Supplemental Information for

Inkjet Aerosol Generator as Monodisperse Particle Number Standard

by

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S1: Coincidence Correction

Theory

This section describes the approach used to estimate the fraction of sampled particles whose scattered light was successfully recognized as a particle detection event by the OPC hardware used in this study. The fraction is denoted by a symbol $\eta_{OPC(II)}$ in the main article. The value of $\eta_{OPC(II)}$ is expressed as a ratio of indicated particle count rate, λ_{OPC} to the rate of aerosol particle exiting from the IAG, λ_{IAG} assuming that there are no transport losses inside the OPC.

$$\eta_{OPC(II)} = \frac{\lambda_{OPC}}{\lambda_{IAG}} \quad (S1)$$

If particle detection events follow a Poisson process the distribution of time between two consecutive particle detection events, which is hereafter called inter-particle time (IPT), is given by the exponential distribution.

$$\frac{dP}{dt} = \lambda_{IAG} \exp(-\lambda_{IAG} \cdot t), \quad (S2)$$

Where P is cumulative probability, and t is IPT. The OPC cannot detect the fraction of the distribution whose IPT is less than the internal deadtime of an OPC hardware t_d . Therefore, the ratio $\lambda_{OPC} / \lambda_{IAG}$ can be estimated by

$$\frac{\lambda_{OPC}}{\lambda_{IAG}} \approx \int_{t_d}^{\infty} \frac{dP}{dt} \cdot dt = \exp(-\lambda_{IAG} \cdot t_d) \quad (S3)$$

which is in a same form as a frequently used formula in aerosol research to perform coincidence correction of particle number concentration measured by OPCs or CPCs (Willeke and Liu 1976).

The value of t_d was about 50 μ s according to its manufacturer. Since the droplet generation rate was set at 100 droplets s^{-1} the value of $\lambda_{OPC} / \lambda_{IAG}$ would be 0.9950 if particle generation efficiencies up to the detection region were all unity. On the other hand, values of $\lambda_{OPC} / \lambda_{IAG}$ is unity if the IPT has a constant value at 0.01 s since there would be no particles detected during t_d . In order to

judge which of these two values should be used for $\lambda_{OPC} / \lambda_{IAG}$ the distribution of IPT was measured experimentally.

Comparison with Experiments

Figure S1 shows frequency distributions of the IPTs when NaCl particles were generated by the IAG. IPT bins of the distribution were normalized by the average of measured IPTs to visually compare distributions having slightly different average particle count rates.

Figure S1. Examples of the frequency distribution of the inter-particle time of the IAG-generated NaCl particles measured using a RION KC-01D1 OPC.

The distributions widened as particle size increased indicating that larger-sized NaCl particles were less evenly spaced with respect to positions along the axis when they were detected by the OPC. The exponential distribution can be rearranged into the following dimensionless form to compare it with measured values.

$$\frac{dP}{d \log \tilde{t}} = \tilde{t} \cdot \exp(-\tilde{t}) \cdot \ln 10, \quad (\text{S4})$$

where $\tilde{t}$ is the product of t and λ_{IAG} . When D_{ve} of the IAG generated particles were 8 μm the

distributions closely matched the exponential distribution indicating the particle detection process was a Poisson process.

In this study a particle detection process was considered as a Poisson process if the standard deviation of measured IPT distribution was close to the value predicted by the exponential distribution. The standard deviations of measured IPT distribution was obtained by

$$u(IPT) = \sqrt{\frac{\sum_i (t - \bar{t})^2 \cdot \Delta N}{\sum_i \Delta N}} \quad (S5)$$

Where ΔN is the number of particles in i th IPT bin. The value of $\bar{t}$ was approximated by the average of measured IPTs, which is the inverse of λ_{OPC} . The standard deviation of the exponential distribution was approximated by

$$u(EXP) = \lambda_{IAG}^{-1} \approx \lambda_{OPC}^{-1} \quad (S6)$$

Figure S2 show the value of $u(IPT)$ normalized by $u(EXP)$ as a function of D_{ve} when the aerosol flowrate of the IAG-OPC system and the particle material used were 0.5 L/min and NaCl, respectively. Particles sizes were varied over a decade ranging from 0.8 to 8 μm .

Figure S2. Ratios of the standard deviation of the inter-particle time (IPT) distribution to the standard deviation of the exponential distribution. Particle material and aerosol flowrates of the AIST-IAG were NaCl and 0.5 L/min, respectively.

When the size reached 8 μm the standard deviation of the IPT distribution was almost equal to that of a Poisson process. In this case a coincidence correction under a Poisson process was applied to a

measured particle count rate. In this study the coincidence correction was applied only when particle material was NaCl and the value of D_{ve} were equal or greater than 8 μm .

S2: Uncertainty of the mass concentration of the solute inside the inkjet solution.

Mass concentration of the solute C_m is defined as the mass of solute per mass of solution, and the mass was measured using a microbalance. (Mettler Toledo, XP-504DR). The expanded uncertainty of the microbalance written on the calibration certificate was ± 1.0 mg, accordingly, the RSU associated with one time measurement is estimated by ± 0.5 mg divided by the measured mass. The inkjet solution was prepared by a series of dilutions, and the dilution factor at each step was almost the same. The solute or the solution from the previous dilution step was added to a volumetric flask which is partially filled with ultrapure water. The added masses were always obtained by taking the difference between before and after the addition; therefore, the standard uncertainty of the microbalance $u(B)$ were included twice in the uncertainty expression of the added mass of the solute or the solution from the previous dilution step. The expression for the RSU of the C_m after i -th dilution, $\tilde{u}_{C_m}^{(i)}$, reduces to

$$\tilde{u}^{(i)}(C_m) = \sqrt{u^2(B) \left(\sum_{k=0}^i \frac{1}{(m_{total}^{(k)})^2} + 2 \left[\frac{1}{m_{solute}^2} + \sum_{k=1}^i \frac{1}{(m_{solution}^{(k-1)})^2} \right] \right)} \quad (S7)$$

It is noted that $i = 0$ corresponds to the step when a solute (NaCl or EMI-TFMS) is added to make the original solution. The symbol $m_{total}^{(k)}$ is the total mass of the solution after k -th dilution was completed, m_{solute} is the solute mass (NaCl or EMI-TFMS) added to make the original solution, and $m_{solution}^{(k-1)}$ is the mass taken from the solution made in the previous dilution step. For example, $m_{solution}^{(0)}$ is the mass of the original solution added at the first dilution step. The presence of the summation in the expression tells that the RSU of C_m increases as C_m decreases since more dilution steps are required.

S3: Analysis of variance (ANOVA)

This section explains how the results of ANOVA were processed when the variations of the rate of particles exiting the IAG λ_{IAG} and the average mass of a droplet generated by the inkjet head m_d were analyzed.

The rate of particles exiting the IAG, λ_{IAG}

As already described in Section 3.1.1. the variations of λ_{IAG} across three elements were considered and evaluated: particle diameters, experiments performed on different day, and continuously repeated measurements within a relatively short time. The input matrix of the λ_{IAG} consisted of three dimensions: seven particle sizes, five days of measurements, and fourteen times of continuously repeated measurements. Table S1 shows the results of ANOVA.

Table S1. Analysis of variance (ANOVA) of λ_{IAG} , which is the rate of particles exiting the AIST-IAG, when the droplet generation rate and aerosol flowrate of AIST-IAG were 100 s^{-1} and 0.5 LPM , respectively

Source of variation	Sum of squares, $(\text{s}^{-1})^2$	Degrees of freedom	Mean square $(\text{s}^{-1})^2$	Expectation of mean square
Particle diameter, [D]	18.4932	6	3.0822	$\sigma_e^2 + 14\sigma_{D \times dd}^2 + 70\sigma_D^2$
Day-to-day, [dd]	3.6530	4	0.9133	$\sigma_e^2 + 14\sigma_{D \times dd}^2 + 98\sigma_{dd}^2$
Interactions, [D $\times$ dd] (replicability)	6.8404	24	0.2850	$\sigma_e^2 + 14\sigma_{D \times dd}^2$
(Pooled replicability [dd'])	(10.4934)	(28)	(0.3748)	$(\sigma_e^2 + 14\sigma_{dd'}^2)$
Error [e] (repeatability)	9.4734	455	0.0208	σ_e^2
Total	38.4600	489		

In the rightmost column of the table, the symbols σ_e^2 , σ_D^2 , σ_{dd}^2 , and $\sigma_{D \times dd}^2$ denote, respectively, population variances of the effects of error [e], particle diameter [D], measurements performed on different days [dd], and interaction between [D] and [dd], [D $\times$ dd]. The 'error' is a terminology used in ANOVA and includes a repeatability of measurements and other random effects not accounted in the analysis. Values of mean squares, which are given in the second column from the right, are expected to be the expressions given in the rightmost column. Standard deviations of

the population with respect to [e], [D], [dd], and [D × dd] were calculated by

$$\sigma_e = \sqrt{V_e} = 0.1443 \text{ s}^{-1} \quad (\text{S8a})$$

$$\sigma_{D \times dd} = \sqrt{\frac{V_{D \times dd} - V_e}{14}} = 0.1374 \text{ s}^{-1} \quad (\text{S8b})$$

$$\sigma_{dd} = \sqrt{\frac{V_{dd} - V_{D \times dd}}{98}} = 0.0801 \text{ s}^{-1} \quad (\text{S8c})$$

$$\sigma_D = \sqrt{\frac{V_D - V_{D \times dd}}{70}} = 0.1999 \text{ s}^{-1} \quad (\text{S8d})$$

where the letter V represents the mean square of each parameter. There was an appreciable amount of interaction between [D] and [dd] indicating that size dependence of the λ_{IAG} had some day-to-day variations. The value of σ_{dd} was the smallest indicating that particle generation efficiencies of the IAG at a fixed particle diameter was reproducible over different days. In order to carry out a concise analysis [dd] and [D × dd] were pooled and expressed as an overall daily variation, [dd'].

$$V_{dd'} \equiv \frac{4 \cdot V_D + 24 \cdot V_{D \times dd}}{28} \quad (\text{S9a})$$

$$\sigma_{dd'}^2 \equiv \sigma_{dd}^2 + \sigma_{D \times dd}^2 \quad (\text{S9b})$$

Standard deviation of the population across [dd'] was calculated by

$$\sigma_{dd'} = \sqrt{\frac{V_{dd'} - V_e}{14}} = 0.1590 \text{ s}^{-1}. \quad (\text{S10})$$

Finally, the coefficients of variation were estimated by normalizing the standard deviations by the average among all data, $\bar{\lambda}_{IAG}$, which was 99.878 s^{-1} , to obtain the coefficient of variations of the particle generation efficiencies given in Table 1

$$\tilde{u}_D(\lambda_{IAG}) \approx \frac{\sigma_D}{\bar{\lambda}_{IAG}} = 0.00200, \quad (\text{S11a})$$

$$\tilde{u}_{dd}(\lambda_{IAG}) \approx \frac{\sigma_{dd'}}{\bar{\lambda}_{IAG}} = 0.00159, \quad (\text{S11b})$$

$$\tilde{u}_{\text{repeat}}(\lambda_{IAG}) \approx \frac{\sigma_e}{\bar{\lambda}_{IAG}} = 0.00144. \quad (\text{S11c})$$

It is noted that the 'error' term in the ANOVA was interpreted as a random variation across continuously repeated measurements.

Average mass of a droplet, m_d

As already described in Section 3.3.1., the input matrix for the ANOVA consisted of the two solute types, three solute concentrations, and five repeated measurements. Solute concentrations were expressed as volume equivalent diameter. Table S2 shows the results of ANOVA.

Table S2. Analysis of variance (ANOVA) of measured average mass of droplets

Source of variation	Sum of squares, $(\times 10^{-12} \text{ kg})^2$	Degrees of freedom	Mean square $(\times 10^{-12} \text{ kg})^2$	Expectation of mean square
Particle Size, [D]	2.9077	1	2.9077	$\sigma_e^2 + 5\sigma_{D \times S}^2 + 15\sigma_D^2$
Solute type, [S]	23.7116	2	11.8558	$\sigma_e^2 + 5\sigma_{D \times S}^2 + 10\sigma_S^2$
Interactions, [D $\times$ S]	51.6657	2	25.8328	$\sigma_e^2 + 5\sigma_{D \times S}^2$
Error [e] (repeatability)	40.7209	24	1.6967	σ_e^2
(Pooled repeatability [e'])	(67.3402)	(27)	(2.4941)	$(\sigma_{e'}^2)$
Total	119.0058	29		

In the rightmost column of the table, the symbols σ_e^2 , σ_D^2 , σ_S^2 , and $\sigma_{D \times S}^2$ denote, respectively, the population variances of the effects of error [e], particle diameter [D], solute type [S], and interaction between [D] and [S], [D $\times$ S]. Mean squares of [D] and [S] turned out to be larger than [D $\times$ S] indicating that the analysis could not detect finite variations across particle sizes at a fixed solute type and across solutes at fixed particle size since the size dependence of m_d had a much stronger variation across different solute types. In this study the effects of [D] and [S] were unphysical; therefore, these two effects were pooled into [e] and considered as a part of a variation over repeated measurements. The pooled error [e'] is given at second row from the bottom in the table.

$$V_{e'} \equiv \frac{V_D + 2V_S + 24V_e}{27} \quad [\text{S12}]$$

The standard uncertainty of m_d due to interactions between [D] and [S], $u_{\text{Size} \times \text{Solute}}(m_d)$, and the error, $u_{\text{repeat}}(m_d)$, were estimated by

$$u_{\text{Size} \times \text{Solute}}(m_d) \approx \sigma_{D \times S} = \sqrt{\frac{V_{D \times S} - V_{e'}}{5}} = 2.1605 \times 10^{-12} \text{ kg}, \quad [\text{S13a}]$$

$$u_{\text{repeat}}(m_d) \approx \sigma_{e'} = \sqrt{V_{e'}} = 1.5793 \times 10^{-12} \text{ kg}. \quad [\text{S13b}]$$

It is noted that the ‘error’ term in the ANOVA was interpreted as a random variation across repeated measurements. The values of $u_{\text{Size}\times\text{Solute}}(m_d)$ and $u_{\text{repeat}}(m_d)$ were normalized by the average m_d among all data, which was 35.1563×10^{-12} kg to obtain relative standard uncertainties

$$\tilde{u}_{\text{Size}\times\text{Solute}}(m_d) \equiv \frac{u_{\text{Size}\times\text{Solute}}(m_d)}{\bar{m}_d} = 0.0609 \quad [\text{S14a}]$$

$$\tilde{u}_{\text{repeat}}(m_d) \equiv \frac{u_{\text{repeat}}(m_d)}{\bar{m}_d} = 0.0445. \quad [\text{S14b}]$$

REFERENCE

Willeke, K. and Liu, B. Y. (1976). Single Particle Optical Counter: Principle and Application, in *Fine Particles*, B. Y. Liu, ed., Academic Press, Inc., 697.