Investigation of Alternative Methods to Determine Particulate Mass Emissions

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Background and Executive Summary

Currently alternative particle measurement techniques for the type approval of exhaust emissions of vehicles in addition to the actual gravimetric procedure are considered within UNECE/WP.29/GRPE due to the ongoing discussion on health effects of fine particles. In this context novel, unconventional particle characteristics like number, size and surface are focussed as measurand as well as the mass of black carbon or the solid particle fraction.

To date still many uncertainties concerning the evidence, strength and kinds of health effects of particles exist and also an alternative health-related particle dose measure besides the traditional mass metric could not yet be proven causally. The introduction of an additional type approval method is therefore questionable, risk of losing consistency in exhaust gas improvements and misguided engine developments must be taken in account. As the limit of detection of the actual type approval procedure is also suitable for future regulatory demands no additional certification testing technique is required.

DaimlerChrysler was motivated to investigate some of the discussed alternative measure-ment methods for elemental carbon due to their potential to act as development tool. Thereby the main quality characteristics and the suitability for practical use of the measurement systems “laser-induced incandescence (Li^2sa)” and “photoacustic sensor (PASS)” in comparison to the standard gravimetric procedure and the actually utilized real time measurement tool (opacimetry) have been the examination items. Measurements were performed with current mass production diesel and gasoline vehicles of different manufacturers.

Both measurement systems for the determination of the mass emission of elemental carbon offered excellent quality characateristics for engine exhaust developmental purposes:

- The correlation to gravimetrically determined particle emissions is significant (regression coefficient = 0,98). For modern vehicle concepts the results of these systems account for about 80 % of total particulate mass.
- The limit of detection is at least one order of magnitude better than this of the standard procedure.
- Because of a time resolution ? 5 Hz particle formation during engine combustion could be cause studied.
- Cross interferences to other exhaust components are not given.
- System calibration is performable via coulometry.

It should be mentioned, that Li^2sa measurements revealed a non-linear relationship between soot mass and signal value. As the PASS system shows additionally advantages regarding practical routine application it seems to be the more preferable technique and has the potential to substitute the actually utilized opacimeter as online development tool.

Li2sa-determined primary particle diameters of different engine concepts did not offer notable size differences, the expressiveness of this measurand is questionable so.

Experimental

Investigations were carried out on a diesel test cell equipped with twin roller chassis dynamometer and a CVS system with diesel particulate tunnel. Several methods were applied in parallel (Figure 2).

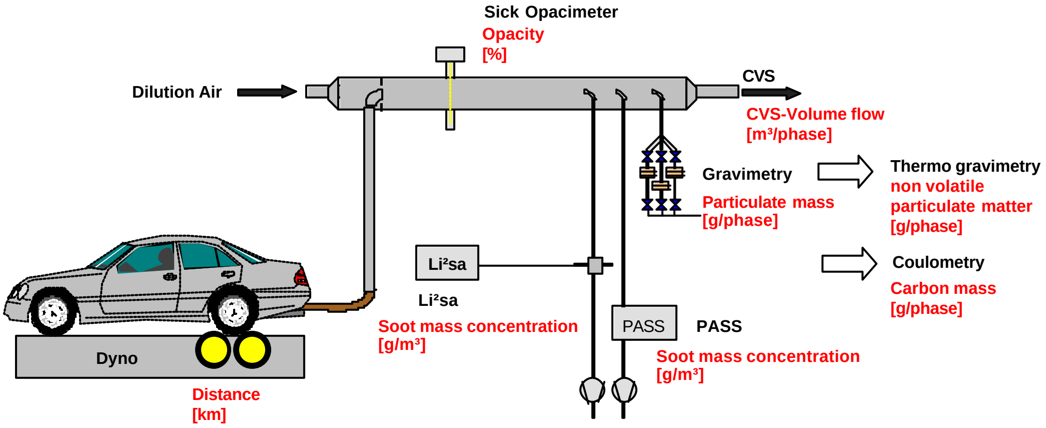

Figure 1: Experimental setup

Applied Methods:

Gravimetry: Standard filter method as described in the regulations
Thermo-gravimetry: After the weighing the standard teflon coated filters are heated to 250 °C for a defined time to eliminate volatile matter (mainly fuel and oil constituents). After this treatment the filters are weighed again and the amount of non volatile particulate matter is calculated.
Coulometry: Special filters (pretreated quartz fiber) are loaded according the standard procedure and are analyzed after the test by coulometry for the total carbon mass.
Opacimetry: The opacity is measured across the tunnel.
Li²sa (laser induced incandescence soot analyzer): A small sample is taken iso-kinetically and delivered to the measuring chamber of the device.
PASS (photo acoustic soot sensor): A small sample is taken iso-kinetically and delivered to the measuring chamber of the device.

Method	sampling	analysis	measured value	# of phase results
Gravimetry	iso-kinetic	off-line	particulate mass on filter	101
Thermo -gravimetry	iso-kinetic	off-line	non volatile particulate mass on filter	62
Coulometry	iso-kinetic	off-line	carbon mass on filter	12
Opacity	in-situ	continuous	opacity	101
Li²sa	iso-kinetc	continuous	soot concentration	101
PASS	iso-kinetc	continuous	soot concentration	76

Table 1: Characteristics of the investigated systems

Testing program

During the evaluation period 47 tests were run, most of which European driving cycles. 8 Tests were conducted at constant speed (50, 100 and 120 km/h).

Vehicle	# of Tests
Diesel (EU2)	3
Direct injection diesel (EU3-4)	27
Gasoline (EU4)	3
Gasoline direct injection (EU4)	14
Blank test	2

Table 2: Tests conducted during testing period

Calibration of Opacimeter

From the opacity T a mass concentration of particulate matter can be calculated according to:

$$c = k * \ln(100/(100-(T-T_0))$$

with
c = mass concentration [g/m³]
k = calibration factor [g/m³]
T = opacity [%]
T_0 = opacity value at zero concentration [%]

Experiments showed very good correlation of opacity data with thermo-gravimetric results. The calibration factor k was determined according figure 3 to k = 0,2381.

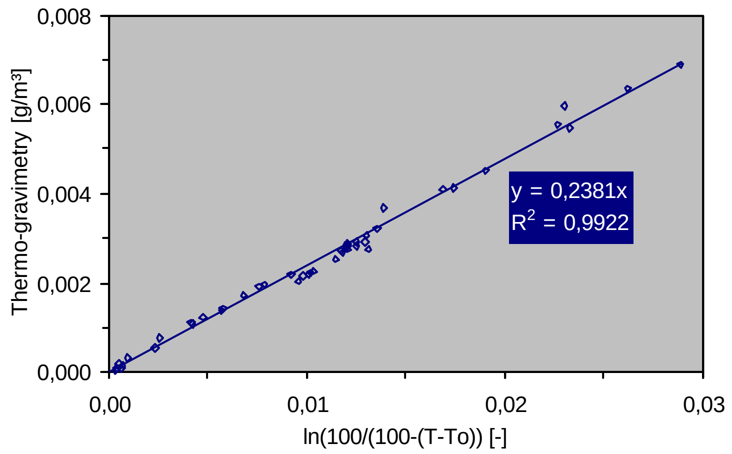

Figure 2: Calibration of opacimetry

Calibration of Li²sa and PASS

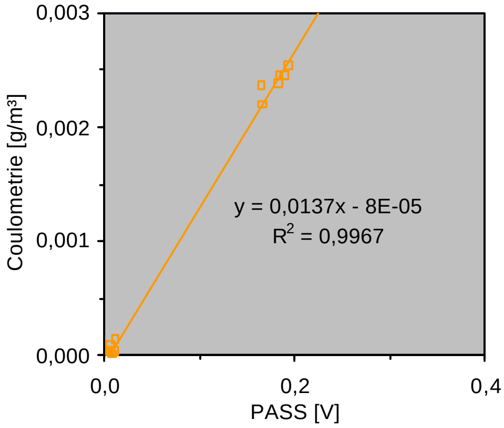

Figure 3: Calibration of the PASS with results from coulometry

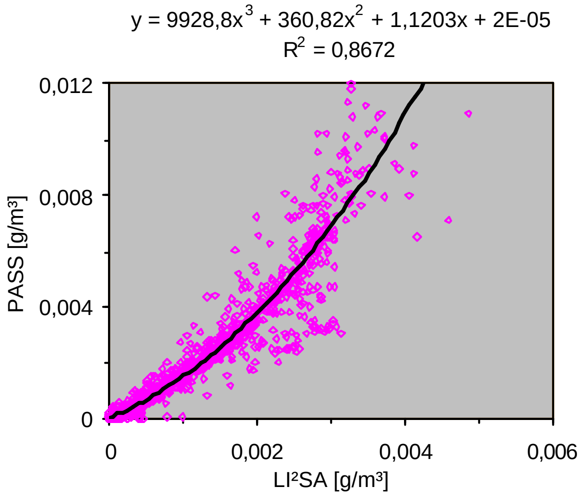

Figure 4: Third order calibration of Li²sa using calibrated values from PASS

The PASS system was calibrated using coulometric results (see figure 4). A linear calibration was applied, since PASS and thermo-gravimetric results showed a good linear correlation.

The Lisa system was calibrated using the calibrated PASS data. This was necessary because of an assumed non-linear relation between soot mass and Lisa signal. Since only few points with coulometric results were available, these were not sufficient for a non linear calibration.

Correlation to standard gravimetric procedure (with/without volatiles)

Figure 6 shows the correlation of the results from the different systems with the standard gravimetric method. Each point represents the average concentration of one phase. As to be expected, the gravimetric method yields the highest results, since all other methods register only part of the particulate matter on the filter. Li²sa, PASS and coulometry give the amount of soot or elementary carbon respectively. In the tests conducted soot was typically about 80 % of the total gravimetric mass. Results from opacimetry and thermo-gravimetry are slightly higher and typically reach values around 90 %.

As can be seen from figure 6, opacimetry, Li²sa and PASS show a very strong correlation to thermo-gravimetric results with coefficients of variation of 0,97 to 0,99.

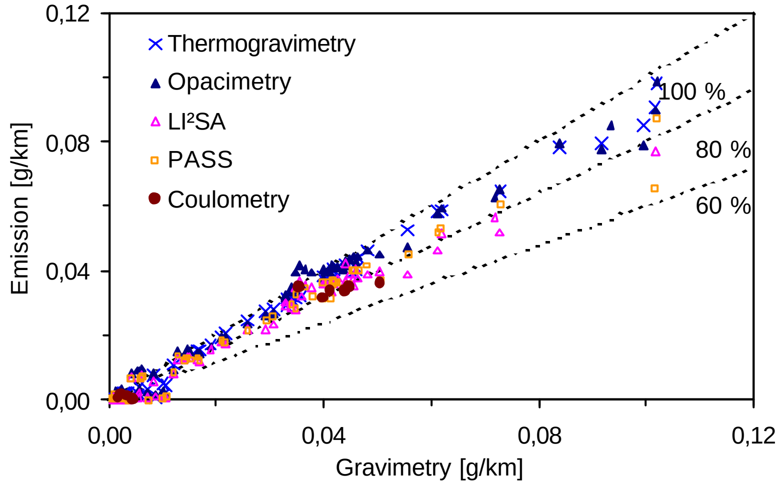

Figure 5: NEDC-Phase average emissions plotted over results from gravimetry

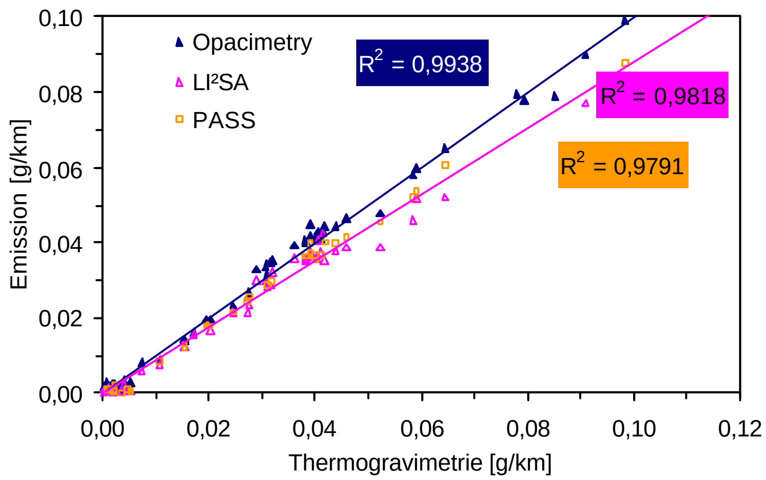

Figure 6: Correlation of mass emissions calculated from opacity, Li²sa and PASS with thermo-gravimetry (NEDC)

At very low emission levels Li²sa and Pass still show a reasonable correlation. This confirms that Li²sa and PASS are applicable for emission levels far below the Euro 4 level.

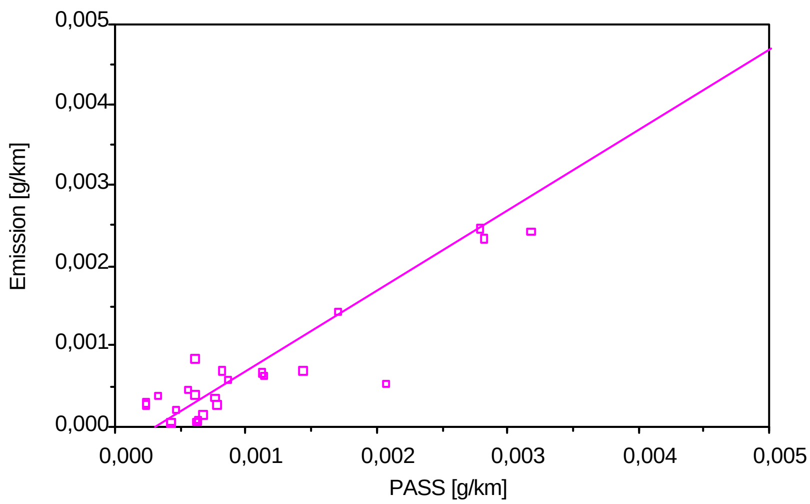

Figure 7: Correlation of opacity, Li²sa, thermogravimetry related mass emissions with PASS results at low emission levels

Time resolution

For development purposes time resolution is an important issue. Figure 9 shows a comparison of the time resolved mass emission during the NEDC. In the investigated setup the opacimeter has the best time resolution since it is directly applied to the bulk gas flow. For the Li²sa and PASS system small samples are extracted and a delay time depending on length of sample line and sample flow can be observed. The Li²sa system at the time of this experiments featured only a sampling rate of 0,5 Hz. This is the reason why the peak at 120 s is not fully resolved. In the meantime a sampling rate of 20 Hz is available. The PASS has a sampling rate of 5 Hz, however, T90-time is in the order of 1 s. Therefore, time resolution is not as good as for the opacimeter, however, it is sufficient for development purposes.

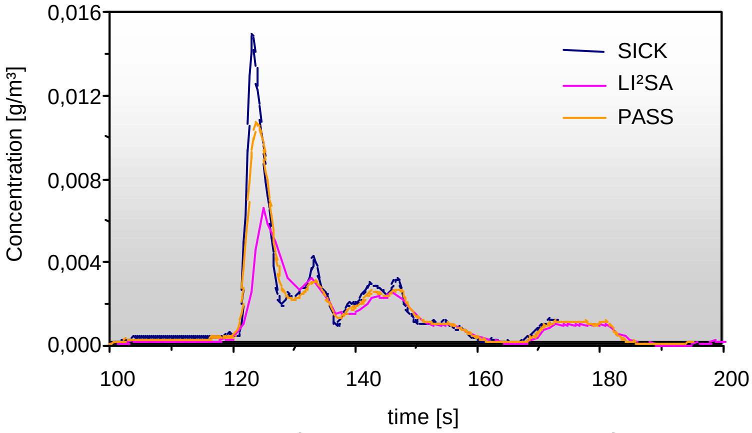

Figure 8: Comparison of time resolution (section of an NEDC)

Signal noise and limit of detection

To study the limit of detection of the measurement methods, blank tests (emission test without vehicle) were carried out. In the case of the gravimetric method these tests indicate the limit of detection of the entire process (weighing, filter handling, loading, weighing). Figure 1 shows the difference in weighing before and after test. The zero scatter (standard deviation ?) is +/- 0,8 mg. Therefore, the LOD (3 * ?) is estimated to be 0,025 mg. This is equivalent to approximately 1 mg/km in an NEDC which is 4 % of the Euro 4 emission limit. By optimization of the gravimetric method (optimized flow, micro balance with increased accuracy) it will be possible to decrease the LOD to approximately 0,01 mg/filter.

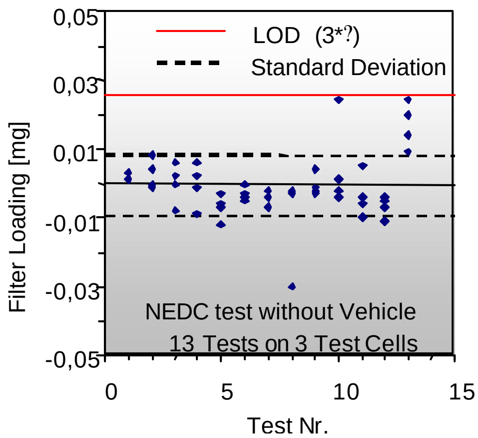

Figure 9: Determination of LOD of gravimetric method by blank tests

For the continuous measurement techniques signal noise and stability of the base line are important criteria for the achievable limit of detection. Figure 10 shows the signals during a blank test. The opacimeter has the highest signal noise. In addition a baseline drift can be observed. PASS has a very low signal noise and offers the highest potential for low emission measurement. The offset of opacimeter and PASS is due to contamination (see below). For the repeatability and accuracy of test results the scatter of the phase average is incisive.

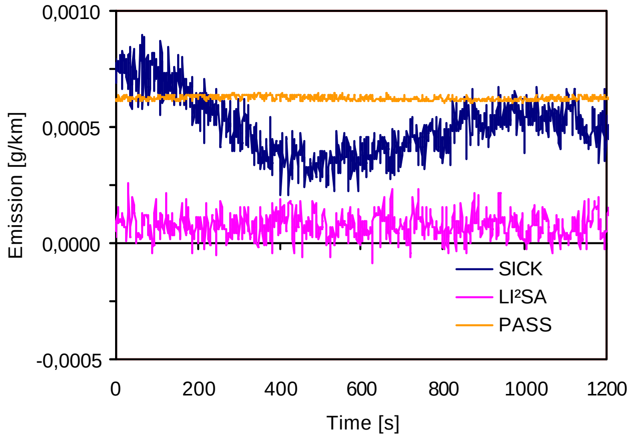

Figure 10: Signal noise during blank test

Zero drift

In figure 11 the zero signal prior to each test is shown. A pronounced increase of the zero signal due to fouling of the optical interface can be observed for the opacimetry. The PASS also shows an increasing zero signal, although fouling is much less pronounced. The zero signal of Li²sa is very stable. No influence from fouling can be seen. Due to the zero drift opacimetry requires a zero correction. This is done by the determination of T_0 prior to each test. The same is possible for the PASS system.

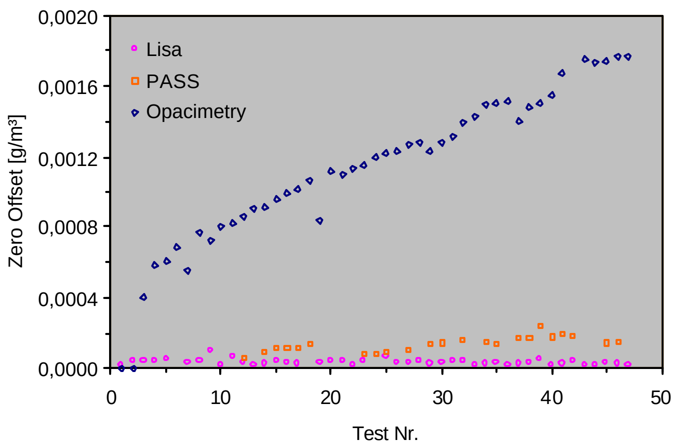

Figure 11: Zero drift due to fouling

Cross interference

It is known that the opacimetry suffers a slight cross interference from NO_2. For vehicles with high NO_2 and low particulate emissions results are influenced noticeably (Figure 13). A NO_2 concentration of 100 ppm causes an interference of 4 mg/m³. For Li²sa and PASS no cross interference was observed.

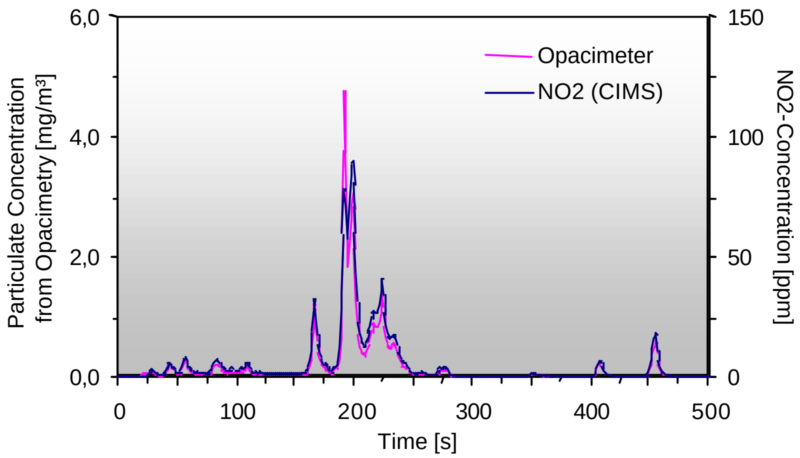

Figure 112: NO_2 interference of Sick opacimeter

Measurement of primary particle diameter with Li²sa

The Li²sa system offers the possibility to determine the primary particle diameter of the soot particulate. As figure 13 shows, this diameter is independent on particle concentration (and thus engine load) and combustion principle. For all investigated vehic les it was in the range of 25 – 35 nm.

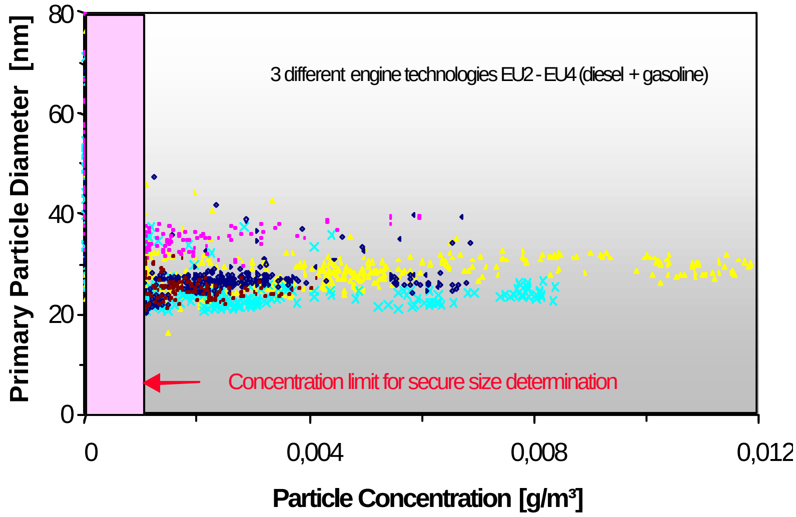

Figure 13: Primary particle size plotted over particle concentration for different vehicles