



PMP 33RD MEETING

**Institute for Energy and Transport
Joint Research Centre**

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30 Sept 2014

Outlook

- *Regeneration*
- *Sub23nm*
 - Status / Need of change?
 - Vehicles
 - PN systems
- *Catalytic Stripper (CS)*
- *Calibration*
 - Status / Need of change?
 - PNC
 - VPR



Calibration

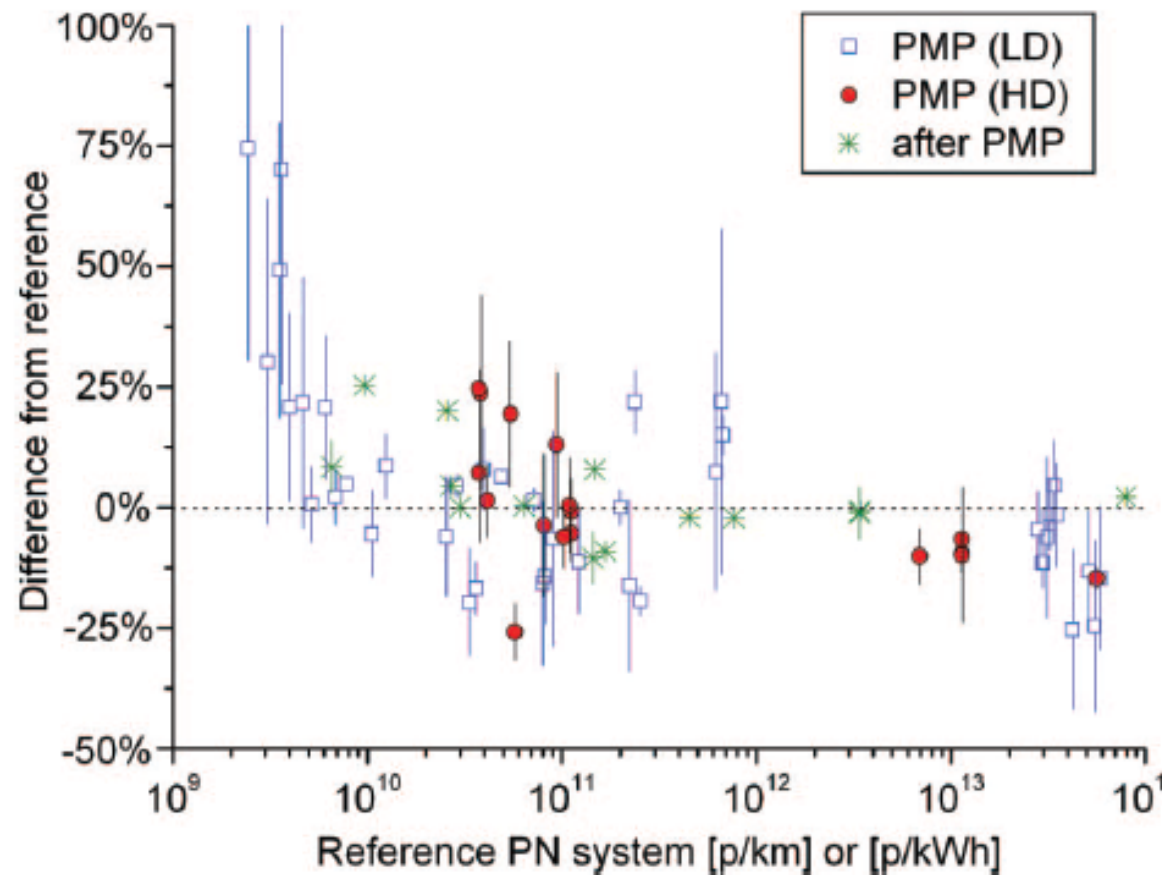


Calibration topics overview

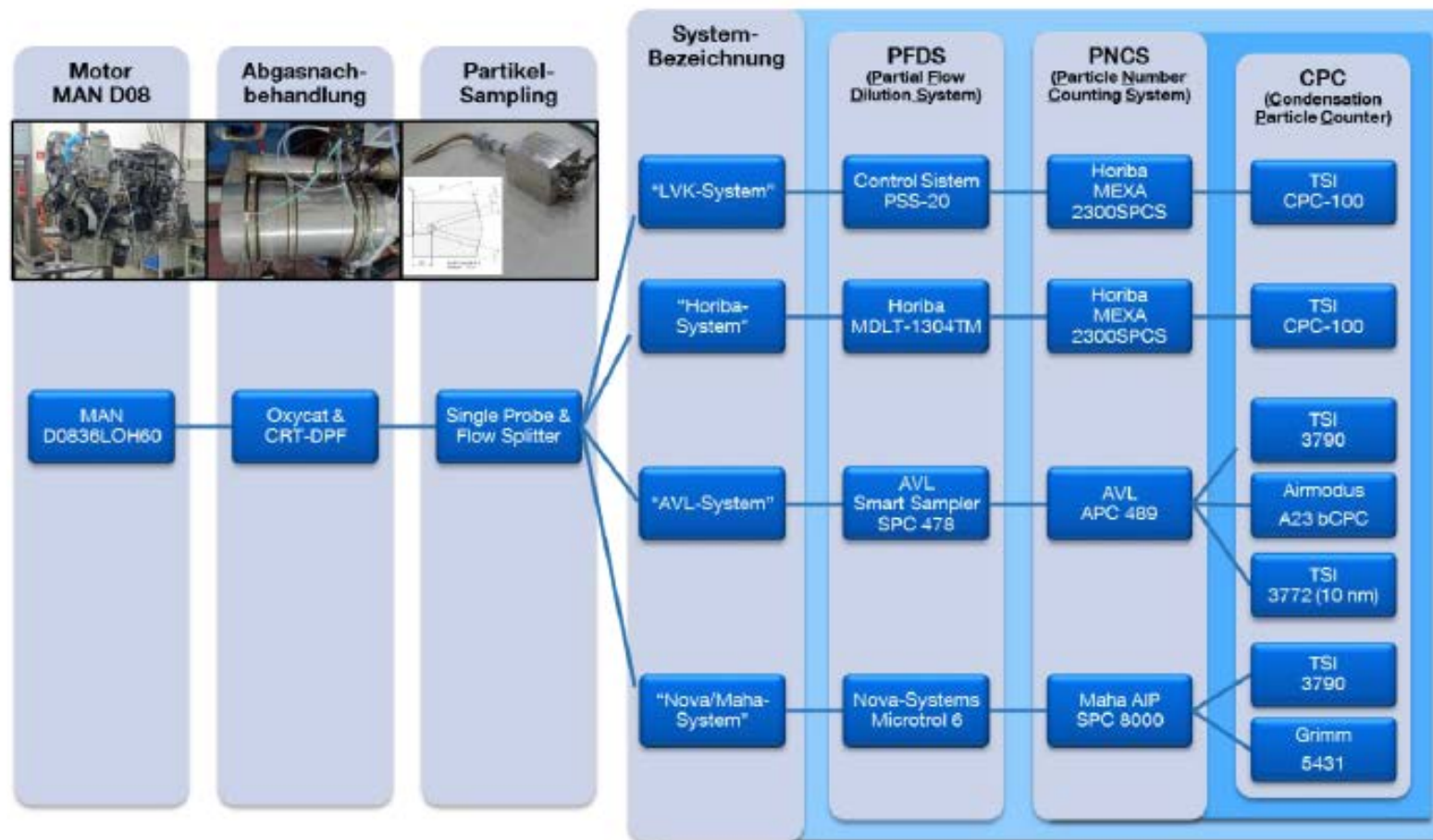
- *Is there a need?*
- *Status PNC*
- *Status VPR*
- *Open issues VPR*

PN systems: Comparability

*From $\pm 30\%$ (PMP)
to $\pm 15\%$ (R83, 49)*

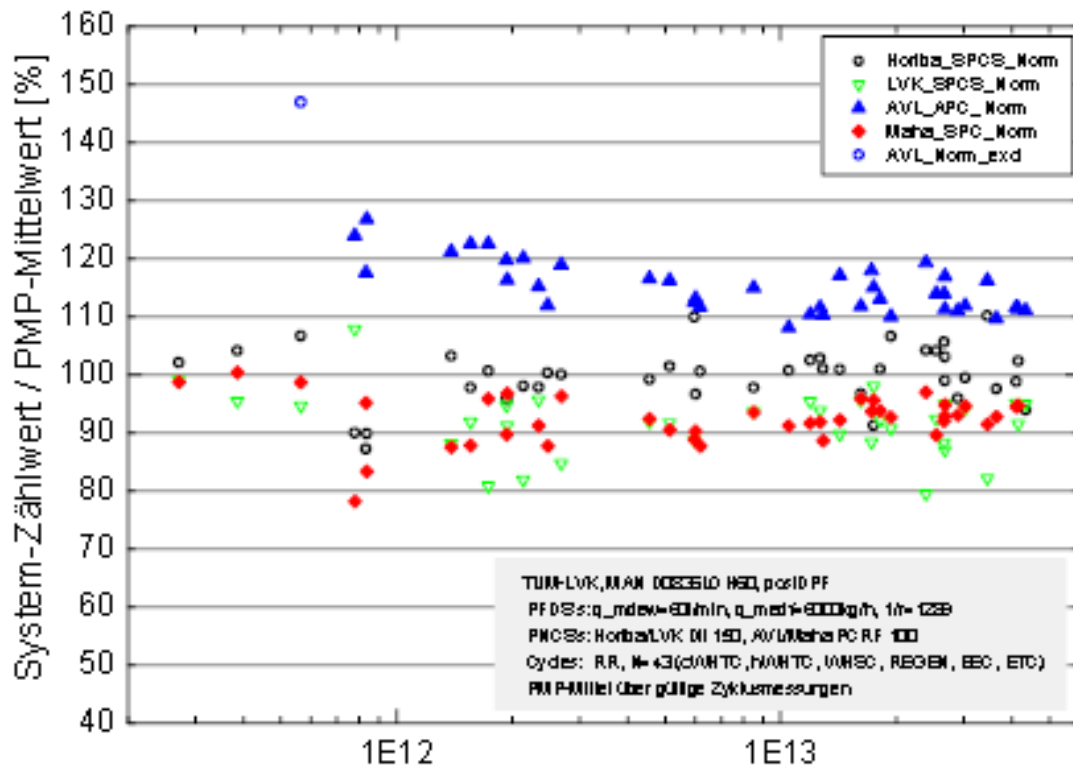


FVV: HD partial flow systems



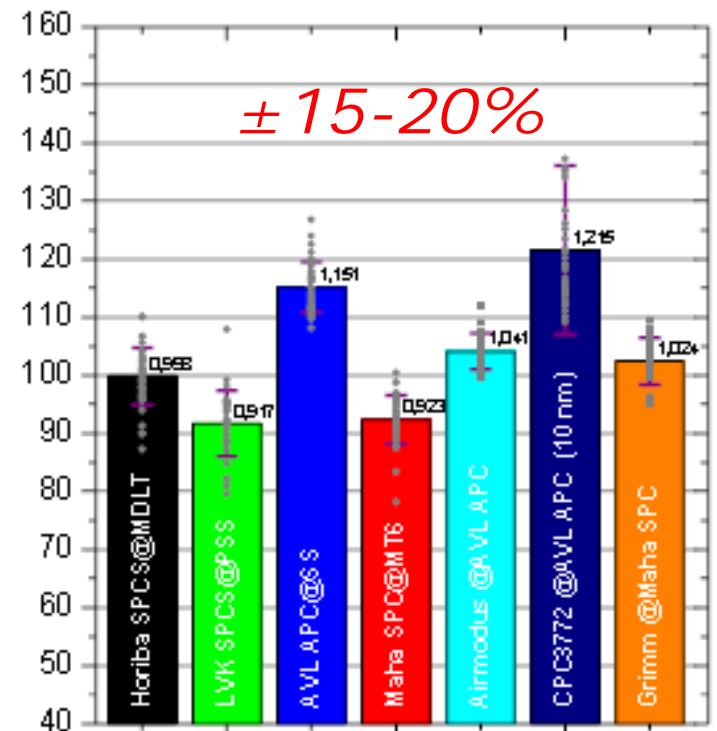
FVV: PN systems comparability

Phase 1 - Normalisierte Systemzählwerte über PMP-Mittelwert



PMP-Mittelwert d. zyklusintegrierten Partikelanzahl [# / Zyklus]

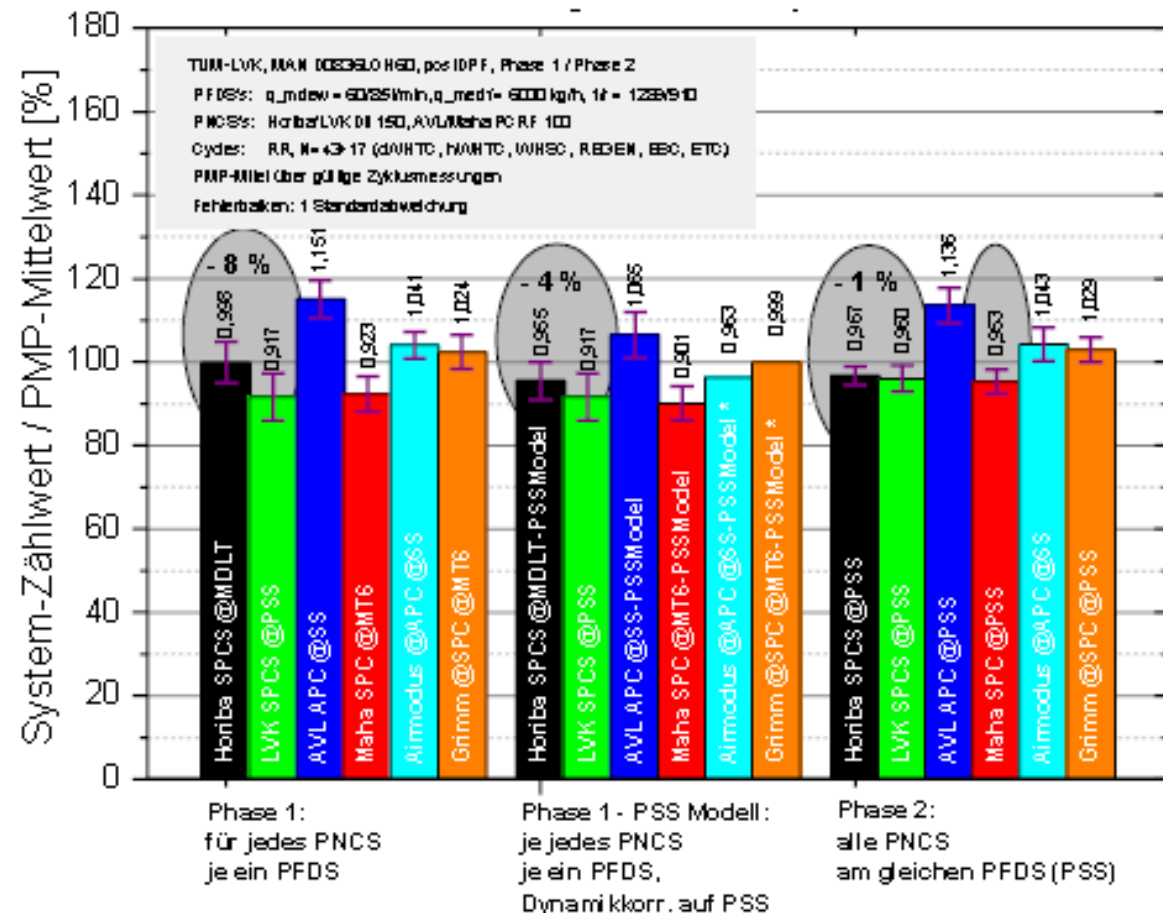
Phase 1 - Kampagnengemittelte Systemzählwerte



PMP-Systembezeichnung

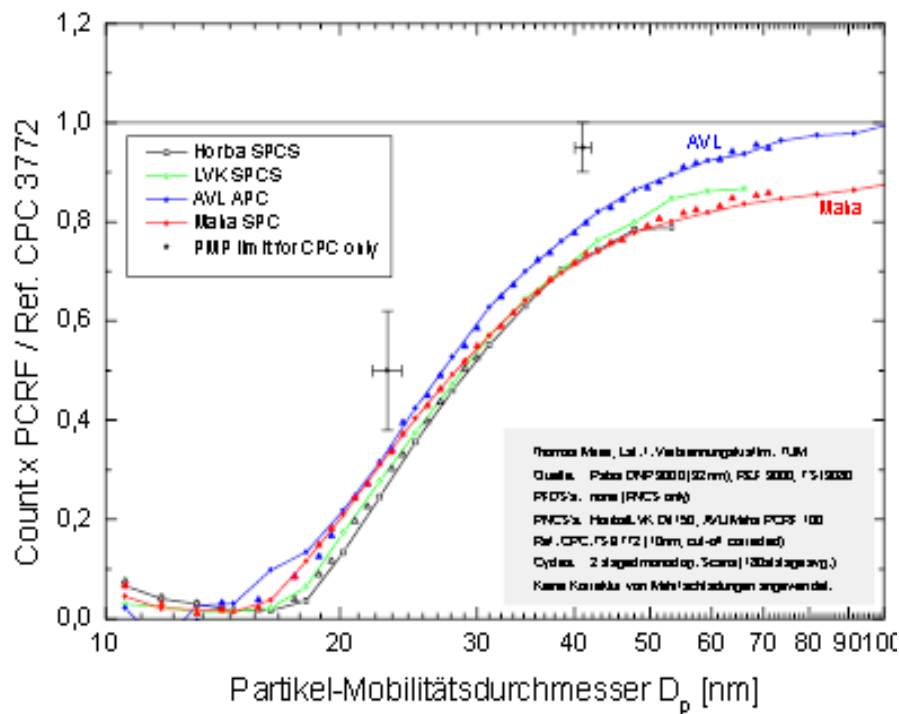
FVV: Influencing factors

- *Partial flow system response $\pm 4\%$*
- *Partial flow system calibration and losses $\pm 4\%$*
- *PN system calibration $\pm 7-12\%$*

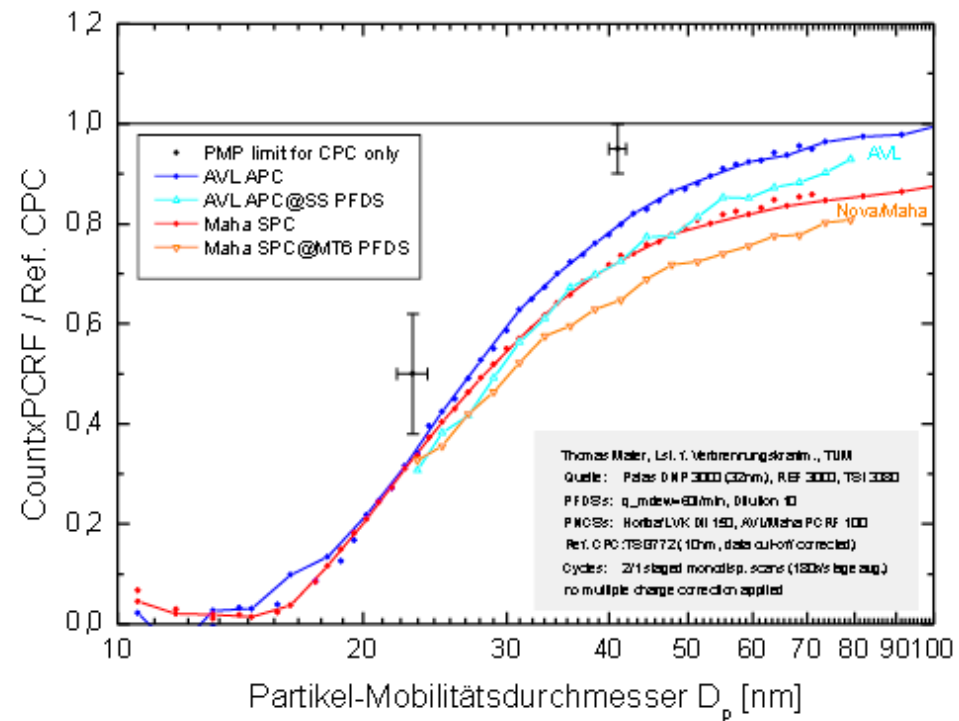


FVV: Calibration of systems

PNCS Gesamt-Cut-off



(PNCS) vs. (PFDS & PNCS) Gesamt-Cut-off Vergleich



10-15% improvement can be achieved (BOTH VPR and PNC)



PNC calibration

PNCs (CPCs) status

- *Legislation and AEA document (Dec 2007)*
- *Bibliographic review*
- *ISO 27891 covers procedures*
 - Multiply charged particles
 - Reference PNC cut-off
 - Procedure
- *EMRP*
- *Open issues*



Legislation / AEA

PNC requirements

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

PNC check

- *Zero < 0.2 p/cm³*
- *External flow check (monthly)*

PNC calibration (yearly)

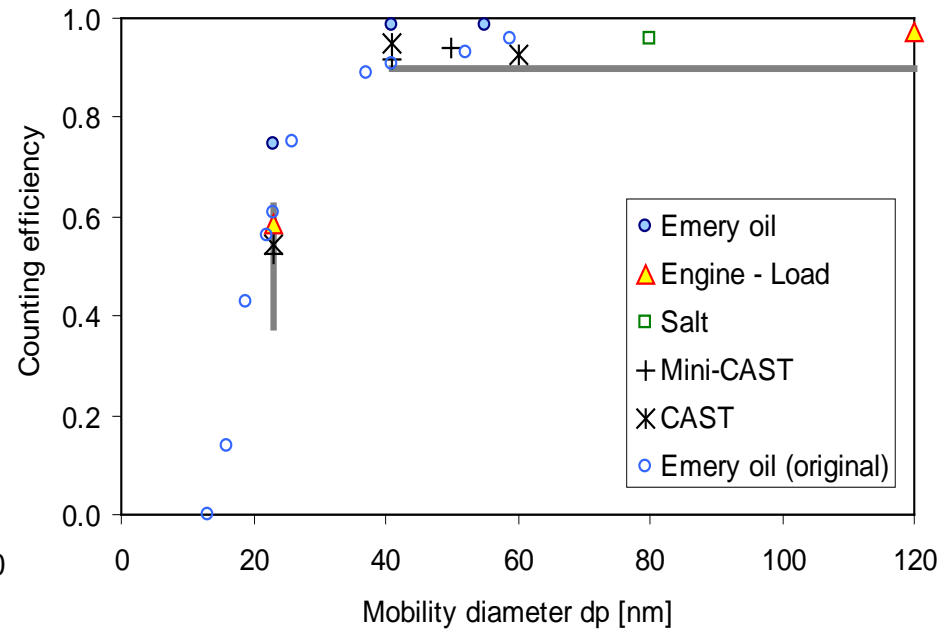
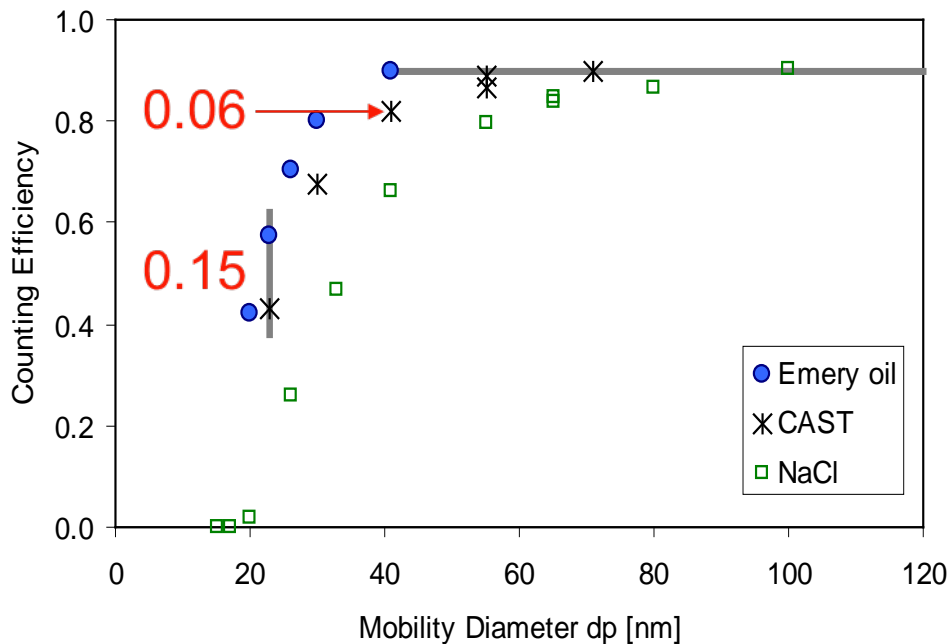
- *Comparison with electrometer (primary) or reference PNC (secondary method)*
- *Linearity: Slope 0.9-1.1, $R^2 > 0.97$, all six concentrations $\pm 10\%$*
- *Counting Efficiency $CE_{23} = 0.50 \pm 0.12$, (optional $CE_{41} = \geq 0.9$)*

PNC issues

- *Cut-off ($d_{50\%}$) of Reference PNC not specified*
- *Calibration material*
 - For linearity any material is allowed
 - For $d_{50\%}$ only emery oil and CAST
 - Emery oil gives higher CE
- *Allowed (Non-) Linearity (20%)*
- *k factor correction*
 - If applied $d_{50\%}$ might be outside the limits
 - If not the $d_{50\%}$ range is wider (0.38 – 0.68)
- *Drift / degradation over time*

Effect of material

- *NaCl gave the lowest counting efficiencies*
- *CAST and mini-CAST gave similar results with diesel exhaust particles*
- *Emery oil gave higher counting efficiencies than CAST*



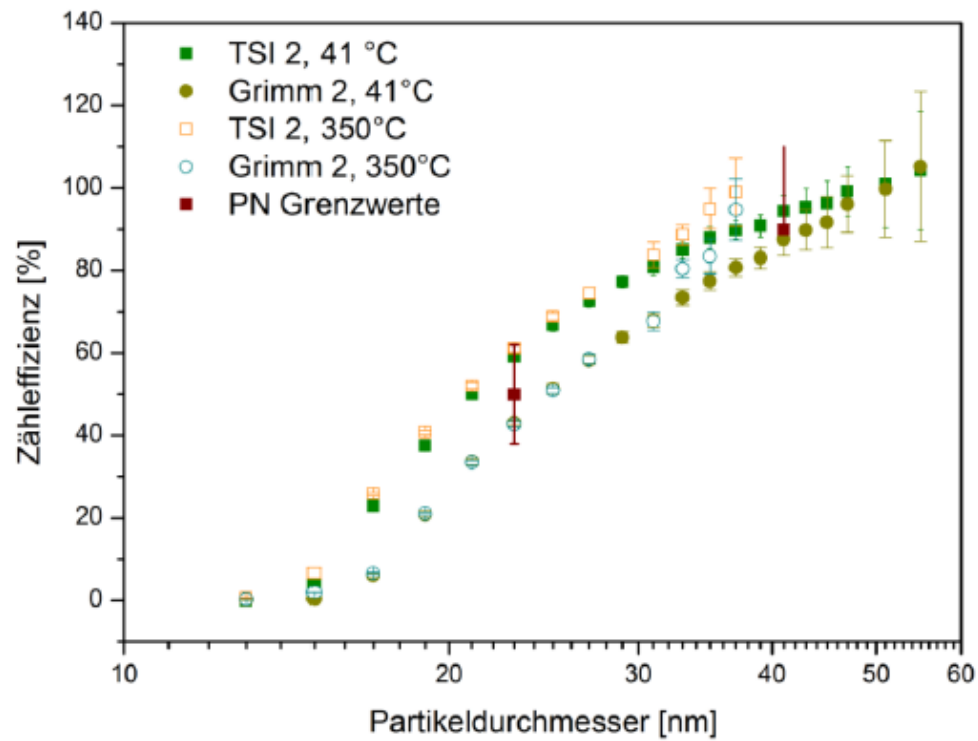
Effect of material: mini CAST

FVV:

no effect of thermal pre-treatment of mini CAST on CE

JRC:

low CE (33-39%, APG mode 15nm) to normal (47%, APG mode 70 nm)



Effect of material

- *Emery oil*
Difficult to reproduce in other labs
- *CAST*
Different counting efficiencies with different CAST settings with thermal pre-treatment.
Concerns for different CAST models

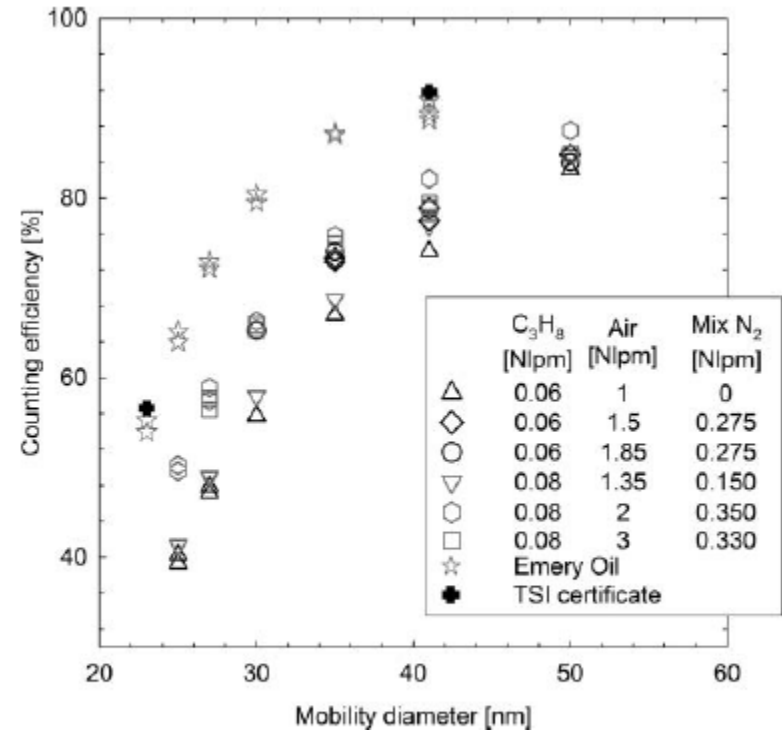
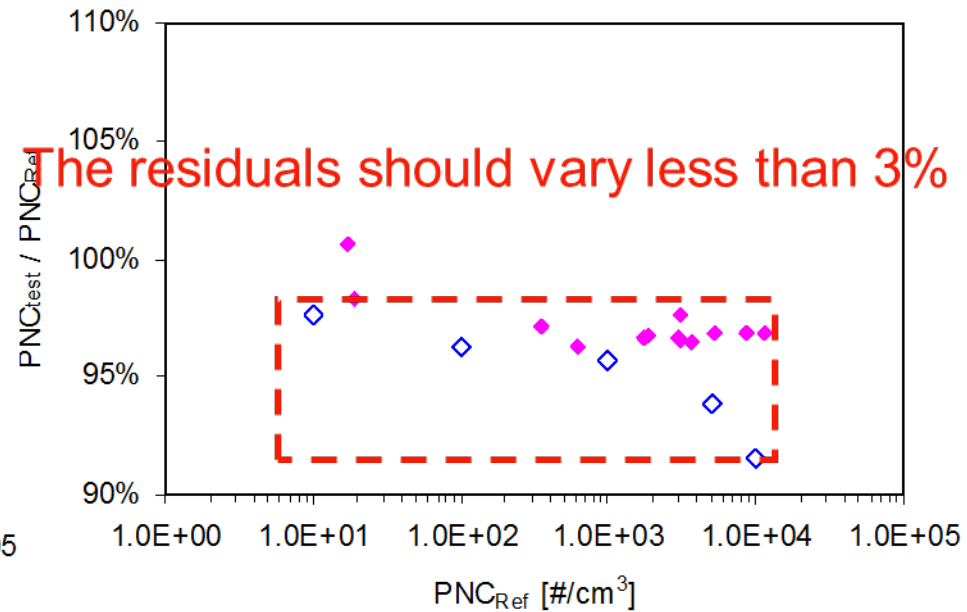
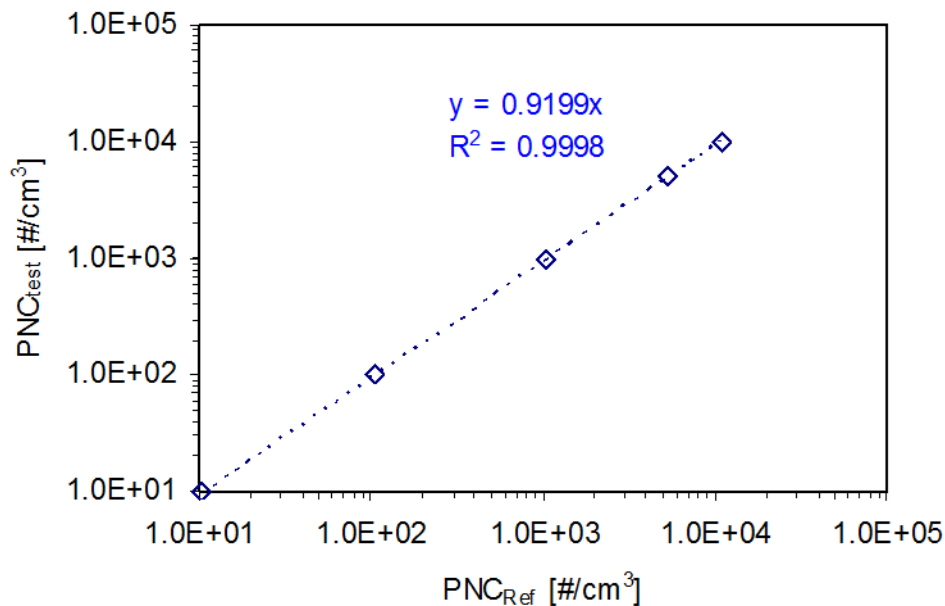


FIG. 5. Counting efficiencies of the TSI 3790 CPC against emery oil (star symbols) and different mini-CAST particles. The certification values by TSI, determined using emery oil, are also shown (crosses).

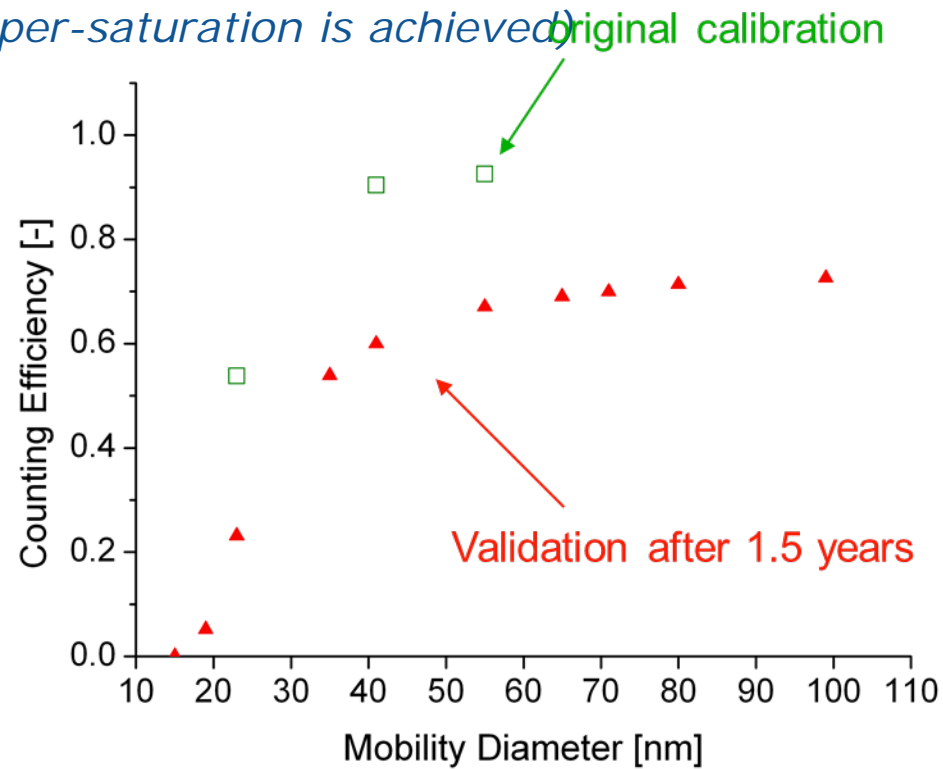
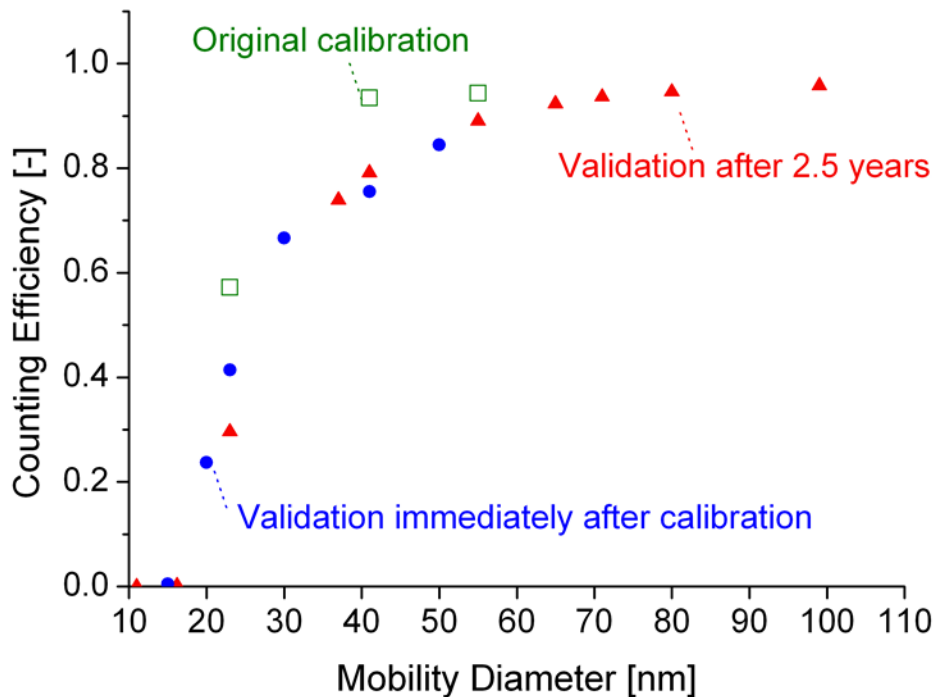
(Non-) Linearity

- *Linear regression might be misleading. The residuals are necessary*
- *The non-linearity can affect both VPR calibration and measurements with different dilutions (thus concentrations)*



Degradation 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)



ISO 27891

- *More detailed/strict calibration setup/procedure*
 - Set-up / position of instruments
 - Repetitions
 - Multiply charged particles
 - Adds uncertainty of calibration value
- *Possibility to check/calibrate $< 1000 \text{ p/cm}^3$*
- *PNC reference d_{min} (almost at the plateau)*

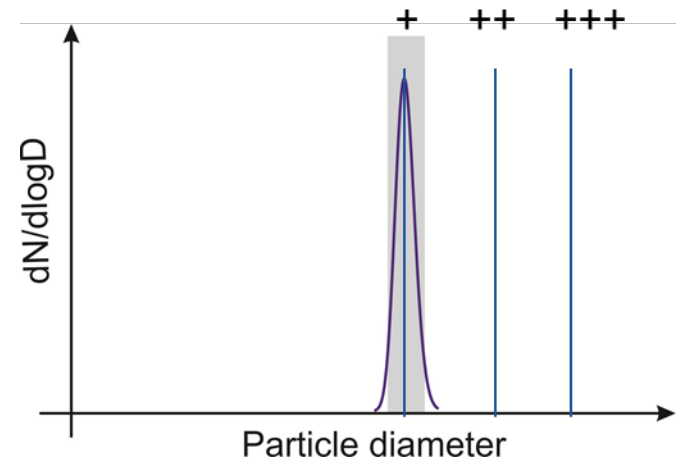
EMRP

- *DMA size standards below 80 nm:*
 - The particle mobility diameter for particles below 80 nm is calculated using the equations from ISO 15900 (e.g. slip correction) and is assumed to be correct by convention.
- *Difficult to define soot-like aerosol (high variability)*
 - “soot-likeness” is not the best criterion for a calibration aerosols considering the intrinsic variability of real soot and tested aerosols

Aerosol	Efficiency @ 23 nm	Efficiency @ 41 nm
miniCAST	26.5 % - 48.5 %	77.5 % - 79.9 %
graphite spark	41.4 % - 48.5 %	79.9 % - 93.3 %
«real soot»	42.5 % - 56.6 %	83.5 % - 89.2 %

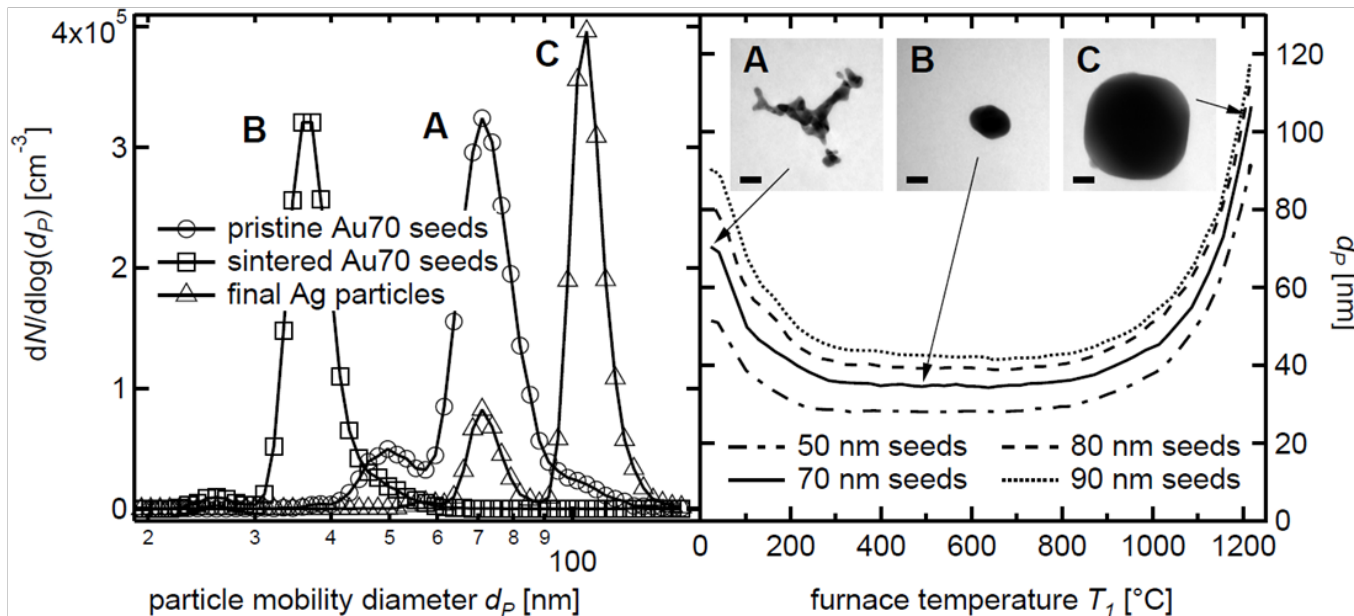
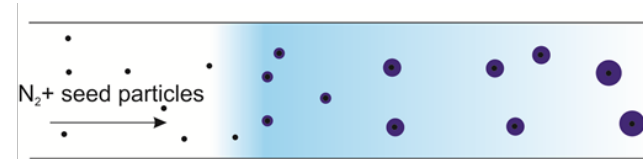
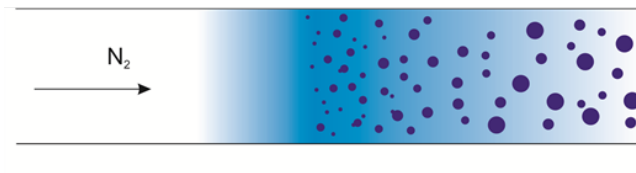
PNC calibration material criteria

- *Monodispersity*
Single charge
Tunable size
Sufficient number concentration
Controlled morphology (spherical)
Thermal stability
...
- *Calibration of the particle number concentration of a test CPC by comparison with an electrometer according to ISO/DIS 27891.*
SI-Traceability to units Volume, Time and Ampere.
Linear interpolation for small number concentrations.



Promising “primary” calibr. aerosol

- Heterogeneous nucleated silver particles*





From NMI to field

- *The dissemination from the NMI's to the field level will need "secondary" calibration aerosols with less stringent criteria*
- *The uncertainty of the particle number measurement will subsequently increase*
- *Not valid according to ISO:*
 - For electrometer it should be ok
 - For ref PNC same material would be required
- *Action: ISO to give possible traceability chain charts from NMI to user*



NMI s FCE intercomparison

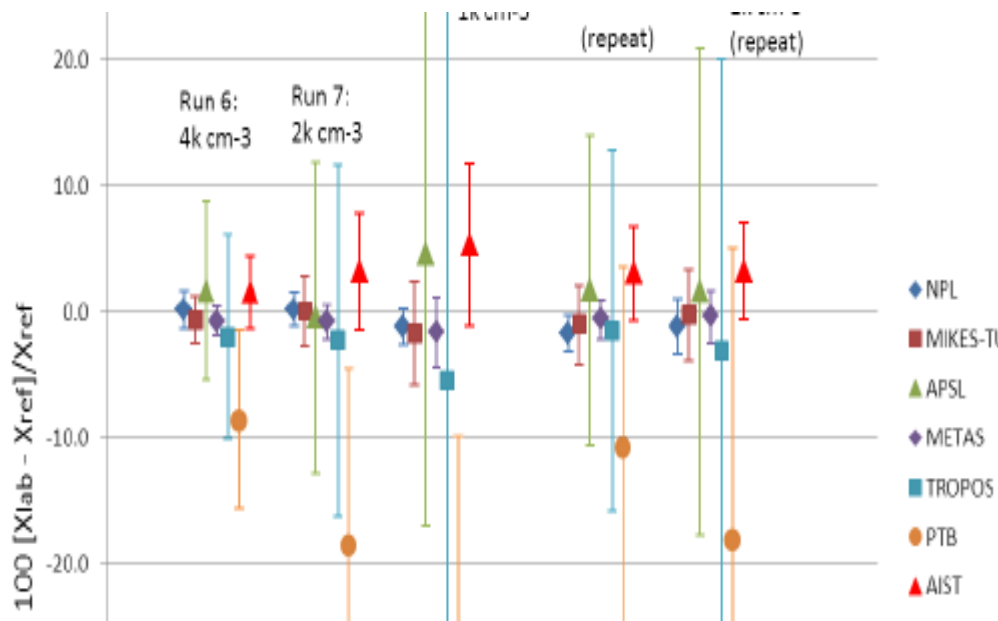
- *Participants generally agree within 2 % in the size range 20 nm to 100 nm and number concentrations above 5000 cm⁻³ for singly charged synthetic particles.*
- *Larger deviations result at lower particle sizes and particle concentrations and soot particles.*



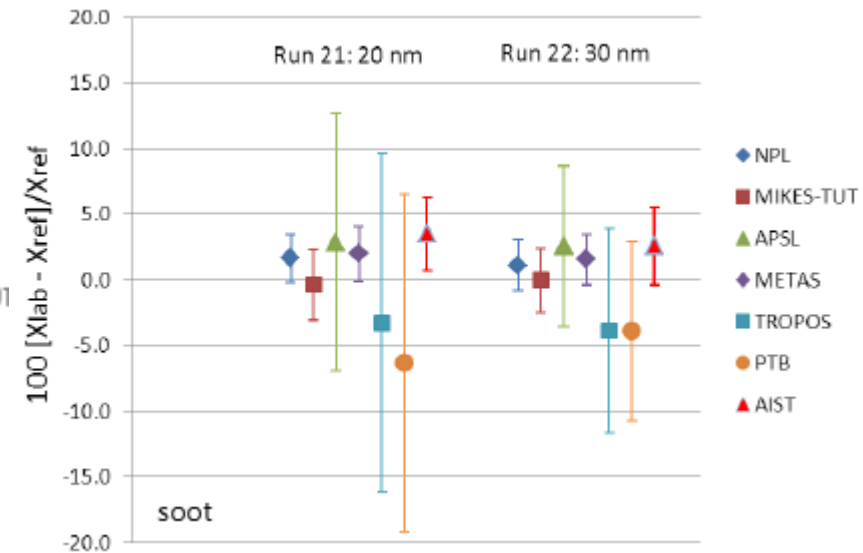
NMI s PNC calibration

- *Preliminary results suggest that the agreement of participants is less good than in the FCE comparison.*
- *Increased uncertainties down the traceability chain from primary FCE → reference CPC (ISO/DIS 27891).*

SCAR



Soot



- *Not evident that soot has higher variability (at least in one lab)*

Aviation (PNC)

- *Adhere to ISO 27891 recommendations*
- *Use reagent grade **n-butanol** as working fluid*
- *Operate under full flow operating conditions (flow splitting inside the CPC is not allowed)*
- *single count mode only with up to 10% coincidence correction*
- *Linearity $0.90 \leq \text{slope} \leq 1.10$*
- *Have counting efficiency of $\geq 50\%$ at 10 nm and $\geq 90\%$ at 15 nm electrical mobility diameter respectively, using an **emery oil** aerosol or equivalent*
- *Report in Standard conditions: The pressure should be measured with accuracy better than **2%***

Final open issues

- *Calibration material* → *PMP group*
 - Aviation: The calibration aerosol shall be Emery oil, or an aerosol that can be shown to provide an equivalent response. For example, if the efficiency curve is measured with a different aerosol, such as soot, the correlation to the Emery Oil curve must be provided as a chart that compares the counting efficiency obtained using both test aerosols
 - Minimize adaptation of PNCs / past data inconsistencies
 - (10nm PNC in future)
- *k factor correction*
 - Mandatory to be applied (?) → *TSI comments*
 - Stricter linearity differences range → *TSI comments*



VPR calibration

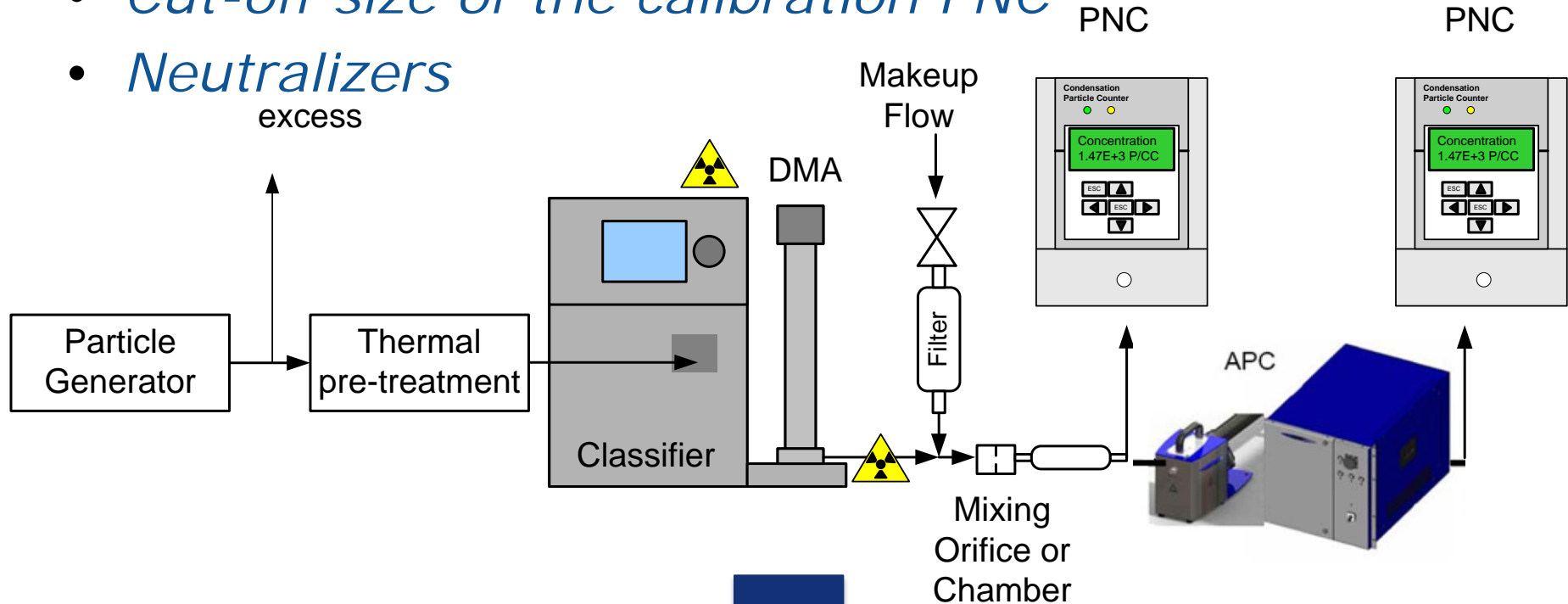


Status VPR (September 2014)

- *Legislation and AEA report (Dec 2007)*
- *VPR Round Robin recommendations*
- *EMRP*
- *Bibliographic review*

Open (major) points VPR

- *Calibration material / thermal pre-treatment*
- *One or two PNC method, monitor PNC*
- *Cut-off size of the calibration PNC*
- *Neutralizers*



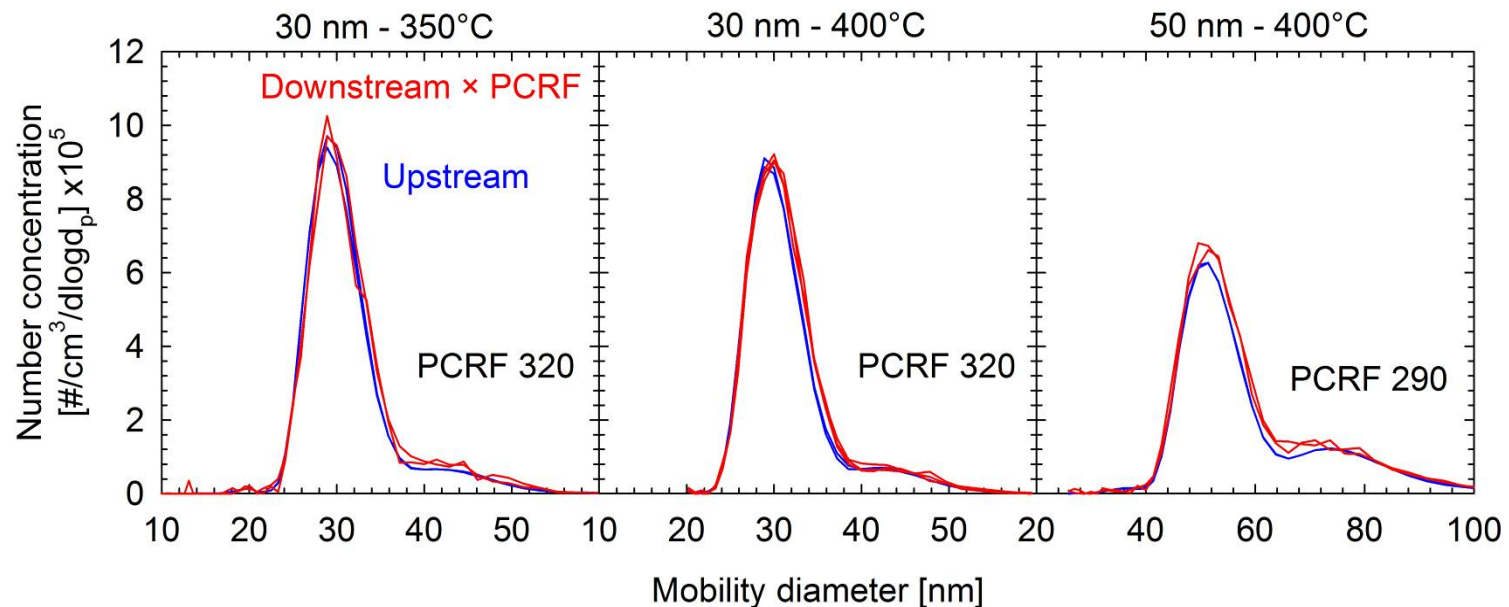


Open (minor) issues VPR

- *Pressures (and temperatures) during calibration effect on VPR (calibration PNC is corrected)*
- *Addition of polydisperse (validation check)*
- *Measurement of penetration for WLTP*
- *Stability criterion*
- *C40 might not be the right material for volatile removal efficiency*

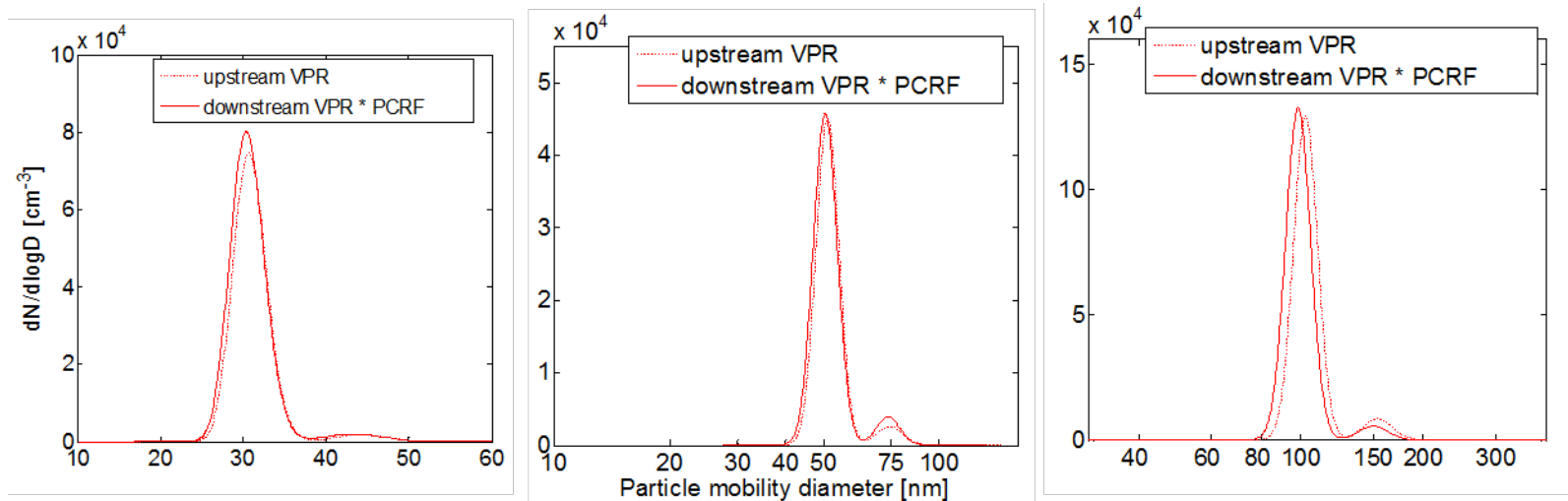
EMRP

- Graphite spark generator by PALAS (DNP300) was thermally stable up to 400°C*



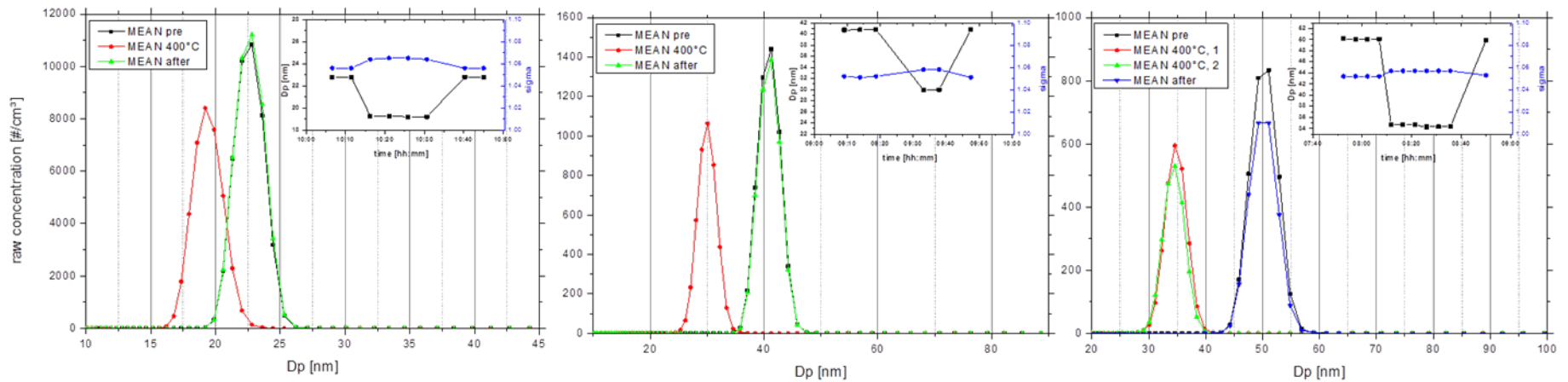
Mini CAST

- *Thermally pre-treated miniCAST is stable inside a VPR*
- *Concerns for adequate concentration for low sizes*



Silver

- *Silver particle aerosols need sintering at 400°C for thermal stability*
- *Upper size limited to 50 nm*



Aviation (VPR)

- Achieve **>99.9%** removal of 30 nm tetracontane particles with an inlet concentration of **$\geq 50,000$** particles/cm³ respectively.
- If a **CS** is used then the diluent must be air (minimum oxygen content of 10%). If a CS is not used, a heated dilution stage shall be placed upstream, which outputs a sample at a temperature of ≥ 423 K (150 °C) and ≤ 623 K ± 15 K (350 °C), and dilutes by a factor of at least **8**
- **Instead of PCRF \rightarrow DF**. Note that number measurements are **NOT corrected for particle loss in the VPR** (different to PMP). However, particle penetration measurement through VPR is required for sampling system transport performance, with minimum specifications of **30%, 55%, 65% & 70% at 15, 30, 50 & 100nm respectively**.



FVV: Tetracontane

- *A PNC can respond differently to C40 depending on the generation method (with or without oxygen). Oxidized C40 has higher counting efficiency.*
- *Importance for calibration (C40 volatile removal efficiency) but also for the real tests (already discussed)*
- *FVV: Temperature, residence time must be defined*

Next steps

- *The comments were included in the report*
- *Extra comments were added based on calibration experience*
- *Clearly define open points and alternatives*
- *Gather data*
- *Organize a meeting to take decisions*



Actions (both 23nm and 10nm PMP, separately)

- *Non calibration issues*
 - PNC drift, or stabilization time effect
 - Pressure (and temperature) effect on VPRs and corrections applied (for CVS minor effect)
- *PNC*
 - Argumentation k factor correction
 - Emery oil or CAST or possibility to 'correct' for the different material
 - Relative differences +/-3% from slope (which could be within 0.9-1.1)
 - Traceability chain chart
- *VPR*

640 on other material (640 with air, customized oil, sulfuric

