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Supplement of

An instrument for the rapid quantification of PM-bound ROS: the Particle Into Nitroxide Quencher (PINQ)

Reece A. Brown et al.

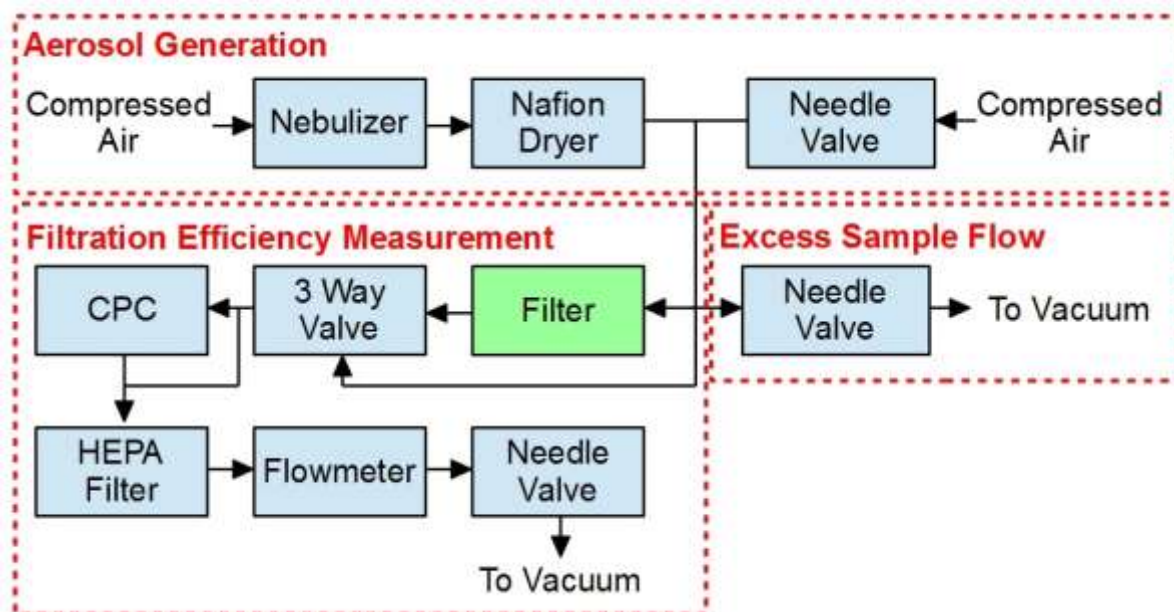
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Supplementary Material (SM) For:

An instrument for the rapid quantification of PM-bound ROS: the Particle Into Nitroxide Quencher (PINQ)

S1. Filter Collection Efficiency



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Figure S1 Flow diagram of setup used to measure the collection efficiency of the filters used in the IAC mass characterization. Aerosol generation stage is identical to the setup used in the characterization experiments. Aerosol is generated through a nebulizer and dried with a nafion dryer. Makeup air at a flowrate dilutes the aerosol sample to provide similar particle number concentrations to the mass collection efficiency studies. Excess sample flow is removed using vacuum line regulated by a needle valve. CPC was used to measure particle concentrations before and after the filter by way of a 3-way valve. CPC exhaust was connected to a CPC bypass flow which is filtered, measured with a flowmeter and regulated by a needle valve to vacuum to maintain the same filter sample flowrate used in mass collection efficiency studies.

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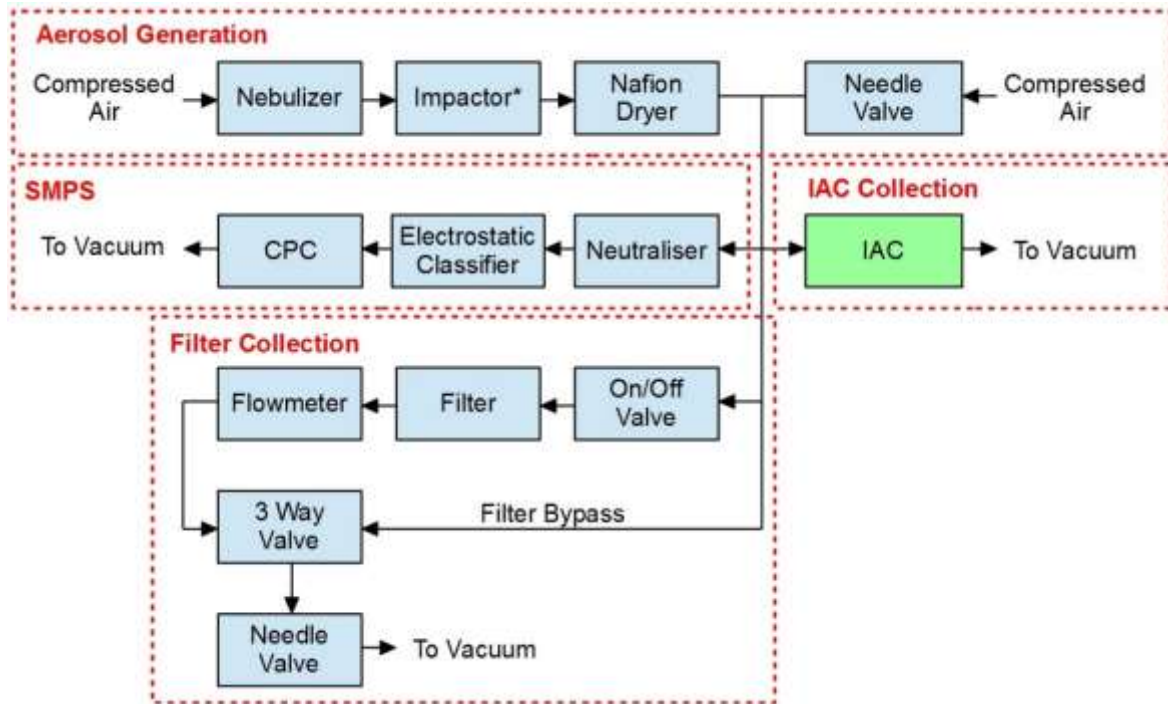
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The filter collection efficiency was measured through the measurement of ammonium sulphate particle number concentrations before and the filter (Whatman Nuclepore polycarbonate membrane, 25 mm diameter, 0.2 μm pore size). The setup was made using the same aerosol generation stage as described in Sect. 3.1.1. to ensure comparable aerosol properties. A 5 g.L^{-1} solution of ammonium sulphate in water was dispersed using a multi-jet nebulizer (Mesa Labs 6 Jet Collision Nebulizer). The generated aerosol was dried using a nafion dryer and mixed with a dry, HEPA-filtered makeup air with the same flowrate as used in Sect. 3.1.1. to ensure the same dilution was achieved. Excess sample aerosol was removed using a vacuum line regulated through a needle valve. A 3 way valve was used to alternate between flowing through the filter, and bypassing it. The resulting aerosol particle number concentration was measured using a TSI 3025 CPC. The exhaust of the CPC was connected to a bypass line to a needle valve running to vacuum in order to regulate the total flow through the filter to 5 L.min^{-1} . The flowrate was measured for each sample using a TSI 4043 mass flow meter to account for any dilution changes. 10 samples before and after the filter were taken. The collection efficiency of the filters (CE_f) was calculated as:

$$CE_f = 1.000 \pm 0.009$$

S2. Mass Collection Efficiency

S2.1 Mass Collection Efficiency Methodology



5 *Figure S2 Flow diagram of experimental setup for particle mass collection efficiency investigation. Aerosol is generated through a nebulizer and dried with a nafion dryer. *Impactor is installed to remove large particles for ultrafine particle ($PM_{0.1}$) collection experiments. Makeup air dilutes the aerosol sample to provide sufficient sample flowrate for the setup. The corresponding aerosol sample is split between the SMPS, IAC and filter. Filter collection contains a bypass flow enabling filters to be installed and replaced without disrupting flow conditions in the setup.*

10 *Figure S2 provides a detailed description of the experimental setup used to investigate the mass collection efficiency of the IAC for both fine ($PM_{2.5}$) and ultrafine ($PM_{0.1}$) particles discussed in Sect. 3.1.1. A 5 g.L^{-1} solution of ammonium sulphate in water was dispersed using a multi-jet nebulizer (Mesa Labs 6 Jet Collision Nebulizer). The generated aerosol was dried using a nafion dryer and mixed with a dry, HEPA-filtered makeup air to provide the required combined sample flowrate. The sample aerosol was then split three ways to the PINQ, filter*
 15 *(Whatman Nuclepore polycarbonate membrane, 25 mm diameter, $0.2 \mu\text{m}$ pore size), and SMPS (TSI 3071 Classifier, TSI 3772 Condensation Particle Counter, Aerosol Instrument Manager (AIM) software).*

The filter sample rate was nominally set to 5 L.min^{-1} using a needle valve and monitored throughout the sample with a TSI 4043 mass flow meter. The IAC aerosol flowrate was set to 16.7 L.min^{-1} , and a 1.5 mL.min^{-1} water flow was input into the steam generator using a peristaltic pump.

20 The IAC relies on condensational growth to successfully capture ultrafine particles into liquid. A consequence of this is that a certain amount of water will dilute the liquid sample exiting the base of the vortex collector, due to both: the collection of grown water droplets containing ultrafine particles for analysis; and the condensation of water inside the cyclone due to the excess supersaturation required to grow hydrophobic ultrafine particles. In order to correct for this effect a 0.5 g.L^{-1} solution of sodium chloride in deionized water was prepared for use as
 25 the liquid sample flow in the IAC. The chloride ion concentrations of each sample were measured before and after each sample, and a correction referred to as the steam dilution factor (SDF) was calculated using *Equation S1*.

Equation S1

$$SDF = \frac{C_{Cl^-}(\text{sample})}{C_{Cl^-}(\text{supply})}$$

Where: $C_{Cl^-}(\text{sample})$ is the chloride ion concentration in ppm of the collected sample which has been diluted by condensed steam from the aerosol; and $C_{Cl^-}(\text{supply})$ is the chloride ion concentration in ppm of the initial sample liquid.

5 Fine (PM_{2.5}) samples were collected without the impactor in the setup detailed in *Figure S2*. A 1 mL.min⁻¹ flowrate regulated by a peristaltic pump was set for both the collection liquid entering into the vortex collector and the sample liquid exiting. Eight filter samples with corresponding simultaneous IAC samples were taken over 15 minutes. SMPS size distribution scans with a three minute scan time were taken continuously throughout the experiment.

10 Ultrafine (PM_{0.1}) samples were collected with an impactor (TSI, 0.0508 cm nozzle size) in front of the nebulizer as in the setup detailed in *Figure S2*. The purpose of the impactor was not to generate a sharp cut-off at 100nm corresponding to ultrafine size range boundary, but to make the resultant size distribution as small as possible so that the mass distributions were predominantly in the ultrafine range. Placing the impactor before the dryer lowered the effective cut-off size as the particles would shrink further during drying, enhancing this effect. The cut-off size can be estimated as ~74 nm based on the logistic function portion of the fitted curve for the particle size distribution with the impactor present (See *Figure S4*).

15 Due to the significantly reduced mass of these samples generated by the removal of larger particles, the sampling methodology was altered to ensure a detectable result. The collection liquid and sample liquid flows entering and exiting the vortex collector were reduced to 0.15 mL.min⁻¹. This significantly increased the concentration of aerosol in the IAC sample liquid at the expense of a higher steam dilution effect. Furthermore, the collection time for samples was extended to 60 min to increase the aerosol mass deposited on the filters.

S2.2. Mass Collection Efficiency Calculations

The sulphate mass collected for each IAC sample (M_{IAC}) in mg was calculated through *Equation S2*.

Equation S2

$$M_{IAC} = \frac{CI_{SO_4^{2-}}}{SDF} * T * q_{ls} * \rho_{water}$$

25 Where: $CI_{SO_4^{2-}}$ is the sulphate concentration of the IAC sample in ppm; SDF is the steam dilution factor of the sample; T is the sample period in minutes; q_{ls} is the liquid sample flowrate in L.min⁻¹; and ρ_{water} is the density of water in g.L⁻¹.

The sulphate mass collected for each filter sample (M_f) in mg was calculated through *Equation S3*.

Equation S3

$$30 \quad M_f = CF_{SO_4^{2-}} * V_l * \rho_{water}$$

Where: $CF_{SO_4^{2-}}$ is the sulphate concentration of the filter sample in ppm; V_l is the volume of liquid used in the filter extraction in L.

The collection efficiency (CE) of each sample was calculated using *Equation S4*.

Equation S4

$$35 \quad CE = \frac{M_{IAC}}{\frac{M_f}{V_f * CE_f} * V_{IAC}}$$

Where: V_f is the air volume sampled by the filter in L; CE_f is the collection efficiency of the filter; and V_{IAC} is the air volume sampled by the IAC.

S2.3. Mass Collection Efficiency Data

The data presented here was used to calculate the final values shown in Sect. 4.1.1. of the manuscript.

Whilst ammonium sulphate tends towards sphericity at small sizes, a dynamic shape factor of 1.02 can be used to correct for a minor aspherical variations (Biskos et al., 2006). In this circumstance applying this factor will negligibly alter the calculations of the percentage of mass in the ultrafine region, as the error margins of the fitted curves are significantly higher than this effect. Hence, to avoid needlessly complicating the analysis the aerosol here is considered to be approximately spherical.

As the collection efficiency calculated using the results of this section are for mass collection, it is important to consider the particles in terms of their mass rather than number distributions. To achieve this, the particle size distributions were fitted with log normal curves of the form given in Equation S5 using the Matlab curve fitting toolbox.

Equation S5

$$N = ae^{\left(\frac{\ln(D)-\ln(b)}{c}\right)^2}$$

Where: N is the number concentration; D is particle diameter; and a, b and c are the fitted coefficients.

To convert the fitted number distributions to mass distributions, the particles were assumed to be spherical and homogenous. This resulted in the mass distribution curve of the form shown in Equation S6.

Equation S6

$$M = ae^{\left(\frac{\ln(D)-\ln(b)}{c}\right)^2} * \frac{4}{3}\pi\left(\frac{D}{2}\right)^3 * \rho$$

Where: M is particle mass; and ρ is particle density.

The averaged SMPS particle size distribution of the ammonium sulphate PM_{2.5} aerosol sample was fitted with a log-normal distribution and a corresponding mass distribution calculated as shown in Figure S3. The ultrafine particles (PM_{0.1}) correspond to approximately 3 % of the total mass of the sample, whilst the entire mass distribution was in the fine particle size range (PM_{2.5}).

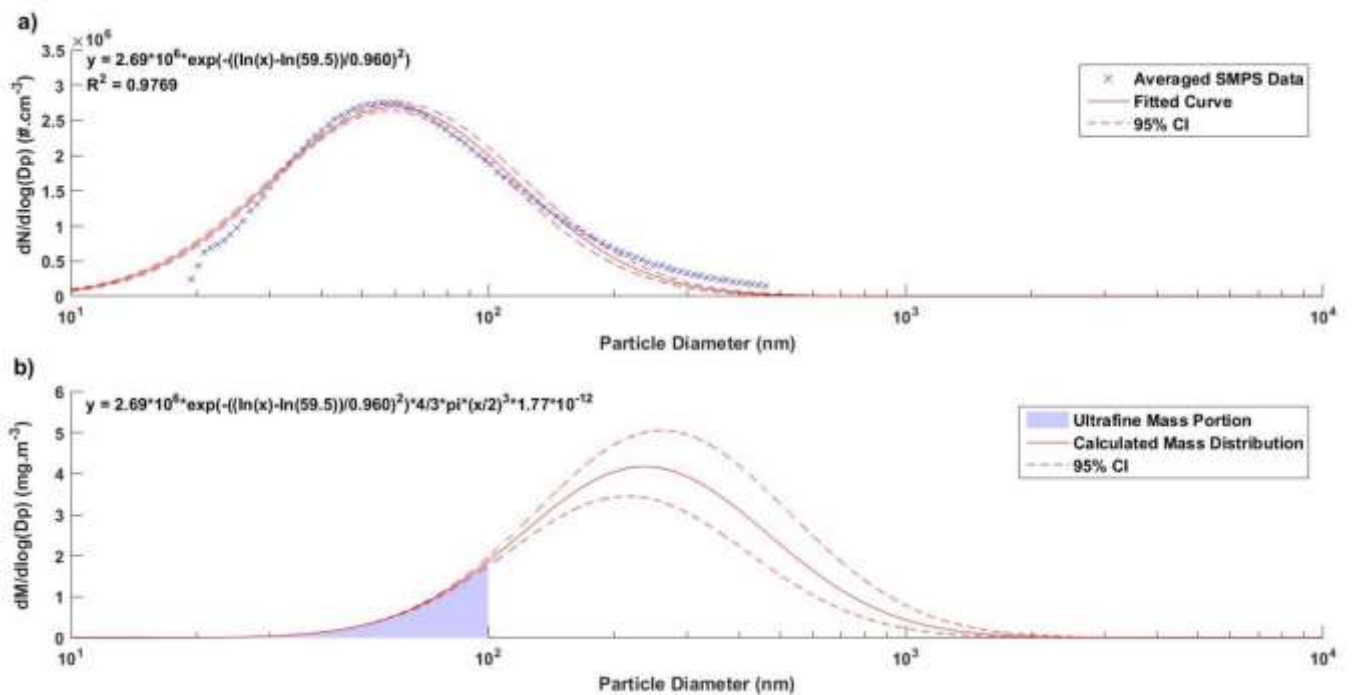


Figure S3 a) is a graph of the averaged SMPS data for the fine particle concentration measurements and a fitted log-normal distribution with 95 % confidence intervals and an R² value of 0.9769. b) shows the calculated mass distribution curve with 95 % confidence intervals. The ultrafine mass portion is shaded, corresponding to ~3% of the total mass.

When an impactor was used to remove larger particles the size cut-off was modelled using a logistic function. Therefore, the fitted number distribution took the form of Equation S7.

Equation S7

$$N = ae^{\left(\frac{\ln(D)-\ln(b)}{c}\right)^2} * \frac{1}{1 + e^{d(x-f)}}$$

5 Where: d and f are fitted coefficients.

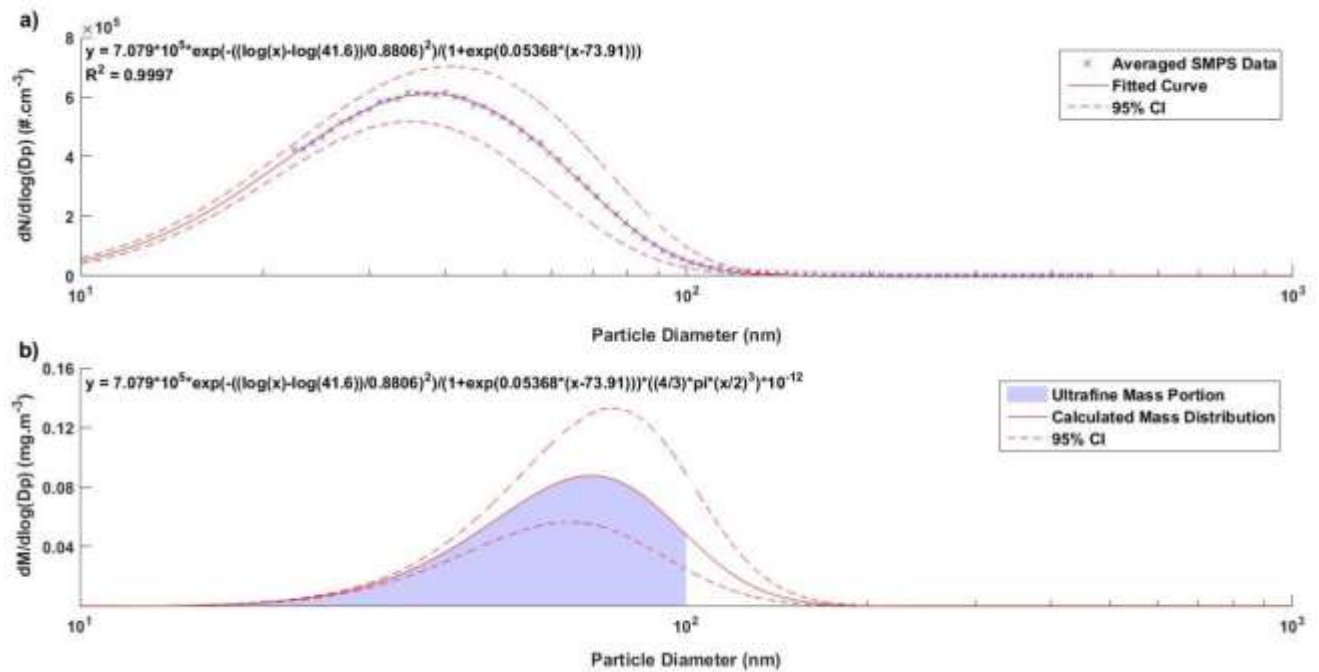
As with the previous distributions, to convert the fitted number distributions to mass distributions the particles were assumed to be spherical and homogenous. This resulted in the mass distribution curve of the form shown in Equation S8.

Equation S8

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$$M = ae^{\left(\frac{\ln(D)-\ln(b)}{c}\right)^2} * \frac{1}{1 + e^{d(x-f)}} * \frac{4}{3}\pi \left(\frac{D}{2}\right)^3 * \rho$$

The averaged SMPS particle size distribution of the ammonium sulphate PM_{0.1} aerosol sample was fitted with a log-normal distribution and multiplied by a logistic function to emulate the size cut-off generated by the impactor. This distribution and a corresponding calculated mass distribution is shown in Figure S4. The ultrafine particles (PM_{0.1}) correspond to approximately 80 % of the total mass of the sample.



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Figure S4 a) The averaged particle number size distribution collected by the SMPS for the ultrafine particle measurements and a fitted log-normal distribution with a logistic function with 95 % confidence intervals and an R² value of 0.9997. b) shows the calculated mass distribution curve from the fitted number concentration distribution with 95 % confidence intervals. The ultrafine mass portion is shaded, corresponding to ~80% of the total mass.

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The sample data used to calculate the results presented in Sect. 4.1.1. for the fine mass collection efficiency are shown below in Table S1.

Sample No.	T (min)	q_{Is} (mL.min ⁻¹)	V_{IAC} (L)	V_f (L)	$CI_{SO_4^{2-}}$ (ppm)	$CF_{SO_4^{2-}}$ (ppm)	SDF	CE
1	15.0	0.966	247	68.1	27.00	124.1	0.88	0.99
2	15.0	0.966	247	69.0	26.99	127.8	0.88	0.98
3	15.0	0.966	247	60.0	30.18	114.8	0.89	1.05
4	15.0	0.966	247	53.7	31.61	113.9	0.88	1.00
5	15.0	0.966	247	59.1	33.48	133.8	0.88	0.99
6	15.0	0.966	247	52.3	36.36	120.7	0.89	1.04
7	15.0	0.966	247	63.1	39.10	159.4	0.89	1.02
8	15.0	0.966	247	63.7	39.47	177.6	0.86	0.97

Table S1 shows the sample time (T), liquid sample flowrate (q_{Is}), total IAC sample volume (V_{IAC}), total filter sample volume (V_f), concentration of sulphate ions in IAC sample ($CI_{SO_4^{2-}}$); concentration of sulphate ions in filter sample ($CF_{SO_4^{2-}}$); Steam Dilution Factor (SDF); and calculated collection efficiency (CE)

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The sample data used to calculate the results presented in Sect. 4.1.1. for the ultrafine mass collection efficiency are shown below in Table S2.

Sample No.	T (min)	q_{Is} (mL.min ⁻¹)	V_{IAC} (L)	V_f (L)	$CI_{SO_4^{2-}}$ (ppm)	$CF_{SO_4^{2-}}$ (ppm)	SDF	CE
1	60.0	0.128	247	274.4	1.64	8.44	0.53	1.01
2	60.0	0.128	247	281.6	1.76	9.31	0.51	1.03
3	60.0	0.128	247	284.5	2.21	10.47	0.54	1.09

Table S2 shows the sample time (T), liquid sample flowrate (q_{Is}), total IAC sample volume (V_{IAC}), total filter sample volume (V_f), concentration of sulphate ions in IAC sample ($CI_{SO_4^{2-}}$); concentration of sulphate ions in filter sample ($CF_{SO_4^{2-}}$); Steam Dilution Factor (SDF); and calculated collection efficiency (CE)

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S3. Size Dependent Collection Efficiency

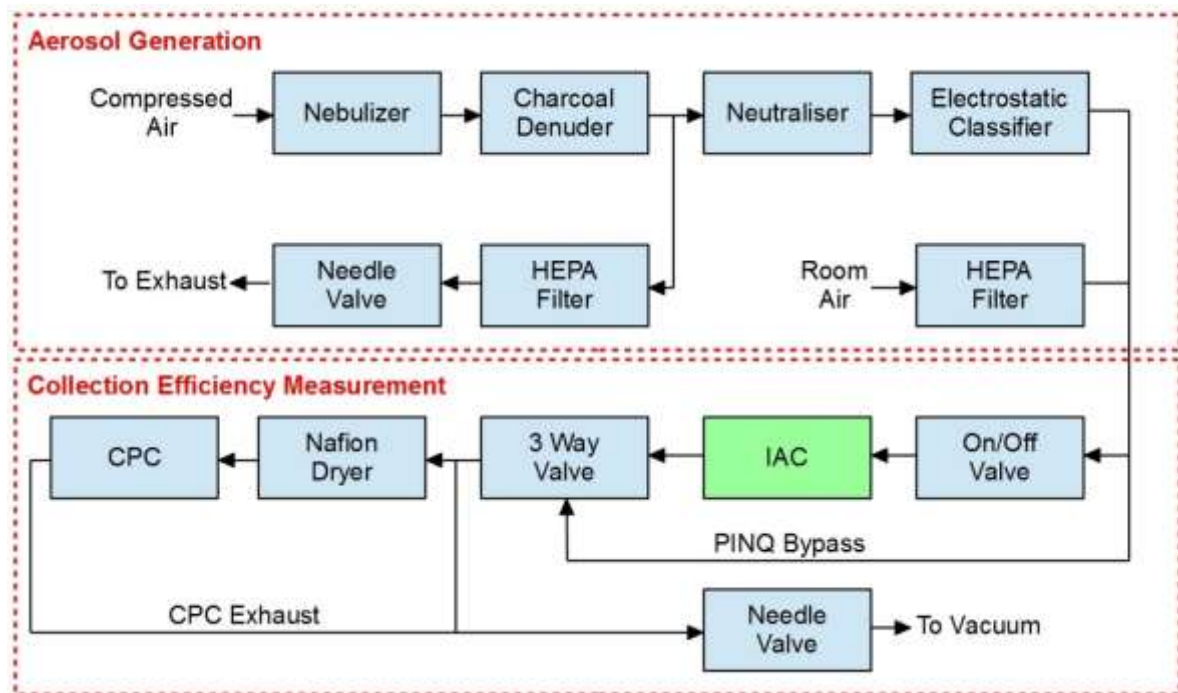


Figure S5 Flow diagram of experimental setup for size dependent collection efficiency experiments. DEHS aerosol is generated through a nebulizer and scrubbed of excess ethanol vapour using a charcoal denuder. Particles are size selected using electrostatic classifier, with classifier aerosol flowrate regulated by the removal of excess aerosol via a filtered needle valve upstream. Monodisperse aerosol sample is mixed with filtered makeup air to generate required sample flowrate. CPC measures PNC before and after the IAC using a bypass flow controlled by a 3-way valve. On/off valve is used to prevent steam backflow into CPC sample when IAC is bypassed. CPC exhaust is connected to the excess flow out of the 3-way valve to prevent pressure differentials in instrument. Sample flowrate is regulated by a needle valve connect to vacuum.

Figure S5 shows a flow diagram of the experimental setup discussed in Sect. 3.1.2 of the manuscript.

The collection efficiency for particles of size d_i was calculated using Equation S9:

Equation S9

$$CE(d_i) = \frac{(1 - CL)C_{in}(d_i) - C_{out}(d_i)}{C_{in}(d_i)}$$

Where: d_i is the particle diameter; $CE(d_i)$ is the number collection efficiency at particle diameter d ; $C_{in}(d_i)$ is the particle number concentration entering the IAC at particle diameter d ; $C_{out}(d_i)$ is the particle number concentration exiting the IAC at particle diameter d_i ; and CL is the chamber losses defined as:

Equation S10

$$CL = 1 - CE_{ultrafine}$$

Where: $CE_{ultrafine}$ is the lower limit of the mass collection efficiency of the ultrafine particle size distribution.

S4. PINQ Characterization

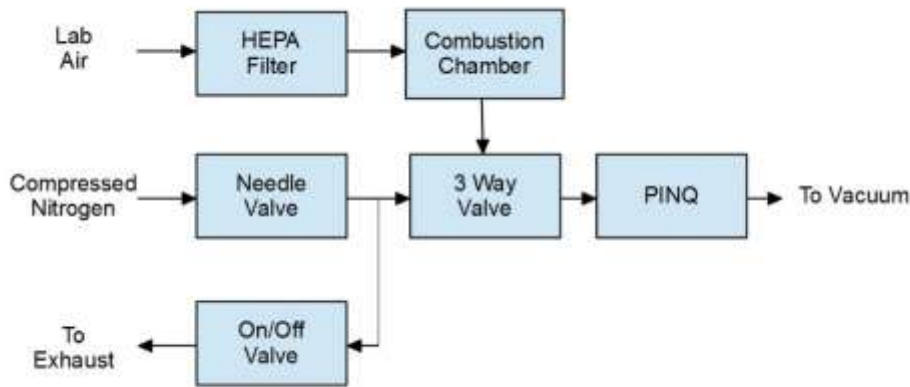


Figure S6 Flow diagram of the experimental setup for measuring the response time of the instrument. A 3-way valve was periodically used to switch between the combustion chamber source and nitrogen. A HEPA filter was attached to the inlet of the combustion chamber which was left open to lab air to prevent the combustion chamber from dropping below ambient pressure. A needle valve was used to regulate the flow of nitrogen to be slightly in excess of the PINQ sample rate, with the excess being removed via an exhaust line to ensure the PINQ sampled at ambient pressure. An on/off valve was used to shut off the nitrogen exhaust flow whilst the combustion chamber was being sampled.

Figure S6 shows a flow diagram of the experimental setup described in Sect. 3.2 of the manuscript.

S5. References

Biskos, G., Paulsen, D., Russell, L. M., Buseck, P. R. and Martin, S. T.: Prompt deliquescence and efflorescence

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