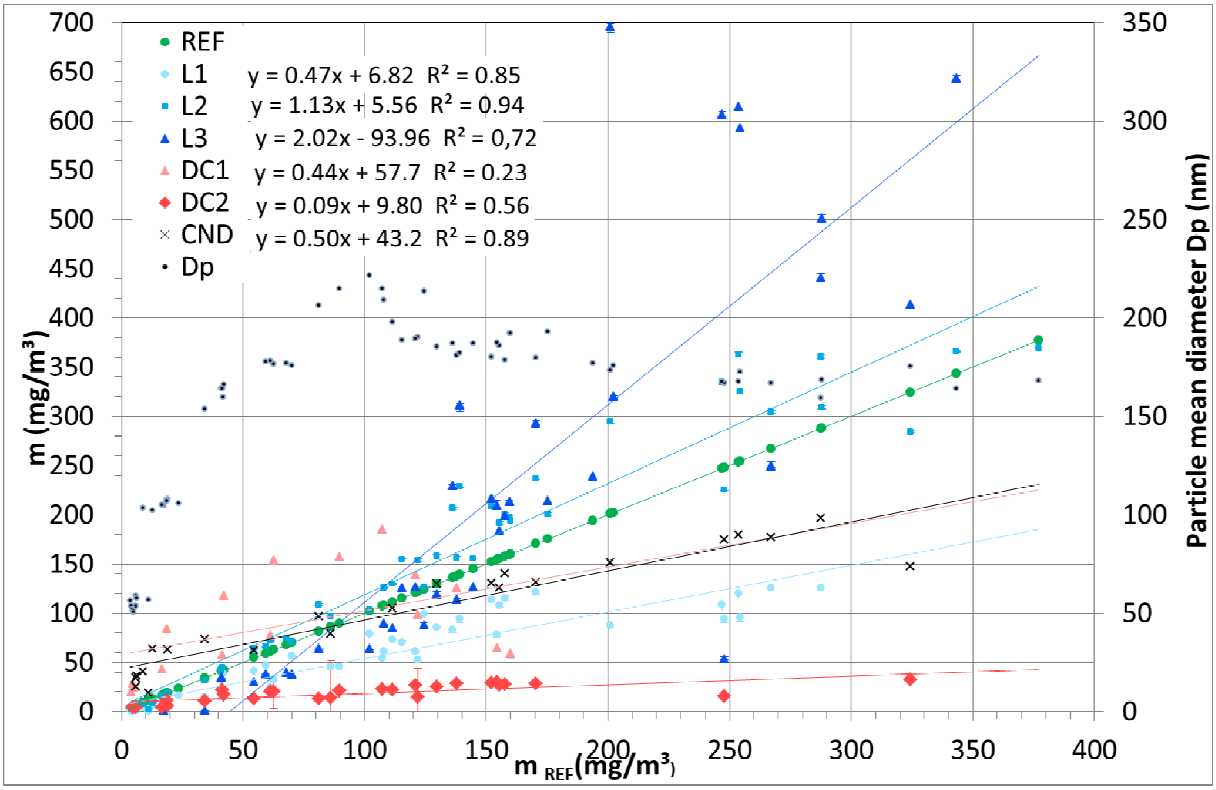

Figure 31. Summary of PTB mass concentration measurements for all candidate instruments (m=0 to 400 mg/m³) including coefficient of determination and a linear fit. Error bars of the devices under test represent standard deviation. Additionally, the mean particle diameter for each configuration is displayed on the right y axis. Note that the particle mean diameter typically found in light-duty diesel exhaust varies between 50-100 nm (Harris & Maricq, 2001).

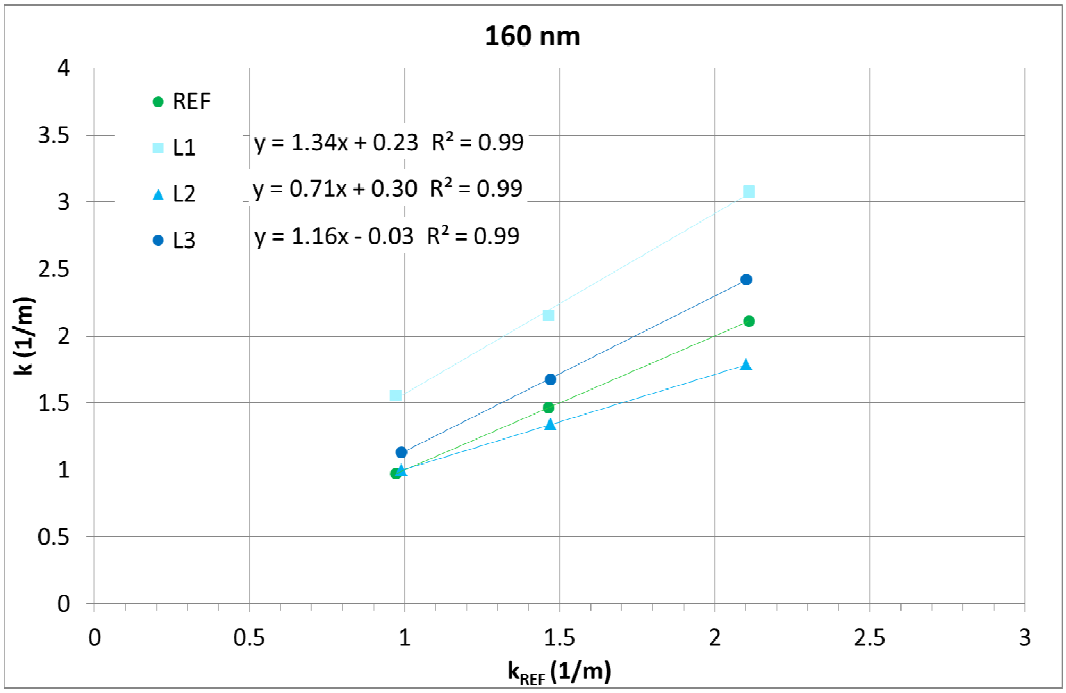

Figure 32: Linearity of light scattering instruments to opacity for a particle size of 160 nm measured at PTB.