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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}).

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PARTICLE NUMBER COUNTERs (PNCs)

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

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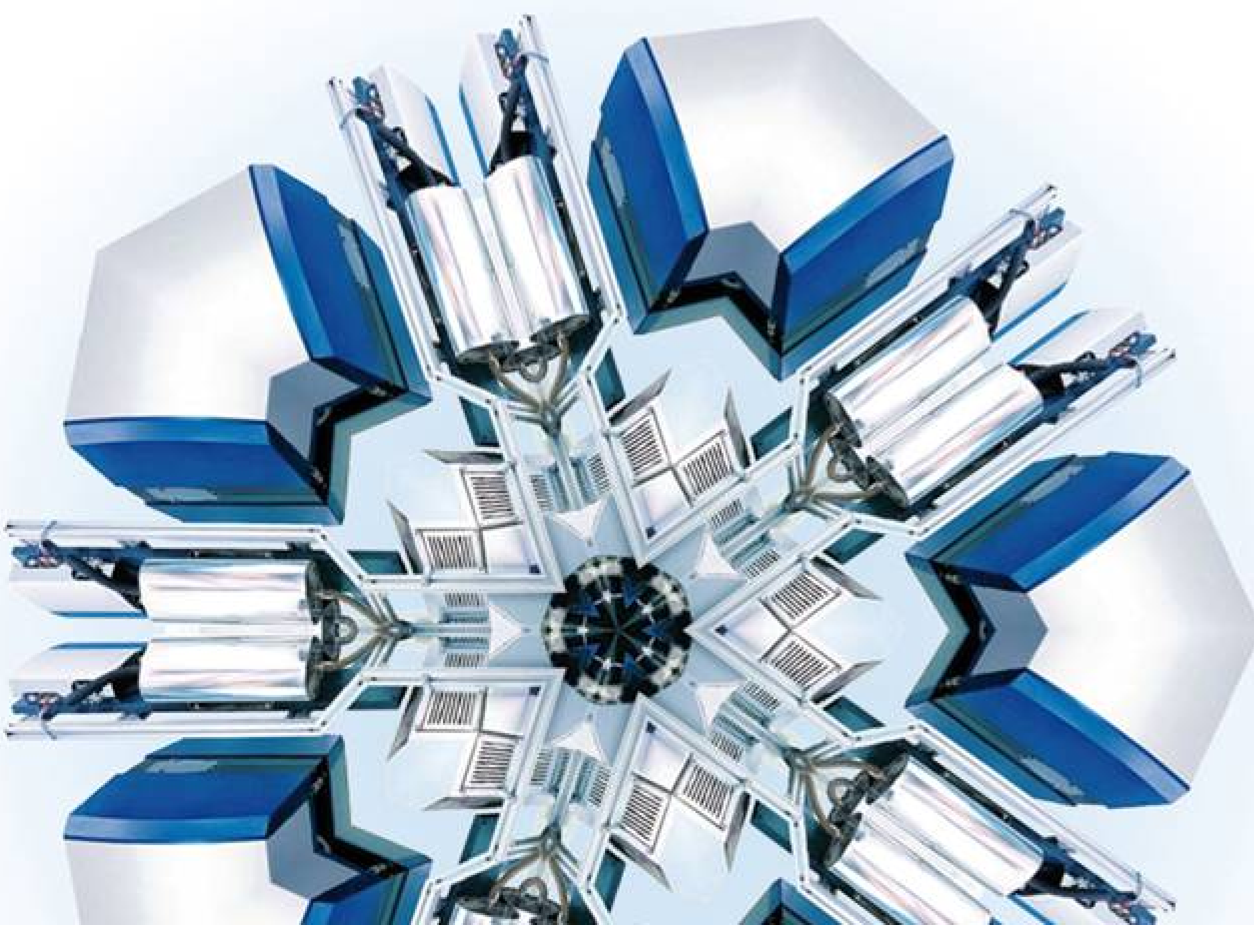


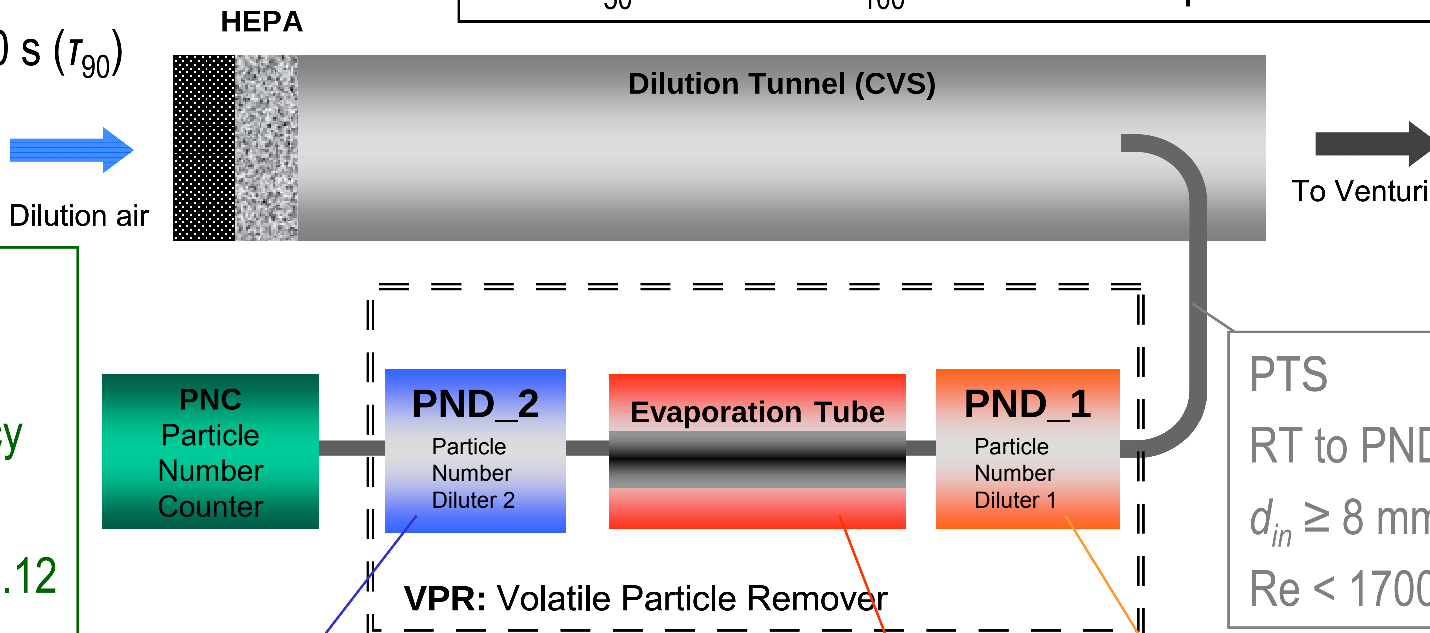
Outline

- Introduction
- Experimental
- Results
- Discussion
- Conclusions

UN-ECE Reg. 83: Light duty particle number regulation

PCRF	Volatile Removal Efficiency
$PCRF_{30} \leq 1.3\ PCRF_{100}$	>99% of ≥30 nm tetracontane
$PCRF_{50} \leq 1.2\ PCRF_{100}$	with 10^4 p/cm^3

Total RT ≤ 20 s (τ_{90})



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

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

PND_2 (Not required)
- t to PNC <35°C
- RT to PNC ≤ 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°C

PNC (Particle Number Counter)

PNC requirements

- Full flow
- τ_{90}<5 s
- Linearity: Slope 0.9-1.1, R2>0.97, all six concentrations ±10%
- Counting Efficiency CE_{23} = 0.50±0.12, CE_{41} = ≥0.9

PNC check

- Light indicators
- External flow check monthly

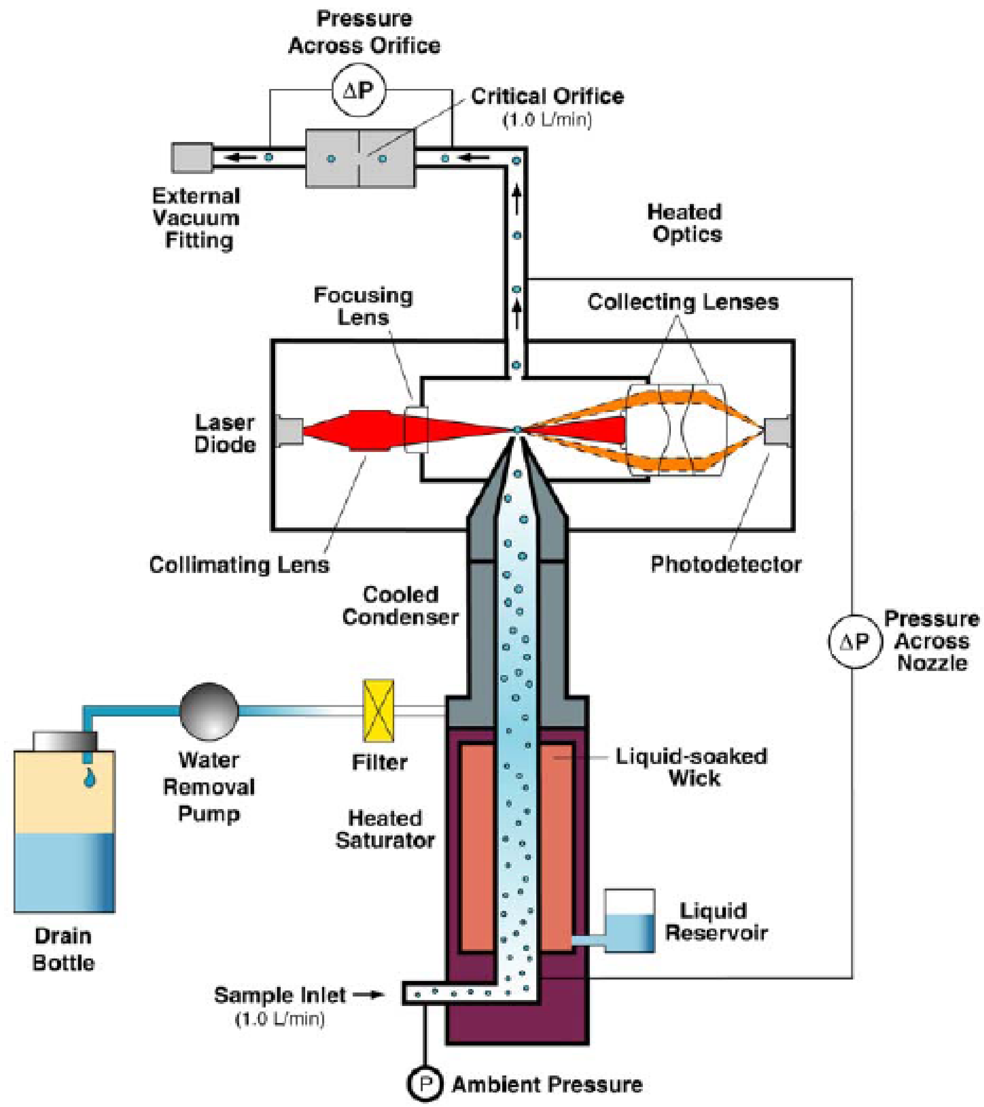
Target was to see if they are within legislation requirements, and if there is any drift over time

PNC calibration (yearly)

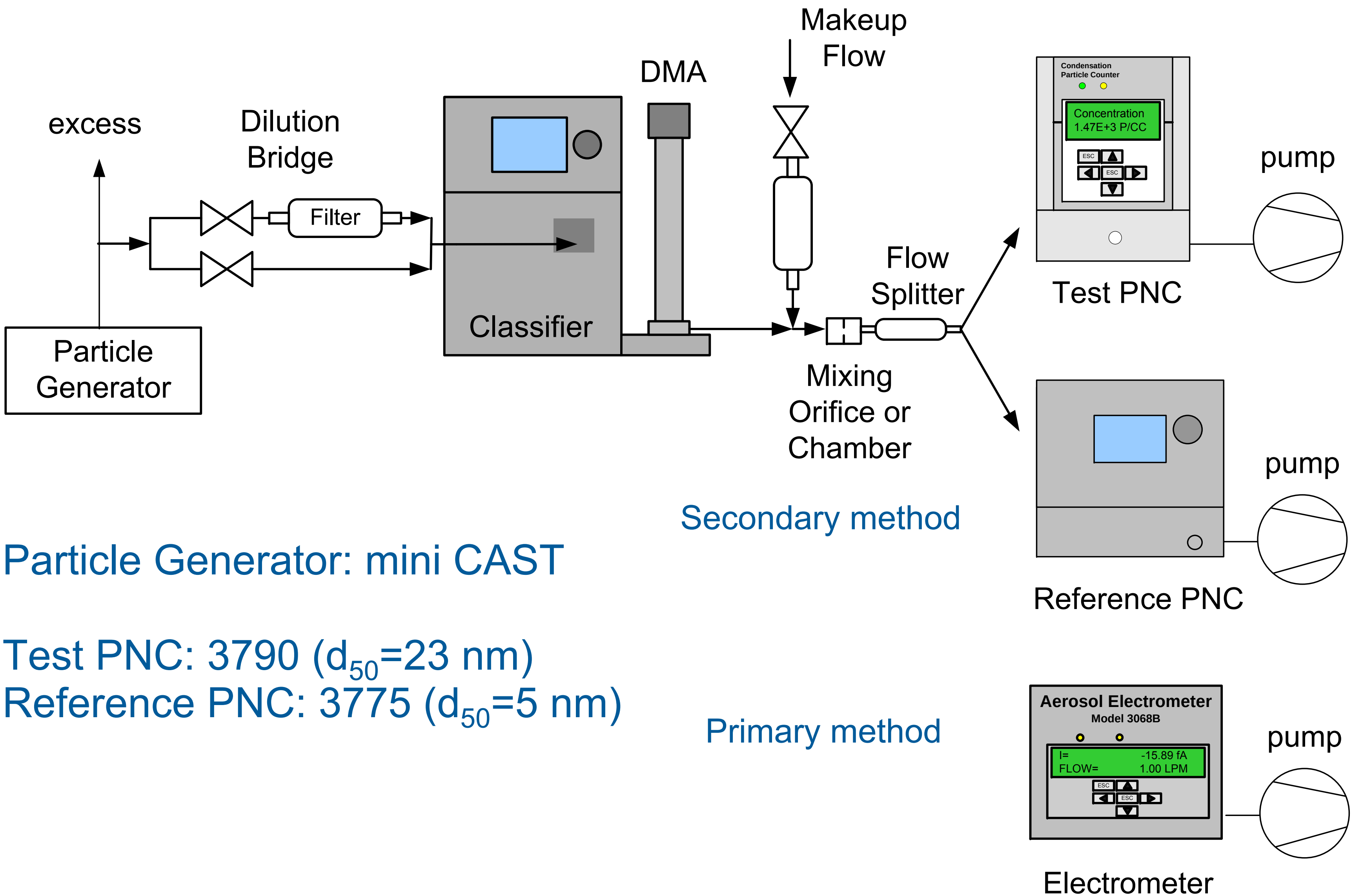
- Comparison with electrometer (primary) or reference PNC (secondary method)
- Linearity: Slope 0.9-1.1, R2>0.97, all six concentrations ±10%
- Counting Efficiency CE_{23} = 0.50±0.12, (optional CE_{41} = ≥0.9)

TSI PNC 3790


Engine Exhaust
Condensation Particle Counter
Concentration
1.47E+03 P/CC
ESC
TSI


Pressure
Across Orifice
ΔP
Critical Orifice
(1.0 L/min)
External
Vacuum
Fitting
Heated
Optics
Focusing
Lens
Collecting Lenses
Laser
Diode
Collimating Lens
Photodetector
Cooled
Condenser
ΔP
Pressure
Across
Nozzle
Water
Removal
Pump
Filter
Liquid-soaked
Wick
Heated
Saturator
Drain
Bottle
Liquid
Reservoir
Sample Inlet
(1.0 L/min)
P
Ambient Pressure

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)

SN	Calibration	ΔT [K]	Flow [lpm]	AE SN	23 nm	41 nm	slope
70734133	2007-09-21	6.7	1.020	E002871	0.57	0.93	0.94
70810498	2008-04-03	6.6	1.010	E003335	0.51	0.91	0.92
70933046	2008-08-28	6.6	1.000	E003432	0.49	0.91	0.94
70831244	2008-09-05	7.1	0.978	E003432	0.59	0.90	0.92
70835093	2008-09-19	6.6	0.996	E003432	0.56	0.90	0.91
70842058	2008-10-21	6.6	0.995	E003432	0.54	0.90	0.93
70734133	2007-09-21	6.7	1.020	E002871	0.57	0.93	0.94
71005189	2010-02-17	6.6	1.020	E003432	0.56	0.94	0.97
71005086	2010-03-03	6.4	1.010	E003432	0.61	0.95	0.97
71011040	2010-03-17	6.6	1.020	E003432	0.57	0.97	0.98
70810498	2010-03-20	7.3	1.000	E006117	0.51	0.90	0.93
70831244	2010-03-23	6.6	1.000	E006117	0.57	0.91	0.93
70949021	2010-04-06	6.5	1.000	E006117	0.54	0.92	0.94

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

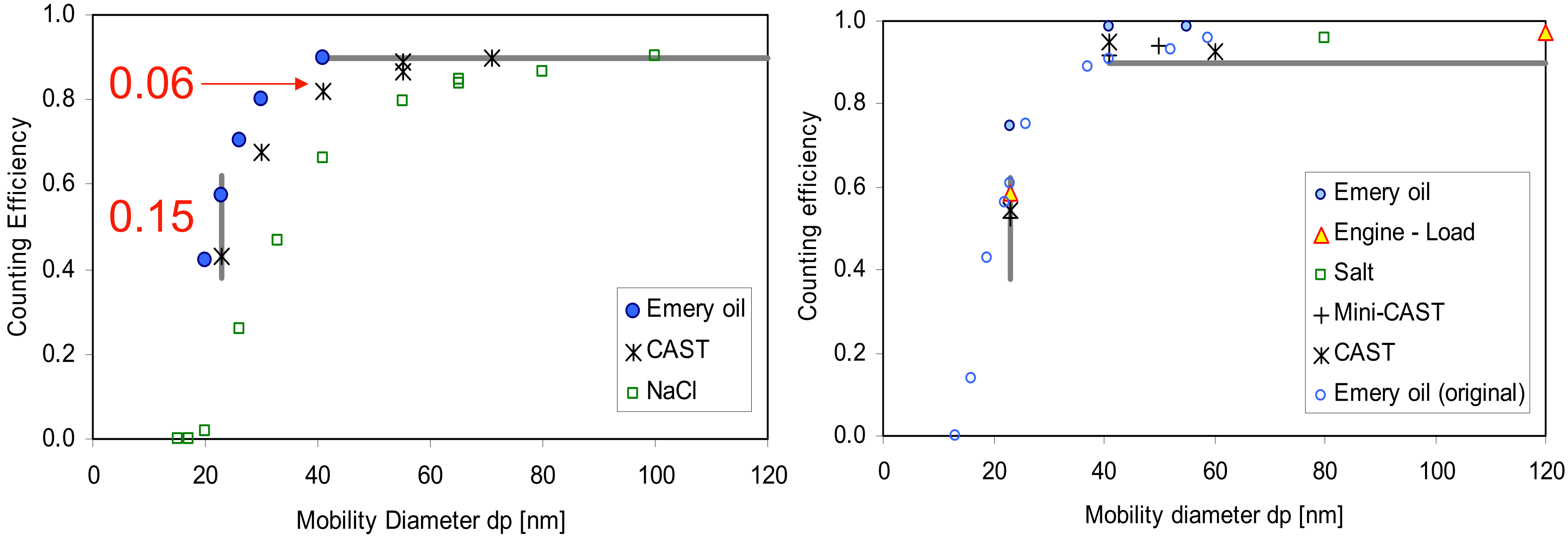
SN	Validation	Flow	Ref	23 nm	41 nm	55 nm	slope	Comment
70734133	2010-04-08	1.023	3775	*0.30*	***0.79***	0.89	0.95	not used
70810498	2010-02-02	-	*3790*	0.50	***0.85***	0.92	0.92	used
70933046	2010-04-06	-	3775	0.38	***0.88***	0.96	1.02	used
70831244	2010-04-16	-	*3790*	0.58	***0.73***	0.77	*0.77*	used
70835093	2010-04-06	-	3775	0.44	***0.87***	0.94	1.00	used
70842058	2010-04-16	1.012	3775	*0.23*	***0.60***	0.67	*0.71*	used
70734133	2007-11-01	-	*AE*	0.41	***0.76***	0.84	*0.84*	new
71005189	2010-04-15	0.990	3775	*0.25*	***0.81***	0.91	0.97	new
71005086	2010-04-15	*0.924*	3775	*0.30*	***0.79***	0.86	0.91	new
71011040	2010-04-16	1.001	3775	0.39	***0.87***	0.95	1.00	new
70810498	2010-04-08	1.034	3775	0.48	*0.95*	1.03	**1.07**	re-calibrated
70831244	2010-04-16	1.007	3775	0.41	***0.84***	0.92	0.97	re-calibrated
70949021	2010-04-16	1.001	3775	0.40	***0.87***	0.95	0.99	re-calibrated

	Flow	23 nm	41 nm	slope
Regulation 83 limits:	0.95 – 1.05	0.38 – 0.62		0.9 – 1.1
Failed:	1	4	(12)	3

In total 6/13 PNCs failed. Reasons:

- Flow (1)
- Different material used for the calibration (3)
- Degrading of PNC parts (2)

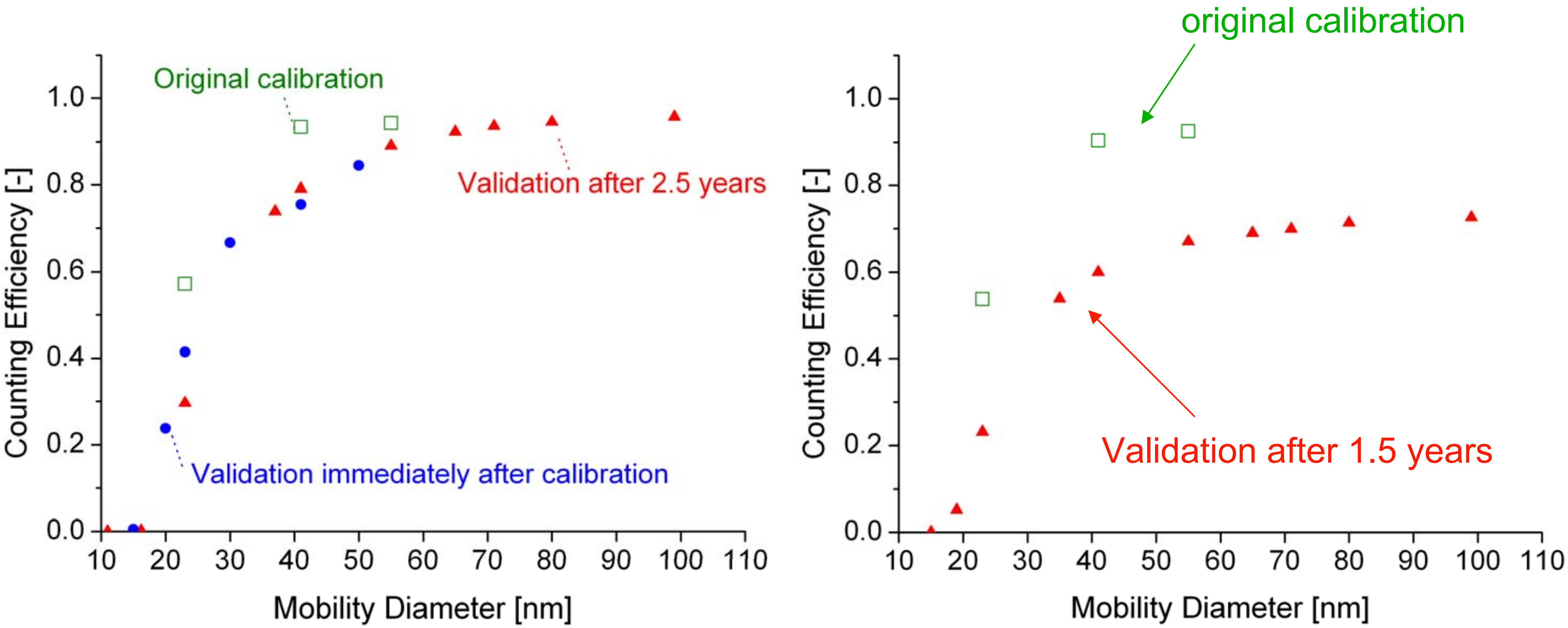
Counting Efficiency: Material (JRC, TSI-NIST workshops)



- 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**

Giechaskiel et al. 2009, AST, 43, 1164
Wang et al. 2010, JAS, 41, 306

Degrading over time

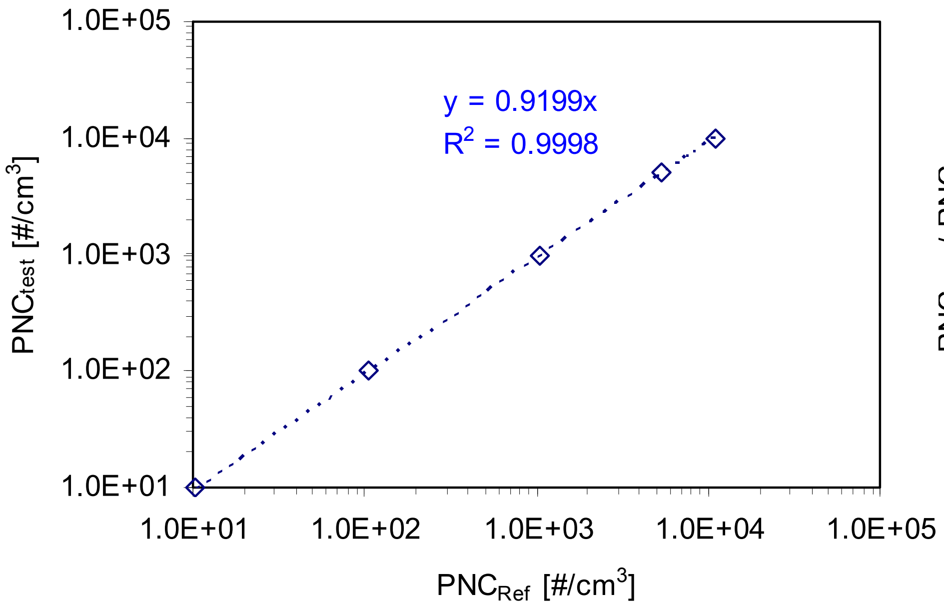


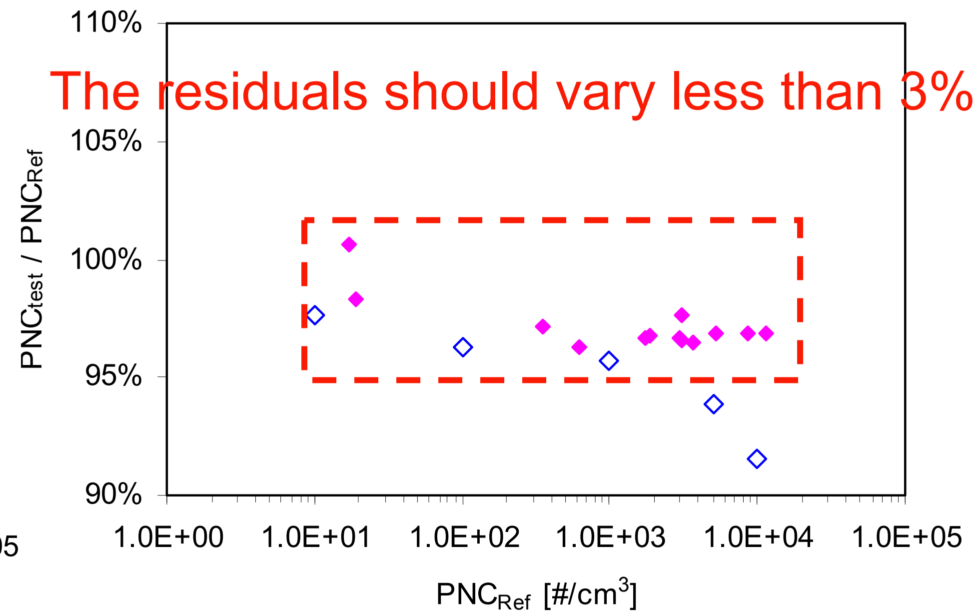
After 2.5 years of no use, no drift was observed
Some PNCs drifted
The reason is the wick (where the super-saturation is achieved)
The critical point: **No light indicator identified this degrading**

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

CPC MODEL 3790 CERTIFICATE OF CALIBRATION

70949133	Serial number	Test Aerosol: Emery Oil
12/29/2009	Date	

Inlet Flow (Volumetric)

Value	Parameter	Units	Low Limit	High Limit
1.02	Inlet Flow Value	L/min	0.95	1.05

Temperature and Pressure

Value	Parameter	Units	Low Limit	High Limit
22	Room Temperature	°C	-	-
45%	Room Relative Humidity	-	-	-
38.3	Saturator Temperature	°C	38	38.7
32	Condensor Temperature	°C	30.5	32
40	Optics Temperature	°C	39.8	40.2
28.6	Cabinet Temperature	°C	20	35
98.4	Ambient Pressure	kPa	88	108
83.2	Pressure Drop across Orifice	kPa	70	88
2.9	Pressure Drop across Nozzle	kPa	1.9	3.2

Laser Check

Value	Parameter	Units	Low Limit	High Limit
17	Laser power (measured)	mW	14	20

Optics

Value	Parameter	Units	Low Limit	High Limit
36	Laser current reading	mA	12	-
1.2	Minimum pulse height	V	1	3.65
110	Minimum pulse width	ns	110	450
3	Maximum pulse height	V	2	3.65
210	Maximum pulse width	ns	110	450

Zero Count Test

Value	Parameter	Units	Low Limit	High Limit
0	Concentration average over 12 hours	p/cc	0	0.001

Lower Detection & Concentration Linearity Test Results

Value	Parameter	Units	Low Limit	High Limit
61.7%	23 nm Particle Counting Efficiency	-	38%	62%
99.5%	41 nm Particle Counting Efficiency	-	90%	-
102.6%	Linearity Test: Slope (up to 10,000 p/cc)	-	90%	110%
0.9981	Linearity of Regression (R^2)	-	0.97	-
N/A	CPC / Electrometer Counting Ratio (25,000 p/cc nom.)	-	-	-
N/A	CPC / Electrometer Counting Ratio (50,000 p/cc nom.)	-	-	-

Final Voltage Measurements

Value	Parameter
Pass	Analog Input and Output Voltages
Pass	Verify flash memory function (pass/fail)

Linearity Response: CPC vs. Electrometer 3068B

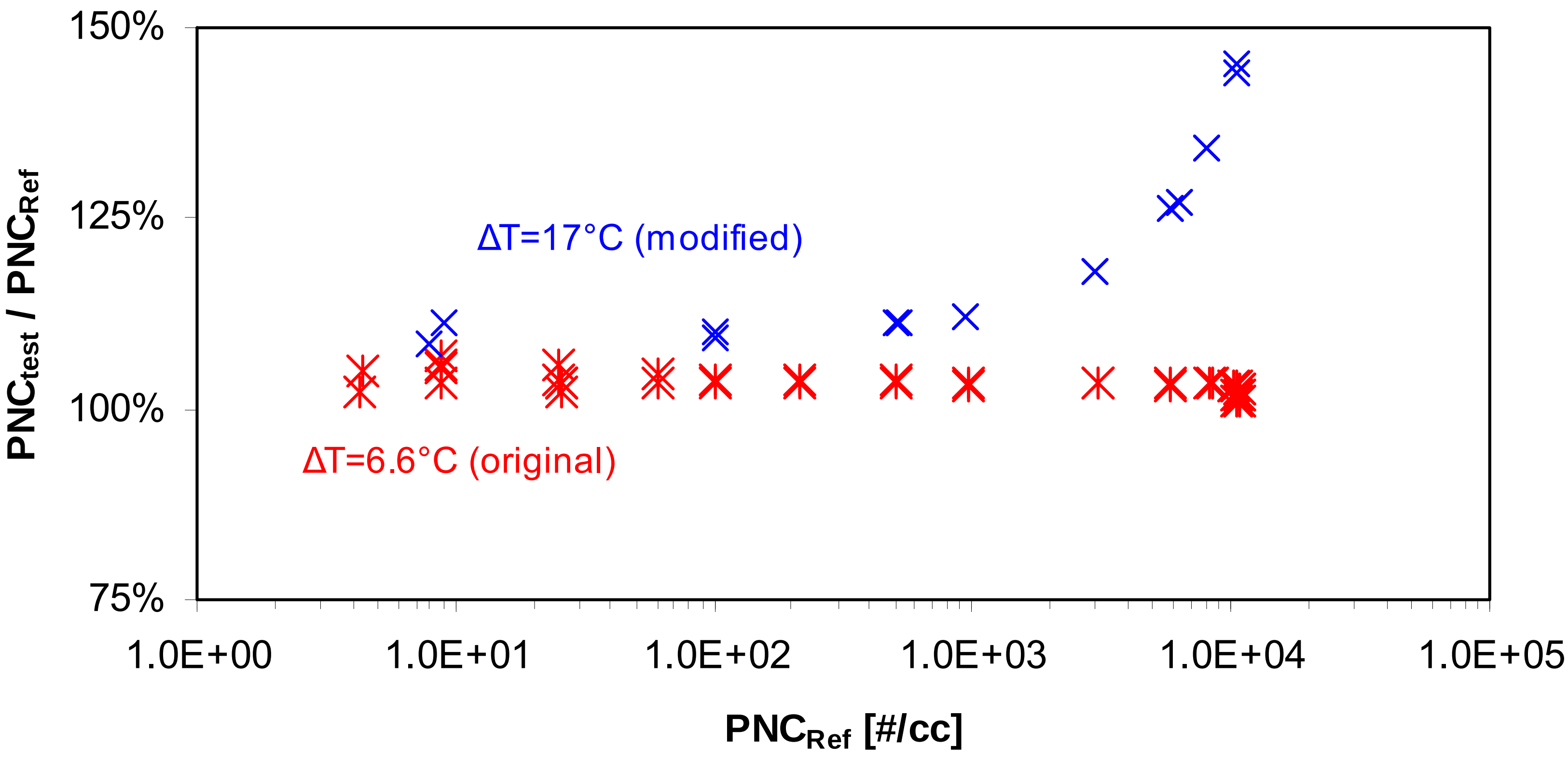
Value	Concentration	Parameter	Units	Low Limit	High Limit
-2.42%	2000 p/cc	CPC Concentration	% Diff.	-10%	10%
-0.81%	4000 p/cc	CPC Concentration	% Diff.	-10%	10%
0.34%	6000 p/cc	CPC Concentration	% Diff.	-10%	10%
1.45%	8000 p/cc	CPC Concentration	% Diff.	-10%	10%
3.66%	10000 p/cc	CPC Concentration	% Diff.	-10%	10%

What about <2000 p/cm^3?

Uncertainty >10%

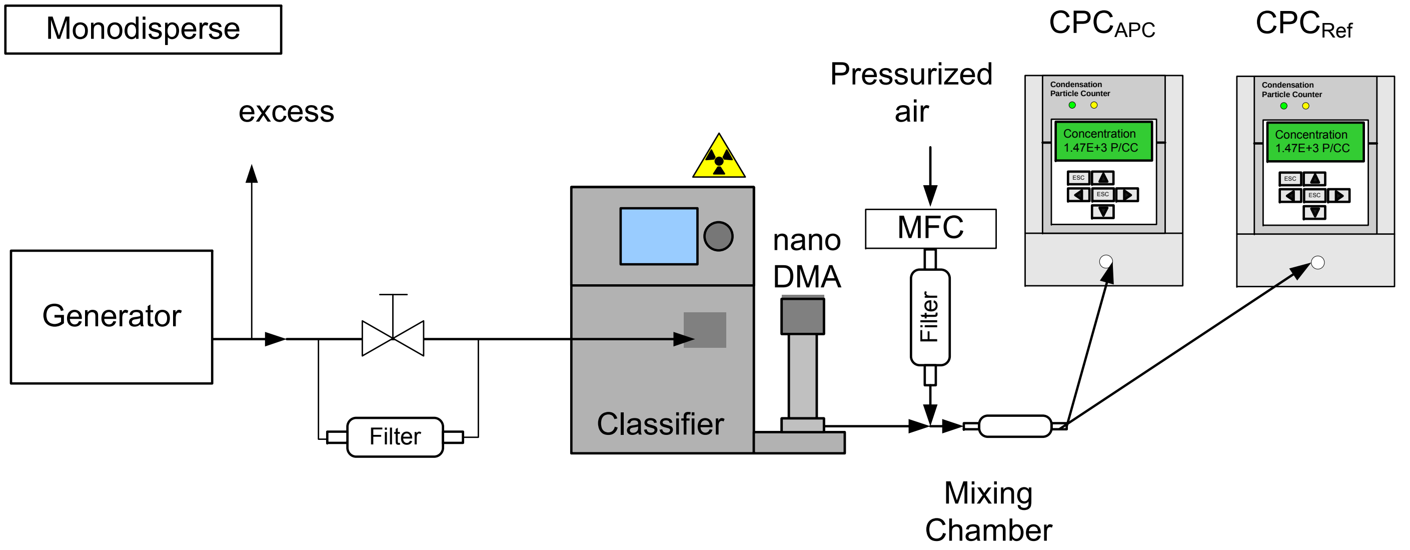
Uncertainty 5%

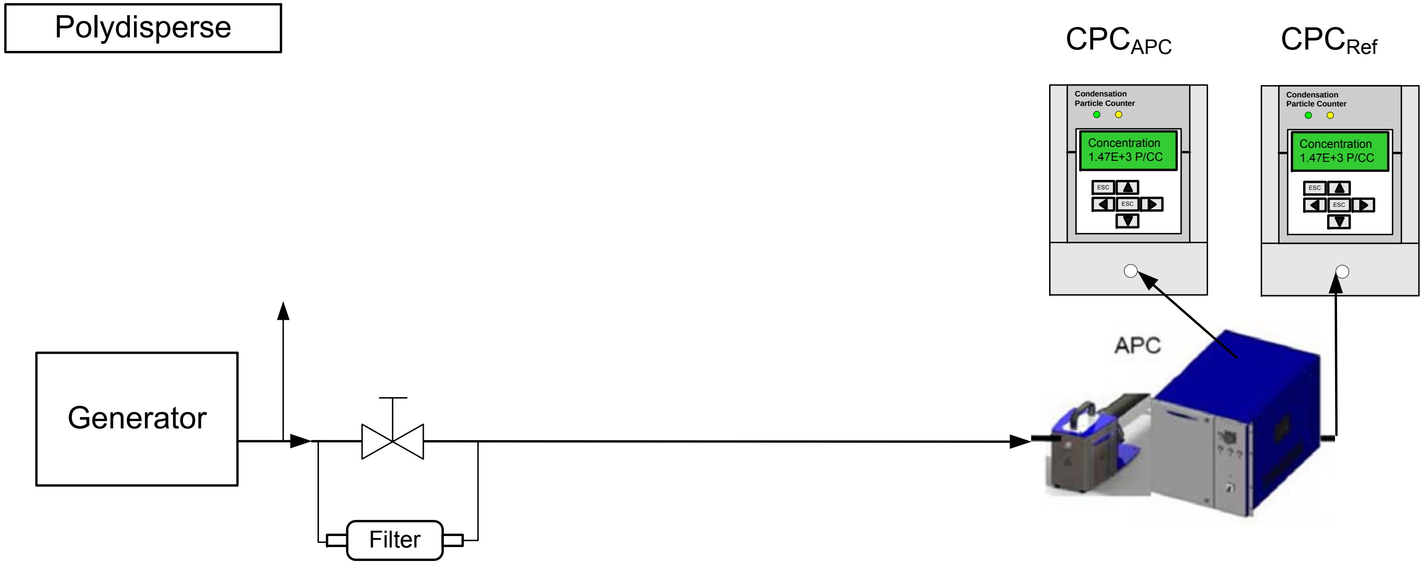
Modified PNCs



- 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.

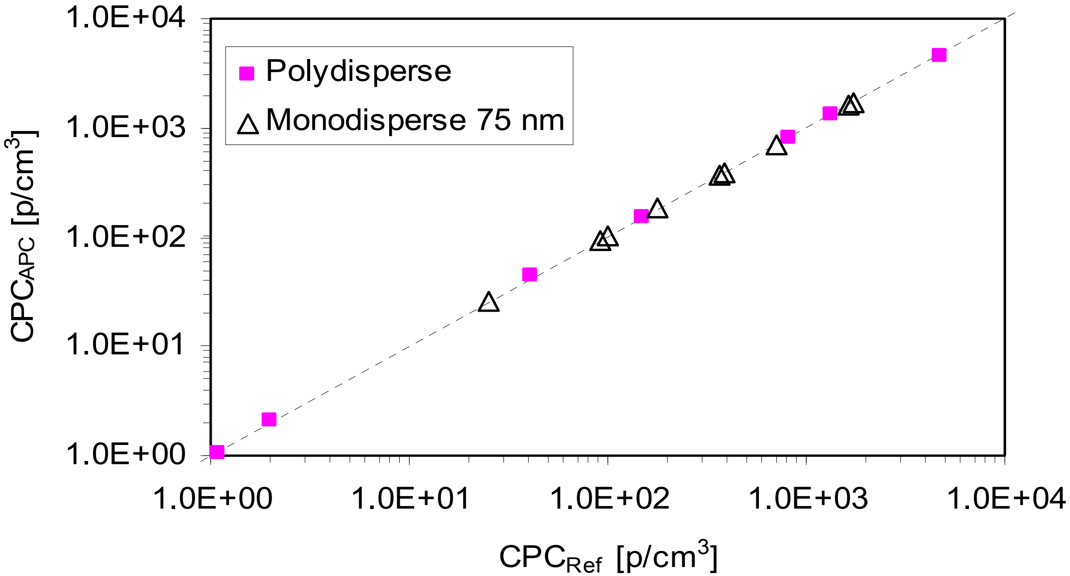
PNC validation (monodisperse) & check (polydisperse)

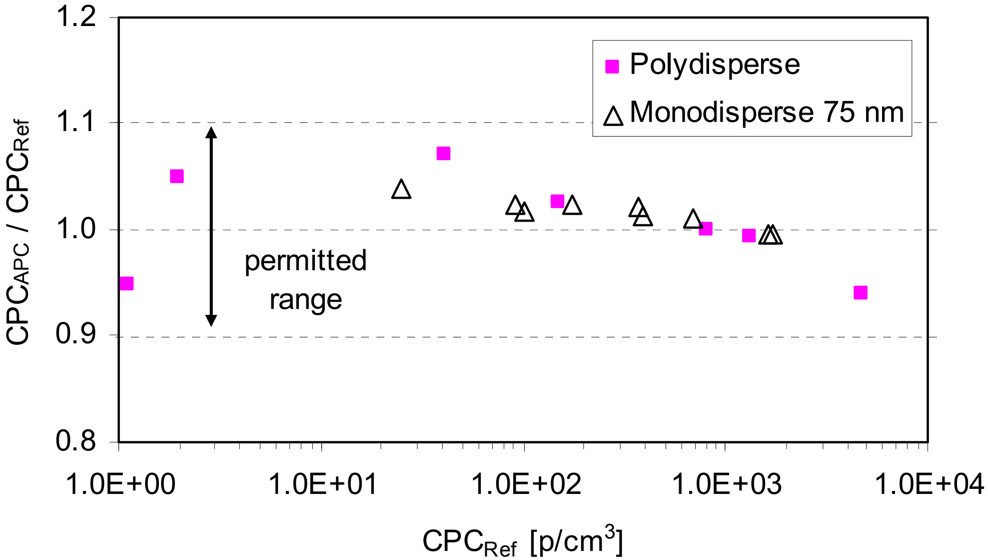




PNC validation (monodisperse) & check (polydisperse)

- 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!