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Zusammenfassung / Résumé / Summary

An experimental setup with associated calibration procedures for the measurement of particle number concentration of diesel engine exhaust gases was proposed from PMP (Particle Measurement Project) to UNECE, the World Forum for Harmonization of Vehicle Regulations (WP 29) to be included as appendix 4a in ECE-R 83. The Automotive industry (OICA) provided experimental data, revealing, that the proposed PMP setup and calibration procedures result in a poorer accuracy than the established gravimetric method. Therefore UNECE has postponed the inclusion of appendix 4 a in the ECE-R 83.

On request by the involved bodies (FOEF, FEDRO and PMP) METAS analysed the proposed experimental setup with associated calibration procedure and detected several points for potential accuracy improvement. The following points should be reconsidered and revised:

- Simplification of the measuring system (e.g. the use of only one diluter instead of two diluters to reduce the bias and uncertainty of the over-all system)
- The proposed "calibration" of the individual components of the measuring system describes procedures that are not calibration in metrological terms but tests, validation etc. These procedures should be rearranged and defined as requirements.
- These elaborated "calibrations" are not equivalent to the calibration of the complete system. The component calibration should be amended by a simple over-all calibration.
- A three-part calibration/validation concept is proposed:
  1. Regular calibration of the particle counters with internationally recognized and accepted standards
  2. Validation of the complete laboratory infrastructure for proper sampling and measuring of particle number concentrations
  3. Calibration of the over-all system prior to each measurement or measurement series

METAS is convinced that the particle number concentration method has, with the proposed improvements, a much higher potential for reliable and sensitive measurement than the established gravimetric measurement.

Sektion, Bereich / Section, Ressort / Section, Field	Unterschrift Sektions- oder Bereichsleiter / Signature du chef de section ou de ressort / Signature head of section or field
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Comments to the PMP setup and Calibration Procedure

1 General view of the PMP

The goal of the proposed experimental setup and calibration procedure is to establish reliable measuring results for the particle number concentration from diesel exhaust. Figure 1 shows the actual PMP measuring system for particle number concentration.

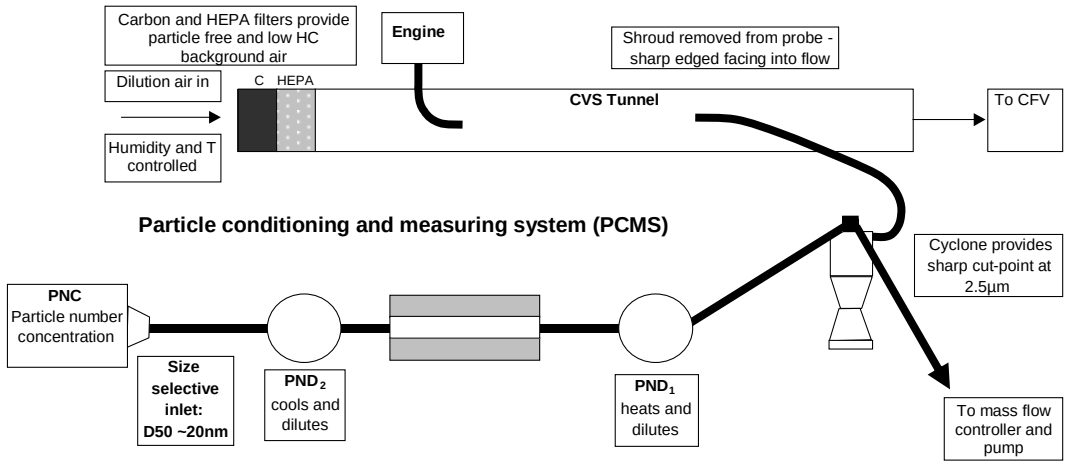

Figure 1 Schematic diagram of particle number emissions measurement system.

The boundary conditions and assumptions are:

- The exhaust gas is available at elevated temperature in the CVS tunnel
- The particle concentration in the CVS Tunnel varies from zero to about 10^8 cm^{-3}
- The temporal relative gradient of the particle concentration $\frac{1}{N} \cdot \frac{\partial N}{\partial t}$ can rise over 0.1 s^{-1}
- The particle conditioning and measuring system (PCMS) consists of several components as cyclone, aerosol heating diluters (PND = particle number diluter), evaporation tube (ET) and a particle counter (PNC = Particle number counter)
- The over-all system – called Particle Conditioning and Measuring System (PCMS) – contains all components from cyclone to PNC.

2 Calibration levels

2.1 *Terminology: calibration*

According to VIM (International Vocabulary of Metrology) the expression "calibration" signifies the "set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards".

Therefore the calibration gives the quantitative information about the bias of the instrument compared to a reference standard. The result of a calibration is summarized in a document called a calibration certificate or a calibration report.

Attention should be paid that the calibration covers only the instrument at the specific circumstances during the calibration procedure. The application of that instrument in another setup can cause deviations, which cannot be predicted by the calibration.

2.2 "Component calibration" (partially in the PMP proposal)

The proposed procedures for the calibration of the measuring system for exhaust describe the "calibration" of single components as PND, ET or PNC. The term calibration is not correct for all the proposed procedures. The procedures are a mixture of calibration, testing and verification.

Following components are or should be considered:

- Cyclone: Up to now no examination of the influence of the cyclone is provided
- PND: Calibration of the dilution factors with gas is not equivalent to dilution factors with particles!
- PND: Control of the penetration efficiency is only used to define specifications. Penetration is evaluated for particle diameters 30 nm, 50 nm and 100 nm
- PNC: Control of the linearity, Calibration of the flows, Calibration with a reference PNC (more significant than linearity check and shall replace it)
- Response Time: Up to now no examination of the behaviour with fast concentration changes is provided. But the response behaviour can be important, if short events with high concentrations contribute a large fraction of particles.
- Each component of the Particle Conditioning and Measuring System (PCMS) contributes a portion of uncertainty. Therefore accuracy can be gained by simplifying the measuring system. The most obvious simplification is to remove one PND.

The "component calibration" characterise the system step by step. This characterisation is not sufficient to guarantee reliable results, because slight modifications for the final setup and interaction of the components can falsify the results. Example: Changing the pressure in the tubes of PND change the dilution flows, dilution ratio, and particle loss and the aerosol flow in the PNC.

2.3 "Over-all calibration" = PCMS calibration (not in PMP proposal)

The ideal case is the calibration of the "Particle conditioning and measuring system" (PCMS) with a reference standard. This is not possible with real exhaust particles at real transient conditions. But a procedure with a test aerosol at constant concentrations or well defined changes of concentrations could substitute it. The necessary tools are prepared with the "Component calibration".

3 "Dilution factor" and "Penetration efficiency" versus "Concentration Reduction Factor"

The proposed calibration procedure demands in a first step the calibration of the diluters with trace gas in order to give a nominal dilution factor. In a second step it defines minimal penetration efficiencies. This procedure in two steps creates bias and uncertainties that are not necessary.

Particle diluters shall be calibrated directly with particles, because particles do not behave like gases. The size dependent losses are too important. The expression "dilution factor" (PND-DF) is misleading; we propose to define a "particle concentration reduction factor".

The term "dilution factor" implies the image of mixing two flows, where the merged volume flow and the merged mass flow correspond to the sum of the initial flows (conservation of mass). Starting with PND-DF and defining minimal penetration efficiencies (PE) always leads to systematically too small particle concentrations, because losses are not compensated. Therefore the concentration of 100 nm particles (diluted with a PE of 80 %) underrates to 20 %, with 30 nm particles even up to 50 %. There is no particle size with a correct concentration measurement. This is a large contribution to the uncertainty.

The term "particle concentration reduction factor" $f_r(d)$ just implies the over-all quotient between the inlet concentration N_{in} and the outlet concentration N_{out} for a given particle diameter d: $f_r(d) = N_{in} / N_{out}$. The reason or the physics for the reduction of the particle concentration is not important, as long as it is reproducible and identical for all particles of the given size. This concept should be applied for the over-all system (from CVS Tunnel to PNC). Working with f_r the deviations are symmetric. While the concentration of 100 nm will be overrated, the concentration of 30 nm will be underrated. The concentration measurement of a size in between will correct. The use of this reference value will lead the smaller uncertainties (see Figure 2).

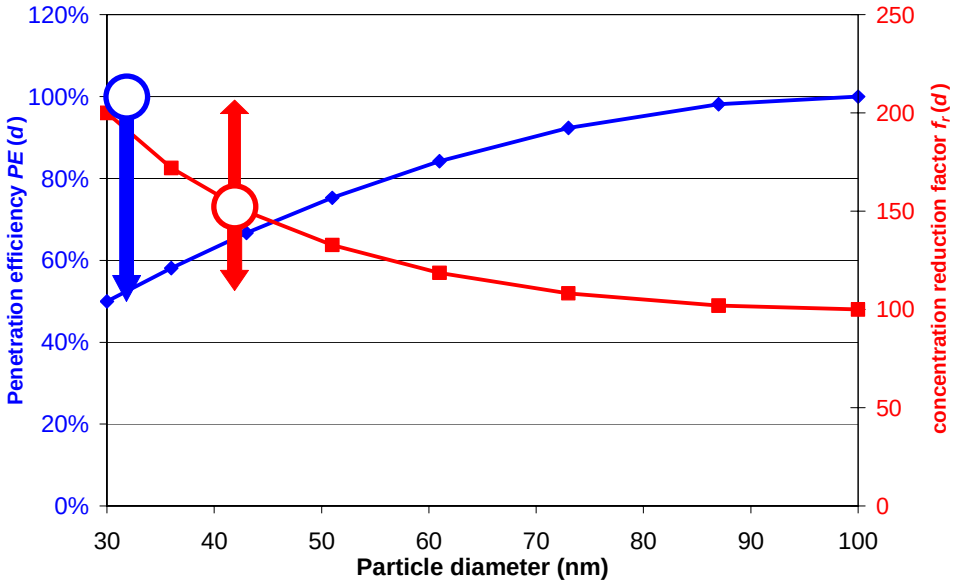

Figure 2 Comparison of the two concepts for the indication of particle dilution (principle): Arrows show the maximal deviation of effective to the reference value (circles). Using f_r instead of PE=100% leads to smaller deviations

In any case (both concepts) in order to get reliable measurements the size dependence of the losses must be reduced. This is the legitimate objection of automotive industry (OICA). The "particle concentration reduction factor" shall not vary more than 20 % in the range from 30 nm to 100 nm, this means $f_r(30\ nm) / f_r(100\ nm) > 0.8$. Probably not all diluter systems can fulfil such tough requirements.

METAS calibrate diluters always just before the measurement and keeps all settings constant afterwards.

4 New Calibration concept (METAS proposal)

This proposal gives a well structured procedure with three calibration or validation levels: Laboratory reference standards, laboratory infrastructure, and measurement preparation.

Most operations are already described in the PMP documents 17-4 and 18-1. They just need to be rearranged and completed by further test points.

4.1 Calibration of the "Laboratory reference standard"

The particle counter (NPC) is the key component of the system. It shall be periodically calibrated with internationally established standards (see also ISO NPWI 27891). This calibration is carried out by specialized laboratories (e.g. national metrology institutes). The periodicity of this calibration is to be defined (e.g. 6 months).

This calibration shall consist in following elements:

- Calibration of the internal flow meter as a function of the aerosol pressure. The flow must be referred to defined conditions (e.g. 0 °C and 1013 hPa).
- Calibration of the number concentration of 30 nm, 50 nm, 100 nm monodisperse particles at 100 cm^{-3}, 200 cm^{-3}, 500 cm^{-3}, 1 000 cm^{-3}, 5 000 cm^{-3}, and 10 000 cm^{-3}. Attention: coincidence may become important above 1 000 cm^{-3} and can not be neglected at 10 000 cm^{-3}. Coincidence shall be detected and its correction shall be accepted to a defined level.
- Evaluation of the detection efficiency for small particles in order to determine the detection limit. This curve shall fulfil defined requirements.
- Evaluation of the temporal response characteristics of the PNC. Here it is assumed that the contribution of the response time of the PNC probably dominates the over-all response time. Then it shall fulfil defined requirements.

4.2 Validation of the "Laboratory infrastructure"

The laboratory infrastructure shall be well known. This means the influence of all parameters is known quantitatively. After that evaluation the tolerances for these parameters can be determined from the sensitivity analysis.

The stability of a parameter defines the interval for the subsequent control of the parameter. Changes in the setup must be followed by a renewed evaluation.

Parameters to evaluate:

- Flows, temperature, and pressure in the diluter define the dilution ratio, the residence time and therefore the time constant and the size sensitive particle loss
- Geometry, flow and gas temperatures at inlet/outlet in the heated tube define the residence time, the suppression of nucleation particles, and solid particle loss
- Temperature in the heated tube (and diluters) define the solid particle loss (thermophoresis)
- The geometry of the tubing between the components defines the residence time and the losses
- Size dependent "concentration reduction factor" $f_r(d)$ for the used setting(s)

4.3 Calibration for the "Measurement preparation"

The evaluation of the components is important for knowing the influence parameters, but it is not equivalent to a calibration of the over-all system PCMS. Therefore the final calibration of the PCMS shall be performed before each measurement or measurement series.

Procedure for the PCMS calibration:

- The final setup of the measuring system with all parameters is fixed
- Aerosol with 100 nm particles is generated
- Number concentration is just below the detection limit of the PNC (maximum calibrated concentration)
- When number concentration is stable at the outlet of the generator the concentration is measured with the calibrated PNC ($N_{u100} \pm u_{u100}$ = upstream concentration and uncertainty of PCMS).
- The same aerosol is fed to the inlet upstream the cyclone and the concentration is measured with the PNC as a part of the PCMS ($N_{d100} \pm u_{d100}$)
- Repeat the procedure with 30 nm particles (N_{u30} and N_{d30} = downstream concentration an uncertainty of PCMS)
- Calculate f_r(100 nm), f_r(30 nm) and $f_r = (N_{u30} + N_{u100}) / (N_{d30} + N_{d100})$ and their uncertainties.

5 Related documents

- Condensation Particle Counter Calibration Procedures; Working paper no. GRPE-PMP-17-4, September 2006
- Volatile Particle Remover Calibration Procedure; AEA/ED48512/DRAFT, September 2006, GRPE-PMP-18-1
- Review of proposed calibration procedures for the PMP Volatile Particle Remover; NPL Report AS (Res) 001, May 2007
- Comment of OICA, Informal document No. GRPE-54-14, June 2007