Notes on „Soot“ Measurement of Diesel Engines

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Why bother about Soot Measurement?

- The measurement of “Soot” is a widely accepted method in Engine R&D since several decades.
- It provides information about the quality of the combustion process.
- PMP has decided that agglomeration mode particles should be counted - Such particles typically consist of “soot” in Diesel exhaust.
- There is some evidence that soot is more relevant with regard to health concerns than the homogeneous, volatile “Nanoparticles”.

Gravimetric measurement of total particulate mass after partial-flow or full-flow dilution.
Properties of Soot from Diesel Engines

- Soot is a combustion product. ("Carbon black" is no "soot").
- Soot consists of "Carbonaceus Particles"
- Soot has a combustion temperature in air of >450 °C, it is not volatile or liquid. (compare the measuring proposal of PMP)
- The size is mainly in the "agglomeration mode" range, the structure irregular (fractal dimension 1.8 to 2.5)
- **Soot is “really black”**
Methods for Diesel Soot Measurement

- Analysis of filtered Diesel Particulates
  - chem. extraction
  - thermogravimetry
  - Coulometry

- PMP method:
  Thermodesorption and particle counting

- Via its optical properties:
  - The mass extinction coefficient of Soot is nearly constant for D < 100 nm
  - The scattering coefficient goes with D/λ⁻⁴
How well can various systems measure Soot Mass?

Criteria:
- accuracy - selectivity - measuring artefacts
- concentration:  
  - resolution, detection limit  
  - dynamic range
- repeatability, reproducibility
- time resolution

Target:
To assess the physical limits of various methods and the practical problems encountered when measuring Diesel Soot.
Advantages:
- Simple method, proven reliability, widely used in R&D
- Selectivity: for soot content >15%, FSN is clearly related to Soot concentration
- Detection limit: with high sampling volume 20 µg/m³ or 0,002 FSN achievable
  ⇒ dynamic range > 1: 10000 (concentration)
- Repeatability: 5% achievable (see below)

Challenges:
- Due to the simplicity of the method it is often used uncritically without observing the basic principles of particle measurement.
- A realistic theory of the relation between FSN and Soot concentration does not exist

Drawback:
- time resolution >10 sec by principle
Influences to FSN Measurement:

- Sample Conditioning. FSN is measured from the raw exhaust ⇒ concentrations are high, particle deposition is of considerable concern.
- Hangup after measurement of large FSN: purging is required to avoid re-entrainment during “white level determination” ( <2 µg allowed !)
- Filter paper: if two different filter papers, at opposite ends of the ISO 10054 specification band are used, results may vary by >20%. (AVL makes a special paper check to guarantee ± 5%).
- Soot content: in aerosols with a very small soot core (<15% by mass) “the absorption coefficient is increased”

If measurements are carried out carefully, even the emissions of a Euro 5 HD engine can be measured reproducibly.
Opacity Measurement

- **Advantages:**
  - Good time resolution, \( \leq 0.1 \text{ sec} \)
  - Theoretically well defined (for fixed \( R \))
  - Detection limit: \( k = 0.002 \text{ m}^{-1} \)
    corresponding to \( \approx 300 \mu g/m^3 \)
    (sufficient for non-trap engines)

- **Challenges:**
  - To achieve a stable “Zero” value \( I_0 \)
  - The mass extinction coefficient \( R \) of soot is slightly size dependent (typical uncertainty \( \pm 20\% \))
  - The influence of \( NO_2 \) on the signal is substantial,
    the influence of \( HC \) and \( SO_4 \) only at high concentrations

- **Drawback:**
  - At the current stage the technology is at its limits
Challenges for good Opacity Sensitivity

Good resolution in \( k \) is achieved if:

- \( I_0 \) is stable
- The measuring length \( L \) is large

To some extent the two requirements contradict each other:

If the temperature of gas and chamber walls are not stable, the thermal lens („mirage effect“) changes \( I_0 \)

Temperature changes of 1.5 °C result in an \( I_0 \) change of 0.1%
"Accuracy" - is Opacity related to Soot?

In other words: is

\[ k \text{ (m}^{-1} \text{)} = R \cdot \text{Conz (mg/m}^3 \text{)} \]

with \textbf{konstant} R?

Quantities influencing R:
- Particulate size.
- Particulate composition: (HC and SO$_4$)

Practical experience:
A constant ($\pm$ 20\%) relation between Opacity and Soot is given if:
- NO$_2$ concentration is < 100ppm
- The particulates consist to less than 50\% of HC and SO$_4$
- The exhaust temperature in the measuring chamber is $\geq 100^\circ$C
- The particle size is in the "typical" Diesel exhaust accumulation mode range

The Particulate size dependence of R decreases with increasing $\lambda$

$\rightarrow$ IR extinction (drawback: R decrease with increasing wavelength)
How about light Scattering?

\[ I_s = Fkt( \vartheta, \varphi, \text{d}/\lambda, n, ff) \]
with \[ n = m+ik, \]
\[ ff = \text{form faktor} \]
\[ I_s \propto d^{-6} \]

**In Principle:** The measurement of \( I_s \) at different \( \vartheta, \varphi \) and at different \( \lambda \) can yield a wealth of information about size, size distribution, number, shape.....

**In Practice:**
- Single particle scattering: with reasonable effort the lower size limit is \( \approx 100 \) nm due to low scattering intensity.
- Multi particle scattering: large particles dominate the Signal.
- Multi-wavelength and -angle scattering: the addition of measuring uncertainties introduces ambiguities into the data evaluation.

⇒ A robust and accepted light scattering instrument has not made its way to the market despite substantial and repeated effort in the last 20 years
Photoacoustics - AVL Micro Soot Sensor

- Periodic heating by a modulated laser beam and subsequent cooling generates an acoustic signal that is detected by a microphone.

- Advantages:
  - Sensor is “directly” sensitive to soot concentration
  - High sensitivity (detection limit < 10 µg/m³)

- Challenges:
  - Signal evaluation at low concentrations
  - Repeatability / reproducibility / calibration
  - Currently for diluted exhaust only
Accuracy: Selectivity, Linearity and Comparability

- **Selectivity:**
  No cross-sensitivity from typical or untypical exhaust gases, if the proper near IR Laser wavelength is used (H₂O, HC, SO₄, NO₂,...).

- **Linearity:**
  Due to the physical principle the signal is linear with soot concentration

- **Comparability:**
  According to experience in various laboratories the signal is comparable to the soot determined with gravimetric soot mass determination

$y = 0.9773x - 6E-05$
$R^2 = 0.9914$

Comparability of Photoacoustics with Gravimetry

**Courtesey V. Scheer, FFA**

Research & Advanced Engineering
Reproducibility, Repeatability, Calibration

- **Reproducibility:**
  The near IR frequency of the laser used guarantees, that $D/\lambda$ is small for typical Diesel particulates. Therefore the mass extinction coefficient $R$ is nearly constant.

- **Repeatability:**

- **Calibration:**
  Calibration must be performed in comparison to gravimetric methods. However, the calibration factor in the „PASS“ has not been changed in the last 2 years, and yields the same results as the AVL Micro Soot Sensor.

Comparability of two Photoacoustic instruments (IWC Munich and AVL)

\[
y = 0.9912x + 0.0004 \\
R^2 = 0.9963
\]
Resolution (concentration, time)

- **Resolution:**
  Challenges: Good resolution (below 10 \(\mu g/m^3\)) can be obtained by:
  - Signal evaluation with high frequency selectivity
  - Low noise in the gas path
  - Correct signal evaluation, subtracting the baseline signal from sooted windows phase-corrected

- **Dynamic range:**
  Photoacoustics allows a dynamic range of 1: 10000 (important to detect peaks on low background)

- **Time resolution:**
  1 sec \(\tau_{90}\) is easily achievable, better time resolution currently sacrifices concentration detectivity
Laser Induced Incandescence (LII)

- High sensitivity for ultra-low emission
- Good time resolution for transient testing
- In-situ raw exhaust gas measurement

However:
- Substantial costs, due to expensive laser
- Serious laser hazards
Summary

- Several Methods exist to measure Soot on the basis of its strong absorption coefficient.
- If these methods are used with attention and some basic knowledge about particulate measurement they can give reliable soot data even for very low soot concentration in the exhaust.
- The method proposed by PMP for measuring particles seems feasible - the interlaboratory exercise has not yet started - but practically it measures only the soot fraction of the Diesel exhaust.
- A second thought on mass-proportional soot measurement methods as a viable alternative seems appropriate.