Evaluation of concentration measurement techniques of colloidal nanoparticles for microfiltration and ultrafiltration applications: Inductively coupled plasma-mass spectrometry, nanoparticle tracking analysis and electrospray-scanning mobility particle sizer

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ABSTRACT

Three different liquid-borne particle concentration measurement methods, including the inductively coupled plasma-mass spectrometry (ICP-MS), nanoparticle tracking analysis (NTA) and electrospray-scanning mobility particle sizer (ES-SMPS), for determining the efficiency of liquid filtration were investigated and compared for their applicability and feasibility. These methods were first calibrated using commercial Au monospheres with various sizes from 5 to 50 nm and several sizes of NIST traceable polystyrene latex (PSL) from 20 to 125 nm. Calibration results showed that the prepared concentrations of liquid-borne particles according to that

provided by the manufacturers were proportional to the concentrations measured by all these methods. The calibration results were then used to determine the filtration efficiencies of Au and PSL nanoparticles through the 0.1 μm pore diameter polycarbonate track-etched (PCTE or Nuclepore filter) membrane filters, which were performed as the dead-end type filtration. It was found that the filtration efficiencies obtained by different measurement methods under the same condition were comparable with each other. The results of this study provide a very useful guidance in selecting the proper method for liquid-borne particle filtrations under different circumstances.

Keywords: Microfiltration; Ultrafiltration; Inductively coupled plasma-mass spectrometry; Nanoparticle tracking analysis; Electrospray-scanning mobility particle sizer; Particle size distribution

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1. Introduction

Due to the boundless potential of nanotechnology, great investments are being made to support the nanotechnology research and development [1,2]. There is a variety of different areas associated with nanotechnologies, e.g., semiconductor, chemical engineering, pharmaceutical, biomedical, energy and environmental applications [3-10]. As the world spurs the development of nanotechnologies, enormous benefits from nanomaterials are discovered but new hazards from nanosized materials may be created and then expose human and environment to health risks [11-14]. Therefore, efforts are needed to remove the nanomaterial contaminants emitted and discharged from different sources [15-18]. For example, researchers have been investigating the release of commercial engineered nanoparticles into various aqueous environments, e.g., groundwater, surface water and synthetic freshwater. Typically, special attentions have been paid on nanoparticle removal for drinking water sources and wastewater discharges from nanotechnology factories [19-23].

Membrane technique has been considered as one of effective and energy-efficient method for removing liquid-borne nanoparticles in various aqueous environments [24-26]. For example, it has been widely applied in semiconductor industries to minimize the negative effects from exposing their products to nanoparticle contaminations during the manufacturing to raise the yield rate. Especially, due to the reduced feature size of circuit components being down to sub-10 nm, high-quality and particle-free process liquids including water and chemicals are more and more in demand. Therefore, many researches have been devoted to study membrane filtration for these important motivations [4,27,28]. In addition to semiconductor industries, in recent few years, drinking water and wastewater plants started applying membrane process as the core

method to replace the traditional treatments [29-31]. Therefore, the importance of membrane filtration in the coming years is expected.

Conventionally, the performance of membrane was rated based on their pore size. However, it has been found pore size alone cannot give a good indication of the quality of membranes [32-35]. Therefore, the most effective way to evaluate the filtration performance is to systematically perform filtration experiments to obtain their retention efficiencies against particles with different sizes. However, there is a lack of research which provides a simple guideline for one to select the most proper method to accurately determine the membrane filtration efficiency, $E(d_x)$, from the measurements of upstream (C_{up}) and downstream (C_{down}) particle concentrations of the membrane filters. The filtration efficiency is calculated as:

$$E(d_x) = 1 - \frac{C_{down}(d_x)}{C_{up}(d_x)} \quad (1)$$

where d_x is particle size. Besides, the comparison of different methods to examine their applicability for adapting different filtration conditions, such as different particle sizes, different concentrations as well as different materials of the challenging particles was also not available. One important issue should be mentioned is if the nanoparticle removal efficiency of the membrane is not accurately determined, environmental aqueous system may be exposed to high risk. For example, an effective removal of nanoparticles from wastewater discharge stream of nanotechnology and semiconductor manufacturing factories should be secured, especially those containing heavy metals, e.g. CMP (Chemical Mechanical Planarization) and nanofabrication processes [36,37], is very important because a strong correlation between negative health effects by the nanoparticles with their number and surface concentration has been found although their mass concentrations may be remained low [12].

In the following, available methods for determining liquid filtration efficiency are briefly discussed. The first widely used method for quantifying liquid-borne particle concentration is the gravimetric analysis. This method is done by measuring the weights of the test filter before and after filtration wherefrom the filtration efficiency is determined [38]. However, this method may not be suitable for determining the size fractional retention efficiency of filters when the challenging particles are polydisperse. Besides, the sensitivity is also an issue when the weight of the deposited particles is too low to be measured, e.g., for filtrations with low concentration or tiny nanoparticles. Another method can be used is optical microscopy. This method can detect particles that deposited on filter surfaces but they should be larger than 2 μm , which limited the application for nanoparticle filtration [39]. The particle size analyzers using a laser light source, e.g., liquid particle counter, laser diffraction analysis and dynamic light scattering, have been widely used for sizing and counting liquid-borne particles [40-45]. For example, a liquid particle counter was used for the size characterization of standard latex particles and irregular shaped particles in liquid media [40]. Besides, the size distribution of 0.2-10 μm silica particles were analyzed by laser diffraction technique [45]. However, liquid particle counter and laser diffraction techniques have the size limit with only down to 20-30 nm. In comparison, dynamic light scattering is able to detect particles as small as 1 nm. However, this technique is known to have some drawbacks due to its inherent measurement principle, which analyzes the particle speed by measuring the rate at which the intensity of the scattered light fluctuates [46]. It is a fact that the intensity is proportional to the sixth power of the particle diameter, which results in the interference with size determination of targeted particles due to only the small number of larger particles [47]. Other than abovementioned techniques, concentration of liquid-borne particles also can be analyzed by electron microscopy and spectrophotometer methods. Because of the

capability of imaging small nanoparticles, transmission and scanning electron microscopy have been widely used [48]. However, these methods are time-consuming and not cost-effectiveness. Also, the results obtained by electron microscopy may not be representative because the detection area is usually only a small portion of the test filter unless an extra effort was made to analyze a large portion of the filter surface. One of the frequently used spectrophotometers is the UV/vis or fluorescence spectroscopy. The spectrophotometers have been widely used for nanoparticles smaller than 30 nm in ultrafiltration tests [49-51]. However, relatively high feed concentrations around or over 50 mg/l were needed for the spectrophotometer due to their low sensitivity which limits their applicability unless for extremely small nanoparticle filtrations, e.g. sub-5 nm [34].

With less limitation, three important and well-received methods for measuring liquid-borne particle concentrations including inductively coupled plasma-mass spectrometry (ICP-MS), nanoparticle tracking analysis (NTA) and electrospray-scanning mobility particle sizer (ES-SMPS) were introduced, compared and investigated for their feasibility for microfiltration and ultrafiltration study. The ICP-MS has become one of the most frequently used methods for analyzing inorganic nanoparticles in liquid [52-54]. It has also been employed to determine the water quality of drinking water [55,56] and marine sediments [57]. The exceptional analytical features, e.g., high sensitivity, of ICP-MS could be of great advantage for filtration study. The NTA consists of laser scattering microscopy with a charge-coupled device (CCD) camera to visualize nanoparticles in solution. This method has become an important technique to size and count liquid-borne particles for various purposes such as characterizing soot agglomerates from automotive engines [58], cellular vesicles [59-61] and aquatic environmental samples, e.g., sea water, lakes and rivers [62]. The last method is the ES-SMPS. **The SMPS has been widely used**

to measure the size distribution of airborne nanoparticles down to 1 nm. Therefore, the ES-SMPS is foreseeable to be widely applied for the liquid filtration of tiny nanoparticles because its sensitivity is expected to be comparable with the mass based ICP-MS for extremely small particles, e.g., < 5 nm. From the comparison of these three methods, the aim of this study is to provide the guideline for one to choose the most proper method for the microfiltration and ultrafiltration evaluations.

2. Materials and methods

2.1. Preparation of colloidal nanoparticles

For applying the three aforementioned methods for microfiltration and ultrafiltration studies, calibration curves, in terms of measured concentration versus prepared (or calculated) concentration according to the data from manufacturer, should be established. Table 1 summarizes the information of colloidal nanoparticles and initial concentration ranges for the three techniques. The test particles used in this study are Au nanospheres (Ted Pella, Inc., Redding, CA) with four sizes of 5, 10, 40 and 50 nm and standard PSL nanoparticles (Thermo Fisher Scientific, Inc., Waltham, MA) with five sizes of 20, 40, 60, 100 and 125 nm. Au nanoparticles were analyzed by all three methods while PSL nanoparticles were measured only by NTA and ES-SMPS because ICP-MS is more preferred for trace metal analysis. To ensure the prepared colloidal nanoparticles were well-dispersed and aggregate-free, they were ultrasonicated for at least 10 min before being measured by each technique.

Table 1

Due to different detection ranges of mass and number concentrations of the three methods, different initial particle number concentrations, as shown in Table 1, were prepared. Then the prepared colloidal nanoparticles were diluted with 18 M Ω cm resistivity ultrapure water (Milli-Q system, Millipore Corp., Bedford, MA) covering several orders of magnitude to allow obtaining decent calibration curves for the use in determining filtration efficiency. Because both Au and PSL nanoparticles are in spherical shape, their number concentrations were converted from the weight percentages, wt%, provided by the manufacturers by considering the density. For example, diluting 0.06 ml of the 1 wt% 40 nm PSL with 10 ml of ultrapure water results in a particle concentration around 1.7×10^{12} particles/ml.

The detection signal for ICP-MS is related to the particle mass concentration since the plasma in ICP-MS is employed to generate ions from elements of interest. Therefore, the smaller the size, a higher number concentration is required, e.g., the initial number concentration was prepared as 4×10^9 and 4×10^{12} particles/ml for 50 and 5 nm Au particles, respectively. The required initial concentration for NTA calibration is much lower than other two methods, which was less than the order of 10^{10} particles/ml. This concentration is around the upper limit of optimum concentration range of the NTA measurement. In comparison, the lower limit is about the order of 10^7 particles/ml and an extended measurement time is required for obtaining statistically reproducible data if the particle concentration is lower than the value. On the other hand, if the concentration is higher than the order of 10^{10} particles/ml, the Brownian motions of particles may not be properly analyzed due to the coincidence effect [63].

ES-SMPS requires the highest initial concentration among the three methods, which was around the order of 10^{12} particles/ml. The upper limit of concentration could be even higher than

174 this range as long as the residue particle distribution does not interrupt the main particle
175 distribution. However, when a high concentration solution is used, which contains a large
176 amount of surfactants and impurities, the residue particles may be enlarged and then interfere
177 with the main particles. We confirmed that all measurements for filtration tests were conducted
178 without the interference of residue particles, which will be discussed more in the session 3.4
179 Control of Residue Particles for ES-SMPS. Due to the much lower concentration in original
180 product of Au nanoparticles (~ 0.005 wt%) compared to that of PSL nanoparticle (~ 1 wt%), the
181 maximum number concentration we could prepare, for example, for 50 nm Au nanoparticles is
182 only 4×10^{10} particles/ml. To be mentioned, the sample solution should have an enough
183 electrical conductivity to be dispersed using ES. The conductivity was controlled by adding
184 ammonium acetate.

185 It should be mentioned that, prior to every measurement, ultrapure water without containing
186 test particles were measured by the three measurement methods to check background particle
187 concentration. For ICP-MS, we confirmed that ultrapure water sample did not show any signal
188 for the Au element. Likewise, no particles were visualized from the NTA measurement for
189 ultrapure water. For the ES-SMPS, we measured the particle number concentration of ultrapure
190 water with only ammonium acetate added from the electrospray to check the background
191 residues. Due to the very low concentration of the impurities in ammonium acetate solution, we
192 observed the size range of the residue particles is smaller than that of the test particles under our
193 test conditions or the number concentration of the residue particles was found to be negligible in
194 comparison with to that of test particles (Figure S1 of Supplementary Material). Therefore, all
195 measurements were conducted without any interference of impurities in ultrapure water.

2.2. Inductively coupled plasma-mass spectrometry (ICP-MS)

The ICP-MS (Agilent 7700s ICP-MS, Agilent Technologies Inc., CA) used in this study was equipped with a quartz double pass spray chamber, triple concentric quartz torch chamber, platinum interface cones and a PFA (perfluoroalkoxy) micro-nebulizer. In addition, an octopole reaction system was in place between the ion lens assembly and the quadrupole mass filter and utilized helium gas at a flow rate of 0.35 l/min. This effectively eliminates the key interferences arising from the sample matrix that are not argon based and cannot be eliminated using traditional approaches. Au nanoparticle measurements were performed by ionizing the sample in a plasma stream generated at a radio-frequency power of 1550 W with a carrier argon gas flow of approximately 1.0 l/min and using a quadrupole mass spectrometer and electron multiplier detector to identify the Au ions. A sample matrix of 5% by volume ultrapure nitric acid (HNO₃) was used to prepare calibration standards in the 0 ppb to 100 ppb range. A calibration curve having an R² value of > 0.99 was required. A minimum of 1.0 ml of each sample was used for the analysis.

2.3. Nanoparticle tracking analysis (NTA)

Concentration measurements using NTA were conducted by the NanoSight LM14 (NanoSight Ltd., Malvern, UK), which was equipped with a sample chamber and 630 nm laser. The NTA measured the diffusive Brownian motion of liquid-borne particles and the sizes of particles were calculated using the Stokes-Einstein relation. The particle concentration was obtained based on the number of particles visualized in the video microscopy of a control volume. Each sample was loaded slowly into the sample chamber using a syringe to avoid

generating pressures and extra care was taken to avoid the induction of bubbles in every sample loading. The chamber was rinsed by flushing ultrapure water through it prior to loading a different sample. The NTA 3.0 software was used for capturing and analyzing the data. The scattered particle motion was recorded for 60 seconds and the analysis was performed for about 30 seconds for each measurement. It should be noted that NTA requires several adjustment steps during the capture and analysis process to obtain accurate results depending on the type of sample, e.g., camera level and detection threshold [63-65]. Usually, different settings were used for different particle size samples.

2.4. Electrospray-scanning mobility particle sizer (ES-SMPS)

Figure S2 in Supplementary Material shows the schematic of the experimental setup, consisting of dispersion and measurement parts, for concentration measurement using ES-SMPS. Diluted colloidal nanoparticles were dispersed by an electrospray aerosol generator (ES, model 3480, TSI Inc., Shoreview, MN). The ES breaks down the liquid jet by the Coulombic force between highly charged droplets. Compared to conventional nebulizer, e.g., **Collison atomizer**, the droplet size dispersed by this mechanism can be much smaller and it is monodisperse and controllable by the electrical property of sample solution and liquid flow rate [66]. In operation of ES, sheath air flow rate and chamber pressure were maintained at 2 l/min and 2 psig, respectively. The liquid flow rate, Q , through the capillary tube with an inner diameter of 40 μm at the 2 psig chamber pressure was 0.128 $\mu\text{l}/\text{min}$ and we found that the liquid flow rate was proportional to the chamber pressure as shown in Figure S3 of Supplementary Material. The reason for choosing the 2 psig chamber pressure was for controlling residue particle size distribution, which will be discussed in the session 3.4 Control of Residue Particles for ES-

SMPS. The applied voltage range of 2 ~ 2.5 kV was found to form the cone-jet mode easily, which is considered a proper dispersion mode of the liquid jet at the tip of the capillary in ES [67].

The droplets dispersed from ES were dried by a diffusion dryer and their charges were brought to be equilibrium by a neutralizer. The airborne nanoparticles were measured by the SMPS consisting of an electrostatic classifier (EC, model 3082, TSI Inc.), a differential mobility analyzer (DMA or nano-DMA, model 3081 or 3085, TSI Inc.) and an ultrafine condensation particle counter (UCPC, model 3776, TSI Inc.). The SMPS was calibrated with a volumetric bubble flowmeter (Giliblator, Gilian Instruments, Wayne, NJ) for sheath flow and with NIST (National Institute of Standards and Technology) traceable standard PSL for particle sizing accuracy. The particle size distributions were measured using the voltage-scanning mode with 50 seconds scanning time. The flow rates of sheath and aerosol flow through the DMA (or nano-DMA) were set to 15 and 1.5 l/min, respectively.

2.5. Experiments for filtration test

The setup for the dead-end type filtration is shown in Figure S4 of Supplementary Material. The 0.1 μm rated PCTE membrane filter was placed in a 47 mm filter holder and ready for evaluating the three measurement methods for determining filtration efficiencies. Prior to each experiment, ultrapure water of 500 ml was drawn by a peristaltic pump to clean the device and the membrane until the number concentration of the downstream water was confirmed to be particle-free or acceptable level, e.g. 3-4 orders of magnitude lower than the upstream particle concentration.

To determine the particle concentration upstream of the filter, $C_{up}(d_x)$, 30 ml sample was passed through the filter holder without a membrane placed and collected for being analyzed by the proposed methods. This upstream sample took the transport loss in the tubing and filter holder into consideration. In comparison, the downstream concentration, $C_{down}(d_x)$, was obtained from analyzing the effluent of two successive 30 ml samples through the filter. Each of the filtered 30 ml sample was collected in a separate centrifuge tube before being analyzed. Therefore, in an experimental run, a total 30 ml upstream and 60 ml downstream samples were collected. The filtration experiment process was repeated for three times with new clean filters under the same experimental condition to obtain statistically reliable data. All filtration tests were conducted at the constant permeation flux of $720 \text{ l/m}^2\cdot\text{h}$ controlled by a peristaltic pump.

3. Results and discussion

3.1. Particle size distribution obtained by NTA and ES-SMPS

Size distributions of Au and PSL nanoparticles measured by NTA and ES-SMPS are shown and compared in Table 2. Only the particles larger than or equal to 40 nm were analyzed by the NTA because its sizing limit is only slightly smaller than 40 nm, especially for non-metallic particles. According to the claim by the manufacturer, it should be able to measure Au particles down to 20 nm (with higher refractive index). However, Au and PSL particles close to these sizes were not studied. In comparison, the ES-SMPS can measure all sizes of test particles from 5 to 125 nm.

Generally, it was found the measurements of both Au and PSL particles by NTA allow obtaining relatively accurate mean diameters close to those provided by the manufacturers. As

one of advantages in particle sizing by NTA, liquid samples are directly analyzed, which avoids the overestimation of particle size and interference of size distribution caused by residue or impurities as occurred in ES-SMPS measurements. For PSL particles of 40 and 60 nm, the geometric standard deviations of 1.14 and 1.09 were measured by NTA, respectively, which are relatively narrower than those estimated by ES-SMPS measurements as shown in Table 2. We believe that NTA measurements may underestimate the geometric standard deviation because the output from NTA measurements is usually dominated by intensities scattered from larger and more popular particles. Therefore, the dominant particles with mode diameters might contribute to the narrow size distributions, by screening the smaller or less popular particles. Moreover, for particles with a mode (or mean) diameter around 40 nm, which is close to the lower detection size limit for NTA, the particles relatively smaller than the mode diameter, below the detection limit, cannot be recognized and analyzed by NTA, resulting in the narrow size distribution.

In comparison, the ES-SMPS measurement is based on the single particle counting and the detectable size range is down to single-digit nanometers, which provides the less sensitivity issue in the size range of tens of nanometers compared to NTA. The ES-SMPS measurements showed smaller mean diameters and broad distributions for 20, 40 and 60 nm PSL particles. It should be noted that the smaller PSL particles generally have the relatively larger standard deviation of size distributions [68]. It was confirmed after the ES-SMPS measurements that the particles exhibited size distributions skewed toward smaller sizes (e.g., the size distribution of 40 nm PSL particles obtained by ES-SMPS in Figure S5). The modes were at 42.9 and 63.8 nm, respectively, for the 40 and 60 nm PSL particles, which were close to those labelled by the manufacturer and measured by NTA. Exceptionally, the distribution of 20 nm PSL particle peaked at 15.7 nm, similar to the mean diameter, and the reason should be studied further in the future.

In addition, in the ES-SMPS measurements, the level of overestimation of particle sizes increased with decreasing particle sizes, i.e. from 1.04% for 125 nm PSL to 56% for 5 nm Au. This trend was also observed in other studies [69-71]. It was mainly due to, taking the 5 nm Au nanoparticles as an example, the surfactants or impurities present in the solution stuck onto the 5 nm Au particles when they were aerosolized and evaporated. The contributions for size growing could become more significant when a high concentration of original solution was used. A simple calculation for estimating the effects of nonvolatile residue particles on the contribution to particle size is shown in Figure S6 of Supplementary Material.

Table 2

3.2. Dilution test of colloidal Au nanoparticles for ICP-MS

Figures 1(a) and (b) show the calibration results for Au nanoparticles with sizes of 5 to 50 nm for the ICP-MS based on mass, C_M , and number concentration, C_N , respectively. The C_M was converted to C_N as:

$$C_N = \frac{C_M}{\left(\frac{\pi}{6} D_p^3\right) \times \rho_p} \quad (2)$$

where D_p and ρ_p are the particle diameter and density, respectively. There was a very good linear relationship between the prepared and measured concentrations. The initial Au colloidal particles were prepared with the mass concentration around 5000 ng/ml (or 0.0005 wt%) for all test particle sizes, which approximately corresponded to the number concentrations of 4×10^{12} , $5 \times$

10¹¹, 7.7 × 10⁹ and 4 × 10⁹ particles/ml for 5, 10, 40 and 50 nm Au nanoparticles, respectively. From these initial particle concentrations, each sample was diluted stepwisely with ultrapure water at a fixed ratio of 1:10 and then measured sequentially until it reached the lowest detectable concentration. We found that ICP-MS could analyze Au nanoparticles with concentration down to a single digit of ppt, e.g., around 5 ppt (0.005 ng/ml). Below this range, the measurement gave negative mass concentrations, indicating the amount of Au nanoparticles was too small to be detected. It was also found that the minimum detectable number concentration increased as the particle size decreased. For example, 5 nm Au nanoparticles had the minimum number concentration around 4 × 10⁷ particles/ml, but that of 50 nm Au nanoparticles could be as low as 4 × 10⁴ particles/ml, which was 1000 times lower concentration. The result is reasonable since the 10 times of diameter leads to the 1000 times of mass. Due to the proportional relationship between prepared and measured concentration, the filtration efficiency can be directly calculated by Eq. (1).

Figure 1

3.3. Dilution test of colloidal nanoparticles for NTA

Figure 2 shows the calibration results of NTA for both PSL and Au nanoparticles with sizes of 40 to 125 nm. It should be noted that because the concentration measured by NTA depends on the characteristics of particles, e.g., material and particle size, the proper adjustment of settings is needed when capturing and analyzing the particle motion. For all calibrations of the NTA measurement shown in Figure 2, we intentionally adjusted the settings, i.e., camera level and

detection threshold, depending on the material and particle size so that the measured initial number concentrations, i.e., the highest number concentrations, were around 9×10^8 particles/ml. Under the same detection threshold condition, for example, the higher camera level is required for measuring 40 nm PSL particles with the lower refractive index than the 40 nm Au particles with the much higher refractive index. The camera level adjusts the length of time for camera shutter to be open and the sensitivity of the camera. The detection threshold determines the minimum gray scale value to allow particles to be traceable. The effects of the settings on analysis of nanoparticles are discussed in Figure S7 of Supplementary Material.

The NTA measurement results with a sequent 1:2 dilution ratio with ultrapure water showed that the proportional relation was observed between the prepared and measured liquid-borne particle concentrations. Therefore, the filtration efficiency can be calculated by the ratio of upstream and downstream concentrations shown in Eq. (1).

Figure 2

3.4. Control of residue particles for ES-SMPS

As mentioned earlier, when using the aerosolization method, residue particles were usually formed from the evaporation of nonvolatile surfactants and impurities for the blank droplets containing no main particles. They could interfere with the size distribution of the main particles and result in the incorrect number concentration and particle size. Figure 3 shows the particle size distributions of 5 nm Au nanoparticles with 2.5 ppm (mg/l) concentration under different electrical conductivity (K) and chamber pressure (P or the corresponding Q) conditions. There

are two clear peaks in these size distributions except for Figures 3(d) and (g). One of the peaks was attributed to the main Au nanoparticles and the other peak was from the residue particles. In these two-peak distributions, the sizes of peaks with smaller sizes (located in the left side) varied with both K and P while the sizes of larger size peaks (located in the right side) remain relatively stable at ~8 nm. It was further observed that the sizes of small size modes increased with increasing P and decreasing K. It becomes clear that the first size distribution can be attributed to residue particles because when dispersing a solution with a higher P (or liquid feed rate, Q), larger blank droplets were formed, which contain more nonvolatile water impurities or surfactants and then formed larger residue particles after being dried. In addition, the lower K can also lead to the generation of larger blank droplets in the ES. This finding is in agreement with that by Chen and Pui [72] in which the size of residue particles was found to be scaled with $(Q/K)^{1/3}$. In comparison, this stable peak should be referred to as the main 5 nm Au particles and the growth of an extra of 3 nm should be associated with the attachment of impurities and surfactant during the evaporation process. They tended to coat on the surface of the Au particles and became part of them. Similarly, as shown in Table 2, there was 1-3 nm growth for other sizes of Au particles. Regardless of the growth of particle size, the particle concentration of the main particles can be obtained from the SMPS measurements as long as the residue particle size distribution does not interrupt the main particle size distribution. In this study, the chamber pressure of 2 psig in ES and the electrical conductivity of 1000 $\mu\text{S}/\text{cm}$ of solutions were chosen to completely separate the two sets of size distributions contributed from residue and main Au nanoparticles as shown in Figure S8 of Supplementary Material.

Figure 3

396

397 *3.5. Dilution test of colloidal nanoparticles for ES-SMPS*

398 Figure 4 shows the ES-SMPS calibration results for all test particles from 5 to 125 nm
399 nanoparticles. As can be seen, a proportional relationship between the prepared liquid-borne and
400 the measured airborne particle concentrations were obtained for all test particles. Besides, all the
401 data appeared to fall in one single linear curve as shown in Figure 4(a). This finding indicated
402 that regardless of material compositions, i.e., Au and PSL nanoparticles, the single linear line can
403 be used to calculate the concentration of liquid-borne particles with unknown concentration from
404 the measured airborne particle concentration. Further normalized the initial prepared liquid-
405 borne and accordingly measured airborne concentrations, Figure 4(b) depicts the relationship
406 between the two concentrations. A fitting curve of $y=1.003x$ with extremely high square root
407 value of 0.998 was obtained for the relationship, indicating that ES is a very powerful method for
408 generating singlet nanoparticles with very less possibility of agglomerate-formation. This is
409 attributed to the very small droplet size generated by the ES. As the proof of the singlet particle
410 generation of ES, the Au nanoparticles with the concentration around 2×10^{12} particles/ml, the
411 highest concentration used in this study, were aerosolized and sampled on a 0.4 μm rated PCTE
412 membrane filter for scanning electron microscopy (SEM) analysis. Figure S9 of Supplementary
413 Material shows the SEM image of the singlet Au nanoparticles deposited on the filter surface.

414 From the calibration results, due to the proportional relationship between the liquid-borne
415 and airborne particle concentrations, the relation can be written as:

416
$$C_{\text{liquid-borne}} = \text{constant} \times C_{\text{airborne}} . \quad (4)$$

417 This correlation allows us to calculate the filtration efficiency again by Eq. (1).

Figure 4

3.6. Filtration efficiency of PCTE membrane filters

To determine filtration efficiency by the ICP-MS, NTA and ES-SMPS, different detection concentration ranges were needed. The collected upstream sample should be adjusted to have adequate concentrations, i.e., around 10^{11} , 10^9 and 10^{12} particles/ml for ICP-MS, NTA and ES-SMPS, respectively. Each corresponding dilution ratio for obtaining proper concentration was also applied to the collected downstream samples for each measurement.

Likewise, each sample was analyzed as described in the aforementioned procedure and the filtration efficiency was obtained by Eq. (1). Figure 5 shows the experimental data of the filtration efficiency for the 0.1 μm rated PCTE membrane filters challenged by Au and PSL nanoparticles. Filtration efficiencies of 5 and 10 nm Au nanoparticles were analyzed by ICP-MS and ES-SMPS and 40, 60 and 100 nm PSL nanoparticles were analyzed by NTA and ES-SMPS. It is seen the pair of filtration efficiencies from the independent experiments by different measurement methods were quite comparable.

For the filtration efficiencies of 40 nm PSL particles with the high geometric standard deviation (= 1.47), it is found that the efficiency calculated by ES-SMPS is slightly lower than the one by NTA. The ES-SMPS is able to detect particles in the smaller size range (the left tail in the size distribution) where NTA cannot detect the particles due to reduced intensities of scattered light from such small particles as shown in Figure S5. Therefore, these smaller particles

were counted in the total number concentrations by the ES-SMPS measurement, which resulted in the lower filtration efficiency compared to the NTA measurement.

It should be noted that PCTE membrane filters, Au and PSL nanoparticles were characterized to be negatively charged in water [34,73,74]. The low filtration efficiencies (< 0.2) were obtained for particles smaller than or equal to 40 nm due to the relatively strong electrostatic double layer repulsion under the unfavorable condition caused by the same polarity of charges of nanoparticles and the filter [75]. As the particle to pore diameter ratio increases, the effects of sieving and interception become significant. For example, the 100 nm PSL nanoparticles, having a close diameter to the pore size of the filter, had a very high filtration efficiency due to the mechanical deposition mechanisms, i.e., sieving and interception, regardless of the unfavorable condition.

Figure 5

4. Conclusions

Three important methods for liquid-borne particle size and concentration measurements, including ICP-MS, NTA and ES-SMPS, for determining liquid filtration efficiency were analyzed and compared to see their feasibility and applicability. ICP-MS provides extremely high sensitivity to a wide range of elements and has a broad analytical working concentration range as long as samples meet the mass requirement. On the other hand, NTA and ES-SMPS have more confined number concentration range compared to ICP-MS but they are eligible to determine the particle size distribution, which can be employed to investigate liquid filtrations

for polydisperse nanoparticles. NTA enables the visualization of dancing particles due to Brownian motion and estimates the particle size distribution from the particle displacements. However, proper handlings and settings are required for acquiring accurate results from NTA, including proper concentration of colloids, camera level and detection threshold, laser wavelength, optical alignment and vibration.

Our results showed that ES-SMPS can be used to evaluate filter performance for nanoparticles in a broad size range from over one hundred down to sub-10 nm. The absolute liquid-borne particle concentration can be obtained from the measured airborne concentration. Due to the outstanding capability of detecting small nanoparticles down to 1 nm (validation data shown only down to 5 nm), ES-SMPS can be a promising method for microfiltration and ultrafiltration even for nanofiltration studies. The important precaution when using ES-SMPS is to avoid the interference of residue particles that can affect the analysis in two ways: (1) overestimating the particle size by nonvolatile impurities and surfactants formed and coated onto the particle surface and (2) interrupting the identification of the main particle distribution by residue particles formed from evaporation of blank droplets that do not contain the main particles.

To demonstrate the feasibility of the proposed measurement methods for the liquid filtration tests, the calibration results of each method were applied to the 0.1 μm rated PCTE membrane filtrations. Results showed that these methods are comparable. Because of the potential of measuring wide size ranges of liquid-borne particles in a real-time and its high sensitivity for tiny nanoparticles, ES-SMPS is foreseeable for future sub-10 nm nanofiltration applications.

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692

Caption

Figure 1. Relationship between prepared and measured liquid-borne nanoparticle concentrations obtained by the ICP-MS based on (a) mass concentration and (b) converted number concentration. Fitting curves with the intercept at zero are $y = 0.9649x$ and $y = 1.122x$ for (a) mass and (b) number concentration, respectively. The sum of error square (R^2) is larger than 0.99 for each case and the units of x and y are the same as the units of the respective axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 2. Relationship between prepared and measured number concentration of liquid-borne nanoparticles obtained by the NTA measurement. A curve fitting with the intercept at zero is estimated as $y = 0.9744x$ with R^2 larger than 0.99 and the units of x and y are the same as the units of the respective axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 3. Size distributions obtained by the ES-SMPS measurement for 5 nm Au nanoparticles under different solution electrical conductivity (K) and electrospray chamber pressure (P). The size distributions consist of residue and Au nanoparticles and the mode diameters are shown in each figure.

Figure 4. Relationship between prepared liquid-borne and measured airborne number concentrations by the ES-SMPS. Axes present (a) prepared and measured concentrations and (b) normalized values by the initial liquid- and airborne concentrations for each particle size. Each fitting curve has R^2 larger than 0.99 and the units of x and y are the same as the units of the

714 respective axis. (For interpretation of the references to color in this figure legend, the reader is
715 referred to the web version of this article.)

716 **Figure 5.** Filtration efficiency of the 0.1 μm rated PCTE membrane filters for particles of 5, 10,
717 40, 60 and 100 nm. The data points and error bars represent the average filtration efficiency and
718 standard deviation. Filtration efficiencies of the same particle size were obtained by two different
719 measurement methods.

720 **Table 1.** Particle sizes and prepared concentrations measured by the three different methods.
721 Generally, the smaller particles, the higher initial concentrations were needed for ICP-MS.

722 **Table 2.** Mean number diameter and standard deviation (and geometric standard deviation) of
723 test particles measured by NTA and ES-SMPS.

725 Table 1. Particle sizes and prepared concentrations measured by the three different methods.

726 Generally, the smaller particles, the higher initial concentrations were needed for ICP-MS.

Material	Density [g/cm ³]	Particle size [nm]	Measurement technique	Prepared initial concentration for calibration [particles/ml]
Au	19.3	5	ICP-MS NTA ES-SMPS	$4 \times 10^9 \sim 4 \times 10^{12}$ (ICP-MS) $\sim 1 \times 10^9$ (NTA) $4 \times 10^{10} \sim 2 \times 10^{12}$ (ES-SMPS)
		10		
		40		
		50		
PSL	1.05	20	NTA ES-SMPS	
		40		
		60		
		100		
		125		

727

728

Table 2. Mean number diameter and standard deviation (and geometric standard deviation) of test particles measured by NTA and ES-SMPS.

Material	Particle size [nm] (manufacturer)	NTA			ES-SMPS		
		Mean number diameter [nm]	Standard deviation [nm]	Geometric standard deviation	Mean number diameter [nm]	Standard deviation [nm]	Geometric standard deviation
Au	5	-	-	-	7.80	1.05	1.14
	10	-	-	-	13.5	0.79	1.08
	40	42.4	7.1	1.13	42.6	4.07	1.10
	50	54.1	8.7	1.10	51.0	6.27	1.11
PSL	20	-	-	-	15.8	4.34	1.36
	40	42.7	6.7	1.14	33.0	10.46	1.47
	60	59.9	6.1	1.09	57.4	12.06	1.24
	100	99.4	8.7	1.09	102.2	6.31	1.07
	125	123.7	9.5	1.07	126.3	9.87	1.09

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5