Ultralow emissions from trap equipped diesel engines, a challenge for instrumentation
Ultralow Emissions from Trap Equipped Diesel Engines, a Challenge for Instrumentation

Markus Kasper
Matter Engineering AG, Wohlen

The use of particulate traps poses new challenges to particle measurement methods. Particle emissions after traps are often claimed to be "very low", "below the detection limit" or "almost not measurable". Other studies find higher particle concentrations after trap than before trap. To clarify this confusing situation, nanoparticle measurement methods are compared to gravimetric and coulometric analysis of filter samples from CVS sampling. Repeatability and sensitivity of the methods are assessed, and the influence of dilution and sampling is investigated.

Repeatability
Fig. 3 shows results from a round robin test carried out with various diesel engines that were sent to different laboratories around the world for particle emission measurement. Gravimetric analysis of the filter samples was repeatable within 10% within lab and among labs. A more recent study showed a similar result for coulometric analysis (elemental carbon content) of filter samples from ambient air measurement and diesel engine emissions (Fig. 4). In September 2000 a round robin test with 11 SMPS systems was carried out at the IGF (Institut für Gefahrstoffforschung) in Dortmund, Germany. After optimizing the measurement conditions among the 11 systems the repeatability of number concentration measurement was of the order of 20% (Fig. 5).

Sensitivity
The relative sensitivity of various methods was assessed by measuring the particulate emissions of a EURO III diesel passenger car, operated at 50 km/h on a roller dynamometer (Fig. 6). At the end of the CVS tunnel, the mass concentration of total PM and elemental carbon was 3.6 mg/m$^3$ and 3.2 mg/m$^3$, respectively (Fig. 7). Assuming that the mass of the filter sample should be more than 100 µg to allow a reliable weighing, the detection limit of the two methods was 0.9 mg/m$^3$. Thus, the measured PM and EC concentrations were only about 4 times the detection limit. The same approach was applied to the particle number spectrum measured with SMPS at the same sampling point. In this case the measured concentration is almost 10'000 times the detection limit of the instrument. Similar results were obtained with the NanoMet sensors.

In Fig. 8 the measured values are displayed as multiples of the detection limit. While being three orders of magnitude more sensitive, the nanoparticle methods are faster, too.

Dilution and Sampling
In all studies about instrumentation, the subject of dilution and sampling has to be addressed in detail, as severe artefacts may occur. Fig. 9 shows PM filters with samples taken before and after a CRT system. Obviously the "particles" after trap are hardly visible and give the filters a slight yellowish color. What cannot be seen in the picture is that the mass on the yellowish filters is about the same, sometimes even more than on the "sooty" blackish filters. In terms of PM measurement, the CRT system is inefficient as not only there is no reduction in particle emissions, but sometimes there is even an increase: The CRT has negative efficiency. Chemical analysis of the samples reveals
that before trap most of the mass is carbonaceous soot, while after trap it is sulfate and water (Fig. 10). The authors of this report showed a good sense of humor in concluding that obviously CRT was a very efficient converter for turning carbonaceous soot into sulfate and water...

Another sampling problem, connected with the particle background in a CVS tunnel is presented in Fig. 11. The dilution air in a CVS system is preconditioned, e.g. it contains less particles - in terms of number concentration - than ambient air (first bar vs. second bar). Particle emissions of a EURO III diesel passenger car typically lead to 1000 times higher particle number at the sampling port of the CVS tunnel (3rd bar). Obviously, the particle background has no significant influence on the measured particle concentration. The situation changes completely when the particle emissions of a car with particulate trap are measured (Peugeot 607 HDI). As the car speed up, the exhaust gas volume increases, but the particle number in the CVS tunnel decreases. The exhaust "dilutes" the dilution air (bars 4 to 7). Using direct tailpipe sampling with particle free dilution air the number concentration just after filter was measured (Fig. 12). This number concentration is ten times lower than the particle background in the CVS (Fig. 11, last bar).

**Conclusions (Fig.13)**

It was shown that the repeatability of nanoparticle measurement methods is not much worse - as sometimes claimed - than that of PM measurement, but is of the same order. As future particle emissions are expected to decrease dramatically due to the use of particulate traps, repeatability and reliability of the gravimetric PM measurement will further decrease. In order to improve the repeatability of nanoparticle methods, a thorough calibration concept is needed, though. The sensitivity of nanoparticle methods is by three orders of magnitude better than that of PM and EC measurement. This provides a much better signal-to-noise ratio, especially when particle emissions are very low. While a gravimetric "zero" measurement may still contain a lot of nanoparticles, a "zero" with a nanoparticle method is by a factor 1000 closer to particle free air.

Addressing the issue of dilution and sampling it is once more shown that condensation of vapors may lead to wrong conclusions about trap efficiency. Such erroneous results can be avoided by applying hot dilution and/or direct sampling, or by using material specific particle detection. In CVS systems the particle background may be higher than the particle emissions of a trap equipped vehicle.

**References**

see Figures
Ultralow Emissions from Trap Equipped Diesel Engines, a Challenge for Instrumentation

Markus Kasper
Matter Engineering AG, Wohlen

5th ETH Workshop "Nanoparticle Measurement"

ETH Zürich, 7.8.2001

Traps - a Challenge for Instrumentation

- Repeatability (Round Robin Tests)
- Sensitivity (Signal-to-Noise Ratio)
- Sampling and Dilution

Conclusions
Repeatability: Gravimetry

Figure 5. Variability of the ISO round robin

Repeatability: Elemental Carbon

Figure 4

from: Stein & Herdan (1998), SAE 982043

Repeatability: SMPS Number

Figure 5


M. Kasper: Traps - a Challenge for Instrumentation

Chassis Dynamometer Setup

Figure 6

from: AFHB

M. Kasper: Traps - a Challenge for Instrumentation
### Particulate Emissions as Multiples of the Detection Limits

**Euro III Diesel Passenger Car, 50 km/h**

<table>
<thead>
<tr>
<th>param</th>
<th>method</th>
<th>units</th>
<th>value</th>
<th>DL</th>
<th>multiples</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>grav</td>
<td>[mg/m³]</td>
<td>3.6</td>
<td>0.900¹</td>
<td>4.0</td>
</tr>
<tr>
<td>EC</td>
<td>coul</td>
<td>[mg/m³]</td>
<td>3.2</td>
<td>0.900¹</td>
<td>3.6</td>
</tr>
<tr>
<td>N</td>
<td>SMPS</td>
<td>[cm⁻³]</td>
<td>4.4e+6</td>
<td>500</td>
<td>8.8e+3</td>
</tr>
<tr>
<td>S_{active}</td>
<td>DC</td>
<td>[µm²/cm³]</td>
<td>1.3e+5</td>
<td>5</td>
<td>2.6e+4</td>
</tr>
<tr>
<td>EC</td>
<td>PAS</td>
<td>[µg/m³]</td>
<td>3.2e+3</td>
<td>0.5</td>
<td>6.4e+3</td>
</tr>
</tbody>
</table>

¹ assumed absolute DL: 100 µg sampled material

---

**Figure 7**

M. Kasper: Traps - a Challenge for Instrumentation

---

### Particulate Emissions as Multiples of the Detection Limits

**Euro III Diesel Passenger Car, 50 km/h**

- **PM_{grav}**: 240 secs
- **EC_{coul}**: 90 secs
- **N_{SMPS}**: 1-5 secs
- **S_{act, DC}**: 1-5 secs
- **EC_{PAS}**: 1-5 secs

---

**Figure 8**

M. Kasper: Traps - a Challenge for Instrumentation
Filters from Upstream/Downstream of Trap


Figure 9

M. Kasper: Traps - a Challenge for Instrumentation

Traps Convert Carbon into Sulphate
(“next attempt: turn carbon into gold”)


Figure 10

M. Kasper: Traps - a Challenge for Instrumentation
CVS Measurement: Peugeot 607 with Trap
particle concentrations: ambient air / CVS / MD19 (at tailpipe)

from: Matter Engineering AG / FH Biel

Figure 11

M. Kasper: Traps - a Challenge for Instrumentation

NanoMet Diluter: Direct Sampling

from: Matter Engineering AG
Conclusions

Repeatability within 10-20% is “normal” for PM&EC
- starting point to judge nanoparticle methods
- with low concentrations
- calibration concept is needed

Sensitivity of nanoparticle methods is >1000x better
- lower detection limit / higher signal-to-noise ratio
- smaller uncertainties when surveying legal limits
- gravimetric “ZERO” ~ 1000 x SMPS “ZERO”

Sampling and Dilution
- condensation should be avoided (high T, direct sampling)
- particle background must be lowered
- material specific particle detection