

International Comparison CCQM-P189

**Particle number concentration (100 to 20 000 cm⁻³) and
particle charge concentration (0.15 to 3 fC cm⁻³)**

FINAL REPORT

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Approved on behalf of NPLML by
Andrew Sims, Group Leader, Air Quality & Aerosol Metrology Group

EXECUTIVE SUMMARY

This report presents the results of CCQM-P189, a pilot comparison between 10 laboratories which tested the participants' capability to measure particle number concentration (in the range of 100 to 20 000 cm⁻³) using condensation particle counters (CPCs), and particle charge concentration (in the range of 0.15 to 3 fC cm⁻³) using aerosol electrometers (AEs).

Measurements of aerosol particle number concentration are needed to demonstrate compliance to vehicle emission legislation and are becoming increasingly important in other areas such as ambient air and workplace monitoring. The measurements are typically carried out using condensation particle counters, which are calibrated using either reference CPCs or reference AEs.

An analogous report is available for the CCQM-K150 comparison. CCQM-K150 was identical to, and used the same experimental data as CCQM-P189 with one exception: data from TROPOS, which is not an National Measurement Institute (NMI) or Designated Institute (DI), were only included in CCQM-P189.

CCQM-P189 was an amount-of-substance Track C comparison.

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1 INTRODUCTION

Aerosol particle number concentration has recently featured in vehicle emission legislation and is becoming increasingly important in other areas such as ambient air and workplace monitoring. Condensation particle counters (CPCs) are the usual type of instrument for measuring particle number concentration in the size range from a few nanometres to a few micrometres. These instruments have a large size range over which they have constant detection efficiency for nanoparticles of all compositions (the 'plateau' region), and an instrument and particle-material dependent drop in detection efficiency at low particle sizes.

Calibration of CPCs can be performed via comparison with a reference CPC or a reference aerosol electrometer (AE). Procedures for doing this calibration have been set out in ISO 27891 [1]. If a source of singly-charged particles is used, particle number concentration (typically in units of cm^{-3}) is directly comparable to particle charge concentration (typically in units of fC cm^{-3}). The standard refers to the role of National Measurement Institutes (NMIs) in providing certification for reference AEs and reference CPCs.

Although not strictly a chemical measurement, the comparison belongs to the domain of the Gas Analysis Working Group (GAWG) of CCQM because of the similarity to gas concentration measurements, following the precedent of earlier EURAMET TC-METCHEM projects 893 [2] (workshops to establish "Metrology infrastructure for airborne nanoparticles"), 1027 [3] ("Comparison of combustion particle number concentration and size"), 1244 [4] ("Comparison of aerosol electrometers"), and 1282 [5] ("Comparison of Condensation Particle Counters").

To date NPL, PTB and METAS have Calibration and Measurement Capabilities (CMCs) in the key comparisons database (KCDB) on particle charge and number concentration. Their claims are based on the evidence from the above EURAMET comparisons.

In April 2015 GAWG organised a particle workshop at the BIPM to initiate the process to establish metrological traceability for aerosol measurements. At the workshop it was agreed to start to organise particle comparisons on a global scale. The GAWG subsequently developed a strategy for particle comparison and agreed to start with the most mature particle charge and particle number metrics.

The aim of the comparison was to compare the results of different laboratories' measurements of particle charge concentration by AEs, and particle number concentration in the CPC plateau region.

This report is for the CCQM-P189 comparison of particle number concentration (100 to 20 000 cm^{-3}) and particle charge concentration (0.15 to 3 fC cm^{-3}). An analogous report is also available for the CCQM-K150 comparison, which was identical to, and used the same experimental data as CCQM-P189 with one exception: TROPOS is not an NMI or Designated Institute (DI), so data from TROPOS were only included in CCQM-P189, not CCQM-K150.

SI traceability for the AEs is through the Ampere, second and metre. SI traceability for the CPCs is to the AEs.

2 DESIGN AND ORGANISATION OF THE COMPARISON

2.1 COMPARISON SCHEDULE

April 2017:	formal approval from the chair of CCQM
June 2017:	Registration of participants
October 2017:	Issue of Final Protocol
13-17 November 2017:	Comparison at TROPOS, Leipzig
February 2018:	Due date for results
December 2021:	Draft A report available

2.2 EXPERIMENTAL OUTLINE

The comparison of CPCs and AEs was carried out by parallel sampling of a common source, at TROPOS, the WMO-GAW World Calibration Centre for Aerosol Physics in Leipzig, Germany, during the week of 13-17 November 2017. TROPOS is not an NMI or DI and had the status of guest laboratory for the comparison, participating in CCQM-P189 but not CCQM-K150.

The CPC and AE comparisons were carried out separately; either the full set of CPCs or the full set of AEs were connected to the manifold at the same time. For each comparison, a range of concentrations was generated at one of two aerosol particle sizes. The aerosol particles were silver nanoparticles at a nominal size of 40 nm or 50 nm, selected from an evaporation-condensation source by their electrical mobility.

The participants in CCQM-K150 and CCQM-P189 are given in Table 1:

Table 1: Participants

Comparison	Laboratory	Country	CPC	AE
CCQM-K150	NPL	UK	Y	Y
	PTB	DE	Y	Y
	METAS	CH	Y	Y
	LNE	FR	Y	Y
	VNIIFTRI	RU	Y	N
	NMIJ	JP	Y	Y
	NIM	CN	Y	Y
	KRISS	KR	Y	Y
	BAM	DE	N	Y
CCQM-P189	TROPOS	DE	Y	Y

2.3 AEROSOL SOURCES AND MANIFOLD

A schematic diagram of the experimental set-up is given in [6] and a photograph shown in Figure 1. Participants sampled from separate ports along a manifold, shown in Figure 2. The second CPC from PTB, labelled PTB PMP, was not part of the comparisons.

The silver particles were generated by evaporation using a tube furnace generator and pure nitrogen as a carrier gas. The silver vapour nucleated in a cooling section to form silver nanoparticles, which agglomerated quickly to form larger particles. The coagulation process was quenched using an additional nitrogen flow. The particles were then sintered in a second

tube furnace to form spherical particles. The mean diameter of polydisperse silver aerosol was regulated by the temperature of the first tube, which determined the silver vapour concentration.

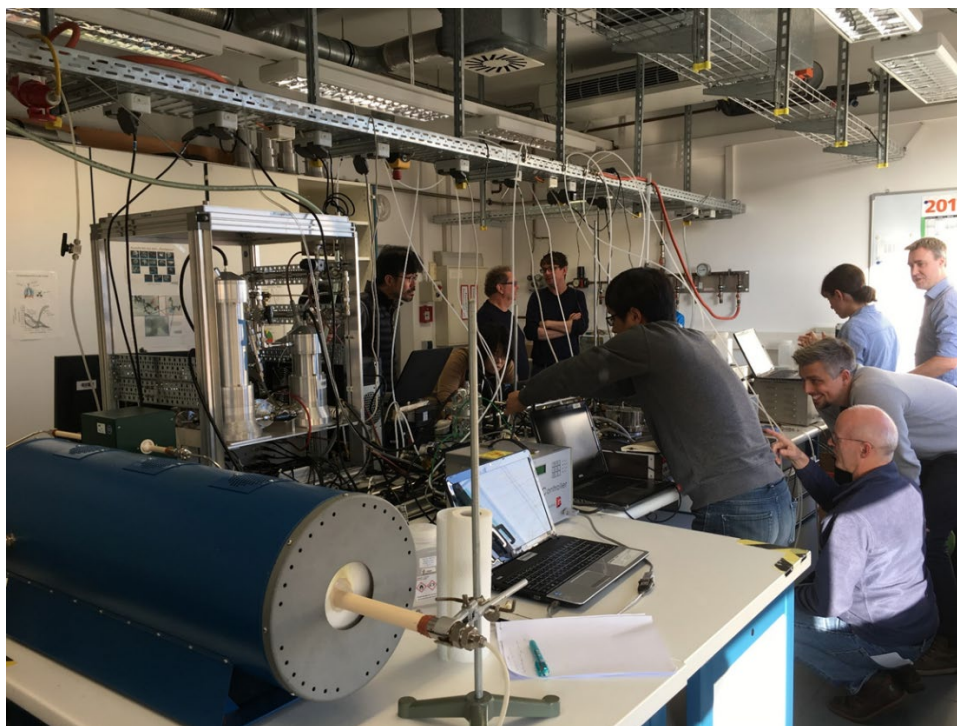


Figure 1: General experimental set-up. The silver nanoparticle source is in the foreground.

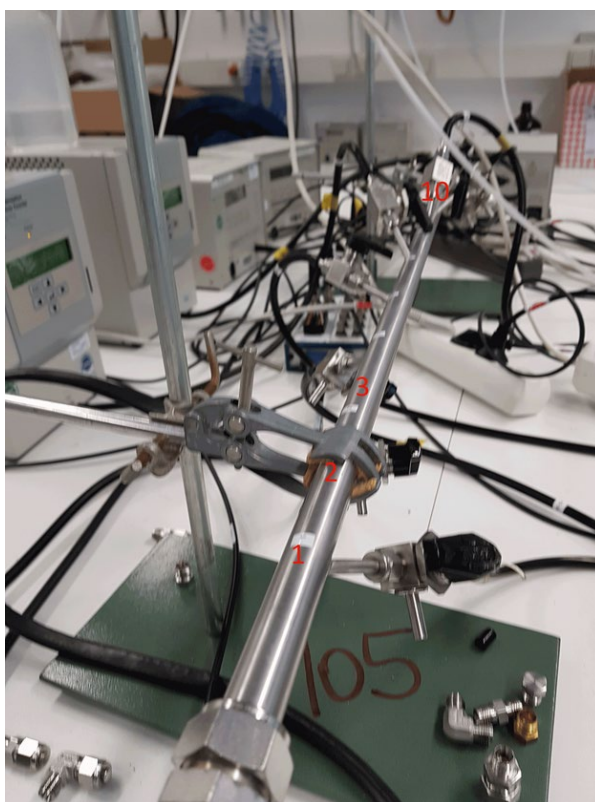


Figure 2: Sampling manifold with numbered ports.

The ports used by each participant are shown in Table 2.

Table 2: Ports assigned to participants. The second CPC from PTB, labelled '(PTB PMP)', was not part of the comparison.

Port	CPC comparison	AE comparison
1	KRISS	KRISS
2	METAS	NIM
3	NIM	METAS
4	NMIJ	LNE
5	PTB	NMIJ
6	LNE	NPL
7	(PTB PMP)	BAM
8	NPL	PTB
9	VNIIFTRI	-
10	TROPOS	TROPOS

2.4 EXPECTED VARIATIONS IN CONCENTRATION BETWEEN INLETS

The causes of losses of aerosol particles along a tube of conducting material are well understood. Sedimentation losses are expected to be negligible for such small particles. Thermophoretic losses (deposition onto cold surfaces) are also expected to be negligible as there are no significant temperature gradients.

Losses by diffusion to the walls can be estimated as a penetration efficiency P , where:

$$P = \frac{n_{\text{out}}}{n_{\text{in}}} = 1 - 5.50\mu^{2/3} + 3.77\mu \quad (1)$$

Where:

$$\mu = \frac{D \cdot L}{Q} \quad (2)$$

And:

n_{in} = particle number concentration at the inlet of the tube
 n_{out} = particle number concentration at the outlet of the tube
 D = particle diffusion coefficient ($\sim 4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 40 nm)
 L = tube length ($\sim 2 \text{ m}$)
 Q = flow rate ($\sim 2 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$)

This gives values for μ of approximately 4×10^{-5} , and for P of approximately 0.994, i.e. a 0.6 % loss at the outlet of the tube compared to the inlet. This compares to reported measurement uncertainties ($k = 2$) - excluding any sampling differences - ranging from approximately 2 % to 35 % for the AE comparison, and 3 % to 8 % for the CPC comparison.

2.5 EXPERIMENTAL CHECKS ON VARIATIONS IN CONCENTRATION BETWEEN INLETS

Measurements were carried out by TROPOS before the comparison (on 6 November 2017) to evaluate the equivalence of the 10 inlet ports, using nominally 30 nm particles at a concentration of approximately $2\,500\text{ cm}^{-3}$. The averaging time of approximately 10 min per port meant that the precision was limited, but the results were consistent with the estimate that the concentrations at ports at the far end of the tube were within 0.6 % of the concentrations at the near end, as shown in Figure 3.

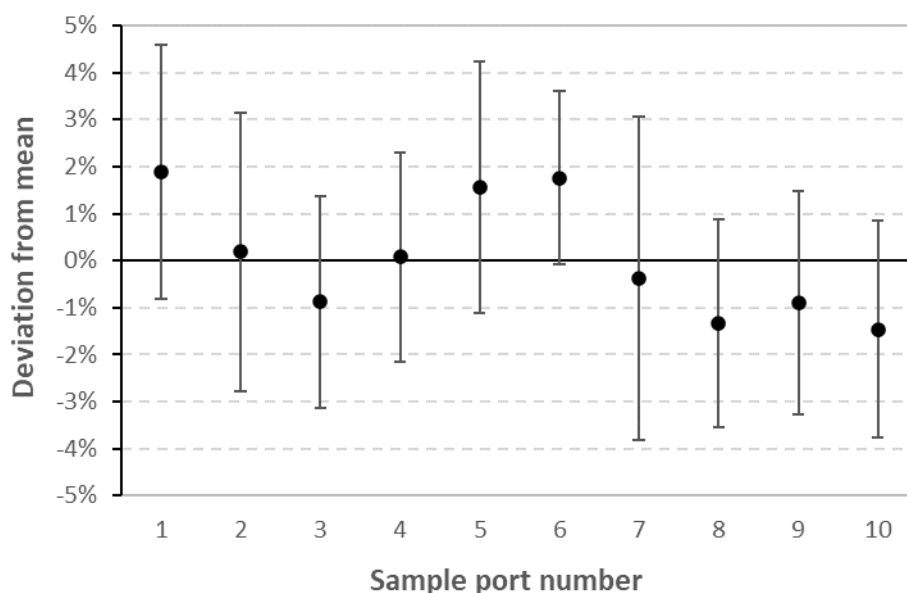


Figure 3: Results of the pre-comparison port variation check. The error bars are equal to 2 standard deviations.

2.6 EXPECTED DIFFERENCES CAUSED BY DIFFERENT INSTRUMENT SAMPLING FLOWS

There will be particle losses from diffusive processes along any tubing, including that between the manifold inlet and the participants' instruments. If all instruments sampled from the inlet at the same flow rate, the differences at the instruments would be minimised by using equal lengths of tubing. However, the participants' instruments were run at a variety of flow rates, as chosen by them. These losses are again governed by the parameter μ (see equation 2).

The small expected losses were equalised by cutting the length of the connecting tube (made of conductive plastic) to be proportional to the instrument flow rate, so that L/Q was the same in each case.

Any residual difference is expected to be fully covered by increasing reported uncertainties by 1 % (2σ) added in quadrature, to cover all differential losses before the test instruments, effectively an uncertainty of the reference value.

Flow meters were in general calibrated before travelling to the intercomparison as described in the participants' measurement reports (Annex 1) and were not calibrated again at TROPOS. Mass flow was converted to volumetric flow by each participant and particle counts were then corrected based on the actual (measured) flow rate.

2.7 CORRECTIONS FOR AEROSOL TEMPERATURE AND PRESSURE

The results were all required to be reported as concentrations with the aerosol volume standardised for a temperature of 25 °C and pressure of 101.3 kPa. The associated calculation depends on the method of flow control and calibration by each participant. For some, but not all, participants, values of the temperature and pressure in the laboratory, supplied by TROPOS, were used to calculate the reported results. NMIJ raised the question of whether this might introduce a bias into the results reported by these participants. In practice, any errors are expected to be negligible, and inspection of results from the participants compared to the rest showed no significant bias. Any differences are considered to be allowed for by the 1 % relative expanded ($k = 2$) uncertainty assigned to the reference value, in addition to the standard error of the mean (see below).

2.8 APPROACH FOR DETERMINATION OF THE REFERENCE VALUE

In the absence of an independently traceable reference value in either comparison, the protocol (Annex 3) stated that the reference value would be by consensus, specifically the mean of all the participants after the removal of outliers.

It was agreed at the GAWG meeting at BIPM in April 2018 that no outliers were apparent in either the CPC or AE results, based on visual inspection.

During discussions of the results, two of the participants, PTB and VNIIFTRI, found significant errors in the calculations of their reported CPC concentrations. In the case of PTB, a correction for detection efficiency could not be applied before the intercomparison, because a technical failure directly before the intercomparison required maintenance in the TROPOS workshop. In the case of VNIIFTRI, it had not been possible to calibrate the CPC before the results were reported, and the subsequent calibration showed that a significant correction factor was necessary. Although these results were not considered outliers, they were removed from the set of eight results used to calculate the CPC reference values, making a set of six results whose mean value was taken to determine the CPC reference value. These were: NPL, METAS, LNE, NMIJ, NIM and KRISS. Note that the results from TROPOS were not used to determine the reference value as TROPOS are not an NMI or a DI.

The reference values for the AE comparison were simply the means of the results from all participants apart from TROPOS (i.e. eight participants). In both cases, there was no attempt to weight the mean according to the uncertainties assigned by the participants – this approach was agreed in a GAWG-led meeting of participants held on 14 October 2020.

The reference values for both the CPC and AE comparisons in CCQM-P189 are therefore identical to the key comparison reference values in the CCQM-K150 final report.

For the purposes of data analysis, an uncertainty must be assigned to the reference value. After extensive discussion among the participants, it was agreed at the GAWG dedicated meeting on 14 October 2020 that the expanded ($k = 2$) uncertainty of the reference value would be twice the standard error of the mean value (as recommended in the CCQM Guidance Note 13-22 [7]), combined in quadrature with 1 %, representing a realistic additional uncertainty for variation between actual sampled concentrations.

3 RESULTS AND DEGREES OF EQUIVALENCE

3.1 RESULTS

The results from all participants in CCQM-K150 are presented in Tables 3 and 4.

Table 3(a): Aerosol electrometer reported results and reference value for 40 nm.

Lab	40 nm, 3.2 fC cm ⁻³				40 nm, 1.6 fC cm ⁻³				40 nm, 0.64 fC cm ⁻³			
	$x_i /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$x_{RV} /$ fC cm ⁻³	$u(x_{RV}) /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$x_{RV} /$ fC cm ⁻³	$u(x_{RV}) /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$x_{RV} /$ fC cm ⁻³	$u(x_{RV}) /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³
NPL	2.972	0.030	2.983	0.050	1.603	0.016	1.595	0.027	0.659	0.007	0.654	0.012
KRISS	3.161	0.083	2.956	0.041	1.682	0.043	1.584	0.023	0.691	0.018	0.649	0.011
METAS	3.075	0.032	2.968	0.048	1.638	0.028	1.590	0.026	0.676	0.022	0.651	0.012
LNE	2.810	0.140	3.006	0.042	1.500	0.090	1.610	0.022	0.610	0.060	0.661	0.010
NMIJ	3.024	0.036	2.975	0.050	1.601	0.020	1.595	0.027	0.660	0.011	0.654	0.012
NIM	3.010	0.060	2.977	0.050	1.649	0.029	1.589	0.026	0.678	0.019	0.651	0.012
BAM	2.798	0.070	3.007	0.040	1.496	0.022	1.610	0.022	0.612	0.018	0.661	0.010
PTB	3.000	0.052	2.979	0.050	1.600	0.041	1.596	0.027	0.650	0.037	0.655	0.012
TROPOS	2.943	0.042	2.981	0.044	1.565	0.042	1.596	0.024	0.641	0.042	0.655	0.011

Lab	40 nm, 0.32 fC cm ⁻³				40 nm, 0.16 fC cm ⁻³			
	$x_i /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$x_{RV} /$ fC cm ⁻³	$u(x_{RV}) /$ fC cm ⁻³	$x_i /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$x_{RV} /$ fC cm ⁻³	$u(x_{RV}) /$ fC cm ⁻³
NPL	0.323	0.004	0.322	0.006	0.1680	0.0020	0.1654	0.0039
KRISS	0.339	0.010	0.319	0.005	0.1760	0.0052	0.1643	0.0035
METAS	0.331	0.012	0.321	0.006	0.1690	0.0060	0.1653	0.0039
LNE	0.320	0.060	0.322	0.006	0.1600	0.0600	0.1666	0.0038
NMIJ	0.320	0.009	0.322	0.006	0.1730	0.0076	0.1647	0.0037
NIM	0.333	0.014	0.320	0.006	0.1730	0.0090	0.1647	0.0037
BAM	0.289	0.022	0.327	0.003	0.1470	0.0200	0.1684	0.0024
PTB	0.320	0.036	0.322	0.006	0.1600	0.0360	0.1666	0.0038
TROPOS	0.321	0.042	0.322	0.005	0.1685	0.0420	0.1658	0.0034

Table 3(b): Aerosol electrometer reported results and reference value for 50 nm.

Lab	50 nm, 3.2 fC cm ⁻³				50 nm, 1.6 fC cm ⁻³				50 nm, 0.64 fC cm ⁻³			
	$x_i /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$x_{RV} /$ fC cm ⁻³	$u(x_{RV}) /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$x_{RV} /$ fC cm ⁻³	$u(x_{RV}) /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$x_{RV} /$ fC cm ⁻³	$u(x_{RV}) /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³
NPL	3.150	0.031	3.177	0.045	1.555	0.016	1.561	0.023	0.604	0.006	0.608	0.008
KRISS	3.309	0.084	3.155	0.039	1.616	0.041	1.552	0.021	0.627	0.016	0.605	0.007
METAS	3.245	0.032	3.164	0.043	1.592	0.027	1.555	0.022	0.620	0.022	0.606	0.008
LNE	3.180	0.160	3.173	0.045	1.560	0.100	1.560	0.023	0.610	0.070	0.607	0.008
NMIJ	3.184	0.039	3.172	0.045	1.563	0.020	1.559	0.023	0.611	0.010	0.607	0.008
NIM	3.221	0.061	3.167	0.044	1.607	0.030	1.553	0.021	0.624	0.015	0.605	0.007
BAM	2.932	0.037	3.208	0.021	1.436	0.025	1.578	0.010	0.566	0.017	0.614	0.004
PTB	3.170	0.053	3.174	0.045	1.550	0.041	1.561	0.023	0.600	0.037	0.609	0.008
TROPOS	3.102	0.042	3.174	0.039	1.512	0.042	1.560	0.020	0.595	0.042	0.608	0.007

Lab	50 nm, 0.32 fC cm ⁻³				50 nm, 0.16 fC cm ⁻³			
	$x_i /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$x_{RV} /$ fC cm ⁻³	$u(x_{RV}) /$ fC cm ⁻³	$x_i /$ fC cm ⁻³	$U(x_i) /$ fC cm ⁻³	$x_{RV} /$ fC cm ⁻³	$u(x_{RV}) /$ fC cm ⁻³
NPL	0.298	0.003	0.301	0.004	0.1650	0.0020	0.1690	0.0021
KRISS	0.309	0.008	0.299	0.004	0.1730	0.0045	0.1678	0.0020
METAS	0.306	0.011	0.300	0.004	0.1710	0.0060	0.1681	0.0021
LNE	0.300	0.060	0.301	0.004	0.1700	0.0600	0.1683	0.0021
NMIJ	0.305	0.008	0.300	0.004	0.1688	0.0079	0.1684	0.0022
NIM	0.310	0.008	0.299	0.004	0.1730	0.0070	0.1678	0.0020
BAM	0.276	0.030	0.304	0.002	0.1570	0.0160	0.1701	0.0010
PTB	0.300	0.036	0.301	0.004	0.1700	0.0360	0.1683	0.0021
TROPOS	0.296	0.042	0.301	0.004	0.1678	0.0420	0.1685	0.0019

Table 4(a): Condensation particle counter reported results and reference value for 40 nm.

Lab	40 nm, 20 000 cm ⁻³				40 nm, 10 000 cm ⁻³				40 nm, 4 000 cm ⁻³			
	x_i / cm^{-3}	$U(x_i) / \text{cm}^{-3}$	x_{RV} / cm^{-3}	$u(x_{RV}) / \text{cm}^{-3}$	x_i / cm^{-3}	$U(x_i) / \text{cm}^{-3}$	x_{RV} / cm^{-3}	$u(x_{RV}) / \text{cm}^{-3}$	x_i / cm^{-3}	$U(x_i) / \text{cm}^{-3}$	x_{RV} / cm^{-3}	$u(x_{RV}) / \text{cm}^{-3}$
NPL	19029	666	19371	326	9751	341	9909	167	3678	129	3731	56
KRISS	19282	591	19320	333	9780	304	9903	169	3705	116	3726	57
METAS	19290	370	19319	333	9920	190	9875	170	3770	80	3713	56
LNE	18245	978	19528	206	9350	491	9989	110	3526	193	3762	31
NMIJ	20000	240	19177	288	10220	120	9815	149	3837	47	3700	50
NIM	20037	801	19169	282	10275	442	9804	141	3819	171	3703	52
VNIIFTRI	21036	1137	19314	272	10843	602	9883	139	4201	247	3723	47
PTB	17777	696	19314	272	9167	359	9883	139	3462	136	3723	47
TROPOS	18071	426	19314	272	9401	222	9883	139	3584	85	3723	47

Lab	40 nm, 1 000 cm ⁻³				40 nm, 100 cm ⁻³			
	x_i / cm^{-3}	$U(x_i) / \text{cm}^{-3}$	x_{RV} / cm^{-3}	$u(x_{RV}) / \text{cm}^{-3}$	x_i / cm^{-3}	$U(x_i) / \text{cm}^{-3}$	x_{RV} / cm^{-3}	$u(x_{RV}) / \text{cm}^{-3}$
NPL	853	30	864	13	113.1	4.0	115.2	1.9
KRISS	861	28	863	13	114.6	4.0	114.9	1.9
METAS	880	20	859	13	118.0	3.0	114.2	1.8
LNE	815	55	872	6	108.0	12.0	116.2	1.0
NMIJ	886	14	858	12	117.7	2.6	114.2	1.8
NIM	880	46	859	13	117.5	5.4	114.3	1.8
VNIIFTRI	1075	61	863	11	137.0	8.0	114.8	1.6
PTB	802	31	863	11	107.3	4.3	114.8	1.6
TROPOS	840	20	863	11	112.1	2.7	114.8	1.6

Table 4(b): Condensation particle counter reported results and reference value for 50 nm.

Lab	50 nm, 20 000 cm ⁻³				50 nm, 10 000 cm ⁻³				50 nm, 4 000 cm ⁻³			
	x_i / cm^{-3}	$U(x_i) / \text{cm}^{-3}$	x_{RV} / cm^{-3}	$u(x_{RV}) / \text{cm}^{-3}$	x_i / cm^{-3}	$U(x_i) / \text{cm}^{-3}$	x_{RV} / cm^{-3}	$u(x_{RV}) / \text{cm}^{-3}$	x_i / cm^{-3}	$U(x_i) / \text{cm}^{-3}$	x_{RV} / cm^{-3}	$u(x_{RV}) / \text{cm}^{-3}$
NPL	17936	628	18081	385	9354	327	9428	191	3486	122	3512	65
KRISS	18003	547	18068	385	9405	292	9418	191	3531	110	3503	65
METAS	18000	360	18068	385	9430	190	9413	191	3540	80	3501	65
LNE	16744	888	18319	213	8747	461	9550	99	3262	179	3556	25
NMIJ	18690	220	17930	353	9690	120	9361	179	3600	44	3489	61
NIM	18968	720	17875	315	9869	424	9325	156	3625	181	3484	58
VNIIFTRI	20697	1102	18057	315	10267	552	9416	156	4087	231	3507	53
PTB	16914	662	18057	315	8868	347	9416	156	3326	130	3507	53
TROPOS	17135	404	18057	315	9046	213	9416	156	3421	81	3507	53

Lab	50 nm, 1 000 cm ⁻³				50 nm, 100 cm ⁻³			
	x_i / cm^{-3}	$U(x_i) / \text{cm}^{-3}$	x_{RV} / cm^{-3}	$u(x_{RV}) / \text{cm}^{-3}$	x_i / cm^{-3}	$U(x_i) / \text{cm}^{-3}$	x_{RV} / cm^{-3}	$u(x_{RV}) / \text{cm}^{-3}$
NPL	1099	39	1106	20	92.6	3.2	92.6	1.7
KRISS	1116	37	1102	20	93.7	3.2	92.4	1.7
METAS	1130	30	1100	19	95.0	2.0	92.2	1.6
LNE	1028	65	1120	6	86.0	10.0	94.0	0.4
NMIJ	1133	21	1099	18	94.9	2.1	92.2	1.6
NIM	1122	49	1101	19	93.6	4.4	92.4	1.7
VNIIFTRI	1189	68	1105	16	112.0	6.0	92.6	1.4
PTB	1048	41	1105	16	87.8	3.5	92.6	1.4
TROPOS	1086	26	1105	16	94.8	2.2	92.6	1.4

3.2 DEGREES OF EQUIVALENCE

The method used to calculate the degrees of equivalence (DoEs) and their uncertainties considers the following:

- (1) An extra expanded uncertainty of 1 % relative to the reference value was added to all degrees of equivalence
- (2) A covariance arises due to the dependence between the laboratory result and the reference value.

As a result of these considerations, the DoEs and their uncertainties were calculated by applying the 'leave-one-out method' [8] to remove the correlation between the results of a laboratory and the reference value. At the same time, point (2) above was addressed by using the following process to properly determine the relative expanded uncertainty in the DoE.

The DoE is defined as:

$$DoE_i = x_i - x_{RV} \quad (3)$$

Where x_i is the concentration reported by participating laboratory i and x_{RV} is the concentration adopted as the reference value.

The standard uncertainty in the DoE, $u(DoE)$ is then:

$$u(DoE_i) = \sqrt{x_i^2 + 0.005^2 x_{RV}^2 + u^2(x_{RV})} \quad (4)$$

Where the third term accounts for the 1 % extra relative expanded uncertainty (which could be considered as a kind of "dark uncertainty").

The expanded uncertainty in the DoE is then:

$$U(DoE_i) = 2 u(DoE_i) \quad (5)$$

And the relative expanded uncertainty in the DoE is:

$$U_{rel}(DoE_i) = \frac{U(DoE_i)}{x_{RV}} \quad (6)$$

The absolute and relative DoEs and their uncertainties for CCQM-P189 are presented in Tables 5 and 6. The relative DoEs and their uncertainties are plotted in Figures 4-7.

In Figures 4 to 7, the five results from each participant are those for decreasing nominal particle concentrations (from 3.2 fC cm⁻³ to 0.16 fC cm⁻³ in the case of AEs, and 20 000 cm⁻³ to 100 cm⁻³ in the case of CPCs), for the specified aerosol particle size (40 nm or 50 nm).

Table 5(a): DoE and U(DoE) for aerosol electrometer results at 40 nm.

Lab	40 nm, 3.2 fC cm ⁻³				40 nm, 1.6 fC cm ⁻³				40 nm, 0.64 fC cm ⁻³			
	DoE / fC cm ⁻³	U(DoE) / fC cm ⁻³	DoE / %	U(DoE) / %	DoE / fC cm ⁻³	U(DoE) / fC cm ⁻³	DoE / %	U(DoE) / %	DoE / fC cm ⁻³	U(DoE) / fC cm ⁻³	DoE / %	U(DoE) / %
NPL	-0.011	0.109	-0.35	3.67	0.008	0.059	0.49	3.70	0.005	0.026	0.79	3.99
KRISS	0.205	0.120	6.95	4.07	0.098	0.065	6.20	4.13	0.042	0.028	6.42	4.39
METAS	0.107	0.106	3.61	3.56	0.048	0.062	3.01	3.89	0.025	0.033	3.77	5.01
LNE	-0.196	0.166	-6.51	5.52	-0.110	0.102	-6.82	6.31	-0.051	0.063	-7.70	9.59
NMIJ	0.049	0.110	1.64	3.71	0.006	0.060	0.35	3.78	0.006	0.027	0.96	4.19
NIM	0.033	0.121	1.10	4.06	0.060	0.061	3.80	3.86	0.027	0.031	4.12	4.69
BAM	-0.209	0.111	-6.96	3.70	-0.114	0.051	-7.11	3.18	-0.049	0.028	-7.35	4.18
PTB	0.021	0.117	0.72	3.94	0.004	0.070	0.28	4.39	-0.005	0.045	-0.78	6.83
TROPOS	-0.038	0.102	-1.29	3.40	-0.031	0.065	-1.95	4.09	-0.013	0.047	-2.00	7.25

Lab	40 nm, 0.32 fC cm ⁻³				40 nm, 0.16 fC cm ⁻³			
	DoE / fC cm ⁻³	U(DoE) / fC cm ⁻³	DoE / %	U(DoE) / %	DoE / fC cm ⁻³	U(DoE) / fC cm ⁻³	DoE / %	U(DoE) / %
NPL	0.001	0.013	0.41	4.15	0.003	0.008	1.55	4.97
KRISS	0.020	0.015	6.14	4.65	0.012	0.009	7.13	5.43
METAS	0.010	0.017	3.26	5.38	0.004	0.010	2.25	6.02
LNE	-0.002	0.061	-0.66	19.04	-0.007	0.061	-3.95	36.32
NMIJ	-0.002	0.016	-0.73	4.87	0.008	0.011	5.03	6.54
NIM	0.013	0.019	3.98	5.80	0.008	0.012	5.03	7.16
BAM	-0.038	0.023	-11.50	7.04	-0.021	0.021	-12.72	12.25
PTB	-0.002	0.038	-0.66	11.85	-0.007	0.037	-3.95	22.11
TROPOS	-0.001	0.043	-0.42	13.50	0.003	0.043	1.68	25.69

Table 5(b): DoE and U(DoE) for aerosol electrometer results at 50 nm.

Lab	50 nm, 3.2 fC cm ⁻³				50 nm, 1.6 fC cm ⁻³				50 nm, 0.64 fC cm ⁻³			
	DoE / fC cm ⁻³	U(DoE) / fC cm ⁻³	DoE / %	U(DoE) / %	DoE / fC cm ⁻³	U(DoE) / fC cm ⁻³	DoE / %	U(DoE) / %	DoE / fC cm ⁻³	U(DoE) / fC cm ⁻³	DoE / %	U(DoE) / %
NPL	-0.027	0.100	-0.86	3.14	-0.006	0.051	-0.36	3.26	-0.004	0.018	-0.70	2.94
KRISS	0.154	0.119	4.90	3.77	0.064	0.061	4.13	3.90	0.022	0.022	3.64	3.70
METAS	0.081	0.098	2.57	3.09	0.037	0.054	2.36	3.49	0.014	0.027	2.31	4.53
LNE	0.007	0.186	0.22	5.87	0.000	0.111	0.01	7.12	0.003	0.072	0.42	11.86
NMIJ	0.012	0.103	0.36	3.24	0.004	0.052	0.23	3.35	0.004	0.020	0.61	3.23
NIM	0.054	0.112	1.70	3.54	0.054	0.055	3.47	3.52	0.019	0.022	3.07	3.63
BAM	-0.276	0.064	-8.62	2.00	-0.142	0.036	-8.97	2.27	-0.048	0.020	-7.77	3.20
PTB	-0.004	0.109	-0.14	3.43	-0.011	0.063	-0.72	4.05	-0.009	0.041	-1.45	6.67
TROPOS	-0.072	0.094	-2.27	2.96	-0.048	0.060	-3.08	3.83	-0.012	0.045	-2.04	7.34

Lab	50 nm, 0.32 fC cm ⁻³				50 nm, 0.16 fC cm ⁻³			
	DoE / fC cm ⁻³	U(DoE) / fC cm ⁻³	DoE / %	U(DoE) / %	DoE / fC cm ⁻³	U(DoE) / fC cm ⁻³	DoE / %	U(DoE) / %
NPL	-0.003	0.010	-0.95	3.25	-0.004	0.005	-2.35	2.91
KRISS	0.010	0.012	3.25	4.00	0.005	0.006	3.08	3.74
METAS	0.006	0.014	2.10	4.77	0.003	0.008	1.72	4.48
LNE	-0.001	0.061	-0.19	20.20	0.002	0.060	1.04	35.76
NMIJ	0.005	0.012	1.72	4.05	0.000	0.009	0.22	5.44
NIM	0.011	0.012	3.63	3.97	0.005	0.008	3.08	4.92
BAM	-0.028	0.030	-9.21	9.99	-0.013	0.016	-7.71	9.54
PTB	-0.001	0.037	-0.19	12.37	0.002	0.036	1.04	21.57
TROPOS	-0.005	0.043	-1.56	14.24	-0.001	0.042	-0.41	25.05

Table 6(a): DoE and U(DoE) for condensation particle counter results at 40 nm.

Lab	40 nm, 20 000 cm ⁻³				40 nm, 10 000 cm ⁻³				40 nm, 4 000 cm ⁻³			
	DoE / cm ⁻³	U(DoE) / cm ⁻³	DoE / %	U(DoE) / %	DoE / cm ⁻³	U(DoE) / cm ⁻³	DoE / %	U(DoE) / %	DoE / cm ⁻³	U(DoE) / cm ⁻³	DoE / %	U(DoE) / %
NPL	-341.9	951.5	-1.76	4.91	-158.0	488.2	-1.59	4.93	-53.5	174.9	-1.43	4.69
KRISS	-37.9	911.0	-0.20	4.72	-123.3	464.4	-1.25	4.69	-20.7	166.9	-0.56	4.48
METAS	-28.7	786.0	-0.15	4.07	44.8	402.1	0.45	4.07	56.9	142.7	1.53	3.84
LNE	-1282.7	1079.0	-6.57	5.53	-639.2	546.9	-6.40	5.48	-235.9	206.2	-6.27	5.48
NMIJ	823.3	652.1	4.29	3.40	404.8	336.0	4.12	3.42	137.3	116.4	3.71	3.15
NIM	867.7	998.3	4.53	5.21	470.8	533.1	4.80	5.44	115.7	203.7	3.13	5.50
VNIIFTRI	1722.1	1275.1	8.92	6.60	960.4	670.5	9.72	6.78	478.5	266.7	12.85	7.16
PTB	-1536.5	904.2	-7.96	4.68	-715.6	464.7	-7.24	4.70	-260.3	168.9	-6.99	4.54
TROPOS	-1242.8	717.7	-6.43	3.72	-481.7	369.4	-4.87	3.74	-138.2	131.5	-3.71	3.53

Lab	40 nm, 1 000 cm ⁻³				40 nm, 100 cm ⁻³			
	DoE / cm ⁻³	U(DoE) / cm ⁻³	DoE / %	U(DoE) / %	DoE / cm ⁻³	U(DoE) / cm ⁻³	DoE / %	U(DoE) / %
NPL	-11.46	40.61	-1.33	4.70	-2.06	5.62	-1.79	4.88
KRISS	-1.50	39.50	-0.17	4.58	-0.26	5.69	-0.23	4.95
METAS	20.94	33.22	2.44	3.87	3.82	4.78	3.35	4.19
LNE	-57.06	57.10	-6.54	6.55	-8.18	12.22	-7.04	10.51
NMIJ	28.14	28.99	3.28	3.38	3.46	4.59	3.03	4.02
NIM	20.94	53.10	2.44	6.18	3.22	6.62	2.82	5.79
VNIIFTRI	212.45	65.30	24.63	7.57	22.18	8.68	19.32	7.56
PTB	-60.26	39.16	-6.99	4.54	-7.53	5.45	-6.56	4.74
TROPOS	-22.14	30.59	-2.57	3.55	-2.72	4.28	-2.37	3.73

Table 6(b): DoE and U(DoE) for condensation particle counter results at 50 nm.

Lab	50 nm, 20 000 cm ⁻³				50 nm, 10 000 cm ⁻³				50 nm, 4 000 cm ⁻³			
	DoE / cm ⁻³	U(DoE) / cm ⁻³	DoE / %	U(DoE) / %	DoE / cm ⁻³	U(DoE) / cm ⁻³	DoE / %	U(DoE) / %	DoE / cm ⁻³	U(DoE) / cm ⁻³	DoE / %	U(DoE) / %
NPL	-145.0	1009.3	-0.80	5.58	-74.1	511.4	-0.79	5.42	-25.6	181.5	-0.73	5.17
KRISS	-64.5	962.3	-0.36	5.33	-13.3	490.7	-0.14	5.21	28.5	173.6	0.81	4.96
METAS	-68.2	869.8	-0.38	4.81	17.1	437.4	0.18	4.65	39.2	155.9	1.12	4.45
LNE	-1575.4	1001.8	-8.60	5.47	-802.5	510.6	-8.40	5.35	-294.4	189.2	-8.28	5.32
NMIJ	759.8	761.2	4.24	4.25	329.1	389.3	3.52	4.16	111.2	134.3	3.19	3.85
NIM	1093.4	972.7	6.12	5.44	543.9	534.4	5.83	5.73	141.2	218.2	4.05	6.26
VNIIFTRI	2640.2	1282.1	14.62	7.10	851.2	641.2	9.04	6.81	579.7	256.7	16.53	7.32
PTB	-1142.6	931.6	-6.33	5.16	-548.2	476.4	-5.82	5.06	-181.8	171.7	-5.18	4.90
TROPOS	-921.4	770.0	-5.10	4.26	-369.4	389.9	-3.92	4.14	-86.2	138.0	-2.46	3.93

Lab	50 nm, 1 000 cm ⁻³				50 nm, 100 cm ⁻³			
	DoE / cm ⁻³	U(DoE) / cm ⁻³	DoE / %	U(DoE) / %	DoE / cm ⁻³	U(DoE) / cm ⁻³	DoE / %	U(DoE) / %
NPL	-6.72	56.14	-0.61	5.08	-0.04	4.74	-0.04	5.12
KRISS	13.20	54.65	1.20	4.96	1.28	4.71	1.38	5.10
METAS	30.48	49.20	2.77	4.47	2.84	3.86	3.08	4.18
LNE	-91.92	67.06	-8.21	5.99	-7.96	10.08	-8.47	10.73
NMIJ	34.08	43.85	3.10	3.99	2.72	3.92	2.95	4.26
NIM	20.88	63.28	1.90	5.75	1.16	5.60	1.25	6.06
VNIIFTRI	84.40	76.04	7.64	6.88	19.37	6.67	20.91	7.20
PTB	-56.80	53.37	-5.14	4.83	-4.82	4.55	-5.21	4.91
TROPOS	-19.03	42.60	-1.72	3.86	2.13	3.67	2.30	3.96

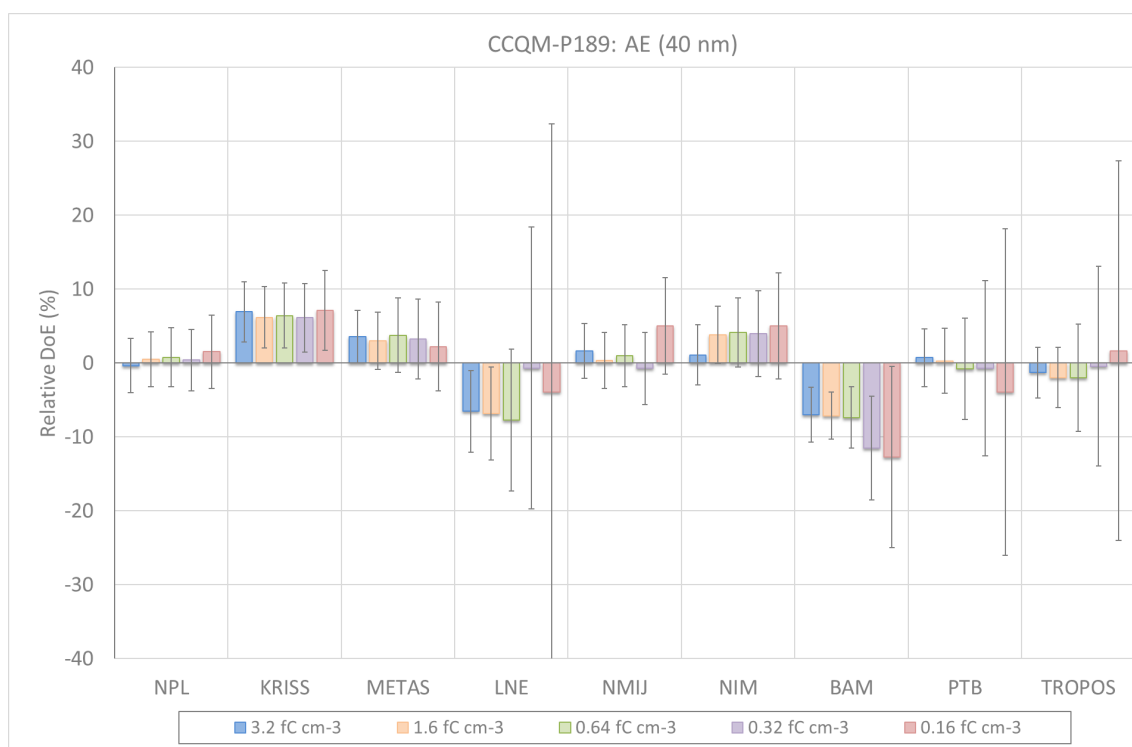


Figure 4: Aerosol electrometer comparison results for 40 nm aerosol particles, with nominal particle charge concentrations.

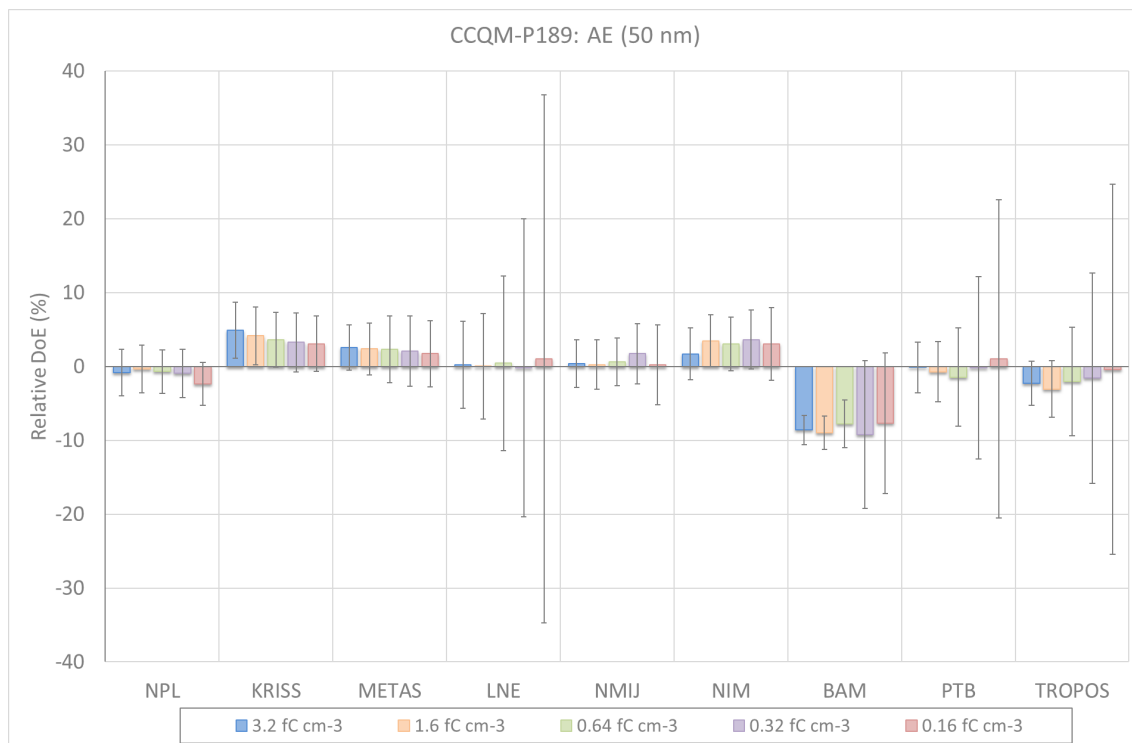


Figure 5: Aerosol electrometer comparison results for 50 nm aerosol particles, with nominal particle charge concentrations.

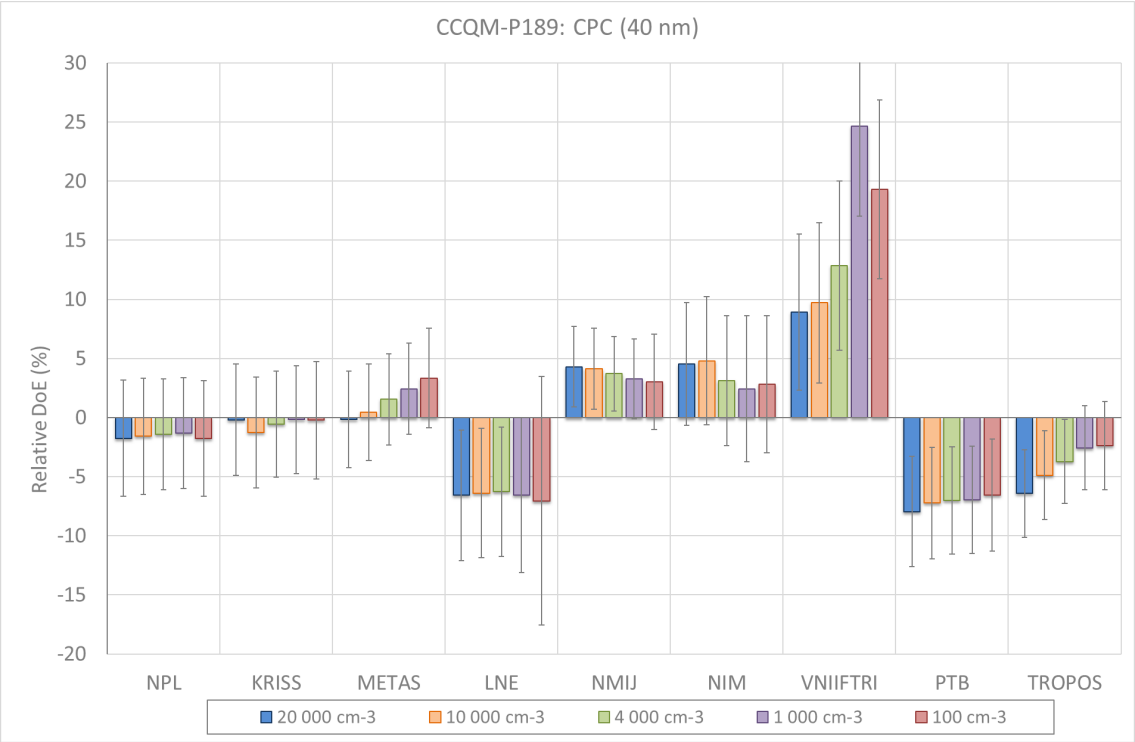


Figure 6: Condensation Particle Counter comparison results for 40 nm aerosol particles, with nominal particle number concentrations.

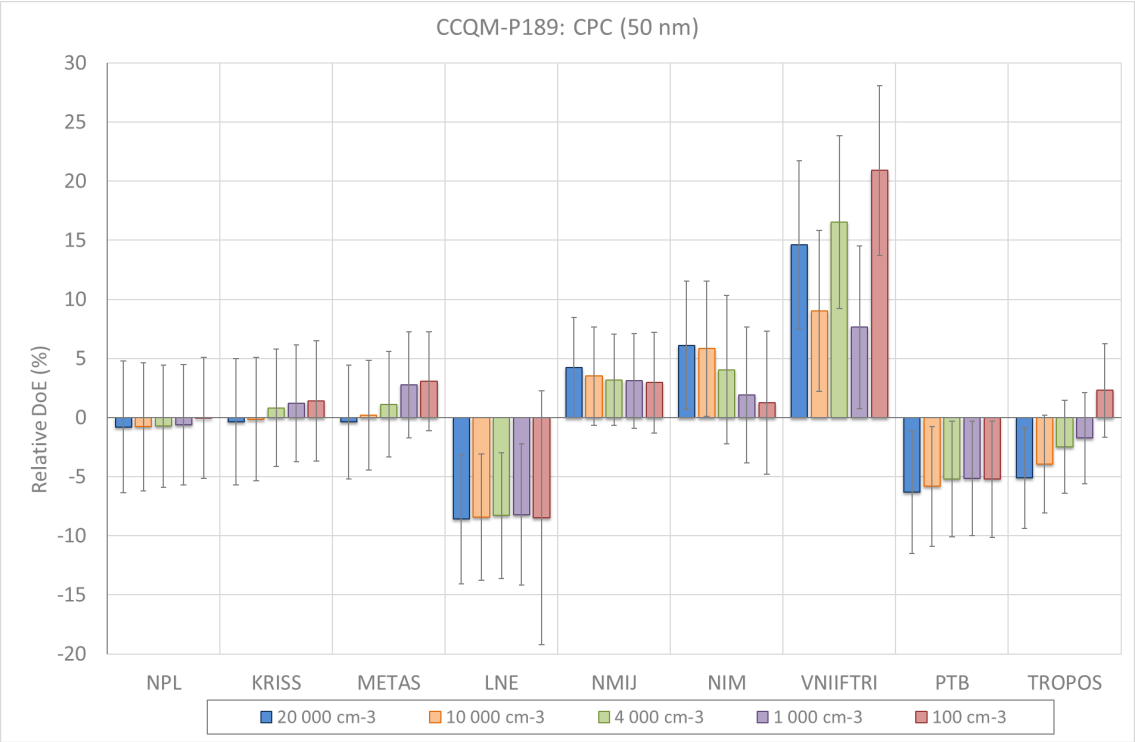


Figure 7: Condensation Particle Counter comparison results for 50 nm aerosol particles, with nominal particle number concentrations.

4 INFORMATION PROVIDED AND QUESTIONS RAISED AFTER THE SUBMISSION OF RESULTS

After the results had been submitted and circulated, LNE found errors in the way that they had handled their uncertainties. Their revised uncertainties are not included in the reported results, but are included as Annex 2. These errors were in addition to the errors found after submission of CPC results by PTB and VNIIFTRI that are described in Section 2.8.

PTB raised questions about how participants had calculated their uncertainties for the charge concentration results, especially at low concentrations. It was agreed in November 2020 that PTB should add a second set of plots to the Annex of this report with a different representation of the difference from the consensus value for the AE data and a further plot showing the range of CMCs (in femtoamperes) for each NMI. This additional information is presented in Annex 4.

Note that the data in Annex 4 have been calculated using a different method to that used in Section 3 to calculate the reference values and DoEs and their uncertainties. For example, it does not account for covariance arising due to the dependence between the laboratory result and the reference value.

The data in Annex 4 cannot therefore be used for claiming CMCs – the data in Section 3 must instead be used for that purpose.

5 CONCLUSIONS

The results from the CCQM-P189 comparison are presented in this report. The results were obtained from the same participants as in CCQM-K150, but also including TROPOS.

For CPCs, claimed expanded ($k = 2$) uncertainties were generally between 2 % and 6 %, with NMIJ's uncertainties being significantly lower (1.2 % at higher concentrations), and LNE's uncertainties being significantly higher at the lowest concentrations (11 %).

For AEs, claimed expanded ($k = 2$) uncertainties were generally lower than for CPCs, at 1 % to 3 %, but some participants estimated much higher uncertainties at low concentrations, notably PTB and TROPOS whose uncertainties rose to over 20 %. The calculation of realistic uncertainties for these measurements merits further study.

For CPCs, three of the nine laboratories demonstrate equivalence with the reference value to within their stated expanded ($k = 2$) uncertainty for all concentrations and both particle sizes, and a further five laboratories demonstrate equivalence for a subset of the measurements. For AEs, four out of nine laboratories demonstrate equivalence with the reference value for all concentrations and sizes, and the remaining five demonstrate equivalence for a subset of the measurements.

ANNEX 1: PARTICIPANTS' RESULTS

A.1.1 RESULTS FROM NPL

a) CCQM K150/P189 Comparison of particle **charge** concentration TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

National Physical Laboratory, UK

Paul Quincey

Jordan Tompkins

Isabel Hessey

Model / origin of aerosol electrometer:

Grimm Faraday Cup Electrometer Model 5.705

Method of flow control and nominal flow rate:

Volumetric flow control by a critical orifice, with a nominal flow rate of 1.0 litres per minute. Charge concentrations recorded were adjusted for the flow rate on the day of measurement. This was calculated using a mean value of three flow measurements taken at the start of the day, and three measurements taken at the end. Flow measurements were taken with a calibrated Mass Flow Meter, assuming a temperature of 25°C and a pressure of 101.3kPa.

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

No.

Calibration methods and traceability:

Mass Flow Meter (model MKS 1179A)-

Calibrated by NPL in February 2017 and January 2018, with both calibration factors taken into account for the calculations. The calibration method is determination of mass loss from a cylinder of synthetic air during a measured time interval and is traceable to NPL Mass Standards.

Faraday Cup Electrometer

Calibrated by NPL in September 2017 and December 2017, with both calibration factors taken into account in the calculations. The calibration method is application of a reference current derived from a measured voltage drop across a 1GOhm standard resistor. A Keithley 213 voltage source, Welwyn resistor and HP 3458A voltmeter were used, and the calibration is traceable to primary standards of voltage and resistance.

Components included in the uncertainty calculation:

- 1- Electrometer current calibration.
- 2- Flow meter calibration.
- 3- Short-term random uncertainty and zero correction.
- 4- Flow variation.

CCQM FCE Comparison Results

Notes:

- 1) The reported concentration is the participant's best estimate of the mean particle charge concentration entering the inlet of their instrument during the designated period.
- 2) For each run, the designated period is the ten minute period prior to the end of the run. Typically the two minutes of data preceding this period will be ignored. The only exception to this is the 40 nm 10,000 cm⁻³ run, where the designated period is the seven minute period prior to the end of the run.
- 3) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (fC·cm ⁻³)	Number of one- second outlier points removed
40 nm 20,000 cm ⁻³	2.972	0.030	0
40 nm 10,000 cm ⁻³	1.603	0.016	0
40 nm 4,000 cm ⁻³	0.659	0.007	0
40 nm 2,000 cm ⁻³	0.323	0.004	0
40 nm 1,000 cm ⁻³	0.168	0.002	0
50 nm 20,000 cm ⁻³	3.150	0.031	0
50 nm 10,000 cm ⁻³	1.555	0.016	0
50 nm 4,000 cm ⁻³	0.604	0.006	0
50 nm 2,000 cm ⁻³	0.298	0.003	0
50 nm 1,000 cm ⁻³	0.165	0.002	0

Supplementary FCE data

These data were obtained at the time of the comparison to provide information about internal losses of the electrometers at low particle sizes. Participants should make corrections for flow rate, and their electrometer calibration results at larger particle sizes. Participants may choose to correct for expected particle losses at low sizes within their instruments, and indicate this in the table. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were nominally 2,000 to 3,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Low-size loss correction applied ?
7 nm FCE	0.374	No
10 nm FCE	0.350	No
23 nm FCE	0.361	No

Date results submitted: 5 Feb 2018

b) CCQM K150/P189 Comparison of particle **number** concentration TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

National Physical Laboratory, UK

Paul Quincey

Jordan Tompkins

Isabel Hessey

Model / origin of CPC:

TSI CPC 3775

Method of flow control and nominal flow rate:

Volumetric flow control by a critical orifice, with a nominal flow rate of 0.3 litres per minute. Particle concentrations recorded were adjusted for the flow rate on the day of measurement. This was calculated using a mean value of three flow measurements taken at the start of the day, and three measurements taken at the end. Flow measurements were taken with a calibrated Mass Flow Meter, assuming a temperature of 25°C and a pressure of 101.3kPa.

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

No.

Calibration methods and traceability:

Mass Flow Meter (model MKS 1179A)-

Calibrated by NPL in February 2017 and January 2018, with both calibration factors taken into account for the calculations. The calibration method is determination of mass loss from a cylinder of synthetic air during a measured time interval and is traceable to NPL Mass Standards.

CPC

Calibrated by NPL in October 2017 and January 2018, with both calibration factors taken into account in the calculations. Calibration is against a reference Faraday Cup Electrometer (GRIMM FCE model 5.705). This was calibrated by NPL in September 2017 and December 2017, with both calibration factors taken into account in the calculations. The calibration method is application of a reference current derived from a measured voltage drop across a 1GOhm standard resistor. A Keithley 213 voltage source, Welwyn resistor and HP 3458A voltmeter were used, and the calibration is traceable to primary standards of voltage and resistance.

Components included in the uncertainty calculation:

1- CPC efficiency calibration.

2- Flow meter calibration.

3- Short-term random uncertainty.

4- Flow variation.

CCQM CPC Comparison Results

Notes:

- 1) The reported concentration is the participant's best estimate of the mean particle number concentration entering the inlet of their instrument during the designated period.
- 2) For each run, the designated period is the full measurement period, approximately 10 minutes in length.
- 3) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (particles cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (cm ⁻³)
40 nm 20,000 cm ⁻³	19029	666
40 nm 10,000 cm ⁻³	9751	341.3
40 nm 4,000 cm ⁻³	3678	128.7
40 nm 1,000 cm ⁻³	853	29.9
40 nm 100 cm ⁻³	113.1	4.0
50 nm 20,000 cm ⁻³	17936	628
50 nm 10,000 cm ⁻³	9354	327.4
50 nm 4,000 cm ⁻³	3486	122.0
50 nm 1,000 cm ⁻³	1099	38.5
50 nm 100 cm ⁻³	92.6	3.2

Supplementary CPC data

These data were obtained at the time of the comparison to provide information about the detection efficiency of the CPCs at low particle sizes. Participants should make corrections for flow rate, and for their plateau-region detection efficiency calibration, but NOT for the expected low-size detection efficiency curve of their CPC. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were in the approximate range 2,000 - 5,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Detected concentration (particles cm ⁻³ at 25°C and 101.3 kPa)
40 nm CPC	2134
30 nm CPC	2584
28 nm CPC	2561
27 nm CPC	2722
26 nm CPC	2466
25 nm CPC	2553
23 nm CPC	2600
20 nm CPC	2339
15 nm CPC	2248
12 nm CPC	2335
10 nm CPC	2117
9 nm CPC	1885
8 nm CPC	2191
7 nm CPC	1797
6 nm CPC	1802
5 nm CPC	1664

Date results submitted: 5 Feb 2018

A.1.2 RESULTS FROM PTB

a) CCQM K150/P189 Comparison of particle **charge** concentration
TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

Andreas Nowak (uncertainty calculation, final analysis) and Carlo Schaefer (preparation of measurements and first data analysis), both from PTB

Model / origin of aerosol electrometer:

Faraday Cup Electrometer (TSI 3068B)

Method of flow control and nominal flow rate: internalWere the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

No. We corrected the flow for the stated conditions here at 25°C and 101.3 kPa. We used the internal flow readings of the mass flow meter of the FCAE. During the comparison, we checked regularly the flow against an external mass flow meter.

Calibration methods and traceability:

The FCAE was calibrated against two primary standards of PTB. For the electrical signal the FCAE was calibrated against an air capacitor for the positive and negative electrical current. The mass flow of the FCAE was calibrated against an oil gas meter.

Components included in the uncertainty calculation:

Based on the calibration certificates of the primary standards, the uncertainty budget for the FCAE includes two parts for the estimation of the uncertainties like the nonlinearity, noise ratio, and offset for both calibration. Also, the resolution of the digital display for both signals like mass flow and current was included of the uncertainty budget.

CCQM FCE Comparison Results

Notes:

- 4) The reported concentration is the participant's best estimate of the mean particle charge concentration entering the inlet of their instrument during the designated period.
- 5) For each run, the designated period is the ten minute period prior to the end of the run. Typically the two minutes of data preceding this period will be ignored. The only exception to this is the 40 nm 10,000 cm⁻³ run, where the designated period is the seven minute period prior to the end of the run.
- 6) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (fC.cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (fC.cm ⁻³)	Number of one- second outlier points removed
40 nm 20,000 cm ⁻³	-3.00	-0.052	30
40 nm 10,000 cm ⁻³	-1.60	-0.041	8
40 nm 4,000 cm ⁻³	-0.65	-0.037	31
40 nm 2,000 cm ⁻³	-0.32	-0.036	22
40 nm 1,000 cm ⁻³	-0.16	-0.036	12
50 nm 20,000 cm ⁻³	-3.17	-0.053	5
50 nm 10,000 cm ⁻³	-1.55	-0.041	13
50 nm 4,000 cm ⁻³	-0.60	-0.037	20
50 nm 2,000 cm ⁻³	-0.30	-0.036	20
50 nm 1,000 cm ⁻³	-0.17	-0.036	11

Supplementary FCE data

These data were obtained at the time of the comparison to provide information about internal losses of the electrometers at low particle sizes. Participants should make corrections for flow rate, and their electrometer calibration results at larger particle sizes. Participants may choose to correct for expected particle losses at low sizes within their instruments, and indicate this in the table. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were nominally 2.000 to 3.000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Concentration (fC.cm ⁻³ at 25°C and 101.3 kPa)	Low-size loss correction applied ?
7 nm FCE	-0.39	<i>No, only flow corrected for stated conditions here</i>
10 nm FCE	-0.36	
23 nm FCE	-0.37	

Date results submitted:

b) CCQM K150/P189 Comparison of particle **number** concentration TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

Andreas Nowak (uncertainty calculation, final analysis) and Carlo Schaefer (preparation of measurements and first data analysis), both from PTB

Model / origin of CPC:

TSI 3772 and TSI 3790 (reference CPC for engine exhaust emission)

Method of flow control and nominal flow rate:

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

No. We corrected the flow for the stated conditions here at 25°C and 101.3 kPa. The flow of both CPCs was checked regularly after and before one measurement interval.

Calibration methods and traceability:

During the comparison, we have used an external flow meter by Voegtlin to check the flow for both CPCs. The calibration report given by the manufacture was used to calculate the uncertainty for both CPC flows.

Components included in the uncertainty calculation:

Several components were implemented in the uncertainty calculation like nonlinearity, noise ratio and offset based on the calibration certificate of manufacture for the mass flow meter (Voegtlin). Also, the resolution of the digital display for the CPC has to be taking into account for the calculation.

CCQM CPC Comparison Results

Notes:

- 4) The reported concentration is the participant's best estimate of the mean particle number concentration entering the inlet of their instrument during the designated period.
- 5) For each run. the designated period is the full measurement period. approximately 10 minutes in length.
- 6) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration 3772 (particles cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (cm ⁻³)
40 nm 20.000 cm ⁻³	17777.39	695.98
40 nm 10.000 cm ⁻³	9167.04	358.87
40 nm 4.000 cm ⁻³	3462.24	135.59
40 nm 1.000 cm ⁻³	802.29	31.48
40 nm 100 cm ⁻³	107.29	4.28
50 nm 20.000 cm ⁻³	16914.28	662.17
50 nm 10.000 cm ⁻³	8867.62	347.17
50 nm 4.000 cm ⁻³	3325.53	130.24
50 nm 1.000 cm ⁻³	1047.80	41.11
50 nm 100 cm ⁻³	87.81	3.50

Run designation (concentrations are the nominal particle number concentrations)	Concentration 3790 (particles cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (cm ⁻³)
40 nm 20.000 cm ⁻³	15207.06	595.39
40 nm 10.000 cm ⁻³	7725.48	302.45
40 nm 4.000 cm ⁻³	2898.07	113.51
40 nm 1.000 cm ⁻³	673.11	26.43
40 nm 100 cm ⁻³	90.54	3.61
50 nm 20.000 cm ⁻³	15932.11	623.72
50 nm 10.000 cm ⁻³	8243.50	322.76
50 nm 4.000 cm ⁻³	3054.74	119.63
50 nm 1.000 cm ⁻³	960.76	37.69
50 nm 100 cm ⁻³	80.53	3.22

Supplementary CPC data

These data were obtained at the time of the comparison to provide information about the detection efficiency of the CPCs at low particle sizes. Participants should make corrections for flow rate, and for their plateau-region detection efficiency calibration, but NOT for the expected low-size detection efficiency curve of their CPC. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were in the approximate range 2.000 - 5.000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Detected concentration 3772 (particles cm ⁻³ at 25°C and 101.3 kPa)
40 nm CPC	2038,70
30 nm CPC	2430,08
28 nm CPC	2400,56
27 nm CPC	2550,57
26 nm CPC	2305,57
25 nm CPC	2380,80
23 nm CPC	2420,01
20 nm CPC	2139,17
15 nm CPC	1945,26
12 nm CPC	1840,62
10 nm CPC	1456,31
9 nm CPC	1149,85
8 nm CPC	1089,40
7 nm CPC	644,10
6 nm CPC	321,09
5 nm CPC	19,45

Run designation	Detected concentration 3790 (particles cm ⁻³ at 25°C and 101.3 kPa)
40 nm CPC	1718,54
30 nm CPC	1529,69
28 nm CPC	1338,40
27 nm CPC	1318,05
26 nm CPC	1086,83
25 nm CPC	1007,98
23 nm CPC	747,04
20 nm CPC	198,25
15 nm CPC	0,52
12 nm CPC	0,01
10 nm CPC	0,00
9 nm CPC	0,00
8 nm CPC	0,00
7 nm CPC	0,00
6 nm CPC	0,00
5 nm CPC	0,00

Date results submitted:

A.1.3 RESULTS FROM METAS

a) CCQM K150/P189 Comparison of particle **charge** concentration TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

METAS, Felix Lüönd

Model / origin of aerosol electrometer:

TSI 3068B (S/N 70701106), METAS laboratory for particles and aerosols

Method of flow control and nominal flow rate:

Nominal flow rate: 1.0 lpm. Internal flow control via solenoid valve. The aerosol flow was measured externally with a Vögtlin Red-y flow meter (GSM-B4PA-BN00, S/N 122021 or S/N 150874, respectively) downstream the solenoid valve. A needle valve was used between the flow meter and the vacuum pump in order to increase the operating pressure of the flow meter from to 840 +/- 10 mbar absolute. The flow meters were calibrated at the respective absolute pressure with N₂.

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

No, since the used flow meters measure mass flow.

Calibration methods and traceability:

Current: The electrometer was electrically calibrated at METAS in July 2017. In this calibration, currents between 10 fA and 5 pA were applied to the electrometer. The reference current was generated with a precisely controlled voltage ramp and a reference capacitance with low frequency dependence. Flow rate: The used mass flow meters have been calibrated with the METAS primary reference standard between 300 mbar and 960 mbar absolute pressure.

Components included in the uncertainty calculation:

Flow rate: Type B contribution according to the flow meter calibration, and a Type A contribution according to the fluctuation in measurement.

Current: Type B contribution according to the electrical calibration of the electrometer. Type A contribution according to the fluctuation in the measurement. For details please refer to the document about data evaluation.

As the flow was measured externally with a mass flow meter, no pressure or temperature measurements enter the formula for the calculation of the charge concentration.

CCQM FCE Comparison Results

Notes:

- 7) The reported concentration is the participant's best estimate of the mean particle charge concentration entering the inlet of their instrument during the designated period.
- 8) For each run, the designated period is the ten minute period prior to the end of the run. Typically the two minutes of data preceding this period will be ignored. The only exception to this is the 40 nm 10,000 cm⁻³ run, where the designated period is the seven minute period prior to the end of the run.

- 9) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (fC·cm ⁻³)	Number of one- second outlier points removed
40 nm 20,000 cm ⁻³	3.075	0.032	3
40 nm 10,000 cm ⁻³	1.638	0.028	1
40 nm 4,000 cm ⁻³	0.676	0.022	12
40 nm 2,000 cm ⁻³	0.331	0.012	5
40 nm 1,000 cm ⁻³	0.169	0.006	6
50 nm 20,000 cm ⁻³	3.245	0.032	4
50 nm 10,000 cm ⁻³	1.592	0.027	3
50 nm 4,000 cm ⁻³	0.620	0.022	3
50 nm 2,000 cm ⁻³	0.306	0.011	5
50 nm 1,000 cm ⁻³	0.171	0.006	7

Supplementary FCE data

These data were obtained at the time of the comparison to provide information about internal losses of the electrometers at low particle sizes. Participants should make corrections for flow rate, and their electrometer calibration results at larger particle sizes. Participants may choose to correct for expected particle losses at low sizes within their instruments, and indicate this in the table. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were nominally 2,000 to 3,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Low-size loss correction applied ?
7 nm FCE	0.406	No
10 nm FCE	0.368	No
23 nm FCE	0.367	No

Date results submitted:

b) CCQM K150/P189 Comparison of particle **number** concentration TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:
METAS, Felix Lüönd

Model / origin of CPC:
Grimm CPC 5412 (S/N 54121103), METAS laboratory for particles and aerosols

Method of flow control and nominal flow rate:
Internal pump and flow controller, flow was continuously monitored by an external mass flow meter (Vögtlin Red-y smart series, S/N 150874) at the exhaust of the CPC. A cold trap was used downstream of the CPC exhaust to prevent butanol vapour from influencing the flow measurement.

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?
No, since the used flow meter reports mass flow.

Calibration methods and traceability:
The flow meter was calibrated with Nitrogen against the corresponding METAS primary standard in August 2017. The corresponding calibration data were used to correct the measured flow. As the flow meter measures mass flow, no information about aerosol temperature and pressure during the measurements is required.

The CPC was calibrated prior to the intercomparison against the METAS primary standard for particle number concentration (TSI 3068B electrometer, S/N 70701106). This calibration also involved two mass flow meters calibrated against the METAS primary standard for flow. The electrical part of the electrometer was calibrated in July 2017 against the METAS primary standard for small DC current (as low as 10 fA). Number concentration values reported in this document have been corrected by the counting efficiency of the CPC.

The calibration of the CPC was done according to ISO 27891 with sintered Ag particles at the sizes 10 nm, 15 nm, 20 nm, 30 nm, 40 nm, and 50 nm for concentrations $\leq 5'000 \text{ cm}^{-3}$. For each particle size, the counting efficiency of the CPC was measured in 6 repetitions. Each repetition included subtraction of the electrometer offset and a correction for multiply charged, larger particles. The uncertainty in the counting efficiency averaged over the 6 repetitions contains contributions from both the variability of the instrument readings recorded at 1 Hz frequency and from the variability of the counting efficiency between the individual repetitions (this results in a conservative estimate of the uncertainty because the two mentioned variabilities can partly have the same origin). The fraction of multiply charged particles in the calibration aerosol was below 1% for all particle sizes. Small particle size or size selection in the far downslope of the initial size distribution reduced the number of required voltage levels usually to two or even one (i.e. no multiple charge correction at all).

For particles smaller than 10 nm where no calibration data exist, the CPC counting efficiency was extrapolated using a cutoff curve of the form

$$\eta_{CPC} = \eta_0 \left(1 - \exp \left(- \frac{(d - d_1)^\alpha}{d_2} \right) \right),$$

with $\eta_0 = 0.95$, $d_1 = -8 \text{ nm}$, $d_2 = 22 \text{ nm}$, and $\alpha = 1.25$.

Components included in the uncertainty calculation:

- Variability (type A uncertainty) of the CPC reading during a 10 min measurement, i.e. standard deviation of the measured values divided by the square root of the number of 1s readings.
- Uncertainty in flow measurement: This includes the variability (type A) of the flow measured during the used 10 min period of a measurement as well as a type B contribution from the calibration of the flow meter.
- Uncertainty in the counting efficiency of the CPC as determined during the calibration of the CPC against the reference electrometer.

CCQM CPC Comparison Results

Notes:

- 7) The reported concentration is the participant's best estimate of the mean particle number concentration entering the inlet of their instrument during the designated period.
- 8) For each run, the designated period is the full measurement period, approximately 10 minutes in length.
- 9) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (particles cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (cm ⁻³)
40 nm 20,000 cm ⁻³	19290	370
40 nm 10,000 cm ⁻³	9920	190
40 nm 4,000 cm ⁻³	3770	80
40 nm 1,000 cm ⁻³	880	20
40 nm 100 cm ⁻³	118	3
50 nm 20,000 cm ⁻³	18000	360
50 nm 10,000 cm ⁻³	9430	190
50 nm 4,000 cm ⁻³	3540	80
50 nm 1,000 cm ⁻³	1130	30
50 nm 100 cm ⁻³	95	2

Supplementary CPC data

These data were obtained at the time of the comparison to provide information about the detection efficiency of the CPCs at low particle sizes. Participants should make corrections for flow rate, and for their plateau-region detection efficiency calibration, but NOT for the expected low-size detection efficiency curve of their CPC. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were in the approximate range 2,000 - 5,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Detected concentration (particles cm ⁻³ at 25°C and 101.3 kPa)
40 nm CPC	2202
30 nm CPC	2657
28 nm CPC	2652
27 nm CPC	2822
26 nm CPC	2569
25 nm CPC	2688
23 nm CPC	2732
20 nm CPC	2478
15 nm CPC	2475
12 nm CPC	2743
10 nm CPC	2603
9 nm CPC	2358
8 nm CPC	2805
7 nm CPC	2412
6 nm CPC	2508
5 nm CPC	2457

Date results submitted:

A.1.4 RESULTS FROM LNE

a) CCQM K150/P189 Comparison of particle **charge** concentration
TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

LNE, Lola Brégonzio-Rozier

Model / origin of aerosol electrometer:

Electrometer, Keithley, model 642

Electrometer remote head, Keithley

Method of flow control and nominal flow rate:

Method of flow control: TSI 4040 Mass Flowmeter

Nominal flow rate: Mass flow controller (Bronkhorst)

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ? NoCalibration methods and traceability: Calibration using standard signal connected to FCE inlet with a SI traceability.Components included in the uncertainty calculation: Flow measurement accuracy of the TSI 4040 Mass Flowmeter and FCE uncertainty.**CCQM FCE Comparison Results**

Notes:

- 10) The reported concentration is the participant's best estimate of the mean particle charge concentration entering the inlet of their instrument during the designated period.
- 11) For each run, the designated period is the ten minute period prior to the end of the run. Typically the two minutes of data preceding this period will be ignored. The only exception to this is the 40 nm 10,000 cm⁻³ run, where the designated period is the seven minute period prior to the end of the run.
- 12) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (fC·cm ⁻³)	Number of one- second outlier points removed
40 nm 20,000 cm ⁻³	-2.81	0.14	113 (missing)
40 nm 10,000 cm ⁻³	-1.50	0.09	0
40 nm 4,000 cm ⁻³	-0.61	0.06	0
40 nm 2,000 cm ⁻³	-0.32	0.06	0
40 nm 1,000 cm ⁻³	-0.16	0.06	0
50 nm 20,000 cm ⁻³	-3.18	0.16	0
50 nm 10,000 cm ⁻³	-1.56	0.10	0
50 nm 4,000 cm ⁻³	-0.61	0.07	0
50 nm 2,000 cm ⁻³	-0.30	0.06	0
50 nm 1,000 cm ⁻³	-0.17	0.06	33 (missing)

Supplementary FCE data

These data were obtained at the time of the comparison to provide information about internal losses of the electrometers at low particle sizes. Participants should make corrections for flow rate, and their electrometer calibration results at larger particle sizes. Participants may choose to correct for expected particle losses at low sizes within their instruments, and indicate this in the table. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were nominally 2,000 to 3,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Low-size loss correction applied ?
7 nm FCE	-0.37	No
10 nm FCE	-0.34	No
23 nm FCE	-0.35	No

Date results submitted:

b) CCQM K150/P189 Comparison of particle **number** concentration TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:
LNE, Lola Brégonzio-Rozier

Model / origin of CPC:
Butanol CPC TSI 3775

Method of flow control and nominal flow rate:
Method of flow control: TSI 4040 Mass Flowmeter
Nominal flow rate: Internal flow control

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ? No

Calibration methods and traceability: FCE traceability

Components included in the uncertainty calculation: Flow measurement accuracy of the TSI 4040 Mass Flowmeter and standard deviation on CPC count for the 10 minutes measurements

CCQM CPC Comparison Results

Notes:

- 10) The reported concentration is the participant's best estimate of the mean particle number concentration entering the inlet of their instrument during the designated period.
- 11) For each run, the designated period is the full measurement period, approximately 10 minutes in length.
- 12) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (particles cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (cm ⁻³)
40 nm 20,000 cm ⁻³	18245	978
40 nm 10,000 cm ⁻³	9350	491
40 nm 4,000 cm ⁻³	3526	193
40 nm 1,000 cm ⁻³	815	55
40 nm 100 cm ⁻³	108	12
50 nm 20,000 cm ⁻³	16744	888
50 nm 10,000 cm ⁻³	8747	461
50 nm 4,000 cm ⁻³	3262	179
50 nm 1,000 cm ⁻³	1028	65
50 nm 100 cm ⁻³	86	10

Supplementary CPC data

These data were obtained at the time of the comparison to provide information about the detection efficiency of the CPCs at low particle sizes. Participants should make corrections for flow rate, and for their plateau-region detection efficiency calibration, but NOT for the expected low-size detection efficiency curve of their CPC. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were in the approximate range 2,000 - 5,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Detected concentration (particles cm ⁻³ at 25°C and 101.3 kPa)
40 nm CPC	2039
30 nm CPC	2434
28 nm CPC	2403
27 nm CPC	2556
26 nm CPC	2314
25 nm CPC	2390
23 nm CPC	2425
20 nm CPC	2166
15 nm CPC	2044
12 nm CPC	2083
10 nm CPC	1856
9 nm CPC	1638
8 nm CPC	1878
7 nm CPC	1516
6 nm CPC	1468
5 nm CPC	1291

Date results submitted:

A.1.5 RESULTS FROM VNIIFTRI

CCQM K150/P189 Comparison of particle number concentration

TROPOS

13-17 November 2017

Results Proforma

Participant laboratory and people involved:

VNIIFTRI
Dmitrii Belenkii
Narine Oganyan

Model / origin of CPC:

TSI CPC 3775

Method of flow control and nominal flow rate:

Tachometric transducer
Nominal flow rate: 0,3 lpm

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

Yes

Calibration methods and traceability:

CPC was calibrated against reference FCAE Palas Charme and flow meter.
Traceability to primary standards of flow rate, current and resistance.

Components included in the uncertainty calculation:

1. Standard deviation of the mean concentration.
2. Flow rate uncertainty.
3. Calibration uncertainty.
4. Temperature correction uncertainty.
5. Pressure correction uncertainty

CCQM CPC Comparison Results

Run designation (concentrations are the nominal particle number concentrations)	Concentration (particles cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (cm ⁻³)
40 nm 20,000 cm ⁻³	21036	1137
40 nm 10,000 cm ⁻³	10843	602
40 nm 4,000 cm ⁻³	4201	247
40 nm 1,000 cm ⁻³	1075	61
40 nm 100 cm ⁻³	137	8
50 nm 20,000 cm ⁻³	20697	1102
50 nm 10,000 cm ⁻³	10267	552
50 nm 4,000 cm ⁻³	4087	231
50 nm 1,000 cm ⁻³	1189	68
50 nm 100 cm ⁻³	112	6

Supplementary CPC data

Run designation	Detected concentration (particles cm ⁻³ at 25°C and 101.3 kPa)
40 nm CPC	2376
30 nm CPC	2871
28 nm CPC	2823
27 nm CPC	2802
26 nm CPC	2719
25 nm CPC	2832
23 nm CPC	2844
20 nm CPC	2578
15 nm CPC	2730
12 nm CPC	2520
10 nm CPC	2287
9 nm CPC	2012
8 nm CPC	2528
7 nm CPC	1819
6 nm CPC	2069
5 nm CPC	1509

Date results submitted: 8 February 2017

A.1.6 RESULTS FROM NMIJ

a) CCQM K150/P189 Comparison of particle **charge** concentration
TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

National Metrology Institute of Japan (NMIJ)
Hiromu Sakurai and Yoshiko Murashima

Model / origin of aerosol electrometer:

Model 3068B, manufactured by TSI Inc.

Method of flow control and nominal flow rate:

With the internal flow control and measurement of the FCAE for constant actual volumetric flow rate,
with connection to the vacuum line of TROPOS
1 L/min

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

Yes

Calibration methods and traceability:

Calibrated against the primary standard FCAE of NMIJ in the size range between 10 nm and 100 nm and in the charge concentration range between 0.15 fC cm^{-3} and 3 fC cm^{-3} with positively singly-charged poly-alpha-olefin, polystyrene latex, or sucrose particles.

The primary standard FCAE of NMIJ had metrological traceability to SI for electrical current and flow rate.

Components included in the uncertainty calculation:

- Uncertainty of the detection efficiencies of the travelling standard FCAE (TSI 3068B) that were determined in the calibration against NMIJ's primary standard FCAE, which included:
 - Uncertainty of the electrical current of NMIJ's primary standard
 - Uncertainty of the flow rate of NMIJ's primary standard
 - Uncertainty of the splitter bias correction factor during the calibration against NMIJ's primary standard
 - Uncertainty for the repeatability during the calibration against NMIJ's primary standard
- Uncertainty for the variation of the detection efficiency due to flow rate variation of the travelling standard FCAE during the trip to/from TROPOS.
- Uncertainty for the repeatability expected to measurements of 10-min average concentrations by the travelling standard FCAE

Note that the uncertainties for the temperatures and pressures, which were provided by TROPOS and were used in the conversion of the concentrations to the standard condition of 25 °C and 101.3 kPa, were not included. The temperatures and pressures given by TROPOS were consistently lower by 1-

3 °C and 0.4-1 kPa than the temperatures and pressures that we recorded for the laboratory air at our FCAE during the measurements, respectively. We understand that those differences may have been due to the difference in the measurement locations. The differences, however, still make us concerned about the accuracy of the temperatures and pressures given by the TROPOS. Error of 3 °C and 1 kPa would each give about 1 % of bias to the converted concentrations. I hope that, in future comparisons, the temperature and pressure in the sampling manifold are measured accurately with a thermometer and a pressure gauge with known, small uncertainties.

It should be also noted that the concentration biases among the sampling ports and biases due to difference in losses among the sampling tubes between the sampling ports and FCAEs are not considered in the uncertainty evaluation.

CCQM FCE Comparison Results

Notes:

- 13) The reported concentration is the participant's best estimate of the mean particle charge concentration entering the inlet of their instrument during the designated period.
- 14) For each run, the designated period is the ten minute period prior to the end of the run. Typically the two minutes of data preceding this period will be ignored. The only exception to this is the 40 nm 10,000 cm⁻³ run, where the designated period is the seven minute period prior to the end of the run.
- 15) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (fC·cm ⁻³)	Number of one-second outlier points removed	Temper ature (°C)	Pressur e (kPa)
40 nm 20,000 cm ⁻³	3.024	0.036	0	25.0	100.4*
40 nm 10,000 cm ⁻³	1.601	0.020	0	25.3	100.5
40 nm 4,000 cm ⁻³	0.660	0.011	0	25.5	100.6
40 nm 2,000 cm ⁻³	0.3198	0.0092	0	25.4	100.5
40 nm 1,000 cm ⁻³	0.1730	0.0076	0	25.7	100.4
50 nm 20,000 cm ⁻³	3.184	0.039	0	25.9	100.5
50 nm 10,000 cm ⁻³	1.563	0.020	0	26.0	100.4
50 nm 4,000 cm ⁻³	0.611	0.010	0	26.3	100.3
50 nm 2,000 cm ⁻³	0.3050	0.0079	0	26.2	100.2
50 nm 1,000 cm ⁻³	0.1688	0.0079	0	26.6	100.5

* Note 1 We modified the tables by adding two columns for the temperatures and pressures that were given by TROPOS for each run.

* Note 2 For the run at 40 nm and 20 000 cm⁻³, while we think that the pressure given by TROPOS was 103.6 kPa, we believe that the pressure was read incorrectly and that the correct pressure was 100.36 kPa.

Supplementary FCE data

These data were obtained at the time of the comparison to provide information about internal losses of the electrometers at low particle sizes. Participants should make corrections for flow rate, and their electrometer calibration results at larger particle sizes. Participants may choose to correct for expected

particle losses at low sizes within their instruments, and indicate this in the table. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were nominally 2,000 to 3,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Low-size loss correction applied ?	Temper ature (°C)	Pressur e (kPa)
7 nm FCE	0.371	Y	24.4	100.6
10 nm FCE	0.350	Y	25.1	100.6
23 nm FCE	0.370	Y	25.6	100.6

Date results submitted:

12 February 2018

b) CCQM K150/P189 Comparison of particle **number** concentration TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

National Metrology Institute of Japan (NMIJ)
Hiromu Sakurai and Yoshiko Murashima

Model / origin of CPC:

Model 3772, manufactured by TSI Inc.

Method of flow control and nominal flow rate:

With the internal flow control with a critical orifice of the CPC, with connection to the vacuum line of TROPOS
1 L/min

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

Yes

Calibration methods and traceability:

Calibrated against the primary standard FCAE of NMIJ in the size range between 10 nm and 100 nm and in the number concentration range between 100 cm⁻³ and 20 000 cm⁻³ with positively singly-charged poly-alpha-olefin, polystyrene latex, or sucrose particles.

The primary standard FCAE of NMIJ had metrological traceability to SI for electrical current and flow rate.

Components included in the uncertainty calculation:

- Uncertainty of the detection efficiencies of the travelling standard CPC (3772) that were determined in the calibration against NMIJ's primary standard FCAE, which included:
 - Uncertainty of the electrical current of NMIJ's primary standard
 - Uncertainty of the flow rate of NMIJ's primary standard
 - Uncertainty of the splitter bias correction factor during the calibration against NMIJ's primary standard
 - Uncertainty for the multiple-charge correction
 - Uncertainty for the repeatability during the calibration against NMIJ's primary standard
- Uncertainty for the variation of the detection efficiency due to flow rate variation of the travelling standard CPC during the trip to/from TROPOS. We observed an unusual variation of the flow rate of the CPC during the shipping from NMIJ to TROPOS, which completely invalidated the calibration at NMIJ before the shipping to TROPOS. Since the flow rate did not change significantly during the shipping from TROPOS to NMIJ, the CPC was recalibrated after the trip from TROPOS. The uncertainty for the stability of the flow meter used to check the CPC flow rate was included in the evaluation of the overall uncertainty.

Note that the uncertainties for the temperatures and pressures, which were provided by TROPOS and were used in the conversion of the concentrations to the standard condition of 25 °C and 101.3 kPa, were not included. As already noted in the FCAE report, the temperatures and pressures given by TROPOS were consistently lower by 1-3 °C and 0.4-1 kPa than the temperatures and pressures that we recorded for the laboratory air at our CPC during the measurements, respectively. We understand that those differences may have been due to the difference in the measurement locations. The differences, however, still make us concerned about the accuracy of the temperatures and pressures given by the TROPOS. Error of 3 °C and 1 kPa would each give about 1 % of bias to the converted concentrations. I hope that, in future comparisons, the temperature and pressure in the sampling manifold are measured accurately with a thermometer and a pressure gauge with known, small uncertainties.

It should be also noted that the concentration biases among the sampling ports and biases due to difference in losses among the sampling tubes between the sampling ports and CPCs are not considered in the uncertainty evaluation.

CCQM CPC Comparison Results

Notes:

- 13) The reported concentration is the participant's best estimate of the mean particle number concentration entering the inlet of their instrument during the designated period.
- 14) For each run, the designated period is the full measurement period, approximately 10 minutes in length.
- 15) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (particles cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (cm ⁻³)	Temperature (°C)	Pressure (kPa)
40 nm 20,000 cm ⁻³	2.000×10^4	0.024×10^4	26.4	100.5
40 nm 10,000 cm ⁻³	1.022×10^4	0.012×10^4	26.5	100.5
40 nm 4,000 cm ⁻³	3.837×10^3	0.047×10^3	26.6	100.4
40 nm 1,000 cm ⁻³	0.886×10^3	0.014×10^3	26.6	100.5
40 nm 100 cm ⁻³	1.177×10^2	0.026×10^2	26.4	100.5
50 nm 20,000 cm ⁻³	1.869×10^4	0.022×10^4	26.0	100.6
50 nm 10,000 cm ⁻³	0.969×10^4	0.012×10^4	25.9	100.6
50 nm 4,000 cm ⁻³	3.600×10^3	0.044×10^3	25.9	100.5
50 nm 1,000 cm ⁻³	1.133×10^3	0.021×10^3	25.9	100.5
50 nm 100 cm ⁻³	0.949×10^2	0.021×10^2	26.0	100.6

Supplementary CPC data

These data were obtained at the time of the comparison to provide information about the detection efficiency of the CPCs at low particle sizes. Participants should make corrections for flow rate, and for their plateau-region detection efficiency calibration, but NOT for the expected low-size detection efficiency curve of their CPC. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were in the approximate range 2,000 - 5,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Detected concentration (particles cm ⁻³ at 25°C and 101.3 kPa)	Temperature (°C)	Pressure (kPa)
40 nm CPC	2.22×10^3	24.9	100.8
30 nm CPC	2.68×10^3	25.4	100.4
28 nm CPC	2.65×10^3	25.5	100.8
27 nm CPC	2.83×10^3	25.7	100.5
26 nm CPC	2.55×10^3	25.6	100.6
25 nm CPC	2.64×10^3	25.9	100.8
23 nm CPC	2.69×10^3	26.0	100.7
20 nm CPC	2.41×10^3	26.0	100.7
15 nm CPC	2.22×10^3	26.0	100.7
12 nm CPC	2.15×10^3	26.1	100.4
10 nm CPC	1.76×10^3	26.1	100.4
9 nm CPC	1.44×10^3	26.3	100.5
8 nm CPC	1.41×10^3	26.4	100.5
7 nm CPC	0.87×10^3	26.5	100.7
6 nm CPC	0.46×10^3	26.5	100.6
5 nm CPC	0.03×10^3	26.5	100.6

Date results submitted:

12 February 2018

A.1.7 RESULTS FROM NIM

a) CCQM K150/P189 Comparison of particle **charge** concentration
TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

National Institute of Metrology, China.
Liu Junjie

Model / origin of aerosol electrometer:

GRIMM 5.705 aerosol electrometer

Method of flow control and nominal flow rate:

Using the built-in pump of the instrument to control the flow rate, and the nominal flow rate is 1L/min.

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

Yes.

Calibration methods and traceability:

For calibrating electrical current (zero values and respondent electrical current) of the NIM FCAE (GRIMM, 5705), the FCAE is connected into a circuit using copper wires, where the reference electrical current of the circuit could be obtained by using a $10T\Omega$ reference resistance and a DC voltage source. The annual stability of resistance is better than 0.075%, and the temperature coefficient is better than 0.05% within (18~28) °C. For ensuring the accuracy of reference electrical, both the resistance and DC voltage source are calibrated by Electricity and Magnetism Division of National Institute of Metrology (NIM) with uncertainty of 0.1% (k=2) and 0.005% (k=2) respectively. In electrical current calibration, for the purpose of preventing external electromagnetic interference, all instruments were put in a shielding case, which is made of steel mesh frame, and the outer lining is full of aluminum skin.

Components included in the uncertainty calculation:

In the aerosol electrometer calibration procedures, there are several uncertainty sources effecting the accuracy of calibration results, e.g., uncertainty budget result from electrical current calibration, flow rate calibration, electron charge and FCE measurement repeatability. Among them, the uncertainty budget from electron charge can be ignored.

CCQM FCE Comparison Results

Notes:

- 1) The reported concentration is the participant's best estimate of the mean particle charge concentration entering the inlet of their instrument during the designated period.
- 2) For each run, the designated period is the ten minute period prior to the end of the run. Typically the two minutes of data preceding this period will be ignored. The only exception to this is the 40 nm 10,000 cm⁻³ run, where the designated period is the seven minute period prior to the end of the run.
- 3) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (fC.cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (fC.cm ⁻³)	Number of one- second outlier points removed
40 nm 20,000 cm ⁻³	3.010	0.060	0
40 nm 10,000 cm ⁻³	1.649	0.029	4
40 nm 4,000 cm ⁻³	0.678	0.019	14
40 nm 2,000 cm ⁻³	0.333	0.014	17
40 nm 1,000 cm ⁻³	0.173	0.009	13
50 nm 20,000 cm ⁻³	3.221	0.061	3
50 nm 10,000 cm ⁻³	1.607	0.030	8
50 nm 4,000 cm ⁻³	0.624	0.015	6
50 nm 2,000 cm ⁻³	0.310	0.008	22
50 nm 1,000 cm ⁻³	0.173	0.007	12

Supplementary FCE data

These data were obtained at the time of the comparison to provide information about internal losses of the electrometers at low particle sizes. Participants should make corrections for flow rate, and their electrometer calibration results at larger particle sizes. Participants may choose to correct for expected particle losses at low sizes within their instruments, and indicate this in the table. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were nominally 2,000 to 3,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Concentration (fC.cm ⁻³ at 25°C and 101.3 kPa)	Low-size loss correction applied ?
7 nm FCE	0.380	No
10 nm FCE	0.353	
23 nm FCE	0.364	

Date results submitted:

Filled proformas are to be sent to paul.quincey@npl.co.uk and volker.ebert@ptb.de by 2 February 2018.

b) CCQM K150/P189 Comparison of particle **number** concentration TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

National Institute of Metrology, China.
Liu Junjie

Model / origin of CPC:

TSI 3775 condensation particle counter

Method of flow control and nominal flow rate:

Using the built-in pump of the instrument to control the flow rate, and the nominal flow rate is 1.5L/min.

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

Yes

Calibration methods and traceability:

CPC calibration is essentially the calibration of counting efficiency, which is the ratio of CPC measurement value to standard value of particle number concentration. In this calibration process, stable and single-charged particles aerosol were firstly produced, and then after through a flow splitter, particles aerosol is equivalently separated into two ways, and pumped into FCE and CPC separately, where FCAE counting efficiency has already been well calibrated.

Components included in the uncertainty calculation:

There are several uncertainty sources: CPC calibration standard uncertainty, CPC flow rate uncertainty, CPC measurement repeatability.

CCQM CPC Comparison Results

Notes:

- 1) The reported concentration is the participant's best estimate of the mean particle number concentration entering the inlet of their instrument during the designated period.
- 2) For each run, the designated period is the full measurement period, approximately 10 minutes in length.
- 3) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (particles cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (cm ⁻³)
40 nm 20,000 cm ⁻³	20037	801
40 nm 10,000 cm ⁻³	10275	442
40 nm 4,000 cm ⁻³	3819	171
40 nm 1,000 cm ⁻³	880	46
40 nm 100 cm ⁻³	117.5	5.4
50 nm 20,000 cm ⁻³	18968	720
50 nm 10,000 cm ⁻³	9869	424
50 nm 4,000 cm ⁻³	3625	181
50 nm 1,000 cm ⁻³	1122	49
50 nm 100 cm ⁻³	93.6	4.4

Supplementary CPC data

These data were obtained at the time of the comparison to provide information about the detection efficiency of the CPCs at low particle sizes. Participants should make corrections for flow rate, and for their plateau-region detection efficiency calibration, but NOT for the expected low-size detection efficiency curve of their CPC. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were in the approximate range 2,000 - 5,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Detected concentration (particles cm ⁻³ at 25°C and 101.3 kPa)
40 nm CPC	2245
30 nm CPC	2694
28 nm CPC	2667
27 nm CPC	2829
26 nm CPC	2560
25 nm CPC	2650
23 nm CPC	2690
20 nm CPC	2404
15 nm CPC	2275
12 nm CPC	2339
10 nm CPC	2108
9 nm CPC	1879
8 nm CPC	2177
7 nm CPC	1795
6 nm CPC	1794
5 nm CPC	1687

Date results submitted:

A.1.8 RESULTS FROM KRISS

a) CCQM K150/P189 Comparison of particle **charge** concentration
TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

KRISS

Jinsang Jung

Model / origin of aerosol electrometer:

GRIMM FCE model: 5.705

Method of flow control and nominal flow rate:Volumetric flow control with a nominal flow rate of 1.0 L min⁻¹.Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations? NOCalibration methods and traceability:

GRIMM FCE: calibrated using a voltage source (Wavetek, model 9100), a 1 TOhm standard resistor (Guilcline, model 9337-1T) traceable to the KRISS primary standard of resistance, and a voltmeter (HP, model 34401A) traceable to the KRISS primary standard of voltage.

Volumetric flow meter (COSMOS, model DF-241BA): The flow meter was traceable to the KRISS primary standard of flow.

The resulting particle charge concentration, C_{FCE} is given by

$$C_{FCE} = \frac{C_{meas}}{\eta_{FCE}} f_q$$

where

$$f_q = \frac{q_{nom}}{q_{cal}}$$

where, q_{nom} is the nominal volumetric flow rate of the FCE (1.0 L min⁻¹). The flow rate of the FCE (q_{cal}) was calibrated against the volumetric flow meter which is traceable to the KRISS primary standard of flow. The calibration of the critical orifice was performed near the standard conditions (23.3 °C, 101.3 kPa). The difference in temperature between the calibration condition (23.3 °C) and standard condition (25 °C) was not corrected but included in the flow rate uncertainty. C_{meas} denotes the measured particle charge concentration by the FCE, and η_{FCE} is the detection efficiency of the FCE.

Components included in the uncertainty calculation:Uncertainty budget of FCE detection efficiency, $u(\eta_{FCE})$

Source of uncertainty	Relative standard uncertainty (%)
Regression fit uncertainty	0.72
Reproducibility	0.61
Repeatability	0.50
Voltage uncertainty	0.065
Resistance uncertainty	0.0001
Relative combined standard uncertainty	1.07

Relative expanded uncertainty ($k=2$)	2.13
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Inlet flow rate uncertainty of FCE including temperature difference during the calibration and comparison, $u(q_{\text{FCE}})$

Parameter	Value
Indicated flow rate (L m^{-1})	1
Measured flow rate (L m^{-1})	1.017
Correction factor	0.9838
Deviation (L m^{-1})	-0.017
Deviation (%)	-1.625
S.D. (L m^{-1})	0.0019
$u(\text{flow repeat})(\text{L m}^{-1})$	0.0027
$u(\text{flow reprod})(\text{L m}^{-1})$	0.0033
$u(\text{flow reprod})$ (%)	0.331
T Cal (K)	296.3
T STD (K)	298
$u(T)$ (%)	0.57
$u(\text{flow})$ (%)	0.66
$U(\text{flow})$ (%) ($k=2$)	1.32

Repeatability of FCE measurement, $u(\text{repeatability})$

Repeatability of FCE measurement	$u(\text{repeatability})$	0.39
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Uncertainty budget of C_{FCE} , $u(C_{\text{FCE}})$

Example: 20K concentration, 40 nm particles

Component	Symbol	Relative uncertainty [%]
FCE detection efficiency	$u(\eta_{\text{FCE}})$	1.07
FCE flow rate uncertainty	$u(q_{\text{FCE}})$	0.66
Repeatability of FCE measurement	$u(\text{repeatability})$	0.39
Relative combined uncertainty	$u(C_{\text{FCE}})$	1.32
Relative expanded uncertainty($k=2$)	$U(C_{\text{FCE}})$	2.63

CCQM FCE Comparison Results

Notes:

- 16) The reported concentration is the participant's best estimate of the mean particle charge concentration entering the inlet of their instrument during the designated period.
- 17) For each run, the designated period is the ten minute period prior to the end of the run. Typically the two minutes of data preceeding this period will be ignored. The only exception to this is the 40 nm 10,000 cm^{-3} run, where the designated period is the seven minute period prior to the end of the run.
- 18) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (fC cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (fC cm ⁻³)	Number of one- second outlier points removed
40 nm 20,000 cm ⁻³	3.161	0.083	NONE
40 nm 10,000 cm ⁻³	1.682	0.043	NONE
40 nm 4,000 cm ⁻³	0.691	0.018	NONE
40 nm 2,000 cm ⁻³	0.339	0.0095	NONE
40 nm 1,000 cm ⁻³	0.176	0.0052	NONE
50 nm 20,000 cm ⁻³	3.309	0.084	NONE
50 nm 10,000 cm ⁻³	1.616	0.041	NONE
50 nm 4,000 cm ⁻³	0.627	0.016	NONE
50 nm 2,000 cm ⁻³	0.309	0.008	NONE
50 nm 1,000 cm ⁻³	0.173	0.0045	NONE

Supplementary FCE data

These data were obtained at the time of the comparison to provide information about internal losses of the electrometers at low particle sizes. Participants should make corrections for flow rate, and their electrometer calibration results at larger particle sizes. Participants may choose to correct for expected particle losses at low sizes within their instruments, and indicate this in the table. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were nominally 2,000 to 3,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Concentration (fC cm ⁻³ at 25°C and 101.3 kPa)	Low-size loss correction applied?
7 nm FCE	0.4525	NO
10 nm FCE	0.3944	NO
23 nm FCE	0.3829	NO

Date results submitted: 2018/02/09

b) CCQM K150/P189 Comparison of particle **number** concentration TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

KRISS

Jinsang Jung

Model / origin of CPC:

GRIMM CPC, model 5.416

Method of flow control and nominal flow rate:

Volumetric flow control with a nominal flow rate of 0.3 L min⁻¹.

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations? NO

Calibration methods and traceability:

CPC: calibrated against the reference FCE (GRIMM FCE, model 5.705). The reference FCE was calibrated using a voltage source (Wavetek, model 9100), a 1 TOhm standard resistor (Guildline, model 9337-1T) traceable to the KRISS primary standard of resistance, and a voltmeter (HP, model 34401A) traceable to the KRISS primary standard of voltage.

Volumetric flow meter (COSMOS, model DF-241BA): The flow meter was traceable to the KRISS primary standard of flow.

The resulting particle number concentration, N_{CPC} is given by

$$N_{CPC} = \frac{N_{meas}}{\eta_{CPC}} f_q$$

where

$$f_q = \frac{q_{nom}}{q_{cal}}$$

where, q_{nom} is the nominal volumetric flow rate of the CPC (0.296 L min⁻¹). The flow rate of the CPC (q_{cal}) was calibrated against the volumetric flow meter which is traceable to the KRISS primary standard of flow. The calibration of the critical orifice was performed near the standard conditions (23.3 °C, 101.3 kPa). The difference in temperature between the calibration condition (23.3 °C) and standard condition (25 °C) was not corrected but included in the flow rate uncertainty. N_{meas} denotes the measured particle number concentration by the CPC, and η_{CPC} is the detection efficiency of the CPC.

Components included in the uncertainty calculation:

Uncertainty budget of CPC detection efficiency, $u(\eta_{CPC})$

Example: 20K concentration, 40 nm particles

Component	Symbol	Value [%]
FCAE detection efficiency	$u(\eta_{FACE})$	1.07
Multiple charge correction	$u(MCC)$	0.3
Splitter bias correction factor	$u(\beta)$	0.0058
FCE flow rate deviation of FCE	$u(q_{FCE})$	0.5
FCE flow rate deviation of CPC	$u_r(q_{CPC})$	0.5

Repeatability	$u(\eta_{\text{CPC}})$	0.461
Relative combined uncertainty	$u(\eta_{\text{CPC}})$	1.40
Relative expanded uncertainty ($k=2$)	$U(\eta_{\text{CPC}})$	2.79

Inlet flow rate uncertainty of CPC including temperature difference during the calibration and comparison, $u(\text{flow})$

Parameter	Value
Indicated flow rate (L m^{-1})	0.296
Measured flow rate (L m^{-1})	0.300
Correction factor	0.9877
Deviation (L m^{-1})	-0.004
Deviation (%)	-1.234
S.D. (L m^{-1})	0.0007
$u(\text{flow repeat})(\text{L m}^{-1})$	0.0005
$u(\text{flow reprod})(\text{L m}^{-1})$	0.0009
$u(\text{flow reprod})$ (%)	0.294
T Calibration (K)	296.3
T STD (K)	298
$u(T)$ (%)	0.57
$u(\text{flow})$ (%)	0.64
$U(\text{flow})$ (%) ($k=2$)	1.29

Repeatability of CPC measurement, $u(\text{repeat}) = 0.3 \%$

Uncertainty budget of N_{CPC} , $u(N_{\text{CPC}})$

Example: 20K concentration, 40 nm particles

Component	Symbol	Relative uncertainty [%]
CPC detection efficiency	$u(\eta_{\text{CPC}})$	1.36
Flow rate deviation of CPC	$u(q_{\text{CPC}})$	0.64
Repeatability of CPC measurement	$u(\text{repeat})$	0.30
Relative combined standard uncertainty	$u(N_{\text{CPC}})$	1.52
Relative expanded uncertainty ($k=2$)	$U(N_{\text{CPC}})$	3.06

CCQM CPC Comparison Results

Notes:

- 16) The reported concentration is the participant's best estimate of the mean particle number concentration entering the inlet of their instrument during the designated period.
- 17) For each run, the designated period is the full measurement period, approximately 10 minutes in length.
- 18) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (particles cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (cm ⁻³)
40 nm 20,000 cm ⁻³	19282.3	590.8
40 nm 10,000 cm ⁻³	9779.9	303.7
40 nm 4,000 cm ⁻³	3705.3	115.9
40 nm 1,000 cm ⁻³	861.3	28.0
40 nm 100 cm ⁻³	114.6	4.0
50 nm 20,000 cm ⁻³	18003.1	546.8
50 nm 10,000 cm ⁻³	9404.7	292.4
50 nm 4,000 cm ⁻³	3531.1	110.0
50 nm 1,000 cm ⁻³	1115.6	36.6
50 nm 100 cm ⁻³	93.7	3.2

Supplementary CPC data

These data were obtained at the time of the comparison to provide information about the detection efficiency of the CPCs at low particle sizes. Participants should make corrections for flow rate, and for their plateau-region detection efficiency calibration, but NOT for the expected low-size detection efficiency curve of their CPC. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were in the approximate range 2,000 - 5,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Detected concentration (particles cm ⁻³ at 25°C and 101.3 kPa)
40 nm CPC	2165.1
30 nm CPC	2593.9
28 nm CPC	2569.0
27 nm CPC	2722.0
26 nm CPC	2466.5
25 nm CPC	2548.9
23 nm CPC	2587.6
20 nm CPC	2321.4
15 nm CPC	2209.6
12 nm CPC	2275.6
10 nm CPC	2049.3
9 nm CPC	1808.2
8 nm CPC	2075.3
7 nm CPC	1673.8
6 nm CPC	1631.3
5 nm CPC	1443.1

Date results submitted: 2018/02/09

A.1.9 RESULTS FROM BAM

a) CCQM K150/P189 Comparison of particle **charge** concentration
TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved:

BAM Federal Institute for Materials Research and Testing, FG 4.2 – Materials and Air Pollutants
Richard-Willstätter-Strasse 11, D-12489 Berlin, Germany

Dr. Stefan Seeger (stefan.seeger@bam.de)
Dipl. Meteorol. Fabian Rasch (fabian.rasch@bam.de)

Model / origin of aerosol electrometer:

Faraday cup based on design from Dr. Yli-Ojanperä, Tampere University of Technology, Finland.
Amperemeter: Keithley 6517B Multimeter. Preamplifier: FEMTO DDPCA-300.

Method of flow control and nominal flow rate:

Active flow control by thermal flowmeter and valve. Nominal flow rate 1 l/min @ 0 deg C and 101,25 hPa

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ?

Yes, the flow rate was corrected according to sample line pressure and temperature.

Calibration methods and traceability:

Factory calibrations of all FCAE components by respective component manufacturers (Keithley, Bronkhorst, FEMTO). Diffusion losses of FCAE were not determined.

Components included in the uncertainty calculation:

Zero level arithmetic means and zero level standard deviations of particle charge concentrations were determined during the runs at least one minute before and after a particle charge concentration level was set by the operator. In each run particle charge concentration arithmetic means and standard deviations were calculated from data recorded over the full length.

Particle charge concentration arithmetic means were corrected for the respective means of zero levels. Standard deviations of zero and concentration levels were used to calculate absolute measurement uncertainties of the charge concentration measurements based on error propagation. Uncertainty of the FCAE sample flow rate was considered negligible for the uncertainty estimation because its relative uncertainty during the measurements was < 0.2 %.

CCQM FCE Comparison Results

Notes:

- 1) The reported concentration is the participant's best estimate of the mean particle charge concentration entering the inlet of their instrument during the designated period.
- 2) For each run, the designated period is the ten minute period prior to the end of the run. Typically the two minutes of data preceding this period will be ignored. The only exception to this is the 40 nm 10,000 cm⁻³ run, where the designated period is the seven minute period prior to the end of the run.
- 3) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (fC·cm ⁻³)	Number of one- second outlier points removed
40 nm 20,000 cm ⁻³	2.798	0.070	0
40 nm 10,000 cm ⁻³	1.496	0.022	0
40 nm 4,000 cm ⁻³	0.612	0.018	0
40 nm 2,000 cm ⁻³	0.289	0.022	0
40 nm 1,000 cm ⁻³	0.147	0.020	0
50 nm 20,000 cm ⁻³	2.932	0.037	0
50 nm 10,000 cm ⁻³	1.436	0.025	0
50 nm 4,000 cm ⁻³	0.566	0.017	0
50 nm 2,000 cm ⁻³	0.276	0.030	0
50 nm 1,000 cm ⁻³	0.157	0.016	0

Supplementary FCE data

These data were obtained at the time of the comparison to provide information about internal losses of the electrometers at low particle sizes. Participants should make corrections for flow rate, and their electrometer calibration results at larger particle sizes. Participants may choose to correct for expected particle losses at low sizes within their instruments, and indicate this in the table. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were nominally 2,000 to 3,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Low-size loss correction applied ?
7 nm FCE	0.367	no
10 nm FCE	0.332	no
23 nm FCE	0.328	no

Date results submitted:

Filled proformas are to be sent to paul.quincey@npl.co.uk and volker.ebert@ptb.de by 2 February 2018.

A.1.10 RESULTS FROM TROPOS

a) CCQM K150/P189 Comparison of particle **charge** concentration
TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved: TROPOS, Dr. Thomas TuchModel / origin of aerosol electrometer: TSI 3068 B S/N 70838596Method of flow control and nominal flow rate: Volumetric Flow Controller (internal)Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ? yesCalibration methods and traceability: PTB fA source, PTB flow standardComponents included in the uncertainty calculation:**Uncertainty budget EM TSI 3068 B, S/N 71133020, current measurement, k=2:**

$$I_{\text{display}} = \prod_i Q_i$$

$$I_{\text{display}} = I_{\text{display}} * Q_{\text{calibration}} * Q_{\text{offset}} * Q_{\text{other}}$$

 $Q_{\text{calibration}}$ (short term stability, non linearity, noise, display resolution, offset during calibration)

 Q_{offset} (Offset during measurement)

 Q_{other} (long term stability, temperature, RH), not used, not sufficient data

$$Q_{\text{offset}} = 1 - I_{\text{offset}} / I_{\text{display}}$$

$$u(I_{\text{offset}}) = 0,5 * 0,001 \text{ pA} * 2 / \sqrt{3}$$

$$u(Q_{\text{offset}}) = u(I_{\text{offset}}) / I_{\text{display}}$$

from the manual: accuracy $\pm 2\%$ or $\pm 5 \text{ pA}$ whichever is bigger.

$$u(Q_{\text{other}}) = 2 * \text{Max}(0,02; 0,005 \text{ pA} / I_{\text{display}}) / \sqrt{3}$$

$$Q_{\text{Sother}} = 1$$

$$Q_{\text{calibration}} = y_1 + y_2 (I'_{\text{display}} - I_0)$$

 y_1 : intercept

 y_2 : slope

 I'_{Anzeige} : offset corrected display

 I_0 : center of calibration ($\rightarrow r_{y_1, y_2} = 0$)

$$I'_{\text{display}} = I_{\text{display}} * Q_{\text{offset}} = I_{\text{display}} - I_{\text{offset}}$$

$$Q_{\text{calibration}} = y_1 + y_2 (I_{\text{display}} - I_{\text{offset}} - I_0)$$

CCQM FCE Comparison Results

Notes:

- 1) The reported concentration is the participant's best estimate of the mean particle charge concentration entering the inlet of their instrument during the designated period.
- 2) For each run, the designated period is the ten minute period prior to the end of the run. Typically the two minutes of data preceding this period will be ignored. The only exception to this is the 40 nm 10,000 cm⁻³ run, where the designated period is the seven minute period prior to the end of the run.
- 3) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (fC.cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (fC.cm ⁻³)	Number of one- second outlier points removed
40 nm 20,000 cm ⁻³	2.9428227	0.04199916	0
40 nm 10,000 cm ⁻³	1.5649383	0.04199916	3
40 nm 4,000 cm ⁻³	0.6413992	0.04199916	4
40 nm 2,000 cm ⁻³	0.3205019	0.04199916	0
40 nm 1,000 cm ⁻³	0.16853	0.04199916	8
50 nm 20,000 cm ⁻³	3.1017786	0.04199916	0
50 nm 10,000 cm ⁻³	1.5118364	0.04199916	8
50 nm 4,000 cm ⁻³	0.5953692	0.04199916	6
50 nm 2,000 cm ⁻³	0.295814	0.04199916	9
50 nm 1,000 cm ⁻³	0.1677782	0.04199916	8

Supplementary FCE data

These data were obtained at the time of the comparison to provide information about internal losses of the electrometers at low particle sizes. Participants should make corrections for flow rate, and their electrometer calibration results at larger particle sizes. Participants may choose to correct for expected particle losses at low sizes within their instruments, and indicate this in the table. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were nominally 2,000 to 3,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Concentration (fC.cm ⁻³ at 25°C and 101.3 kPa)	Low-size loss correction applied ?
7 nm FCE	0.4190641	No
10 nm FCE	0.378263	No
23 nm FCE	0.365616	No

Date results submitted: 19.2.2018

b) CCQM K150/P189 Comparison of particle **number** concentration TROPOS; 13-17 November 2017

Results Proforma

Participant laboratory and people involved: TROPOS Thomas Tuch

Model / origin of CPC: TSI 3772 S/N 71011008

Method of flow control and nominal flow rate: Critical orifice, 1 l/min

Were the sample temperature and pressure data provided by TROPOS used in the calculation of the reported concentrations ? yes

Calibration methods and traceability:

CPC counting efficiency calibrated at concentrations $> 1000 \text{ cm}^{-3}$ with aerosol electrometer and flow meter. Traceability to SI units is through the ampere and mass flow rates.

CPC linearity calibrated at high and low concentrations with dilution proportionality test, and validated at high concentration against aerosol electrometer linearity test.

Components included in the uncertainty calculation:

Two components are included in the uncertainty calculation of concentration measurements with the CPC. The type B uncertainties in CPC counting efficiency are taken from repeated calibrations of this reference CPC over a period of one year. CPC inlet flow rate are taken from the CPC and flow meter calibration certificates.

CCQM CPC Comparison Results

- 1) The reported concentration is the participant's best estimate of the mean particle number concentration entering the inlet of their instrument during the designated period.
- 2) For each run, the designated period is the full measurement period, approximately 10 minutes in length.
- 3) The measurement uncertainty is the participant's estimate of uncertainty relating to their mean concentration estimate. Any variation of the short-term-average concentration during the designated period does not contribute to this uncertainty.

Run designation (concentrations are the nominal particle number concentrations)	Concentration (particles cm^{-3} at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (cm^{-3})
40 nm 20,000 cm^{-3}	18071.10	426.48
40 nm 10,000 cm^{-3}	9400.97	221.86
40 nm 4,000 cm^{-3}	3584.35	84.59
40 nm 1,000 cm^{-3}	840.41	19.83
40 nm 100 cm^{-3}	112.10	2.65
50 nm 20,000 cm^{-3}	17135.42	404.40
50 nm 10,000 cm^{-3}	9046.39	213.49
50 nm 4,000 cm^{-3}	3421.20	80.74
50 nm 1,000 cm^{-3}	1085.57	25.62
50 nm 100 cm^{-3}	94.76	2.24

Supplementary CPC data

These data were obtained at the time of the comparison to provide information about the detection efficiency of the CPCs at low particle sizes. Participants should make corrections for flow rate, and for their plateau-region detection efficiency calibration, but NOT for the expected low-size detection efficiency curve of their CPC. The results will be presented in the CCQM report, but will not form part of the evaluation of participants' CMCs.

Particle number concentrations were in the approximate range 2,000 - 5,000 cm⁻³. Uncertainty estimates are not needed.

Run designation	Detected concentration (particles cm ⁻³ at 25°C and 101.3 kPa)
40 nm CPC	2089.5
30 nm CPC	2522.7
28 nm CPC	2496.5
27 nm CPC	2646.1
26 nm CPC	2401.1
25 nm CPC	2482.7
23 nm CPC	2521.7
20 nm CPC	2258.0
15 nm CPC	2102.2
12 nm CPC	2058.8
10 nm CPC	1723.9
9 nm CPC	1429.2
8 nm CPC	1476.9
7 nm CPC	1016.9
6 nm CPC	753.1
5 nm CPC	242.9

Date results submitted: 19.2.2018

Additional information: FCAE concentrations – may be used to create counting efficiency curves.

Run designation	Detected concentration FCAE (particles cm ⁻³ at 25°C and 101.3 kPa)
40 nm CPC	2137.7
30 nm CPC	2597.6
28 nm CPC	2570.2
27 nm CPC	2726.5
26 nm CPC	2475.4
25 nm CPC	2571.4
23 nm CPC	2627.4
20 nm CPC	2382.0
15 nm CPC	2326.4
12 nm CPC	2509.9
10 nm CPC	2356.7
9 nm CPC	2167.6
8 nm CPC	2589.4
7 nm CPC	2246.4
6 nm CPC	2399.9
5 nm CPC	2507.6

ANNEX 2 POST-SUBMISSION INFORMATION FROM LNE



CCQM K150/P189

Comparison for particle number and charge concentration

Revised uncertainties

After further examination of the results submitted on 9th february 2018, it was noted that submitted uncertainties needed to be revised as follows :

- Revision of uncertainty calculation of concentration measurements with the CPC :

Two components are included in the uncertainty calculation of concentration measurements with the CPC (uncertainty in CPC count and uncertainty in flow measurement). The uncertainty in CPC count u_{count} was mistakenly calculated as the standard deviation of the measured values for each measurement $s(count_k)$. It was thus corrected by calculating the standard deviation of the mean for each measurement $s(\overline{count})$ (standard deviation of the measured values divided by the square root of the number of measured values) instead :

$$u_{count} = s(\overline{count}) = \sqrt{\frac{s^2(count_k)}{n}}$$

where

$$s(count_k) = \sqrt{\frac{\sum_{j=1}^n (count_j - \overline{count})^2}{n-1}}$$

and

$$\overline{count} = \frac{1}{n} \sum_{k=1}^n count_k$$

Results for CPC concentration measurements with revised uncertainties are below :

Run designation (concentrations are the nominal particle number concentrations)	Concentration (particles cm ⁻³ at 25°C and 101.3 kPa)	Revised measurement uncertainty (95% confidence, k=2) (cm ⁻³)
40 nm 20,000 cm ⁻³	18245	929
40 nm 10,000 cm ⁻³	9350	476
40 nm 4,000 cm ⁻³	3526	180
40 nm 1,000 cm ⁻³	815	42
40 nm 100 cm ⁻³	108	6
50 nm 20,000 cm ⁻³	16744	853
50 nm 10,000 cm ⁻³	8747	446
50 nm 4,000 cm ⁻³	3262	166
50 nm 1,000 cm ⁻³	1028	52
50 nm 100 cm ⁻³	86	4

- Revision of uncertainty calculation of concentration measurements with the FCE :

Two components were included in the uncertainty calculation of concentration measurements with the FCE (uncertainty in FCE measurements from calibration certificate and uncertainty in flow measurement).

As the uncertainty in FCE measurements from calibration certificate was relatively high in comparison with the measured values, results were reprocessed considering a correction from reference values of the calibration certificate. As a result, uncertainty in FCE measurements u_{FCE} was corrected by calculating the maximum deviation between the reference values and the measured values divided by $2\sqrt{3}$, and by calculating the standard deviation of the mean for each measurement (standard deviation of the measured values divided by the square root of the number of measured values).

Results for CPC concentration measurements with revised uncertainties are below :

Run designation (concentrations are the nominal particle number concentrations)	Concentration (fC·cm ⁻³ at 25°C and 101.3 kPa)	Measurement uncertainty (95% confidence) (fC·cm ⁻³)
40 nm 20,000 cm ⁻³	-2.81	0.13
40 nm 10,000 cm ⁻³	-1.50	0.07
40 nm 4,000 cm ⁻³	-0.61	0.03
40 nm 2,000 cm ⁻³	-0.32	0.01
40 nm 1,000 cm ⁻³	-0.16	0.01
50 nm 20,000 cm ⁻³	-3.18	0.15
50 nm 10,000 cm ⁻³	-1.56	0.07
50 nm 4,000 cm ⁻³	-0.61	0.03
50 nm 2,000 cm ⁻³	-0.30	0.01
50 nm 1,000 cm ⁻³	-0.17	0.01

ANNEX 3 COMPARISON PROTOCOL**CCQM K150/P189****Comparison for particle number and charge concentration**

Coordinating Laboratories: NPL, UK and PTB, Germany

Host: TROPOS, Leipzig, Germany

Protocol 2017-11-17

(with clarification of reporting, as discussed during the comparison)

Background

Aerosol particle number concentration has recently featured in vehicle emission legislation and is becoming increasingly important in other areas such as ambient air and workplace monitoring. Condensation Particle Counters (CPCs) are the usual type of instrument for measuring particle number concentration in the size range from a few nanometres to a few micrometres. These instruments have a large size range over which they have constant detection efficiency for nanoparticles of all compositions (the “plateau” region), and an instrument and particle-material dependent drop in detection efficiency at low sizes.

Calibration of CPCs can be done via comparison with a reference CPC or a reference aerosol electrometer. Procedures for doing this have been set out in ISO 27891. If a source of singly-charged particles is used, number concentration (typically in units of cm^{-3}) is directly comparable to charge concentration (e.g. in $\text{C}\cdot\text{cm}^{-3}$). The standard refers to the role of NMIs in providing certification for reference aerosol electrometers and reference CPCs.

Although not strictly a chemical measurement, the comparison belongs in the GAWG (gas analysis working group) because of the similarity to gas concentration measurements, following the precedent of earlier EURAMET TC-METCHEM projects 893 (workshops to establish “Metrology infrastructure for airborne nanoparticles”), 1027 (“Comparison of combustion particle number concentration and size”), 1244 (“Comparison of aerosol electrometers”), and 1282 (“Comparison of Condensation Particle Counters”).

To date NPL, PTB and METAS have CMCs in the key comparisons database (KCDB) on particle charge and number concentration. Their claims are based on the evidence from the EURAMET particle comparisons.

On April 2015 GAWG organised a particle workshop at the BIPM to initiate the process to establish metrological traceability for aerosol measurements. At the workshop it was agreed to start to organise particle comparisons on a global scale. The GAWG subsequently developed a strategy for particle comparison and agreed to start with the most mature particle charge and number metrics.

The aim of the proposed comparison is to compare the accuracy of different laboratories’ measurements of particle charge concentration by aerosol electrometers and particle number concentration in the CPC plateau region.

Aerosol metrics

a) Particle charge concentration of silver aerosol particles in $\text{C}\cdot\text{cm}^{-3}$

b) Particle number concentration of silver aerosol particles in cm^{-3}

Comparison protocol

As transportable measurement standards for aerosol particles are not easily available, participants will bring their instruments and any associated equipment to a single location. The aerosol electrometers (a) and CPCs (b) will be connected to common aerosol sources. The comparison will be conducted at the unique facility of the World Calibration Center for Aerosol Physics (WCCAP) at the Leibniz-Institute for Tropospheric Research (TROPOS) from November 13 to 17, 2017.

Participants will be responsible for the transport of their particle measuring instruments to and from the measuring site, and for their setting up and operation. This includes the independent calibration of their particle measuring instruments and any flow meters used, and the collection of data. The CPC condensation fluid will be provided on site if necessary.

The electricity supply at TROPOS is 230V 50Hz with CEE 7/4 socket (plug type F). Participants must provide their own electrical adaptors if necessary.

Participants will sample the test aerosol (particles and nitrogen) at flow rates that have been arranged individually (in the range 0.3 to 1.5 litre/min (at 25°C and 101.3 kPa)), with diffusion losses compensated by corresponding lengths of sample tubing. Participants are expected to take readings every second. Participants' particle measuring instruments must connect to 1/4-inch TSI conductive tubing. The outlet connection of each CPC (i.e. connection to the vacuum line, if needed) should be either a 1/4" Swagelok tube connector or a 1/4" tube. Participants must provide their own adaptors if needed.

Particle counters with a digital pulse output can be logged via the TROPOS software.

Particles will be silver in the size range 10 nm to 100 nm in diameter. Where possible, there will be 5 target concentrations between 0.15 to 3 $\text{fC}\cdot\text{cm}^{-3}$ or 100 and 20,000 particles cm^{-3} , respectively.

The measurement period for each run will last for 10 minutes, with a "clean air" interval between runs lasting 5 minutes.

Particle charge and number concentrations are to be reported at standard conditions (25°C and 101.3 kPa). Data on the sample temperature and pressure will be supplied.

Reporting of the results

The final results are to be reported, with volume corrected to standard conditions, on the pro-forma sheets attached. It is expected that these will be submitted by participants after they have returned to their laboratories to allow subsequent checks on the equipment.

Participating laboratories should specify the method and calibration procedure used for the comparison in detail. They should also state the route through which the calibration procedure provides traceability to the SI.

The expanded uncertainty for each measurement should also be calculated. Information should be provided about how the uncertainty budget was calculated.

NPL and PTB together will be responsible for collecting and reporting measurement results.

Reference values

The reference values will be calculated as the mean of all participants' results, after the removal of outliers.

How far the light shines

The comparison will be considered to cover the range 0.15 to 3 fC·cm⁻³ for charge concentration and 100 to 20,000 particles cm⁻³ for number concentration.

Participants

NPL, UK; PTB, Germany; METAS, Switzerland; LNE, France; VNIIFTRI, Russia (CPC only); NMIJ, Japan; NIM, China; KRISS, S Korea; BAM, Germany (FCE only) and TROPOS.

Tentative Schedule

April 2017:	Approval of comparison
July 2017:	Registration of participants
October 2017:	Issue of Final Protocol
13-17 Nov 2017:	Comparison
2 Feb 2018:	Due date of results
August 2018:	Draft A report available
Feb 2019:	Draft B report available

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ANNEX 4 ADDITIONAL INFORMATION PROVIDED BY PTB FOR THE AEROSOL ELECTROMETER INTERCOMPARISON IN CCQM-P189

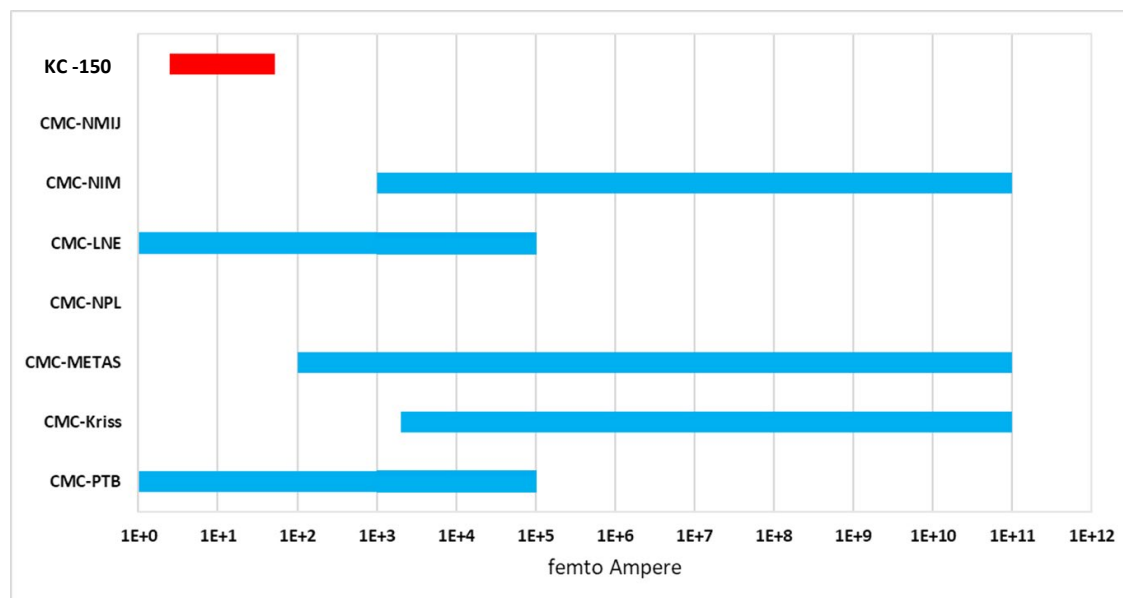


Figure A4.1: Electricity and Magnetism CMCs for current (in fA) for each NMI (blue bars) and the fA range of CCQM-K150 (red, marked as 'KC-150'). CMC data obtained from the BIPM KCDB.

Additional plots for the aerosol electrometer comparison with the uncertainty in the consensus value calculated using $2u(\bar{x})$ and an additional component of 1 % shown in Figures A4.1 to A4.11. This makes full allowance for the statistical uncertainty of the mean value (as in CCQM Guidance Note 13-22 [7]), with a realistic additional uncertainty for variation between sampling ports.

Note that the data in this Annex 4 have been calculated using a different method to that used in Section 3 to calculate the reference values and DoEs and their uncertainties. For example, it does not account for covariance arising due to the dependence between the laboratory result and reference values.

The data in this Annex 4 cannot therefore be used for claiming CMCs – the data in Section 3 must instead be used for that purpose.

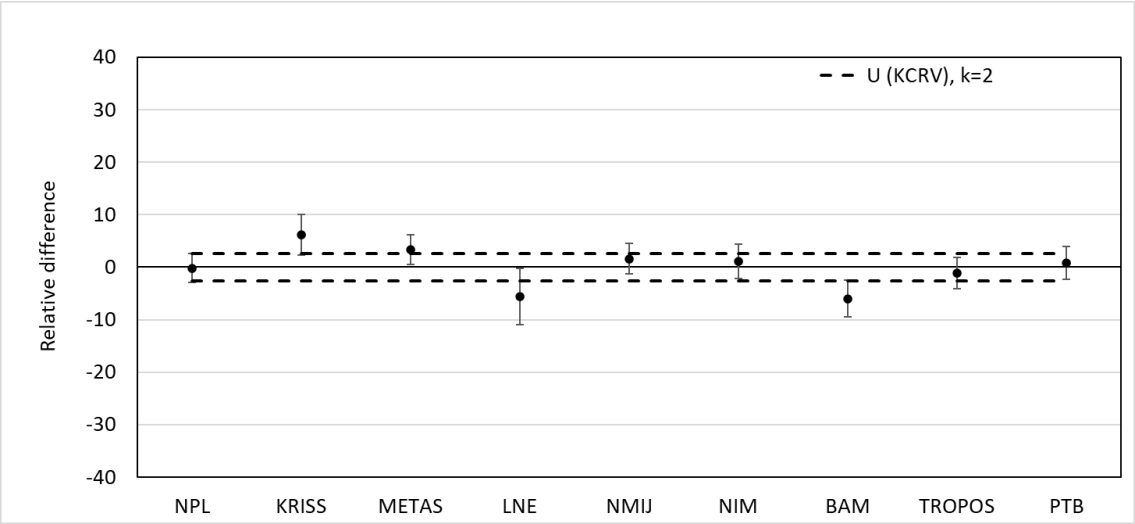


Figure A4.2: Relative difference to the consensus value and related uncertainty for each participant for the aerosol electrometers in CCQM-P189 for 40 nm aerosol particles and 3.2 fC cm⁻³ nominal charge concentration (equivalent to a nominal particle number concentration of 20 000 cm⁻³).

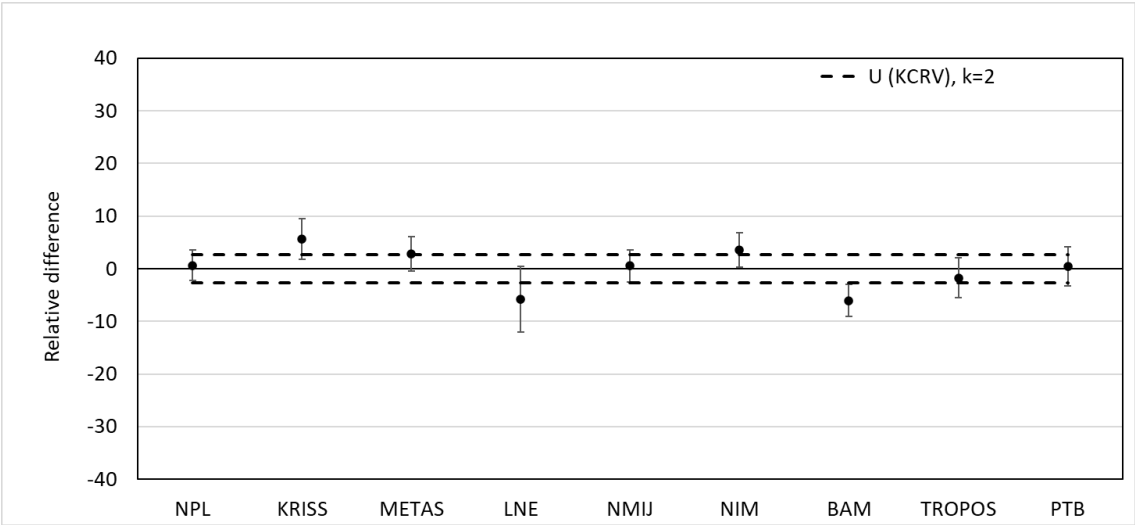


Figure A4.3: Relative difference to the consensus value and related uncertainty for each participant for the aerosol electrometers in CCQM-P189 for 40 nm aerosol particles and 1.6 fC cm⁻³ nominal charge concentration (equivalent to a nominal particle number concentration of 10 000 cm⁻³).

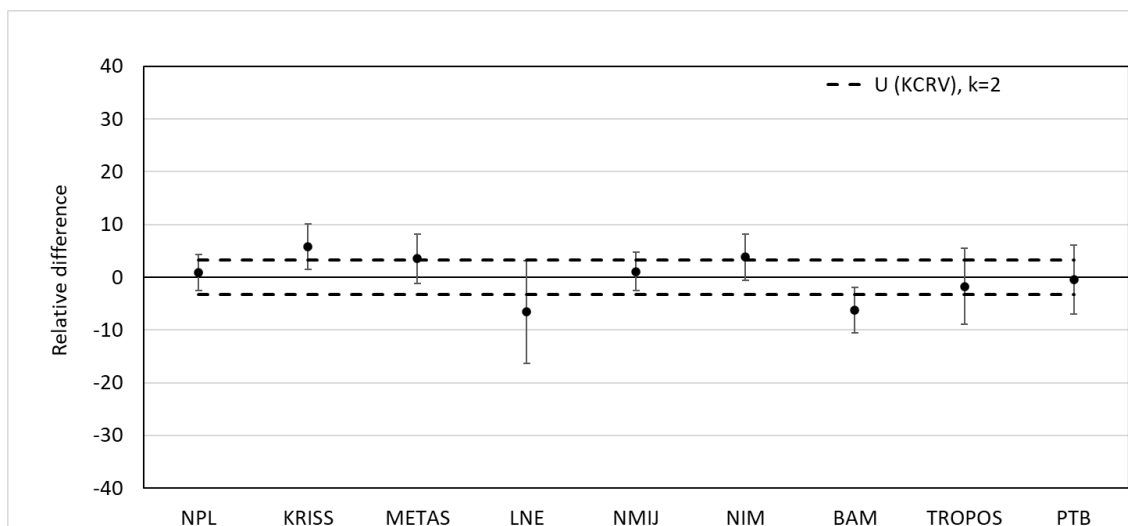


Figure A4.4: Relative difference to the consensus value and related uncertainty for each participant for the aerosol electrometers in CCQM-P189 for 40 nm aerosol particles and 0.64 fC cm⁻³ nominal charge concentration (equivalent to a nominal particle number concentration of 4 000 cm⁻³).

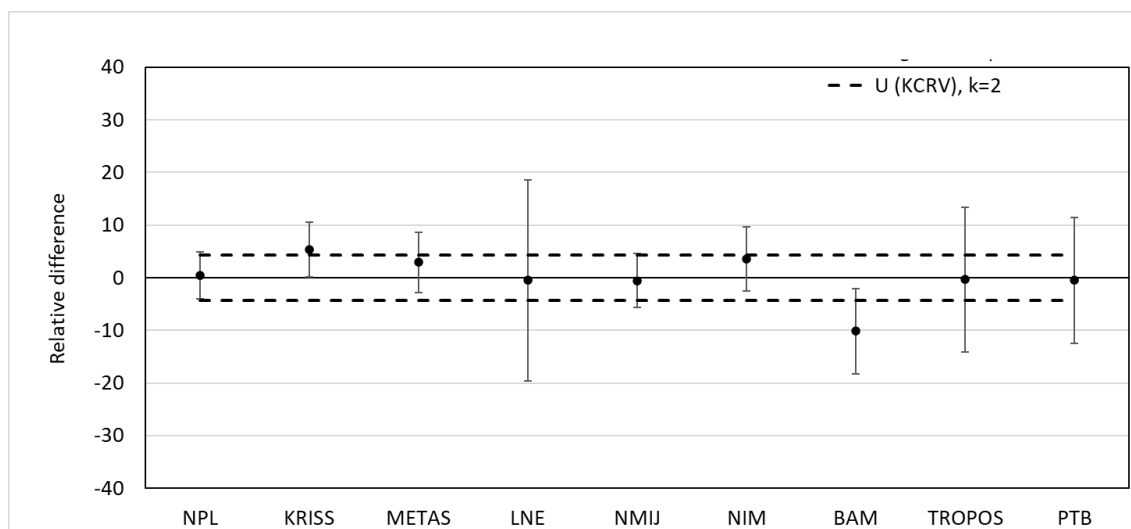


Figure A4.5: Relative difference to the consensus value and related uncertainty for each participant for the aerosol electrometers in CCQM-P189 for 40 nm aerosol particles and 0.32 fC cm⁻³ nominal charge concentration (equivalent to a nominal particle number concentration of 2 000 cm⁻³).

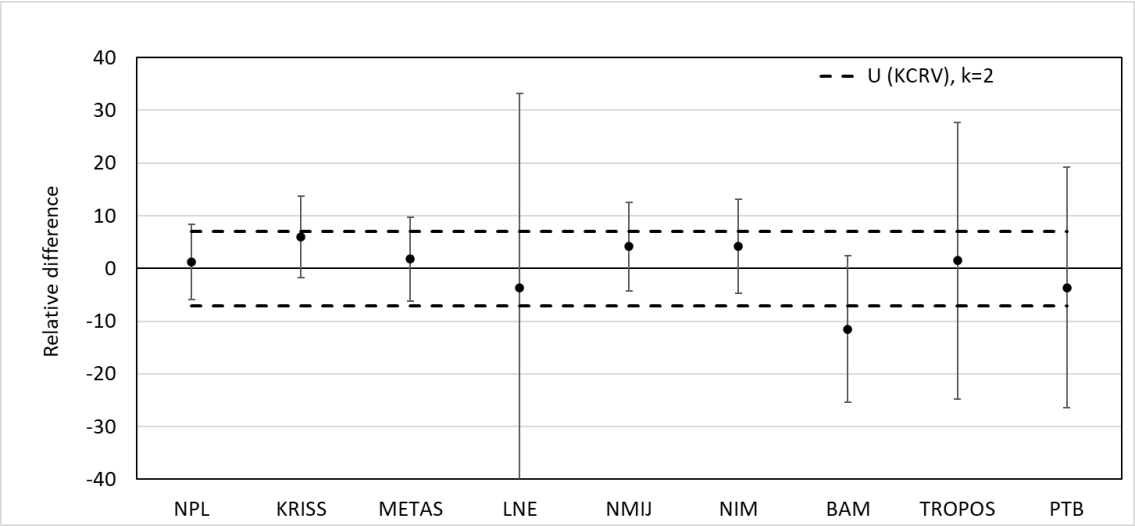


Figure A4.6: Relative difference to the consensus value and related uncertainty for each participant for the aerosol electrometers in CCQM-P189 for 40 nm aerosol particles and 0.16 fC cm⁻³ nominal charge concentration (equivalent to a nominal particle number concentration of 1 000 cm⁻³).

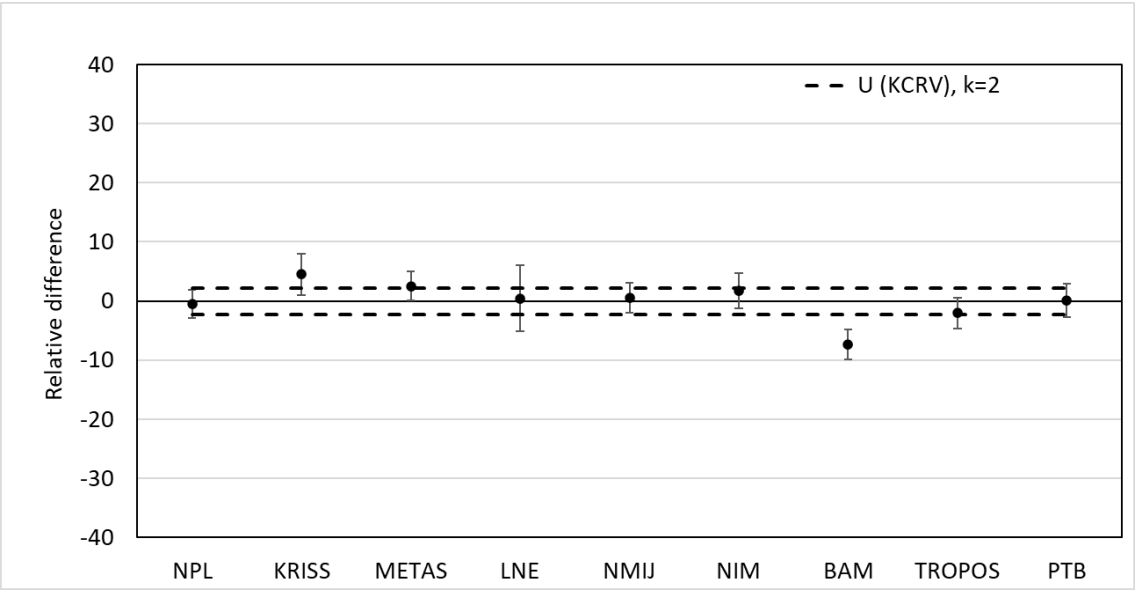


Figure A4.7: Relative difference to the consensus value and related uncertainty for each participant for the aerosol electrometers in CCQM-P189 for 50 nm aerosol particles and 3.2 fC cm⁻³ nominal charge concentration (equivalent to a nominal particle number concentration of 20 000 cm⁻³).

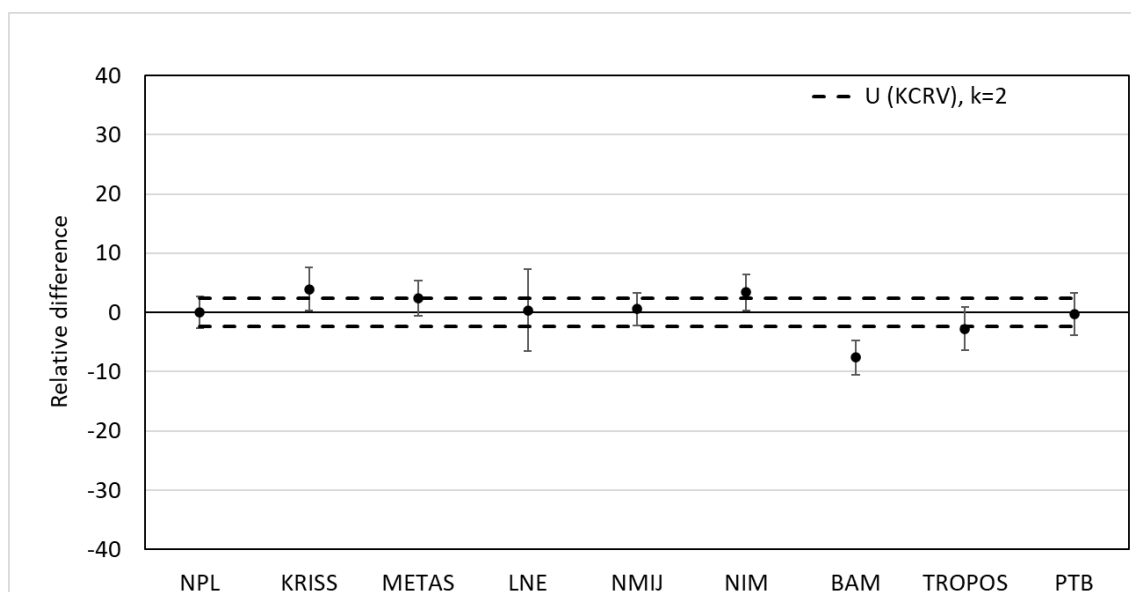


Figure A4.8: Relative difference to the consensus value and related uncertainty for each participant for the aerosol electrometers in CCQM-P189 for 50 nm aerosol particles and 1.6 fC cm⁻³ nominal charge concentration (equivalent to a nominal particle number concentration of 10 000 cm⁻³).

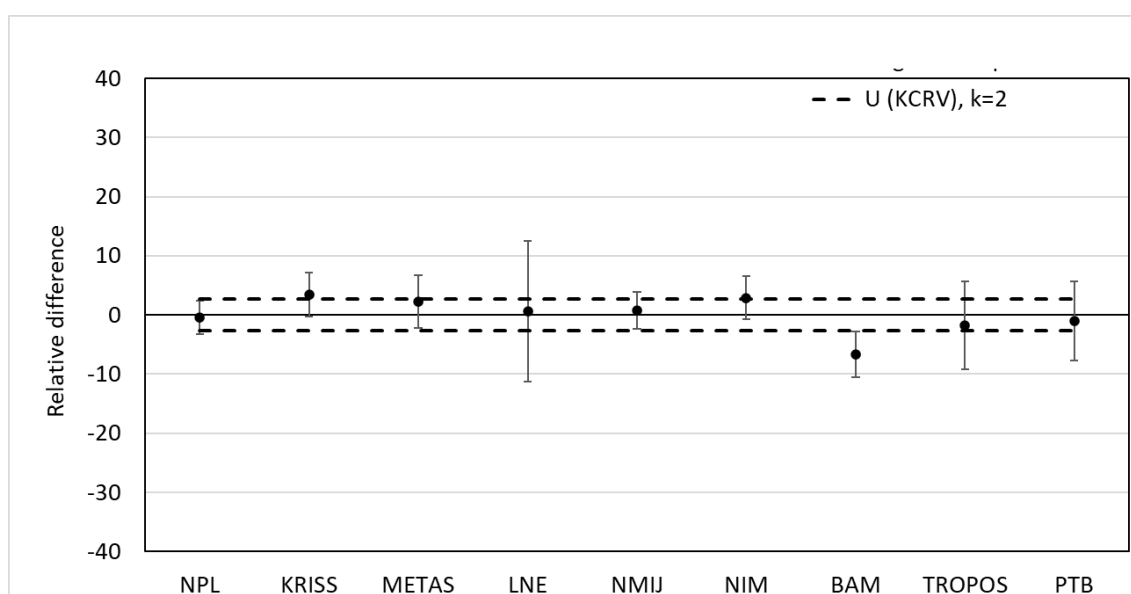


Figure A4.9: Relative difference to the consensus value and related uncertainty for each participant for the aerosol electrometers in CCQM-P189 for 50 nm aerosol particles and 0.64 fC cm⁻³ nominal charge concentration (equivalent to a nominal particle number concentration of 4 000 cm⁻³).

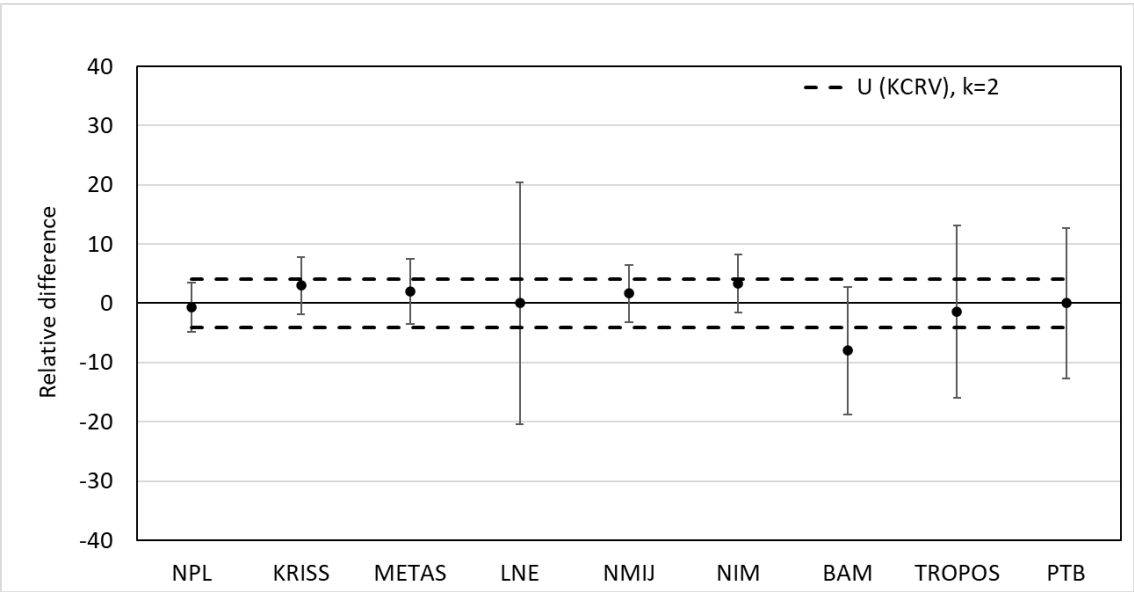


Figure A4.10: Relative difference to the consensus value and related uncertainty for each participant for the aerosol electrometers in CCQM-P189 for 50 nm aerosol particles and 0.32 fC cm⁻³ nominal charge concentration (equivalent to a nominal particle number concentration of 2 000 cm⁻³).

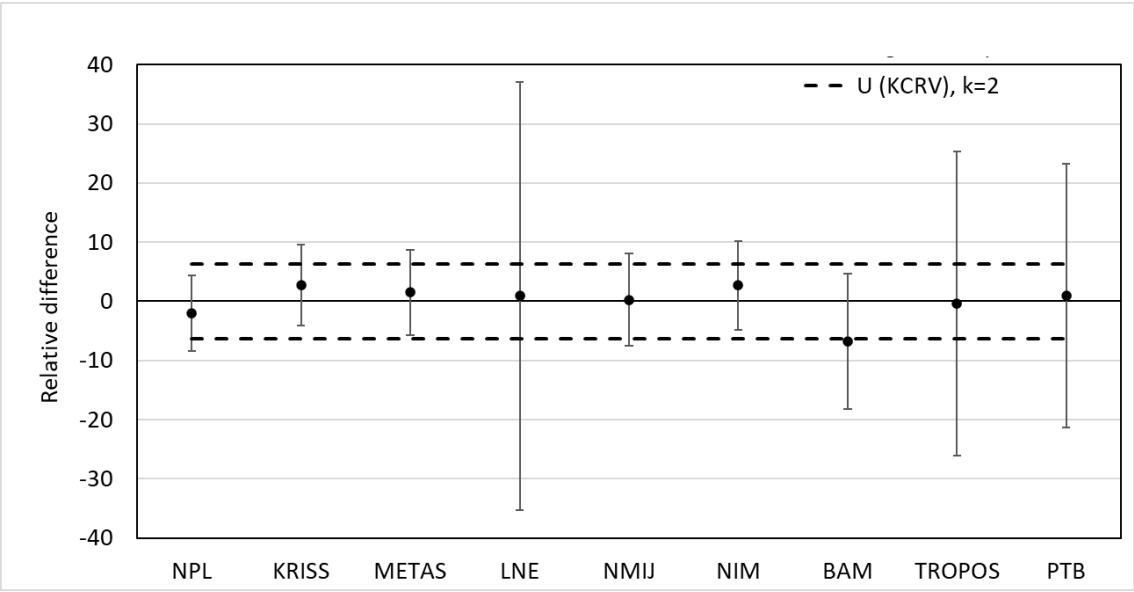


Figure A4.11: Relative difference to the consensus value and related uncertainty for each participant for the aerosol electrometers in CCQM-P189 for 50 nm aerosol particles and 0.16 fC cm⁻³ nominal charge concentration (equivalent to a nominal particle number concentration of 1 000 cm⁻³).

REFERENCES

- [1] International Standard ISO 27891:2015, Aerosol particle number concentration — Calibration of condensation particle counters
- [2] EURAMET project 893, Metrology infrastructure for airborne nanoparticles, <https://www.euramet.org/technical-committees/tc-projects/details/project/metrology-infrastructure-for-airborne-nanoparticles/>
- [3] J. Schlatter, EURAMET Project 1027, Comparison of nanoparticle number concentration and size distribution - report of results, V2.0, September 2009.
- [4] P. Quincey *et al*, NPL Report AS 85, EURAMET comparison 1244, Comparison of aerosol electrometers, Issue 2: EURAMET Report, June 2014.
- [5] P. Quincey *et al*, NPL Report 94 EURAMET comparison 1282, Comparison of condensation particle counters, Final Report, November 2014.
- [6] A. Wiedensohler, A. Wiesner, K. Weinhold, W. Birmili, M. Hermann, M. Merkel, T. Müller, S. Pfeifer, A. Schmidt, T. Tuch, F. Velarde, P. Quincey, S. Seeger and A. Nowak, Mobility particle size spectrometers: Calibration procedures and measurement uncertainties, *Aerosol Science and Technology*, 52:2 (2018), 146-164, DOI: 10.1080/02786826.2017.1387229
- [7] CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, version 10, 12 April 2013. <https://www.bipm.org/documents/20126/28430045/working-document-ID-5794/49d366bc-295f-18ca-c4d3-d68aa54077b5>
- [8] M. J. T. Milton and M. G. Cox, Evaluating degrees of equivalence using 'exclusive' statistics, *Metrologia* 40 (2003) L1–L2. DOI: 10.1088/0026-1394/40/2/101