First comprehensive inter-comparison of aerosol electrometers for particle sizes up to 200 nm and concentration range 1000 cm^{-3} to 17 000 cm^{-3}

2014 Metrologia 51 293

(http://iopscience.iop.org/0026-1394/51/3/293)

IOP Publishing | Bureau International des Poids et Mesures Metrologia

Metrologia **51** (2014) 293–303 doi:10.1088/0026-1394/51/3/293

First comprehensive inter-comparison of aerosol electrometers for particle sizes up to 200 nm and concentration range 1000 cm^{-3} to 17 000 cm^{-3}

Richard Högström[1,10], **Paul Quincey**[2], **Dimitris Sarantaridis**[2], **Felix Lüönd**[3], **Andreas Nowak**[4], **Francesco Riccobono**[5], **Thomas Tuch**[6], **Hiromu Sakurai**[7], **Miles Owen**[8], **Martti Heinonen**[1], **Jorma Keskinen**[9] and **Jaakko Yli-Ojanperä**[9,10]

[1] Centre for Metrology and Accreditation (MIKES), Tekniikantie 1, FI-02151 Espoo, Finland
[2] National Physical Laboratory (NPL), Hampton Road, Teddington TW11 0LW, UK
[3] Federal Institute of Metrology (METAS), Lindenweg 50, CH-3003 Bern-Wabern, Switzerland
[4] Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, D-38116 Braunschweig, Germany
[5] European Commission, Joint Research Centre (JRC), Via E Fermi 2749, I-21027 Ispra, Italy
[6] Leibniz Institute für Troposphärenforschung (TROPOS), Permoserstraße 15, D-04318 Leipzig, Germany
[7] National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki, Japan
[8] US Army Primary Standards Laboratory (APSL), Bldg 5435 Fowler Rd, Redstone Arsenal, AL 35898, USA
[9] Tampere University of Technology (TUT), Department of Physics, Aerosol Physics Laboratory, Korkeakoulunkatu 3, FI-33101 Tampere, Finland

E-mail: richard.hogstrom@mikes.fi and jaakko.yli-ojanpera@tut.fi

Received 10 December 2013, revised 21 March 2014
Accepted for publication 21 March 2014
Published 28 May 2014

Abstract

The concentration of nanometre-sized particles is frequently measured in terms of particle number concentration using well-established measuring instruments, e.g. condensation particle counters. Traceability for these measurements can be achieved by means of calibrations using an aerosol electrometer (AE) as a reference. A number of national metrology institutes (NMIs) and expert laboratories provide such calibrations, but the metrological basis is at present not well established because the equivalence between the unit realizations has not been investigated by means of an inter-laboratory comparison. This paper presents the results of the first comprehensive comparison of AEs involving NMIs and expert laboratories worldwide. The comparison covered the particle size and charge concentrations ranges 20 nm to 200 nm and 0.16×10^{-15} C cm^{-3} to 2.72×10^{-15} C cm^{-3} (equivalent to 1000 cm^{-3} to 17 000 cm^{-3} singly charged particles), respectively. The obtained results agreed to within about ±3%, which was within stated uncertainties, with only a few exceptions, such as at low concentrations. Additional measurements with sub-20 nm particles show that comparisons in this size range are more challenging and require special considerations, though agreement to within about ±5% was still found with 6 nm particles. This comparison is the first and vital step towards internationally recognized SI traceability in particle number concentration measurements.

Keywords: comparison, particle number concentration, aerosols, electrometer

1. Introduction

Aerosol particles play an important role in many areas of technology and science, e.g. global climate change [1], health effects of particulate emissions [2] and nanotechnology [3]. In addition, aerosol particle measurements are widely applied, e.g. in clean room and process technology, ambient air monitoring, as well as in studying emissions from traffic, industry and power production. In recent years the interest in fine and ultrafine particles has increased, as it has been

---

[10] Authors to whom any correspondence should be addressed.

shown that these nanometre-sized particles have adverse health effects [4] and are responsible for particle formation in the atmosphere [5]. The behaviour and effect of nano-sized particles is better described in terms of number concentration, surface area and size distribution rather than simply mass concentration. Moreover, the sensitivity of particle number and surface area concentration measurements is superior to mass concentration measurements owing to the negligible mass of nano-sized particles. Measurement of particle number is, however, preferred over surface area in the regulatory context as it is more clearly defined than surface area, which is ambiguous for aerosols with complex surface structure.

Instruments measuring particle number concentration, e.g. condensation particle counters (CPCs [6]) and optical particle counters (OPCs [7]), are well developed and have been available on the market for a few decades. Number concentration measurements are also often integral to particle size distribution measurements, such as when using a scanning mobility particle sizer (SMPS [8]) or an electrical low pressure impactor (ELPI [9]). Aerosol particle number concentration measurements are frequently applied in clean room monitoring where the measurements are covered by standards [10]. Moreover, particle number concentration has recently featured in the European vehicle emission legislation [11] and it is becoming increasingly important in other areas such as ambient air monitoring. This has generated a growing demand for traceable particle number concentration measurements. Currently some national metrology institutes (NMIs) and research laboratories have primary particle number concentration standards [12–14]. However, the metrological basis is at present incomplete because the equivalence of the actual unit realizations has not been investigated by means of inter-laboratory comparisons.

Most of the standards in use comprise an aerosol particle generator and an aerosol electrometer (AE). The particle generator provides calibration aerosols with known size and average charge, whereas the AE measures charge concentration of the generated aerosol particles. The traceability for charge concentration is achieved by SI traceable measurement of electric current induced by charged particles inside a Faraday cup (FCUP) and the volume flow of the aerosol. If the charge of the particles from the generator is known, the number concentration (expressed typically in cm^{-3}) is directly derived from the charge concentration (e.g. in $\mathrm{C\,cm}^{-3}$). As a primary standard, however, the performance of an AE contributes to the uncertainty of all particle concentration measurements traceable through it. Therefore, a thorough validation comprising a full uncertainty analysis and inter-laboratory comparisons is essential.

In an AE, random noise in the current measurement becomes the prominent source of uncertainty when measuring low particle concentrations (low currents), thus setting a lower limit for the measurement range. In addition, the average charge of the particles must be known and contributes to the uncertainty of the number concentration. Despite these limitations the AE is considered the prime choice for realizing SI traceability for aerosol particle number concentration. The AE is well suited for calibrating CPCs (an instrument type widely in use for measuring particle number concentration in the size range from a few nanometres to a few micrometres) because its response, after correcting for the diffusion losses at the inlet, remains constant at about unity for particles in the size range from 1 nm to 30 nm where the detection efficiency of CPCs drops steeply. In fact, the draft ISO standard ISO/DIS 27891 [15] describes a calibration procedure for CPCs by reference to an AE, and explicitly describes the role of NMIs in providing certification for AEs.

Up to now, only one inter-laboratory comparison on particle number concentration and particle size distribution measurements has been carried out at the NMI level [16]. It was performed using CPCs and SMPS which have been independently calibrated by the participating laboratories. This comparison was performed using combustion aerosol particles and covered the particle size range from 50 nm to 170 nm. However, the comparison involved secondary standards and it did not cover the sub-50 nm particle size range which is relevant for many particle number measurements using CPCs. Recently, a bilateral comparison between the Finnish and Japanese particle number concentration standards [12, 13] was performed at the National Institute of Advanced Industrial Science and Technology (Japan) by calibrating a single CPC in a wide particle size range from 10 nm to 10 µm using three different calibration standards [17]. This comparison was exceptional because the Finnish standard was transported to Japan where the comparison took place allowing direct comparison without transporting the CPC. This approach, however, is not applicable in general since most particle number concentration standards are not suitable for transportation. To overcome this issue but still keeping the influence of the comparison method at minimum, it was agreed in the European Metrology Research Programme (EMRP) PartEmission project to compare the reference AEs directly to each other because accurate determination of charge concentration is a prerequisite for the realization of a particle number concentration scale. This is the first AE comparison (registered also as the EURAMET project 1244—comparison of AEs [18]) involving multiple NMIs and research laboratories with profound expertise in the field.

In the comparison reported here, participant laboratories brought their reference AEs to the Aerosol Physics Laboratory of Tampere University of Technology (TUT) where measurements were conducted from 18 to 22 March 2013. The aim was to investigate the validity of the unit realization among laboratories and to demonstrate the best measurement capability that can be achieved for particle charge concentration. The instruments were operated by the representatives of the owner laboratories. The calibration aerosol was generated using the single charged aerosol reference (SCAR [19]), which generates singly charged particles with known size. The measurement scheme and experimental setup were carefully designed to minimize the uncertainty due to the comparison method. For example special care was taken to ensure symmetric flow splitting of the aerosol such that the particle concentrations at the AE inlets were equal. The comparison measurements were performed at different calibration particle sizes ranging

Table 1. Participants in the study.

Country	Organization	Status	Role
UK	National Physical Laboratory (NPL)	NMI	Coordinator
Finland	Centre for Metrology and Accreditation (MIKES)[a]	NMI	Participant
Finland	Tampere University of Technology (TUT)[a]	Expert lab	Host
Switzerland	Federal Institute of Metrology (METAS)	NMI	Participant
Germany	Physikalisch-Technische Bundesanstalt (PTB)	NMI	Participant
Japan	National Institute of Advanced Industrial Science and Technology (AIST)	NMI	Participant
EU	Joint Research Centre (JRC)	Expert lab	Participant
Germany	Leibniz Institute für Troposphärenforschung (TROPOS)	Expert lab	Participant
USA	US Army Primary Standards Laboratory (APSL)	Expert lab	Participant

[a] MIKES and TUT participated with one instrument.

from 20 nm to 200 nm in order to reveal any particle size dependent losses in the instruments. Measurements were also performed at different charge concentrations from $0.16 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$ to $2.72 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$ using 100 nm singly charged calibration particles (equal to particle concentrations $1000\,\mathrm{cm^{-3}}$ to $17\,000\,\mathrm{cm^{-3}}$). This range of particle concentrations and sizes covers the scope of the calibration requirements set forth in the European regulation on exhaust emissions tests performed in the type approval of passenger vehicles [20]. Additionally, measurements with sub-20 nm particles were performed for studying the applicability of the experimental setup to comparisons with smaller particles.

2. Reference standards

2.1. AE: operating principle and uncertainty sources

The AE is a flow-through instrument measuring charge concentration of aerosol particles. It comprises a FCUP, an electrometer and flow control and measurement. The FCUP consists of a high efficiency particulate filter enclosed in a conducting cup, which is surrounded by a grounded enclosure acting as a shield. The inner cup is connected to ground potential only via a sensitive current-to-voltage amplifier, an electrometer. As charged particles get collected in the filter, an equal but opposite electric charge (so-called image charge) passes through the electrometer so that the net charge on the FCUP is zero. Therefore, the current measured by the electrometer corresponds to the current carried by the particles to the filter. Flow control and measurement is applied to determine the gas volume rate corresponding to the electric current. The aerosol particle charge concentration C is calculated as

$$C = \frac{I}{\dot{V} \cdot \eta_{\mathrm{FCUP}}}, \tag{1}$$

where I is the electric current, $\dot{V}$ is the volume flow rate and η_{FCUP} is the detection efficiency of the FCUP. The particle number concentration can be further calculated from the charge concentration by dividing the charge concentration with the average number of elementary charges carried by particles and the value of one elementary charge. According to [12], particles generated by the SCAR generator are singly charged with an uncertainty of only 0.16%. Therefore, the number concentration is directly obtained in this comparison by dividing the charge concentration with the elementary charge.

It is fairly straightforward to obtain traceable electric current and aerosol flow measurements through calibrations of the volume flow meters and electrometers. A more challenging task is to determine the FCUP detection efficiency. Particle losses may occur inside the FCUP through diffusion losses in the inlet tube and/or deposition of particles outside the detection enclosure. Also, particles might bypass the filter due to leaks or penetrate the filter without being collected. Furthermore, leakage currents and/or improper grounding of the FCUP are possible sources of errors. The effect of the aforementioned defects on the FCUP detection efficiency is hard or even impossible to reliably and accurately quantify. A comparison study is the only way of revealing such defects. However, with careful design these defects can be minimized. Including AEs of different design and manufacturer in the comparison enables us to identify possible model dependent uncertainties in the results.

2.2. Participating laboratories and associated AEs

A total of nine laboratories participated in the comparison study (see details in table 1). MIKES and TUT participated with the AE of the SCAR instrument, which has been designed, built and tested by TUT [19] and validated in co-operation with MIKES [12]. As a consequence, there were eight AEs to be compared as shown in table 2. All laboratories, except AIST, participated with their primary standards. The AIST standard is considered a secondary standard as it is calibrated against the Japanese primary standard [13]. All of these were commercial AEs or modified commercial AEs, except the MIKES–TUT standard, which comprises a self-made FCUP and commercial current and flow measuring instruments. Furthermore, the AIST secondary standard has traceability to the self-made AE of the Japanese primary standard. Each participant took care of the calibrations of the volume flow meter and electrometer used in their AEs. Final results and associated uncertainties were submitted by the participants individually to the Coordinator some weeks after the comparison, to allow for further checks and recalibration at the participants' laboratories.

Table 2. Properties of participating laboratories AEs.

Participant	AE model	Status of standard	Electric current measurement	Flow measurement/control
NPL	GRIMM 5.705	Primary	Internal	MKS 179/internal
MIKES–TUT	Self-made FCUP	Primary	Keithley 6430	Alicat Scientific MC-2SLPM-D/5 M
METAS	TSI 3068B	Primary	Internal	Vögtlin Red-y GSM-B4PA-BN00/internal
PTB	TSI 3068B	Primary	Internal	Internal
AIST	TSI 3068B	Secondary	Internal	Internal
JRC	Ioner EL-5030	Primary	Internal	Alicat Scientific MC-5SLPM-D/5 M
TROPOS	TSI 3068B	Primary	Internal	Internal
APSL	TSI 3068B	Primary	Internal	Bios Defender 510-M/critical orifice

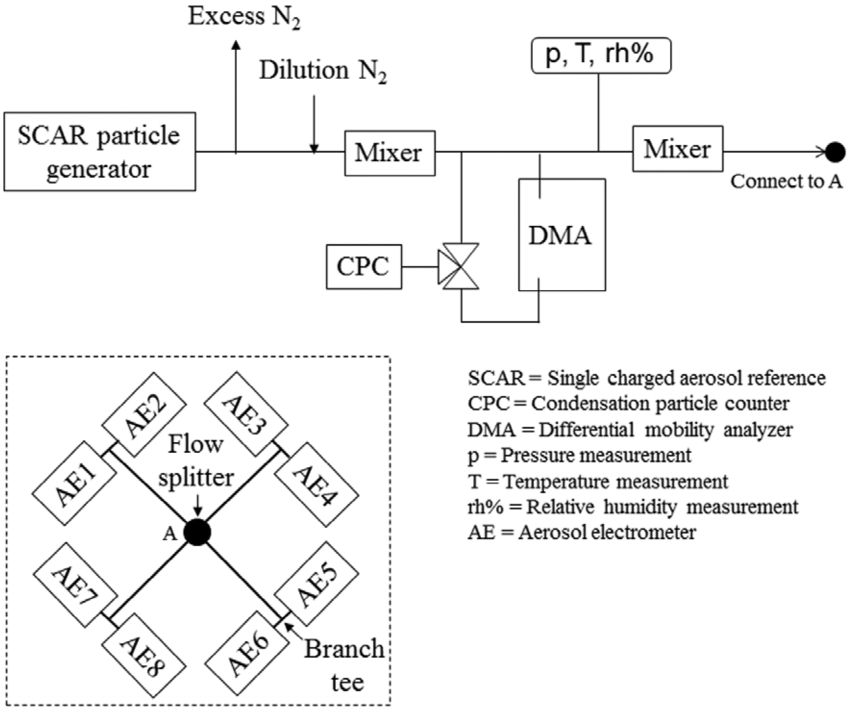

Figure 1. Experimental setup used in the comparison. The arrangement of AEs as seen from above is shown in the figure inside the dashed lines.

3. Comparison procedure

3.1. Experimental setup

The aerosol generator of the SCAR comprises four operational units which are used in numbered order for generating singly charged aerosol particles of known size. (1) Generation of NaCl seed particles by means of tube furnace evaporation/condensation method. (2) Bipolar charging of the 10 nm to 12 nm seed particles. (3) Size classification of the charged seed particles using a differential mobility analyser (DMA). (4) Condensational growth of seed particles to desired size using di-octyl sebacate (DOS) as the working fluid. The condensational growth preserves the particle charge (one elementary charge) acquired as result of steps 2 and 3 [12]. A more detailed description of the operating principle of the SCAR is in [19].

The setup used in the AE comparison is depicted in figure 1. The output flow rate of the aerosol generator is by design constant at 2 l min^{-1}. A dilution flow at the output was used for providing sufficient sample flow for the AEs and to dilute the output particle concentration of the generator. Nitrogen was used as the dilution gas since it corresponds to the carrier gas of the generated aerosol. Nitrogen was also used in calibrations of the flow meters of the participant AEs. This eliminates possible flow measuring inaccuracies caused by mismatch between calibration gas and the actual metered gas.

Special attention was paid to ensuring symmetric flow splitting to the AEs. A static mixer was placed before a flow splitter (TSI flow splitter 3708) in order to guarantee spatially homogeneous particle concentration before the 4-way flow splitter. In addition, a standard stainless steel Swagelok® branch tee was used to further split the sample aerosol to the AEs (figure 1). The sample was drawn through the AEs at a flow rate of 1 l min^{-1} using their own pump or, if not available, using an external pump. All sample lines between the flow splitter and the AEs were of equal length and diameter, thereby the diffusion losses in the sample lines were expected to be similar. In this comparison study, the volume flow rate was set and measured with reference to standard conditions (25 °C and 1013 hPa). This simplifies the measurement setup as no

Table 3. Summary of measurement points in the AE comparison. Measured combinations of charge concentration and particle size are marked with x.

Nominal charge concentration/10^{-15} C cm^{-3}	Equivalent number concentration/cm^{-3}	Nominal particle size/nm 20	30	50	80	100	200
2.72	17 000					x	
1.60	10 000	x	x	x	x	x[a]	x
1.28	8 000					x[a]	
0.64	4 000					x	
0.32	2 000					x[a]	
0.16	1 000					x[a]	
0	0					x	

[a] Measured twice.

additional temperature and pressure sensors for each AE are needed. The validity of the flow splitting was investigated for particle sizes between 20 nm and 200 nm by means of separate measurements, which confirmed that the concentrations at the eight sampling ports agree within experimental uncertainties. However, the uncertainty of these measurements was added to the uncertainty of the comparison results.

The temperature, pressure and humidity of the calibration aerosol were also measured. These measurements were only performed for monitoring purposes, as the flow rate through the AEs was specified as volume flow at standard conditions. In the comparison, the particle size distribution at the generator output was measured before each calibration run using a SMPS consisting of a TSI 3081 DMA, a TSI3080 controller and a TSI 3776 CPC. The SMPS was operated at 1.5 l min^{-1} sample flow and 15 l min^{-1} sheath flow rate. Before each measurement, the nominal calibration concentration was adjusted based on the reading of the TSI 3776 CPC. The uncertainty of the size assigned to the particles, which will be more significant at lower sizes, has not been estimated, as it is not critical to the comparison.

3.2. Comparison measurement scheme

The comparison was performed with different particle sizes ranging from 20 nm to 200 nm in order to reveal any particle size dependent losses within the instruments. These measurements were performed at a nominal charge concentration of 1.6×10^{-15} C cm^{-3} (equal to 10 000 cm^{-3} of singly charged particles) in order to achieve good signal-to-noise ratio and thus minimize the contribution of the uncertainty due to electrometer noise. Moreover, AEs were compared at different particle concentrations ranging from 0.16×10^{-15} C cm^{-3} to 2.72×10^{-15} C cm^{-3} (equal to 1000 cm^{-3} to 17 000 cm^{-3} singly charged particles) using 100 nm calibration particles. This particle size was chosen because particle losses in the tubing are insignificant at this size level. Measurements were repeated for the two lowest concentrations where the AE noise is significant in order to find out the repeatability that can be achieved with the applied measurement cycle and also to compare the repeatability of AEs. The repeatability was also measured at a higher concentration (1.28×10^{-15} C cm^{-3}) where the AE noise is less significant. Moreover, the zero concentration was measured for detecting and compensating drifts in the AEs zero current. A summary of the measurement points included in this comparison is given in table 3.

The measurement cycle at each measurement point consisted of fifteen 1 min long periods of sampling at the nominal concentration (figure 2). Before and after each of these periods, a 1 min period of zero concentration was sampled. This is necessary in order to compensate for the zero current (i.e. zero concentration) offset inherent for AE measurements. An estimate for the concentration during a single measurement cycle was calculated by subtracting the average value of two neighbouring zero concentration periods from the calibration concentration period (see expression inside brackets of equation (2)). After each concentration change, the instruments need some time to stabilize. Therefore, for each 1 min period, the concentration was calculated as an average of the last 30 s of data. As a result, the charge concentration for one measurement point was calculated as an average of 15 zero corrected concentration values as follows:

$$C = \frac{\sum\limits_{k=1}^{15} \left(C_k - \frac{C_{0,k} + C_{0,k+1}}{2} \right)}{15}, \qquad (2)$$

where subscript k denotes the period number and C_0 the zero concentration. The particles were switched on and off by toggling on and off the voltage of the DMA inside of the SCAR. All AEs sampled at a sampling rate of 1 Hz.

3.3. Calculation of results

Each participant calculated their results according to equation (1). The uncertainty of the results was derived as

$$\left(\frac{u(C)}{C}\right)^2 = \left(\frac{u(I)}{I}\right)^2 + \left(-\frac{u(\dot{V})}{\dot{V}}\right)^2 + \left(-\frac{u(\eta_{\text{FCUP}})}{\eta_{\text{FCUP}}}\right)^2 + u^2(\delta C_{\text{s}}), \qquad (3)$$

where $u(\delta C_{\text{s}})$ is the standard uncertainty due to inhomogeneity in flow splitting which was added to the uncertainty reported by each participant. Experimental investigations conducted before the comparison campaign showed that the particle concentration at the sampling ports was equal within the experimental standard uncertainty of 0.5%.

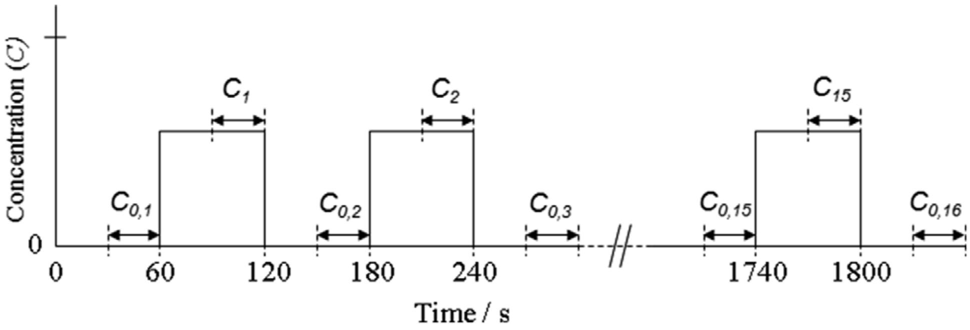

Figure 2. Measurement cycle.

The comparison reference value C_{ref} for each measurement point was determined as the weighted mean of the results reported by the participants ($C_1 \ldots C_N$), in which the weights are given as the inverse square of the associated standard uncertainties [21]:

$$C_{\mathrm{ref}} = \frac{C_1/u^2(C_1) + \cdots + C_N/u^2(C_N)}{1/u^2(C_1) + \cdots + 1/u^2(C_N)}. \tag{4}$$

The standard uncertainty of the reference value is given as

$$\frac{1}{u^2(C_{\mathrm{ref}})} = \frac{1}{u^2(C_1)} + \cdots + \frac{1}{u^2(C_N)}. \tag{5}$$

This method of determining the reference value is, however, only valid if the measurement results are consistent. The measurement results were checked for consistency using the chi-square test as described in [21]. The results were found consistent with 95% confidence for every measurement point when the JRC results were excluded from the reference value calculations.

The results of the comparison are reported in terms of the relative difference d_i between the result C_i of laboratory i and the comparison reference value C_{ref}.

$$d_i = \frac{C_i - C_{\mathrm{ref}}}{C_{\mathrm{ref}}} \times 100\%. \tag{6}$$

The corresponding standard uncertainty was calculated as

$$u(d_i) = \frac{\sqrt{u^2(C_i) - u^2(C_{\mathrm{ref}})}}{C_{\mathrm{ref}}} \times 100\%. \tag{7}$$

The expanded uncertainty of d_i is calculated as

$$U(d_i) = 2u(d_i), \tag{8}$$

which gives a 95% coverage assuming the results are normally distributed [22].

The relative differences and their expanded uncertainties were used for identifying potential anomalies in the results as

$$|d_i| > U(d_i). \tag{9}$$

Concentrations measured by the AE used by the JRC were 10% to 30% lower than the other institutes' concentrations. The deviation was size dependent such that it was larger for larger particle sizes. A possible source of these deviations could be the design of the FCUP inner structure, which might cause a fraction of particles to get deposited onto the grounded inner walls of the FCUP and thus become undetected. Particle deposition mechanisms are known to depend on particle size [23], which would explain the observed size dependent losses. In fact, the FCUP has been redesigned in current models. Due to this apparent shortcoming, it was decided not to report the JRC results, nor take them into account when calculating the comparison reference value.

4. Results

4.1. Comparison results with different particle sizes

The results of the comparison measurements with different particle sizes are summarized in figures 3 and 4, and table 4. No clear dependence of the results on the particle size can be identified in the results of figure 3. For all institutes, the variations of the mean relative differences are smaller than 1.1%. As a typical example of complete results obtained with different particle size, figure 4 shows the results obtained with the particle size of 100 nm and the charge concentration of $1.6 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$. It can be seen that both the AIST and the PTB results show deviations from the reference value that are close to the expanded uncertainty of the deviation. Similar results were obtained with other particle sizes as shown in table 4. The uncertainties increase only slightly for smaller particle sizes, due to uncertainties caused by diffusion losses in the AE inlet. From table 4 it can also be seen that all the mean results are within ±3% of the reference value and that all measurement results, except for the AIST result at 30 nm, agree within the estimated uncertainties. The AIST 30 nm result is, however, in good agreement with the rest of the AIST results and cannot therefore be considered an outlier.

4.2. Comparison results at different particle charge concentrations

The results obtained with different particle charge concentrations with the particle size of 100 nm are presented in figure 5 and table 5. Similar to measurements at different particle sizes, the mean results agree within about ±3% at concentrations larger than $1.28 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$. For these measurements the differences between the institutes are very similar to the results

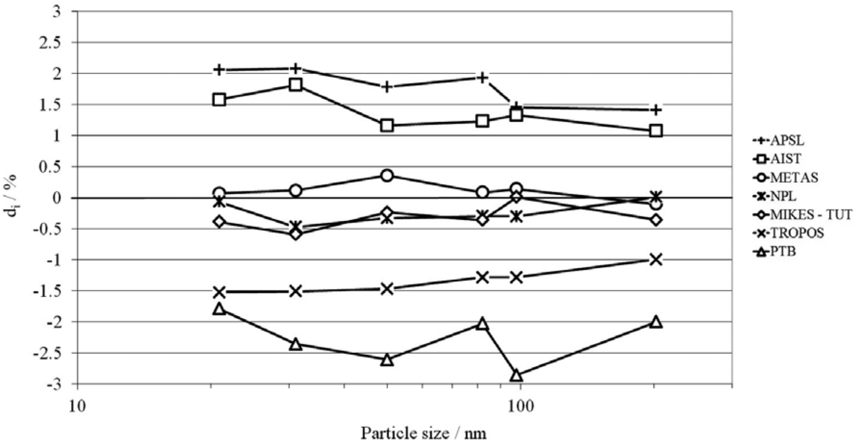

Figure 3. Relative difference between the results obtained by participants and the reference value at different particle sizes with a nominal charge concentration of $1.6 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$ (equal to $10\,000\,\mathrm{cm^{-3}}$).

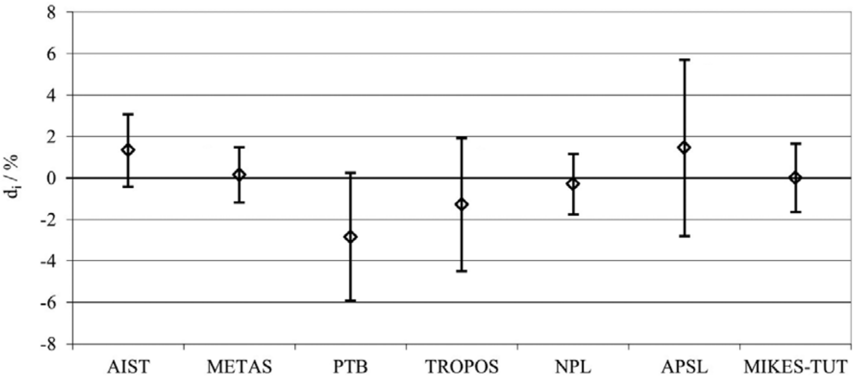

Figure 4. Relative difference between the results obtained by participants and the reference value for a nominal particle size of 100 nm and a nominal charge concentration of $1.6 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$ (equal to $10\,000\,\mathrm{cm^{-3}}$). Error bars show the expanded uncertainties ($k = 2$) of the results.

Table 4. Comparison results at different particle sizes and a nominal particle charge concentration of $1.6 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$ (equal to $10\,000\,\mathrm{cm^{-3}}$). The results are expressed as relative difference d_i from the comparison reference value together with associated uncertainties ($k = 2$).

	Nominal particle size/nm					
d_i/%	20	30	50	80	100[a]	200
NPL	−0.1 ± 1.6	−0.5 ± 1.3	−0.3 ± 1.3	−0.3 ± 1.2	−0.3 ± 1.3	0.0 ± 1.5
MIKES–TUT	−0.4 ± 1.8	−0.6 ± 1.5	−0.2 ± 1.5	−0.4 ± 1.4	0.0 ± 1.5	−0.4 ± 1.5
METAS	0.1 ± 1.5	0.1 ± 1.1	0.4 ± 1.2	0.1 ± 0.9	0.1 ± 1.1	−0.1 ± 1.1
PTB	−1.8 ± 3.1	−2.4 ± 3.0	−2.6 ± 2.9	−2.0 ± 3.0	−2.9 ± 2.9	−2.0 ± 2.7
AIST	1.6 ± 2.1	1.8 ± 1.7	1.2 ± 1.7	1.2 ± 1.5	1.3 ± 1.6	1.1 ± 1.5
TROPOS	−1.5 ± 3.3	−1.5 ± 3.2	−1.5 ± 3.1	−1.3 ± 3.1	−1.3 ± 3.1	−1.0 ± 3.1
APSL	2.1 ± 4.5	2.1 ± 3.2	1.8 ± 3.5	1.9 ± 3.3	1.5 ± 4.3	1.4 ± 2.9

[a] Results illustrated in figure 4.

shown in figure 4. Larger deviations and poorer repeatability can be found in the results obtained with smaller concentrations. This is probably due to the increasing uncertainty of current measurements with smaller concentrations. Figure 6 demonstrates this well: the pattern of the results for particle size and concentrations of 100 nm and $0.16 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$, respectively, is similar to that in figure 4, but the relative differences and associated uncertainties are larger. Similarly to the measurements at different particle sizes, both the PTB and the AIST results show deviations from the reference value that are close, and at some measurement points larger than, the expanded uncertainties. From figure 5 it can also be seen that the dependence on the concentration is very different between the AEs at low concentration levels.

The relative differences of METAS and MIKES–TUT remain constant within 1% for the whole studied concentration range. Also, the NPL results were found independent of particle concentration, but the scattering of results was larger (2.2%) than for the METAS and MIKES–TUT AEs. This scattering is, however, within the estimated uncertainties.

Particle concentration-dependent trends can be identified in the results of APSL, AIST, TROPOS and PTB. From figure 5

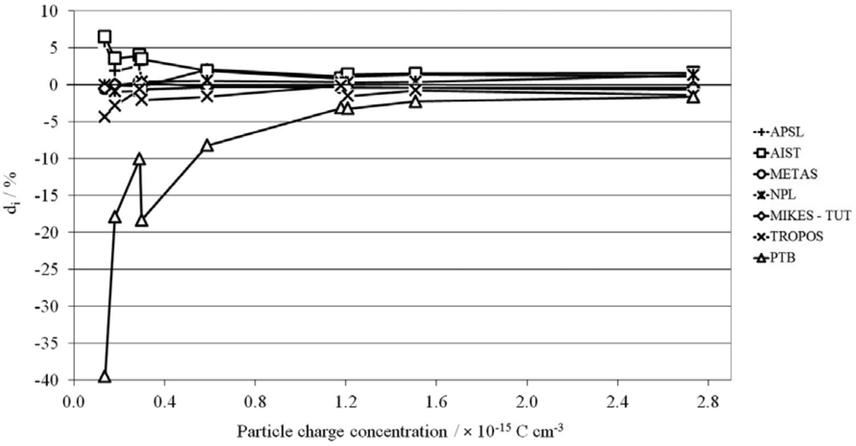

Figure 5. Relative difference between the results obtained by participants and the reference value for different particle charge concentrations of 100 nm size particles.

Table 5. Comparison results with different nominal particle charge concentrations and a nominal particle size of 100 nm. The results are expressed as relative deviation d_i from the comparison reference value and the associated uncertainties ($k = 2$).

	Nominal particle charge concentration/$\times 10^{-15}$ C cm^{-3}								
d_i/%	2.72	1.60	1.28	1.28	0.64	0.32	0.32	0.16[a]	0.16
NPL	1.3 ± 1.4	0.4 ± 1.3	0.3 ± 1.3	0.3 ± 1.3	0.5 ± 1.6	0.4 ± 1.3	−0.8 ± 1.3	−0.9 ± 2.0	−0.1 ± 1.1
MIKES–TUT	−0.4 ± 1.4	−0.4 ± 1.4	−0.4 ± 1.5	−0.2 ± 1.4	−0.3 ± 1.9	0.3 ± 2.7	−0.2 ± 3.1	0.0 ± 3.4	−0.6 ± 4.1
METAS	−0.6 ± 1.1	−0.4 ± 1.1	−0.4 ± 1.0	−0.4 ± 1.2	−0.4 ± 1.2	−0.6 ± 1.3	0.3 ± 1.5	−0.1 ± 1.8	−0.5 ± 2.6
PTB	−1.7 ± 2.0	−2.3 ± 3.1	−3.2 ± 3.7	−3.2 ± 3.8	−8.3 ± 7.2	−18.4 ± 14.1	−10.0 ± 14.5	−17.9 ± 23.2	−39.5 ± 30.6
AIST	1.6 ± 1.5	1.5 ± 1.6	1.4 ± 1.5	0.8 ± 1.6	1.9 ± 2.9	3.4 ± 4.7	4.0 ± 3.8	3.5 ± 3.8	6.5 ± 6.5
TROPOS	−1.4 ± 2.1	−0.8 ± 3.3	−1.5 ± 4.0	−0.1 ± 4.1	−1.6 ± 8.2	−2.1 ± 14.1	−0.6 ± 14.5	−2.8 ± 23.2	−4.4 ± 30.6
APSL	1.1 ± 3.1	1.3 ± 3.5	1.1 ± 3.6	1.1 ± 3.9	2.1 ± 7.2	−0.3 ± 12.4	2.6 ± 12.4	1.8 ± 19.3	5.8 ± 21.9

[a] Results illustrated in figure 6.

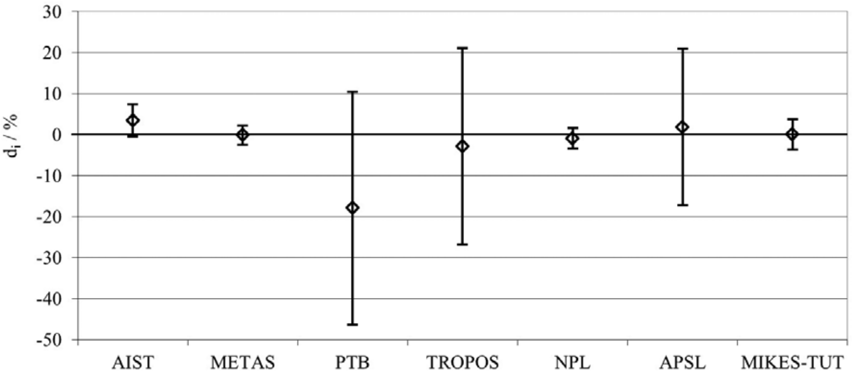

Figure 6. Relative difference between the results obtained by participants and the reference value for a nominal particle size of 100 nm and a nominal charge concentration of 0.16×10^{-15} C cm^{-3} (equal to 1000 cm^{-3}). Error bars show the expanded uncertainties ($k = 2$) of the results.

it can be seen that for the first three of these the difference from the reference value increases as the particle concentration becomes smaller and reaches a value of 5% to 6% for the lowest concentration of 0.16×10^{-15} C cm^{-3}. The differences are, however, less than the stated uncertainties, except for one of the AIST low concentration results. Overall, the AIST results deviated more than the associated expanded uncertainty at 0.32×10^{-15} C cm^{-3} and 2.72×10^{-15} C cm^{-3}. These results were, however, in good agreement with the rest of the AIST results indicating that these results cannot be considered as outliers. The PTB results show a different behaviour from the other AEs. The deviation from the reference value increases notably with decreasing particle concentrations at concentrations smaller than 1.28×10^{-15} C cm^{-3} (equal to 8000 cm^{-3}). The different behaviour of the PTB AE in terms of repeatability and concentration dependency indicates that the results are potentially anomalous. In spite of this, the PTB results were included in the reference value because no clear reason for this odd behaviour was found. Moreover, the PTB results cannot be classified as inconsistent according to the outcome of the chi-square test. Due to the large uncertainties, the PTB results have very small effect on the reference value.

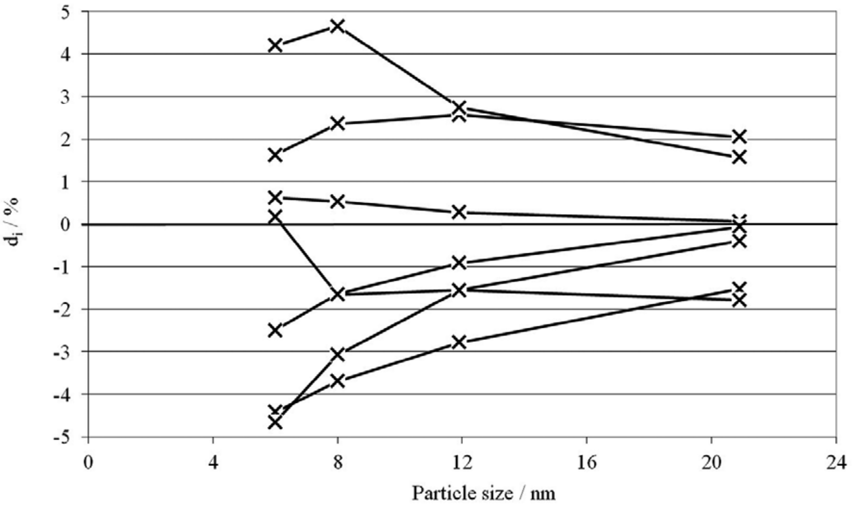

Figure 7. Relative difference between the results obtained by the participants and the reference value for particle sizes 6 nm to 20 nm.

For example, at the lowest concentration point, the reference value would shift upwards by less than 0.1% if the PTB results were excluded from the reference value calculations.

4.3. Additional measurements with sub-20 nm particles

Additional measurements were performed to find out the applicability of the experimental setup for comparisons with sub 20 nm particles. At these particle sizes the diffusion losses in the sampling lines become significant. This has an effect on the maximum particle concentration that can be achieved and also on the symmetry of flow splitting. Even small differences in the dimensions, flow geometry and flow rates of the branches will have a relatively larger effect for small particles.

This is well demonstrated by the results shown in figure 7. The relative differences between the results of the institutes increase as the particle size gets smaller (institute identifications are not shown in the figure). The observed differences cannot exclusively be explained by the slightly increased uncertainties due to diffusion corrections. Because of diffusion losses in the sampling lines, the charge concentration at the sampling ports decreases from a nominal value of $1.6 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$ (equal to $10\,000\,\mathrm{cm^{-3}}$) for 20 nm particles to $0.4 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$ (equal to $2700\,\mathrm{cm^{-3}}$) for 6 nm particles. Therefore, it is not clear to what extent the observed increase of deviation is due size dependent losses inside the AEs or different AE responses to particle concentration or due to uneven flow splitting between sampling ports.

5. Discussion

The relative differences between the participants are fairly constant over the particle sizes and concentrations studied in this comparison. No indication of asymmetric flow splitting was found suggesting that the observed deviations are probably due to uncertainties of volume flow and electric current measurements. If the particle concentration at the sampling ports were asymmetric due to different particle losses in the branches, then this asymmetry would depend on particle size as the loss mechanisms are particle size dependent [23]. Although the mean correction due to the asymmetry was estimated to be zero for all AEs, the associated standard uncertainty of 0.5% was included in the uncertainty analysis.

With large particle concentrations, the most significant sources of uncertainty are related to the volume flow and flow splitting. The uncertainty related to volume flow is around 1% for all institutes, depending on the method of flow control and measurement, and calibration. The differences in the uncertainties reported by the participants are to a large extent caused by different calibration uncertainties of the electric current measurement devices. At low particle charge concentration levels the uncertainty of current measurement becomes the dominating uncertainty component. Increasing relative calibration uncertainty and noise in electric current measurements with smaller concentrations cause the observed poor repeatability and scattering of results at low particle concentrations.

Reasons for the observed non-linear behaviour of the PTB AE are not fully understood. PTB used the same type of AE as METAS, TROPOS, AIST and APSL but showed very different characteristics. Electric current calibration of the PTB AE performed at PTB before the comparison did not show such non-linearity and the same current calibration procedure was performed at PTB for the TROPOS AE. Moreover, recalibration of the PTB AE after the comparison indicated that the AE response had not changed during the comparison. These points indicate that the non-linearity is not due to the electric current calibration nor is it caused by transport of the AE. An error in the measurement of the zero current during the comparison might have caused the observed behaviour, as it would have a relatively larger effect on small current values (small concentrations). After cleaning and recalibration of the AE at the manufacturer, a more stable offset was observed, also interference seen as transient spikes in the current signal was lower than during the comparison at TUT.

Although the results of the institutes show a fairly good agreement, the PTB and the AIST results had a systematic deviation from the reference value that was very close to, and at some measurements points larger than, the expanded uncertainty of the deviation. This does not, however, imply that the results are invalid. It only shows that a mutual agreement of the primary realizations of the charge concentration unit is not achieved at these measurement points. As the disagreement was mostly observed at low particle charge concentrations, it might indicate that there are uncertainties related to electric current measurements that have not been properly accounted for in the uncertainty evaluation. Electric current measurements and calibrations in the femtoampere range are very challenging and further improvements in these areas are needed for accurately measuring non-linearity of electrometers and for better understanding the factors contributing to the uncertainty. Also, the contribution of noise to the uncertainty at low particle concentrations can be further reduced by performing repetitive measurements and/or applying extended measurement cycles.

The anomalies observed in the comparison results emphasize the importance and need for inter-laboratory comparisons. Even a careful validation of the measurement standard (i.e. AE in this work) and calibration of instruments measuring the input quantities (in this case volume flow and electric current) do not guarantee valid realization of the derived measurement quantity, i.e. particle charge concentration. Besides particle charge concentration, also exact knowledge about average particle charge is needed for realizing the particle number concentration unit. Next, a similar comprehensive comparison involving CPCs is needed for investigating the equivalence of complete particle number concentration realizations at different institutes taking also into account the particle generation methods. In fact, such a comparison (registered as the EURAMET project 1252—Comparison of CPCs [24]) has already been initiated.

Overall, the charge concentration measurements of the participating institutes were found to agree within the stated uncertainties except for few measurement points, with the agreement being within about 3%. Additional measurements with sub-20 nm particles show that comparisons in this size range require special considerations regarding sampling lines in addition to a careful characterization of asymmetry in flow splitting in order to minimize the experimental uncertainty. Even so, agreement with 6 nm particles was still observed to be within about ±5%. This outcome is an important step towards internationally recognized traceability in particle number concentration measurements.

6. Conclusions

This paper reports the first comprehensive comparison of aerosol particle charge concentration standards at NMI level. Eight laboratories from seven countries participated in this comparison with their aerosol electrometers. The comparison covered a particle size range of 20 nm to 200 nm and charge concentrations from $0.16 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$ to $2.72 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$ (equal to $1000\,\mathrm{cm^{-3}}$ to $17\,000\,\mathrm{cm^{-3}}$ singly charged particles). The analysed results for all particle sizes and charge concentrations down to $1.28 \times 10^{-15}\,\mathrm{C\,cm^{-3}}$ (equal to $8000\,\mathrm{cm^{-3}}$) agreed within about ±3%. At lower concentrations, and at sizes between 6 nm and 20 nm, the agreement was about ±5%. However, a few potentially anomalous results were observed indicating that further research is needed.

As a summary, the results reported here show that the charge concentration measurements performed by the participating laboratories were mostly equivalent within their stated uncertainties ($k = 2$). This study indicates that the applied comparison protocol and measurement setup is well suited for performing accurate comparisons of AEs in a way that anomalous results can be identified. Additional measurements show, however, that short sampling lines and careful characterization of asymmetry in flow splitting are necessary for comparisons in the size range below 20 nm.

Acknowledgments

This work was supported by European Metrology Research Programme (EMRP) jointly funded by the EMRP participating countries within EURAMET and the European Union, and also by the Cluster for Energy and Environment (CLEEN Ltd, MMEA, WP 4.5.1).

References

[1] IPCC 2013 *Fifth Assessment Report (AR5)* (Geneva: The Intergovernmental Panel on Climate Change)

[2] European Commission 2001 CAFE (Clean Air for Europe) programme

[3] NSF 2003 *Workshop Report on 'Emerging Issues in Nanoparticle Aerosol Science and Technology (NAST)'* (University of California Los Angeles, 27–28 June 2003)

[4] Valavanidis A, Fiotakis K and Vlachogianni T 2008 Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms *J. Environ. Sci. Health* C **26** 339–62

[5] Kulmala M, Vehkamäki H, Petäjä T, Dal Maso M, Lauri A, Kerminen V M, Birmili W and McMurry P H 2004 Formation and growth rates of ultrafine atmospheric particles: a review of observations *J. Aerosol Sci.* **35** 143–76

[6] Agarwal J K and Sem G J 1980 Continuous flow, single particle counting condensation nucleus counter *J. Aerosol Sci.* **11** 343–57

[7] Knollenberg R G and Luehr R 1976 Open cavity laser 'active' scattering particle spectroscopy from 0.05 to 5 microns *Fine Particles—Aerosol Generation, Measurement, Sampling and Analysis* ed B Y H Liu (London: Academic) pp 669–96

[8] Wang S C and Flagan R C 1990 Scanning electrical mobility spectrometer *Aerosol Sci. Technol.* **13** 230–40

[9] Keskinen J, Pietarinen K and Lehtimäki M 1992 Electrical low pressure impactor *J. Aerosol Sci.* **23** 353–60

[10] ISO/DIS 14644-12 *Cleanrooms and Associated Controlled Environments: Part 12. Classification of Air Cleanliness by Nanoscale Particle Concentration Cleanliness* (Geneva: International Organization for Standardization) (still under development)

[11] European Commission 2008 Regulation No. 692 Implementing and amending regulation (EC) No 715/2007 of the European parliament and of the council on the type-approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information *Offic. J. Eur. Union* L:199/1

[12] Högström R, Yli-Ojanperä J, Rostedt A, Iisakka I, Mäkelä J M, Heinonen M and Keskinen J 2011 Validating the single charged aerosol reference (SCAR) as a traceable particle number concentration standard for 10 nm to 500 nm aerosol particles *Metrologia* **48** 426–36

[13] Sakurai H and Ehara K 2011 Evaluation of uncertainties in femtoampere current measurement for the number concentration standard of aerosol nanoparticles *Meas. Sci. Technol.* **22** 024009

[14] Fletcher R A, Mulholland G W, Winchester M R, King R L and Klinedinst D B 2009 Calibration of a condensation particle counter using a NIST traceable method *Aerosol Sci. Technol.* **43** 425–41

[15] ISO/DIS 27891 *Aerosol Particle Number Concentration—Calibration of Condensation Particle Counters* (Geneva: International Organization for Standardization) (still under development)

[16] Schlatter J 2009 *Final Report of EURAMET Project 1027* (www.euramet.org)

[17] Yli-Ojanperä J, Sakurai H, Iida K, Mäkelä J M, Ehara K and Keskinen J 2012 Comparison of three particle number concentration calibration standards through calibration of a single CPC in a wide particle size range *Aerosol Sci. Technol.* **46** 1163–73

[18] EURAMET Project 1244—Comparison of Aerosol Electrometers (www.euramet.org)

[19] Yli-Ojanperä J, Mäkelä J M, Marjamäki M, Rostedt A and Keskinen J 2010 Towards traceable particle number concentration standard: single charged aerosol reference (SCAR) *J. Aerosol Sci.* **41** 719–28

[20] European Commission 2012 Regulation No 83 of the Economic Commission for Europe of the United Nations (UN/ECE)—Uniform provisions concerning the approval of vehicles with regard to the emission of pollutants according to engine fuel requirements *Offic. J. Eur. Union* L:42/1

[21] Cox M G 2002 The evaluation of key comparison data *Metrologia* **39** 589–95

[22] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML 2008 *Evaluation of Measurement Data—Guide to the Expression of Uncertainty in Measurement* (Joint Committee for Guides in Metrology)

[23] Hinds W C 1999 *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles* (New York: Wiley) pp 191–6

[24] EURAMET Project 1252—Comparison of Condensation Particle Counters (www.euramet.org)