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F. Gaie-Levrel, Sébastien Bau, Lola Bregonzio-Rozier, Romain Payet, Sébastien Artous, et al.. An intercomparison exercise of good laboratory practices for nano-aerosols size measurements by mobility spectrometers. *Journal of Nanoparticle Research*, 2020, 22 (103), pp.103. 10.1007/s11051-020-04820-y . hal-03118130

HAL Id: hal-03118130

<https://hal.science/hal-03118130>

Submitted on 21 Jan 2021

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1 **An intercomparison exercise of good laboratory practices for nano-**
2 **aerosols size measurements by mobility spectrometers**

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1 An intercomparison exercise of good laboratory practices for nano- 2 aerosols size measurements by mobility spectrometers

3 An intercomparison campaign on nanoparticle size measurement was organized in the frame of the
4 French nanoMetrology club. The aim of this study is to make an inventory of the metrological capabilities
5 of all measurement techniques in France involved in the “nano” size range, including the SMPS
6 (Scanning Mobility Particle Sizer) concerning aerosol metrology. For this study, four samples have been
7 proposed, namely (1) - a SiO₂ colloidal suspension (FD304) consisting of a monomodal population, (2) -
8 two samples consisting of two nanoparticle populations of SiO₂ having proportions to be determined and
9 (3) - a TiO₂ colloidal suspension. Ten SMPS associated to five participants around a common
10 experimental setup were performed in link with a control SMPS to have simultaneous measurements with
11 a same instrument in each laboratory in parallel with the SMPS used by each partner. This article presents
12 SMPS results of this study associated with the description of the experimental set-up and the sample
13 preparation protocol with an identified schedule and comparison with SEM measurements. The present
14 paper does not focus on the actual capability of the tested mobility spectrometers, but aims to highlights
15 the good laboratory practices using their own but common resources in terms of aerosol generation and
16 measurement set-ups.

17 Keywords: Intercomparison, nano-aerosols, colloidal suspension, SMPS

18 1. Introduction

19 Atmospheric aerosols are known to have a large impact on human health (Vedal et al., 2006; Lawrence et
20 al., 2007), atmospheric chemistry and climate (Forster et al., 2007). Concerning human exposure in
21 workplace and outdoor environments, aerosol inhalation can cause adverse health effects due to the
22 deposition of airborne particles in the respiratory tract (ICRP, 1994). In addition to particle
23 chemistry/chemical composition, such impacts are mainly dependent on particle number size distribution
24 (PNSD), which can be measured by instrumental techniques such as Mobility Particle Size Spectrometer
25 (MPSS), also known as Differential Mobility Particle Sizer (DMPS), Differential Electrical Mobility
26 Analyzer (DEMA) or Scanning Mobility Particle Sizer (SMPS). Such instruments are composed of a
27 Differential Mobility Analyzer (DMA) with a bipolar diffusion charger (aerosol neutralizer), used to
28 select a given particle size, coupled to a Condensation Particle Counter (CPC) allowing particles to be
29 counted individually. Upstream the DMA, an impactor is used to remove larger particles which could
30 disturb neutralizing process and lead to biases in size distribution measurements. Although not best suited
31 for field measurement campaigns (Leskinen et al., 2012; Bau et al., 2013), SMPS is a standardised
32 method already used in the certification process of spherical particle reference materials.

33 Several interlaboratory comparisons of SMPS have been performed over the last 25 years, mainly in the
34 context of atmospheric measurements (Wiedensohler et al. 1993 ; Khlystov et al. 2001 ; Rodrigue et al.
35 2007 ; Helsper et al. 2008 ; Jeong and Evans, 2009 ; Watson et al., 2011; Wiedensohler et al., 2012;
36 Motzkus et al. 2013 ; Gómez-Moreno et al. 2015 ; Fonseca et al., 2016 ; Wiedensohler et al., 2017). Joshi
37 et al. (2012) conducted a metrological study of two different SMPS on both ambient and laboratory test
38 aerosols. Even though they reported an excellent consistency while comparing the mean size and
39 geometric standard deviation from both instruments, the authors highlight the necessity to perform inter-
40 comparison exercises for harmonisation of the measurements.

41 Laboratory performances of four DMAs were evaluated by Fissan et al. (1996) by sampling
42 monodisperse aerosols in the 6–50 nm size range under the same operating conditions for each system,
43 such as sample and sheath air flow rates, input and tubing lengths. Their results provide a quantitative
44 comparison of the mobility selection accuracy and diffusion losses of nanometer aerosols in such
45 systems. Later, Dahmann et al. (2001) reported acceptable comparability of the results obtained in the
46 framework of an international inter-comparison performed in Germany (11 models investigated). This
47 study highlighted the need to guarantee uniform instrument parameters under conditions of good practice
48 and user skills, in line with the conclusions drawn by Kaminski et al. (2013) from a laboratory study
49 which showed a higher comparability between 8 SMPS models. In the paper from Asbach et al. (2009),
50 the response of four different mobility particle sizers was investigated when measuring NaCl and diesel
51 soot particles. The major conclusions of these inter-laboratory comparison studies are the lack of (1)
52 measurement standards with specific recommendations and (2) harmonized and standardized
53 measurement procedures.

1 A lack of metrological traceability can be identified in these studies highlighting the crucial importance to
2 have traceable parameters. Indeed, in the paper from Wiedensohler et al. (2012), the issue of the
3 harmonization of measurement procedures to facilitate high quality long-term observations of
4 atmospheric particle size number distributions obtained by SMPS is raised. In more recent work,
5 Wiedensohler et al. (2017) state that an SMPS calibration facility should have one or several calibrated
6 reference SMPS. For a complete quality assurance, it is therefore proposed that measurement procedures
7 take into account (1) - sizing calibration of the candidate SMPS using a certified particle size standard,
8 (2) - PNSD intercomparison of candidate SMPS against a reference SMPS, (3) - intercomparison of the
9 integral particle number concentration (PNC) of the candidate SMPS against a calibrated reference CPC
10 with pre-calibration of the candidate CPC counting efficiency curve. It is worth mentioning that PNSD
11 measurement is also based on the commonly used equations for the bipolar charge equilibrium (Fuchs,
12 1963) as described in ISO 15900, which is agreed by convention (Wiedensohler et al., 2017) but not SI-
13 traceable

14 In industrial environments where workers are confronted to engineered nanomaterials, inhalation
15 exposure to nano-objects aggregates/agglomerates (NOAAs) must be monitored with adapted techniques.
16 In this context, other intercomparison studies on PNSD measurements by SMPS were performed on TiO₂
17 (Leskinen et al., 2012; Ding et al., 2016). Babick et al., (2016a,b) showed for several nano-added
18 materials that the SMPS number-weighted median diameters deviate from electron microscopy results by
19 a factor not larger than 1.5.

20 In this work, we present an SMPS intercomparison study, which is part of a multi-technical
21 interlaboratory comparison of the measurement of the size of nano-objects performed in the framework of
22 the French nanoMetrology Club (nMC). This nMC (Club nanoMétrologie, 2019) is coordinated since
23 2011 by LNE and represents a French network gathering around 400 members and dealing with the topic
24 of material characterization at the nanoscale by creating bridges between academic and industry
25 communities.

26 The overall objective of this large intercomparison is to make an inventory of the metrological
27 measurement capabilities of various measurement techniques in France. This paper focuses on the results
28 of 10 SMPS associated to five participants around a common experimental setup in link with a control
29 SMPS. Four different samples were investigated: (1) - a SiO₂ monomodal colloidal suspension of
30 reference nanoparticles (ERM-FD304); (2) - two samples (SiO₂-1 and SiO₂-2) consisting of two
31 populations of SiO₂ nanoparticles; (3) - a fourth sample consisting of TiO₂ NOAAs also called E171 as a
32 food additive. The objective of this paper is not to characterize the actual capability of the tested mobility
33 spectrometers, but to demonstrate the good laboratory practices using their own - but common - resources
34 in terms of aerosol generation and measurement set-ups.

36 2. Experimental setup and SMPS types

38 A SMPS intercomparison exercise is highly constrained by the difficulty to move instruments at the same
39 location in the same time especially when they use radioactive sources. The strategy chosen in this study
40 was based on the reproduction of an experimental setup and measurement sequence, associated with a
41 common measurement device. More precisely, each partner from Lab n°1 to Lab n°4 used its own
42 resources to build the experimental set-up presented in Fig1. As a common measurement device, a
43 PALAS control SMPS (Lab n°5) was used during this interlaboratory comparison in order to have
44 simultaneous measurements performed with a same instrument in each laboratory in parallel with the
45 SMPS used by each partner. The common experimental setup implemented by each partner for this study
46 was based on aerosol generation thanks to an atomizer (model 3076, TSI) operated in recirculation mode,
47 coupled to a diffusion dryer system (model 3062-NC, TSI), and a downstream dilution air flow delivering
48 a constant flow rate of 8 L/min allowing multiple measurements to be carried out in parallel (Fig1). It is
49 important to note that atomizer system was chosen for this study as the only generator owned by each
50 participant by keeping in mind that the main objective of this study is to demonstrate the good laboratory
51 practices using common resources in terms of aerosol generation and measurement set-ups and common
52 sample preparation protocols. The particle-free air introduced in the setup was preliminarily dried and
53 filtered by means of a specific device (model 3074B, TSI).

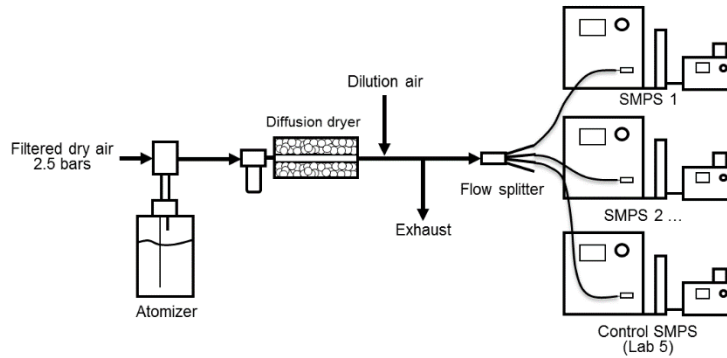


Fig 1: Experimental setup used by each partner for this study.

A four-way flow splitter (model 3708, TSI) was used to simultaneously provide the homogeneous aerosol distribution to the different SMPS operating in parallel, each of them was connected with the same length (~ 1 m) of antistatic tubing. Particle losses within the sampling tubes were supposed to be equivalent due to the range of aerosol flow rates of the instruments; therefore, no correction for particle concentration was performed. Table 1 presents the technical specifications of the different SMPS involved in this study for each laboratory.

Table 1 shows that long columns were mainly used for particle classification. It is important to mention that raw SMPS data are converted into PNSD by assuming that airborne particles reach the target charge distribution imposed by the bipolar charger (Fuchs, 1963; Stolzenburg & McMurry, 2008). This is typically achieved using neutralization sources, which bring aerosols to a steady-state charge distribution, whatever their initial state-of-charge.

Table 1: SMPS types implicated in this intercomparison study.

	Company	DMA + Column	Source	CPC working fluid / d_{50} (nm)	Max concentration for single particle counting ($\#/cm^3$)	Sheath flow / Sample flow (L/min)	Channels / decade	
Lab n°1	SMPS 1.1	3080 + long	^{85}Kr 3077A	3775 butanol / 4	5×10^4			
	SMPS 1.2	TSI	RX 3088	3788 water / 2.5	4×10^5	3 / 0.3	64	
	SMPS 1.3		^{85}Kr 3077	3775 butanol / 4	5×10^4			
Lab n°2	SMPS 2.1	TSI	^{85}Kr 3077	3785 water / 4.2	$< 2 \times 10^4$	3 / 0.3	64	
	SMPS 2.2	GRIMM	Middle Vienna	^{241}Am	5416	1.5×10^5	3 / 0.3	36
			Long Vienna	RX XRC-05	butanol / 4			20
Lab n°3	SMPS 3.1	TSI	RX 3088	3787 water / 5	2.5×10^5	6 / 0.6	64	
Lab n°4	SMPS 4.1		^{85}Kr 3077			15 / 1.5		
	SMPS 4.2	TSI	RX 3087	3775 butanol / 4	5×10^4	3 / 0.3	64	
	SMPS 4.3		RX 3088			15 / 1.5		
Lab n°5	Control SMPS	PALAS	control unit DEMC + long	RX XRC-049	Envi-CPC 100 butanol / 7	1×10^5	9 / 0.9 3.6 / 0.9*	64

* A ¼ sheath/sample flows ratio was used to cover the diameter range for the TiO_2 sample.

In this study, radioactive (^{85}Kr) and soft X-ray sources were used to generate the bipolar ions that diffuse onto the particles and bring them to the charge equilibrium. The bipolar charge equilibrium of Tigges et al. (2015) was used for the soft X-ray charger in the SMPS inversion routine, while the one described by Wiedensohler (1986, 1988) was used for the radioactive neutralizer as an approximation of the Fuchs (1963) diffusion theory for particle sizes in the submicrometer range. It is important to mention that this

1 study does not take into account neutralization efficiency difference between spherical nanoparticles and
2 NOAAs as described by Lall & Friedlander (2005).
3 Wiedensohler et al. (2017) showed that PNSD comparisons between a SMPS with a soft X-ray bipolar
4 charger and a reference SMPS with a ^{85}Kr bipolar diffusion charger is excellent, i.e. in the $\pm 10\%$ target
5 uncertainty. Other work showed a good correlation in the particle number concentration and differences
6 in the count median diameter and geometric standard deviation below 4% for a polydisperse NaCl aerosol
7 measured with GRIMM SMPS equipped with either an X-ray source (TSI RX 3087) or a radioactive
8 source (Nicosia et al., 2014). The results from Nicosia et al. (2018) confirmed that instrumental
9 uncertainties introduced by the use of the X-ray sources rather than a radioactive neutralizer in the size
10 range 10–300 nm are negligible, in line with previous work published by Kallinger et al. (2012).
11 Concerning CPC, water and butanol-based instruments were involved (w&b-CPC respectively). Franklin
12 et al. (2010) compared w&b-CPC for diesel combustion aerosols. They pointed out a disagreement for
13 one of the w-CPC, which was attributed to the use of water as a condensing fluid. This was also pointed
14 out by the work of Bau et al. (2019) which highlighted that the accuracy of w-CPC is dependent on their
15 technical design. To minimize instrumental or model differences, post-data correction equations were
16 proposed by Lee et al. (2013) to adjust the data from TSI water-based CPC using exponential models.
17 Bau et al. (2017, 2019) show that w&b-CPC studied were found to be within $\pm 25\%$ of the reference,
18 except for a w-CPC (TSI model 3787) known to be highly sensitive to particle hydrophobicity. It is
19 important to note that such parameter will have a minor effect in our study due to the sample nature.
20 As stated in Table 1, the main SMPS versions used in the aerosol measurement community are present in
21 this intercomparison study, knowing that TSI models are mainly represented. For each SMPS involved, a
22 sheath flow / sample flow (SSF) ratio of 10 was respected to ensure size resolution with an optimized
23 DMA transfer function. Only the Lab n°5 control SMPS was used with a SSF ratio of 4 in the case of the
24 TiO_2 sample, in order to be capable of covering the range of particle diameter of interest. Indeed, a range
25 of electrical mobility diameters from a few nanometers up to 200 nm was used for ERM-FD304, SiO_2 -1
26 and SiO_2 -2 samples; this range was increased up to 700 nm for the TiO_2 sample.

27 3. Samples, preparation protocol and data acquisition

28 Concerning samples, ERM-FD304 was used as a Certified Reference Material (CRM) to verify
29 instrument calibration and to adjust measurements when required. This CRM is characterized by a
30 reference number-based modal diameter of 27.8 ± 1.5 nm obtained by electron microscopy (EM),
31 knowing that EM measurements correspond to the geometrical diameter of particles, which is not
32 identical but equivalent to the electrical mobility diameter in this case of spherical particles (Kulkarni et
33 al., 2011). SiO_2 -1 and SiO_2 -2 samples were specifically synthesized for this study as bi-populated
34 colloidal suspensions. In parallel of particle size measurements, the determination of the proportions
35 between the two populations was also asked to each participant to this study since both samples are
36 characterized by two different populations proportions. The TiO_2 sample used for this study was a food-
37 grade reference, also known as E171.

38 All stock samples, preliminary prepared by LNE for all techniques, were provided to all participants and
39 stored at room temperature and protected from light. For each participant, preparation protocols for
40 samples to be analyzed were deliberately basic (dilutions in ultrapure water, MilliQ, Millipore,
41 18.2 M Ω .cm resistivity) to be performed as simply as possible. Dilution factors of 750, 600, 500 and 111
42 for ERM-FD304, SiO_2 -1, SiO_2 -2 and TiO_2 stock samples respectively were used. Atomizer cleaning and
43 diffusion drier regeneration protocols were also provided to each participant.

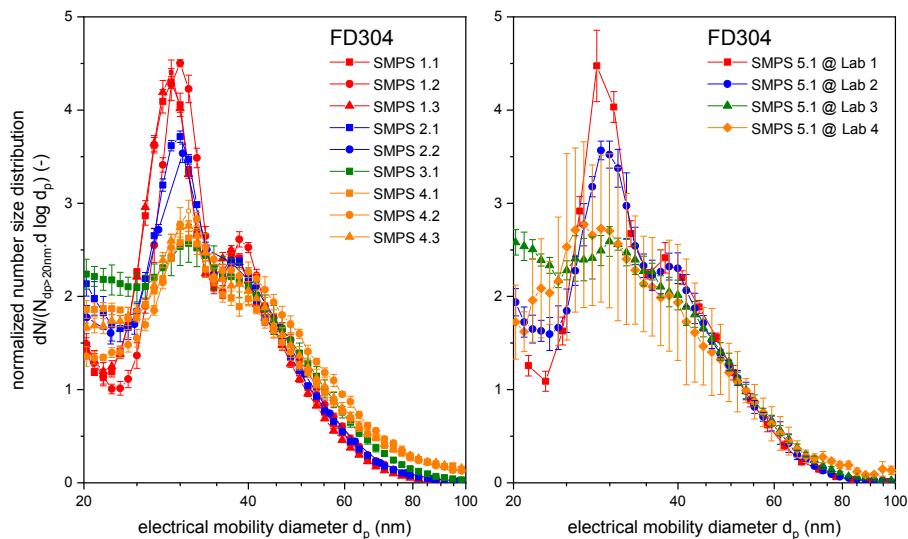
44 As regards to data acquisition, each partner was required to record 5 scans for each sample, with a global
45 duration of 3 min each and a waiting time of 2 min between each scan integrating a 20 s voltage decrease
46 time. A blank level was checked between each scan using ultrapure water nebulization. For TSI SMPS,
47 the AIM software was used by each partner while Grimm nanosoftwares and PDAnalyze software were
48 used for GRIMM and PALAS SMPS, respectively.

50 4. Results

52 4.1 Particle number size distributions

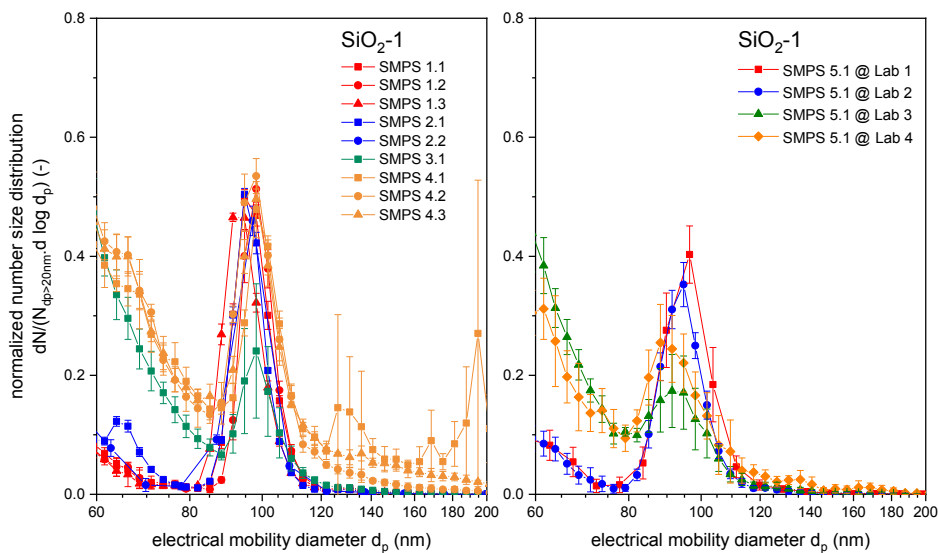
54 Figs 2 to 5 show the average PNSD measured by the different SMPS for aerosols generated by
55 atomization of samples ERM-FD304, SiO_2 -1, SiO_2 -2 and TiO_2 , respectively. The error bars correspond to
56 the standard deviations calculated on the five measurements made for each sample ($k = 1$). The PNSD
57 were normalized with regards to the total number concentration of particles above 20 nm measured by
58 each SMPS for each sample to take into account the different size range of the SMPS involved. For all

1 samples, optimization of sample preparation and dilution protocol was performed during a pilot
 2 laboratory study prior the inter-laboratory exercise. In spite of multiple tests, it remained unsuccessful to
 3 avoid multiplets generation around 40nm using the atomizer generator for the ERM-FD304 sample
 4 (Fig2). For the same sample, the larger error bars associated with the PNSD provided by SMPS5.1@Lab4
 5 are due to a technical problem during the test session. Note that in the case of bimodal suspensions (SiO₂-
 6 1, SiO₂-2 samples), the contribution associated with the MilliQ water nebulization induces the presence of
 7 a non-negligible background aerosol and limits the identification of the first population of these samples.
 8 PNSD of MilliQ water only are available in the appendix associated to this paper (Fig8). Therefore, it was
 9 not possible to calculate the ratios between the two populations of these bi-modal samples. For SiO₂-2
 10 sample (Fig4), the error bars associated with empty symbols for SMPS 4.1 size distribution (> 180 nm)
 11 were deleted due to their large contributions.
 12



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Fig2: Average particle number size distributions for the ERM-FD304 sample.



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 16
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Fig3: Average particle number size distributions for the SiO₂-1 sample.

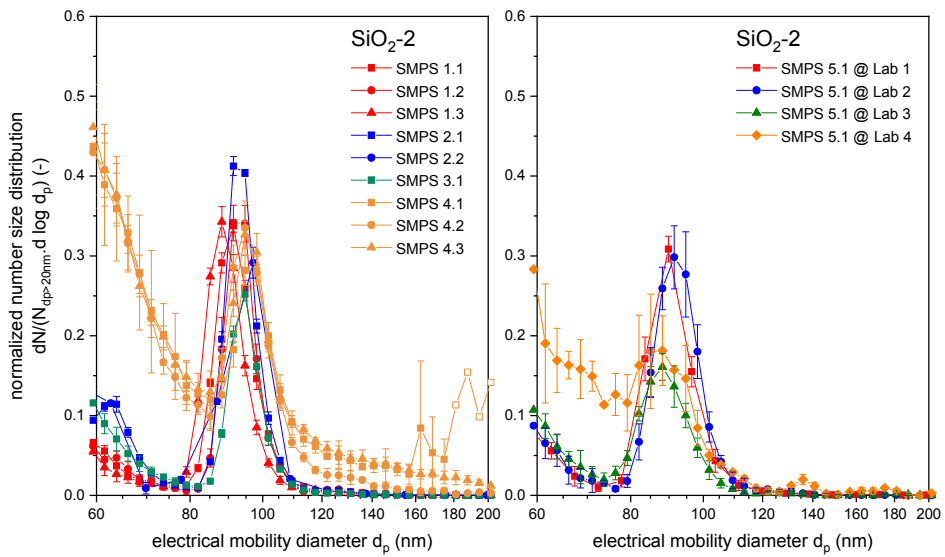


Fig4: Average particle number size distributions for the SiO₂-2 sample.

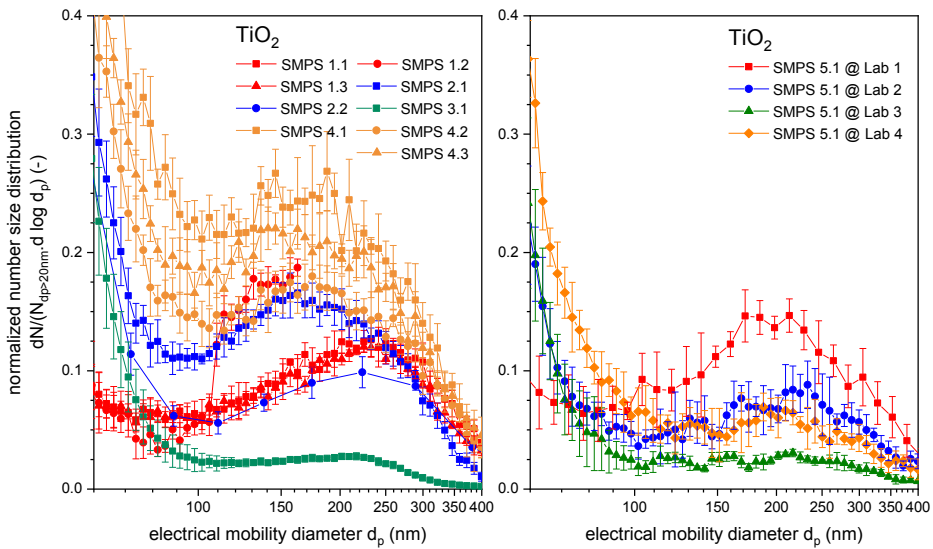


Fig5: Average particle number size distributions for the TiO₂ sample.

From Fig5, greater result variability was obtained for TiO₂. This was associated to the low TiO₂ aerosol concentrations in number linked to the low TiO₂ concentration in the provided stock sample. It is important to note that associated dilutions of stock sample were optimized deliberately by the consortium since the main objective of this study was to demonstrate the good laboratory practices using common resources in terms of aerosol generation and measurement set-ups and common sample preparation protocols. As an example, SMPS3.1 data in Fig2 shows a strong aerosol background due to water nebulisation. This is clearly presented in Fig8 (see appendix) in which a difference in terms of aerosol background due to the water-only nebulisation was observed between the morning and afternoon session during this study due to the cleaning of ultrapure water generation system. This highlights that laboratory practices are important to be considered for such study.

4.2 Modal diameters

Mean, modal and median diameters are commonly used to describe lognormal particle size distributions. Since overlapping size distributions are predominant in this study, it was chosen to take into account only modal diameters in data processing and thus to avoid any deconvolution of size distributions. It is worth mentioning that PNSD in Fig2-5 are presented as curves instead of rigorous histograms in order to improve their readability. Therefore, each point of the curves corresponds to the mid-point diameter of the associated size bin which is defined by the geometric mean diameter. Consequently, in a logarithmic scale, the modal diameter corresponds to the geometric mean diameter of the most frequent channel. Table 2 presents the average modal diameters measured by each laboratory and by the control SMPS (Lab 5) for the four samples involved in this study.

Table 2: Average (Av.) modal diameters measured by each SMPS for each laboratory and for the control SMPS (Lab 5) for each sample. Repeatability and reproducibility standard deviations (STDr (k=1) and STD_R (k=2)) were calculated in accordance with the ISO 5725-2 (1994) standard.

		FD304				SiO ₂ -1				SiO ₂ -2				TiO ₂			
		LAB		Lab 5		LAB		Lab 5		LAB		Lab 5		LAB		Lab 5	
		Av.	STDr	Av.	STDr	Av.	STDr	Av.	STDr	Av.	STDr	Av.	STDr	Av.	STDr	Av.	STDr
		(nm)		(nm)		(nm)		(nm)		(nm)		(nm)		(nm)		(nm)	
Lab n°1	SMPS 1.1	28.9	0.0			95.4	1.6			91.4	0.0			217.2	15.3		
	SMPS 1.2	30.0	0.0	28.4	0.0	98.2	0.0	96.5	0.0	92.7	1.8	89.8	0.0	*---	---	187.3	35.5
	SMPS 1.3	28.9	0.0			92.7	1.8			88.2	0.0			248.8	14.9		
Lab n°2	SMPS 2.1	30.0	0.0			94.7	0.0			92.7	1.8			159.3	10.5		
	SMPS 2.2	30.3	0.0	29.1	0.5	97.1	0.0	94.1	1.5	97.1	0.0	93.4	1.8	203.5	26.7	217.0	29.7
Lab n°3	SMPS 3.1	31.3	0.5	30.2	0.9	98.2	0.0	92.1	2.8	94.7	0.0	87.6	1.4	206.9	19.8	199.1	48.2
Lab n°4	SMPS 4.1	31.3	0.5			98.2	0.0			95.4	1.6			179.7	22.9		
	SMPS 4.2	30.9	0.5	26.9	1.6	97.5	1.6	90.1	1.8	94.7	0.0	89.9	6.9	178.6	5.8	195.7	23.9
	SMPS 4.3	30.7	0.6			98.2	0.0			95.4	1.6			151.6	11.4		
Global Av. / STD_R (k=2)		30.3 / 1.9		28.8 / 3.1		96.7 / 4.3		93.2 / 6.3		93.6 / 5.7		90.2 / 6.7		193.2 / 71.3		199.8 / 70.9	

* not determined (due to inadapted size range [nano column])

Repeatability and reproducibility standard deviations (STDr and STD_R) were calculated in accordance with ISO 5725-2 (1994). For each sample, global average modal diameters (GAMD) were calculated by integrating all SMPS types from Lab n°1 to Lab n°4 and for the control SMPS (Lab n°5) with reproducibility standard deviation (k=2) reported as uncertainties. GAMD for [Lab1-4 / control SMPS] are calculated to be [30.3 ± 1.9 nm / 28.8 ± 3.1 nm]; [96.7 ± 4.3 nm / 93.2 ± 6.3 nm]; [93.6 ± 5.7 nm / 90.2 ± 6.7 nm] and [193.2 ± 71.3 nm / 199.8 ± 70.9 nm] for FD304, SiO₂-1, SiO₂-2 and TiO₂ samples, respectively. SMPS measurements appear consistent for each laboratory especially for SiO₂ samples which are characterized by relative STD_R comprised between 4 and 11% while TiO₂ samples are characterized by relative STD_R around 35%. By taking into account the control SMPS GAMD as reference values, a Z score performance test was performed for each SMPS and each sample as:

$$Z = \frac{d_{mod_{SMPSi}} - d_{mod_{SMPS*}}}{STD_R} \quad (1)$$

where $d_{mod_{SMPSi}}$ is the average modal diameter of a SMPS with $i = 1$ to 9, $d_{mod_{SMPS*}}$ the average modal diameter of the control SMPS and STD_R the estimated reproducibility standard deviation (k=2).

SMPS performance was therefore assessed knowing that:

- absolute Z score values |Z| greater than 3 are considered to be unsatisfactory values (“warning zone”);
- $2 < |Z| \leq 3$ are considered to be questionable values (“surveillance zone”);
- $1 < |Z| \leq 2$ are coherent values and correspond to acceptable performance;
- $|Z| \leq 1$ are optimal values and correspond to excellent performance.

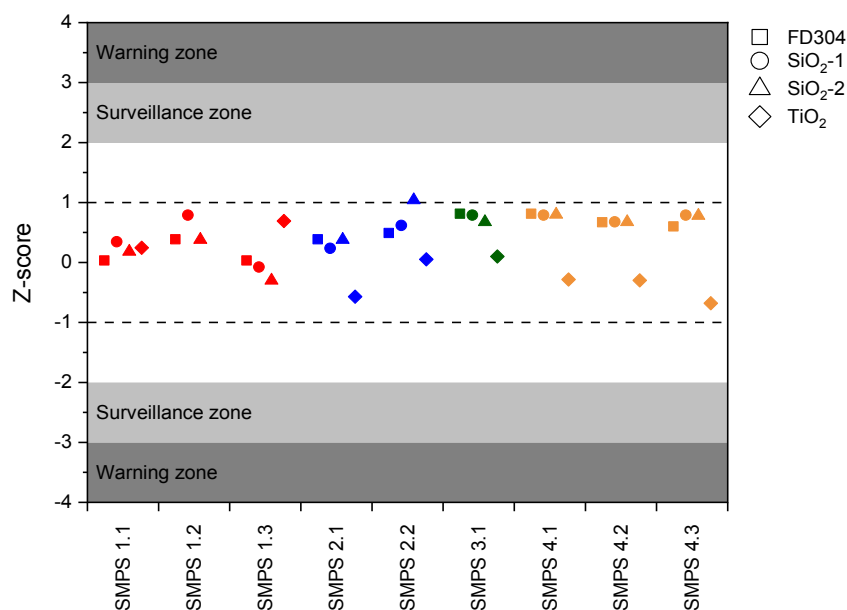


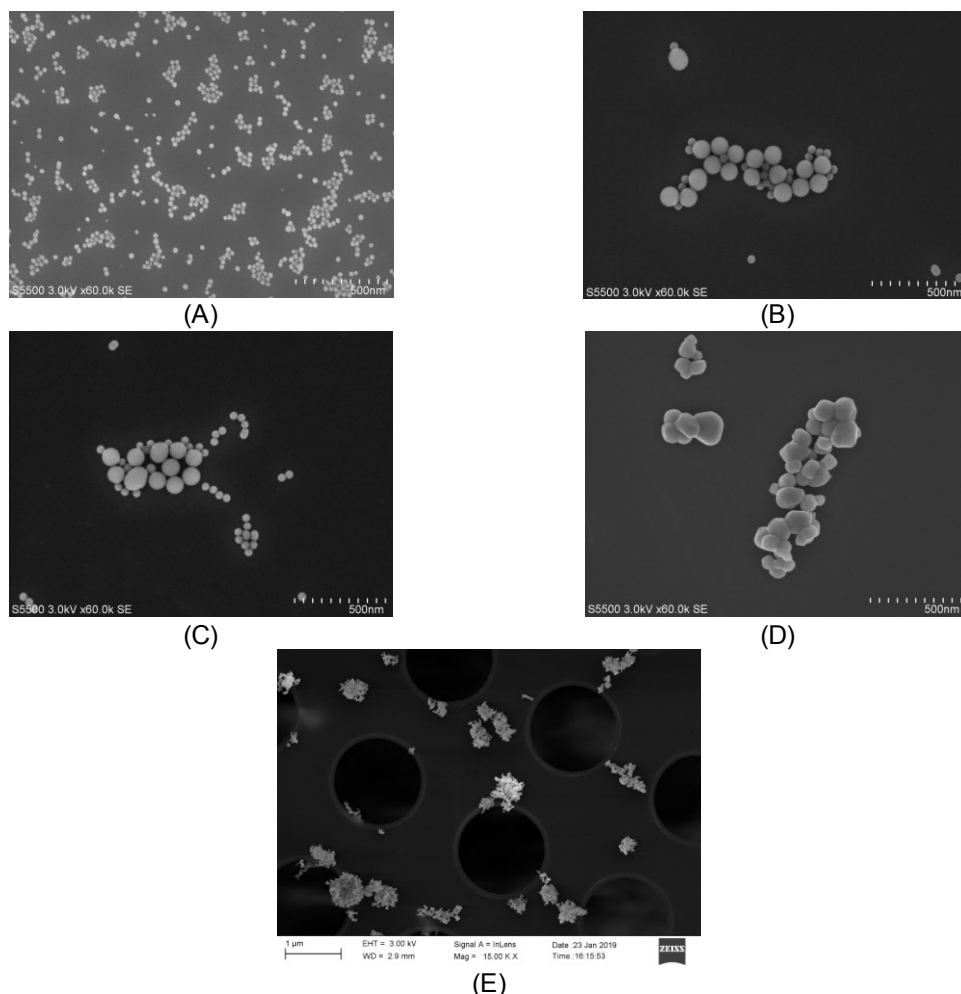
Fig6: Z Score calculation for the average modal diameters measured by each SMPS for the four samples (reference to the control SMPS)

Z score calculation for the average modal diameters measured by each SMPS for the four samples are presented in Fig6. All Z score values are comprised between -1 and 1 for this intercomparison exercise. This highlights the good practices and the ability of each laboratory to measure the modal diameters in connection with the use of provided protocols for each sample studied. In link with discussions in section 4.1, these results clearly show that modal diameter measurements especially for SMPS3.1 are not hindered despite the fact that, in this case, a high background associated to water nebulisation was observed.

4.3 Comparison with electron microscopy measurements

Considering scanning electron microscopy results associated with this intercomparison study, measured average modal diameters were found to be 26.0 ± 0.3 nm, 93.3 ± 1.2 nm, 93.6 ± 1.2 nm and 95.0 ± 0.7 nm for FD304, second modal diameter for SiO₂-1 and SiO₂-2 populations and TiO₂ respectively. Such diameters measured by SEM correspond to projected area equivalent diameter. It should be noted that the ERM-FD304 certified reference material certificate indicates a modal diameter of 27.8 ± 1.5 nm measured by electron microscopy (TEM and SEM) which is slightly higher (7%) than the particle sizes measured by SEM in this study. However, both values are consistent by taking into account associated uncertainties.

According to the SMPS-based modal diameters gathered in Table 2 and by taking into account expanded uncertainty ($k=2$), it can be concluded a satisfying agreement with SEM-based diameters, probably due to the spherical shape of SiO₂ particles (Fig7A, B, C), except for the TiO₂ sample. The default of accordance between SEM- and SMPS-based modal diameter measurements in the case of TiO₂ sample can be due to the fact that primary particles were taken into account for SEM measurements (Fig7D), while SMPS measurements concern NOAAs due to the nebulization process of aqueous colloidal suspension. Indeed, Fig7E shows an example of TiO₂ NOAAs sampled on a carbon TEM grid from an aerosol produced using the experimental setup presented in Fig1 and using the Mini Particle Sampler (MPS) system (R'Mili et al, 2013). The latter clearly shows that airborne TiO₂ particles have an agglomerated/aggregated morphology.



1 Fig7: SEM/TEM pictures of (A) – FD304, (B) – SiO₂-1, (C) – SiO₂-2, (D) – Food-grade TiO₂ sample and
 2 (E) example of TiO₂ aerosol sampled on a carbon TEM grid.

3 5. Conclusions and outlooks

4 This article presents the results from an intercomparison of good laboratory practices dedicated to nano-
 5 aerosols size measurements using harmonized experimental set-up and sample preparation protocols with
 6 an identified schedule and comparison with SEM measurements. Global average modal diameters were
 7 calculated for each sample from all SMPS measurements, i.e. 30.3 ± 1.9 nm; 96.7 ± 4.3 nm;
 8 93.6 ± 5.7 nm; 193.2 ± 71.3 nm for sample ERM-FD304, SiO₂-1, SiO₂-2 and TiO₂ respectively with
 9 reproducibility standard deviation ($k=2$) reported as expanded uncertainties and knowing that ERM-
 10 FD304 sample is a certified reference material characterized by modal diameter of 27.8 ± 1.5 nm.
 11 Complementary scanning electron microscopy results were obtained and average modal diameters were
 12 found to be 26.0 ± 0.3 nm, 93.3 ± 1.2 nm, 93.6 ± 1.2 nm and 95.0 ± 0.7 nm for each sample respectively.
 13 Relative differences of 4% and 7% for SMPS and SEM measurements were obtained for the ERM-
 14 FD304 modal diameter measurements. However, measurements are consistent by taking into account
 15 associated uncertainties. Such a study leads to the global validation of good laboratory practices in terms
 16 of aerosol generation and measurement set-ups involving SMPS since Z score calculations for the average
 17 modal diameters measured by each SMPS for the four samples were comprised between -1 and 1. Such
 18 laboratory practices take into account the variation of technical parameters associated to the experimental
 19 set-up, environmental conditions and experimental operators.

20 As a perspective, new intercomparison studies will be organized on the measurement of the aerosol size
 21 distribution by involving optical (WRAS, WELAS, Dusttrack), aerodynamic (APS, ELPI, cascade
 22 impactors) and electrical mobility sizers (SMPS, FMPS, DMS, nanoscan ...) by sending a same
 23 transportable reference aerosol generator to each participant in the same way of the work performed by
 24 Gaie-Levrel et al. (2017) about particle mass concentration.
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1 **References:**

- 2 Asbach C, Kaminski H, Fissan H, Monz C, Dahmann D, Mülhopt S, Paur HR, Heinz JK, Herrmann F,
3 Voetz M, Kuhlbusch T (2009) Comparison of four mobility particle sizers with different time
4 resolution for stationary exposure measurements, *Journal of Nanoparticle Research* 11:1593–
5 1609.
6
7 Babick F, Mielke J, Wohlleben W, Weigel S, Hodoroaba V-D (2016a) How reliably can a material be
8 classified as a nanomaterial? Available particle-sizing techniques at work, *Journal of*
9 *Nanoparticle Research* 18(6).
10
11 Babick F, Mielke J, Hodoroaba V-D, Weigel S, Wohlleben W (2016b) Critical review manuscript with
12 real world performance data for counting, ensemble and separating methods including in-built
13 mathematical conversion to number distributions submitted for publication - NanoDefine
14 Technical Report D3.3, in NanoDefine.
15
16 Bau S, Witschger O, Gensdarmes F, Thomas D (2013). Determining the count median diameter of
17 nanoaerosols by simultaneously measuring their number and lung deposited surface area
18 concentrations, *J. Nanopart. Res.* 15, 2104.
19
20 Bau S, Toussaint A, Payet R, Witschger O (2017) Performance study of various Condensation Particle
21 Counters (CPCs): development of a methodology based on steady-state airborne DEHS particles
22 and application to a series of handheld and stationary CPCs, *Journal of Physics: Conference*
23 *Series*, IOP Publishing 838, pp.012002.
24
25 Bau S, Payet R, Tritscher T, Witschger O (2019). Intercomparison in the laboratory of various
26 Condensation Particle Counters challenged by nanoaerosols in the range 6 – 460 nm, *Journal of*
27 *Physics: Conference Series*, 1323 012004. doi:10.1088/1742-6596/1323/1/012004
28
29 Club nanoMétrologie, (2019) <http://www.club-nanométrie.fr>
30
31 Dahmann D, Riediger G, Schlatter J, Wiedensohler A, Carli S, Graff A, Grosser M, Hojgr M, Horn H-G,
32 Jing L, Matter U, Monz C, Mosimann T, Stein H, Wehner B, Wieser U (2001) Intercomparison
33 of Mobility Particle Sizers (MPS). *Gefahrstoffe-Reinhaltung der Luft* 61(10):423–428.
34
35 Ding YB, Stahlmecke B, Kaminski H, Jiang Y, Kuhlbusch TAJ, Riediker M (2016) Deagglomeration
36 testing of airborne nanoparticle agglomerates: Stability analysis under varied aerodynamic shear
37 and relative humidity conditions, *Aerosol Science and Technology* 50(11), pp1253-1263.
38
39 Fissan H, Hummes D, Stratmann F, Büscher P, Neumann S, Pui DYH, Chen D (1996) Experimental
40 comparison of four differential mobility analyzers for nanometer aerosol measurements, *Aerosol*
41 *Science and Technology* 24:1–13.
42
43 Fonseca AS, Viana M, Pérez N, Alastuey A, Querol X, Kaminski H, Todea AM, Monz C, Asbach C
44 (2016) Intercomparison of a portable and two stationary mobility particle sizers for nanoscale
45 aerosol measurements *Aerosol Science and Technology* 50:7,653-668, DOI:
46 10.1080/02786826.2016.1174329.
47
48 Franklin L, Bika A, Watts W, Kittelson D (2010) Comparison of Water and Butanol Based CPCs for
49 Examining Diesel Combustion Aerosols, *Aerosol Science and Technology*, 44:8, 629-638, DOI:
50 10.1080/02786826.2010.482112.
51
52 Fuchs NA (1963) On the stationary charge distribution on aerosol particles in abipolar ionic atmosphere,
53 *Pure and Applied Geophysics*, 56(1), 185–193.
54
55 Gaie-Levrel F, Bourrous S, Macé T (2017) Development of a Portable Reference Aerosol Generator
56 (PRAG) for calibration of particle mass concentration measurements, *Particuology*, 37, DOI:
57 10.1016/j.partic.2017.06.005.
58

- 1 Gómez-Moreno FJ, Alonso E, Artñano B, Juncal-Bello V, Iglesias-Samitier S, Piñeiro Iglesias M, López
2 Mahía P, Pérez N, Pey J, Ripoll A, Alastuey A, de la Morena BA, Rodríguez MIG, Sorribas M,
3 Titos G, Lyamani H, Alados-Arboledas L, Latorre E, Tritscher T, Bischof OF (2015)
4 Intercomparisons of Mobility Size Spectrometers and Condensation Particle Counters in the
5 Frame of the Spanish Atmospheric Observational Aerosol Network, *Aerosol Science and*
6 *Technology*, 49:777–785
7
- 8 Helsper C, Horn HG, Schneider F, Wehner B, Wiedensohler A (2008) Intercomparison of Five Mobility
9 Size Spectrometers for Measuring Atmospheric Submicrometer Aerosol Particles. *Gefahrstoffe*
10 *Reinhaltung der Luft.*, 68:475–481
11
- 12 ICRP (1994) Publication 66: Human respiratory tract model for radiological protection, Oxford:
13 Pergamon.
14
- 15 ISO 5725-2 (1994) Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic
16 method for the determination of repeatability and reproducibility of a standard measurement
17 method.
18
- 19 Jeong C-H, Evans GJ (2009) Inter-comparison of a fast mobility particle sizer and a scanning mobility
20 particle sizer incorporating an ultrafine water-based condensation particle counter, *Aerosol*
21 *Science and Technology* 43:364–373
22
- 23 Joshi M, Sapra BK, Khan A, Tripathi SN, Shamjad PM, Gupta T, Mayya YS (2012) Harmonisation of
24 nanoparticle concentration measurements using GRIMM and TSI scanning mobility particle
25 sizers, *Journal of Nanoparticle Research* 14, 1268-1281.
26
- 27 Kallinger P, Steiner G, Szymanski WW (2012) Characterization of four different bipolar charging devices
28 for nanoparticle charge conditioning, *Journal of Nanoparticle Research*, 14, 944-951.
29
- 30 Kaminski H, Kuhlbusch TAJ, Rath S, Götz U, Sprenger M, Wels D, Polloczek J, Bachmann V,
31 Dziurawitz N, Kiesling HJ, Schwegelsohn A, Monz C, Dahmann D, Asbach C (2013)
32 Comparability of mobility particle sizers and diffusion chargers, *Journal of Aerosol Science*, 57,
33 156-178.
34
- 35 Khlystov A, Kos GPA, ten Brink HM, Mirme A, Tuch T, Roth C, Kreyling WG (2001) Comparability of
36 Three Spectrometers for Monitoring Urban Aerosol, *Atmospheric Environment* 35:2045–2051.
37
- 38 Kulkarni P, Baron PA, Willeke K (Eds.) (2011) *Aerosol measurement: principles, techniques, and*
39 *applications*, John Wiley & Sons.
40
- 41 Lall AA, Friedlander SK (2006) On-line measurement of ultrafine aggregate surface area and volume
42 distributions by electrical mobility analysis: I. Theoretical analysis. *Journal of Aerosol Science*
43 37:260-271.
44
- 45 Lawrence MG, Butler TM, Steinkamp J, Gurjar BR, Lelieveld J (2007) Regional pollution potentials of
46 megacities and other major population centers, *Atmos. Chem. Phys.*, 7, 3969–3987,
47 doi:10.5194/acp-7-3969-2007.
48
- 49 Lee ES, Polidori A, Koch M, Fine PM, Mehadi A, Hammond D, Wright JN, Miguel AH, Ayala A, Zhu Y
50 (2013) Water-based condensation particle counters comparison near a major freeway with
51 significant heavy-duty diesel traffic, *Atmospheric Environment* 68 151e161
52
- 53 Leskinen J, Joutsensaari J, Lyyränen J, Koivisto J, Ruusunen J, Järvelä M, Jokiniemi J
54 (2012) Comparison of nanoparticle measurement instruments for occupational health
55 applications, *Journal of Nanoparticle Research*, 14(2), 718.
56
- 57 Motzkus C, Macé T, Gaie-Levrel F, Ducourtieux S, Delvallée A, Dirscherl K et al. (2013) Size
58 characterization of airborne SiO₂ nanoparticles with on-line and off-line measurement
59 techniques: an interlaboratory comparison study, *Journal of Nanoparticle Research* 15(10).
60

1 Nicosia A, Manodori L, Trentini A, Ricciardelli I, Bacco D, Poluzzi V, Di Matteo L, Belosi F (2018)
2 Field study of a soft X-ray aerosol neutralizer combined with electrostatic classifiers for
3 nanoparticle size distribution measurements, *Particuology* 37 99–106.
4

5 Nicosia A, Belosi F, Vazquez B (2014). Application of the soft X-Ray TSI advanced aerosol neutralizer
6 to aerosol measurements made by a Grimm SMPS, *Atmospheric and Climate Sciences* 4(4),
7 636–641.
8

9 R'Mili B, Le Bihan O, Dutouquet C, Aguerre-Chariol O, Frejafon E (2013) Particle Sampling by TEM
10 Grid Filtration, *Aerosol Science and Technology*, Taylor & Francis 47 (7), pp.767-775.
11

12 Rodrigue J, Dhaniyala S, Ranjan M, Hopke PK (2007) Performance comparison of scanning electrical
13 mobility spectrometers, *Aerosol Science and Technology* 41:360–368.
14

15 Stolzenburg MR, McMurry PH (2008). Equations governing single and tan-demDMA configurations and
16 a new lognormal approximation to the transfer function, *Aerosol Science and Technology*, 42(6),
17 421–432.
18

19 Tigges L, Wiedensohler A, Weinhold K, Gandhi J, Schmid H-J (2015) Bipolar Charge Distribution of a
20 Soft X-Ray Diffusion Charger, *Journal of Aerosol Science* 90:77–86.
21

22 Vedal S, Dutton SJ (2006). Wildfire air pollution and daily mortality in a large urban area, *Environ. Res.*
23 102, 29–35.
24

25 Watson JG, Chow JC, Sodeman DA, Lowenthal DH, Chang MCO, Park K, Wang X (2011) Comparison
26 of four scanning mobility particle sizers at the Fresno Supersite. *Particuology*, 9, 204-209.
27

28 Wiedensohler A, Wiesner A, Weinhold K, Birmili W, Hermann M, Merkel M, Müller T, Pfeifer S,
29 Schmidt A, Tuch T, Velarde F, Quincey P, Seeger S, Nowak A, (2017) Mobility particle size
30 spectrometers: Calibration procedures and measurement uncertainties, *Aerosol Science and*
31 *Technology*, 52: 146-164.
32

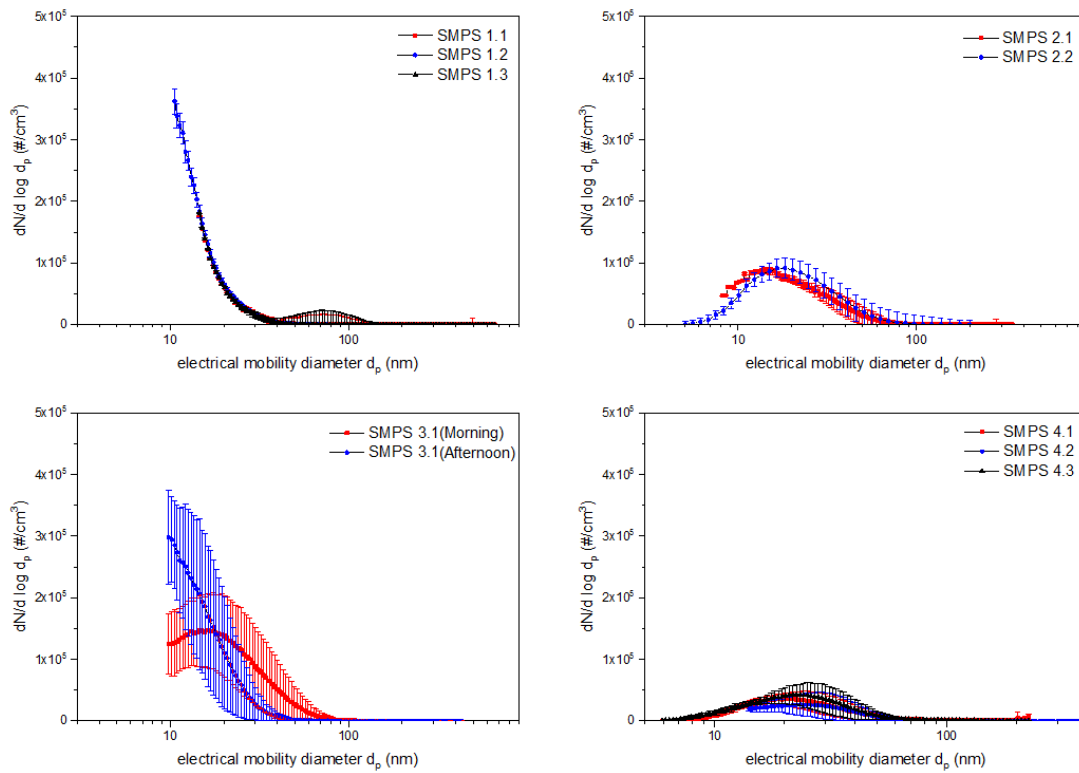
33 Wiedensohler A, Birmili W, Nowak A et al. (2012) Mobility particle size spectrometers: harmonization
34 of technical standards and data structure to facilitate high quality long-term observations of
35 atmospheric particle number size distributions, *Atmos Meas Technol* 5:657–685.
36

37 Wiedensohler A, Aalto P, Covert D, Heintzenberg J, McMurry P (1993) Intercomparison of three
38 methods to determine size distributions of ultrafine aerosols with low number concentrations, *J*
39 *Aerosol Sci* 24:551–554.
40

41 Wiedensohler A, Lütke-meier E, Feldpausch M, Helsper C (1986), Investigation of the Bipolar Charge
42 distribution at various gas conditions, *Journal of Aerosol Science*, 17:413.
43

44 Wiedensohler A (1988) Technical Note: An approximation of the Bipolar Charge distribution for
45 particles in the submicron range, *Journal of Aerosol Science*, 19:3/387-389.
46

1 Appendix:



2

3 Fig8: Average PNSD for aerosols generated from the water nebulization only, by each participant and
4 measured by each involved SMPS.