Validation of new, used and re-calibrated automotive CPCs

Light duty vehicles UN-ECE Regulation 83 introduced the (non-volatile) particle number method based on the findings of PMP. Heavy duty engines UN-ECE Regulation 49 will follow. The volatiles and semi-volatiles are removed with a hot diluter and an evaporation tube; then the non-volatile particles are counted with a Condensation Particle Counter (CPC). The CPC should be calibrated annually either with an electrometer or a CPC that has been calibrated with an electrometer. The calibration includes the counting efficiencies at 23 nm and 41 nm, which should be 0.50 ± 0.12 and >0.90 respectively. In addition, the calibration includes the linearity check at different concentrations across the range from 1 cm⁻³ to the upper threshold of the single particle count mode. The linear regression between the reference instrument and the CPC under calibration should give a slope also within 0.9 and 1.1. This value must be used as the correction factor of the CPC.

Before a certification test of a vehicle, it is required that the CPC has a valid calibration certificate and there is no error message during the measurement (e.g. temperatures, flow etc). This can be achieved either by sending back the CPC to the manufacturer for re-calibration or conducting a validation at the lab (check of linearity and 23 nm cut-point). We checked used, re-calibrated or new CPCs according to the calibration procedures described in UN-ECE Regulation 83 (we validate according to the terminology used herein). The main target was to see if the CPCs are within the legislation requirement, if there are indications of non-linearity and if there is any drift over time.

More specifically, thirteen TSI Condensation Particle Counters (CPCs) (model 3790 for automotive exhaust measurements) were validated with thermally pre-treated mini CAST particles i) immediately after their original calibration from the manufacturer, ii) immediately after a re-calibration or iii) after one and a half years measuring automotive exhaust aerosol. In addition, one CPC was validated after 2.5 years while not being in use. From the 13 cases, 4 cases didn’t meet the 23 nm requirement (the counting efficiency should be between 0.38 and 0.62), and 3 cases the slope (should be between 0.9 and 1.1). The main reason that the 23 nm requirements were not met was that different aerosol was used (emery oil from TSI and mini CAST particles from AVL). The difference of the counting efficiencies between emery oil and mini CAST were found similar with the differences reported in the literature (~0.15, ~0.06 for 23 and 41 nm respectively).

One reason that one CPC had lower counting efficiencies was the decrease of its flow rate (possible the orifice was dirty). This was not identified by the light indicators of the instrument since the flow rate measurement is based on pressure difference measurement and a constant surface area of the orifice. The validation results of one CPC immediately after its calibration and after 2.5 years (the CPC was not in use) were similar indicating that there is no drift when the CPC is not being used. However, from the 5 CPCs that were validated after 1.5 years measuring automotive exhaust aerosol, two had significantly lower counting efficiencies (25% lower). This drift was found to originate from the wick of the instrument. However the drift couldn’t not be identified by the light indicators of the instrument or any other external measurements. The ratios of the test CPCs to the reference CPC were constant with no particular decreasing or increasing trend regardless of the concentration with a few exceptions of older models. For these CPCs a 7% difference was found between low (10 cm⁻³) and high concentrations (10000 cm⁻³). The non-linearity of the CPCs is an important topic, since, theoretically two particle number systems could have 40% differences and still being within legislation requirements.

It was also found that a change of the temperature difference between saturator and condenser affects the linearity of the CPCs and should be avoided. Changing the temperature difference form ~7°C to ~17°C can result in a non-linearity of 50% between low (10 cm⁻³) and high concentrations (10000 cm⁻³).
PARTICLE NUMBER COUNTERs (PNCs)

Validation of new, used, and re-calibrated automotive PNCs

24.08.2010

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Outline

- Introduction
- Experimental
- Results
- Discussion
- Conclusions
UN-ECE Reg. 83: Light duty particle number regulation

PNC
Full flow
±10% accuracy
$\tau_{90} < 5$ s
$CE_{23} = 0.50 \pm 0.12$
$CE_{41} = \geq 0.9$

PND_2 (Not required)
$t$ to PNC $< 35^\circ C$
RT to PNC $\leq 0.8$ s ($d_{in} \geq 4$ mm)

Evaporation Tube
300-400°C wall temperature
no RT restriction

PND_1
DF $> 10$
PND_1 $t_{sample} > 150^\circ C$

Total RT $\leq 20$ s ($\tau_{90}$)

HEPA

Dilution Tunnel (CVS)

VPR: Volatile Particle Remover

PCRF

PCRF_{30} \leq 1.3 \, PCRF_{100}
PCRF_{50} \leq 1.2 \, PCRF_{100}

Volatile Removal Efficiency

$> 99\%$ of $\geq 30$ nm tetracontane with $10^4$ p/cm$^3$

PTS
RT to PND_1 $\leq 3$ s
$d_{in} \geq 8$ mm
Re $< 1700$

±
PNC (Particle Number Counter)

PNC requirements
- Full flow
- \( \tau_{90} < 5 \) s
- Linearity: Slope 0.9-1.1, \( R^2 > 0.97 \), all six concentrations ±10%
- Counting Efficiency \( CE_{23} = 0.50 \pm 0.12 \), \( CE_{41} \geq 0.9 \)

PNC check
- Light indicators
- External flow check monthly

Target was to see if they are within legislation requirements, and if there is any drift over time

PNC calibration (yearly)
- Comparison with electrometer (primary) or reference PNC (secondary method)
- Linearity: Slope 0.9-1.1, \( R^2 > 0.97 \), all six concentrations ±10%
- Counting Efficiency \( CE_{23} = 0.50 \pm 0.12 \), (optional \( CE_{41} \geq 0.9 \))
TSI PNC 3790
PNC calibration setup

Particle Generator: mini CAST

Test PNC: 3790 (d_{50}=23 nm)
Reference PNC: 3775 (d_{50}=5 nm)

Giechaskiel et al. 2009, AST, 43, 1164
# PNCs original calibrations (from TSI)

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Regulation 83 limits:  
- 0.95 – 1.05  
- 0.38 – 0.62  
- 0.9 – 1.1  
- 1.005 (±1%)  
- 0.55 (±6%)  
- 0.94 (±2%)
## PNC validations

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<th>SN</th>
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Regulation 83 limits: \[0.95 \text{ -- } 1.05\] \[0.38 \text{ -- } 0.62\] \[0.9 \text{ -- } 1.1\]

Failed: \begin{align*}
1 & \quad 0.89 \\
4 & \quad 0.92 \\
(12) & \quad 1.02 \\
3 & \quad 0.77
\end{align*}

In total 6/13 PNCs failed. Reasons:
- Flow (1)
- Different material used for the calibration (3)
- Degrading of PNC parts (2)
Labs that produce their own generators should be careful.
NaCl gave the lowest counting efficiencies.
CAST gave similar results with diesel exhaust particles.
Emery oil gave higher counting efficiencies than CAST.
Degrading over time

After 2.5 years of no use, no drift was observed
Some PNCs drifted
The reason is the wick (where the super-saturation is achieved)
The critical point: **No light indicator identified this degrading**

Giechaskiel and Bergmann 2010, submitted to JAS
PNC linearity

The non-linearity can affect both VPR calibration and Measurements with different dilutions (thus concentrations)

- Linear regression might be misleading because the slope is defined by the point with the highest concentration! The residuals are necessary for a correct evaluation.

Giechaskiel and Stilianakis 2009, MST, 20, 077003
Giechaskiel et al. 2008, MST, 19, 095401
Fletscher et al. 2009, AST, 43, 425
New certificate

What about <2000 p/cm³?

Uncertainty >10%

Uncertainty 5%
When the temperature difference of the saturator and evaporator changes, the cut-off size changes.

However, the 3790 PNCs shouldn’t be modified, since the linearity is affected.
PNC validation (monodisperse) & check (polydisperse)
PNC validation (monodisperse) & check (polydisperse)

- For the linearity:
  Monodisperse and polydisperse methods are equivalent
- Slope and ±10% requirements can be checked
- The PNCs might not be completely linear
- The key message is that labs can easily check the linearity of their PNCs
Conclusions PNC

Validation of 13 PNCs (3790 TSI) showed that 4 cases failed the 23 nm requirement, 12 the 41 nm, 3 the slope. The reasons:

- Emery oil and CAST have different counting effic. (0.15, +0.06 for 23, 41 nm).
- The flow of one PNC was lower (dirty orifice?)
- Two out of five used PNCs had lower efficiencies due to a degraded wick

No drift was observed for a PNC not in use

A few PNCs had a minor non-linearity issue.

A change of the temperature difference between saturator and condenser should be avoided.

The linearity of the PNCs can be checked with polydisperse aerosol

The 23 nm cut-off size with polydisperse aerosol needs further investigation.
Thank you for your attention!