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Use of a Condensation Particle Counter and an Optical Particle Counter to Assess the Number Concentration of Engineered Nanoparticles

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There is a need to evaluate nanoparticle (<100 nm) exposures in occupational settings. However, portable instruments do not size segregate particles in that size range. A proxy method for determining nanoparticle count concentrations involves subtracting counts made with a condensation particle counter (CPC) from those of an optical particle counter/sizer (OPC), resulting in an estimation of "very fine" particles <300 nm, where 300 nm is the OPC lower detection limit. However, to determine size distributions from which particles <100 nm may be estimated, the resulting count of particles <300 nm can be used as an additional channel of count data in addition to those obtained from the OPC. To test these methods, the very fine number concentrations determined using a CPC and OPC were compared with those from SMPS measurements and were used to verify the accuracy of a very fine particle number concentration determined by an OPC and CPC. Two "size-distribution" methods, weighted-average and log-probit, were applied to reproduce particle size distributions from OPC and CPC data and were then evaluated relative to their ability to accurately estimate the nanoparticle number concentrations. Various engineered nanoparticles were used to create test aerosols, including titanium dioxide (TiO_2), silicon dioxide (SiO_2), and iron oxide (Fe_2O_3). These materials were chosen because of their different refractive indices and therefore may be measured differently by the OPC. The count-difference method was able to estimate very fine particle number concentrations with an error between 10.9 to 58.4%. In estimating nanoparticle number concentrations using the size-distribution methods, the log-probit method resulted in the lowest percent errors that ranged from –42% to 1023%. Percent error was lower than the instrument manufacturer's indicated level of accuracy when the test aerosol refractive index was similar to that used for OPC calibration standards. Accuracy could be increased if there was an increase in the size resolution for number concentrations measured by the CPC of very fine particles and mitigation of optical effects.

Keywords condensation particle counter, nanoparticles, optical particle counter

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INTRODUCTION

There is an increased concern that the emergence and proliferation of nanotechnology will result in workers being exposed to nanoparticles (particles with diameters <100 nm) through inhalation.[1,2] Exposure to engineered nanomaterials can elicit adverse cardiopulmonary health effects, such as inflammation, progressive pulmonary fibrosis, blood platelet activation, plaque formation, and thrombosis.[3–5]

Traditional methods to measure particulate exposures may be inadequate for engineered nanoparticles. In occupational settings, the regulatory-approved method (National Institute for Occupational Safety and Health [NIOSH] Method 0500) involves gravimetric analysis of a filter sample to measure mass concentration.[6] However, nanoparticles often have negligible mass when compared with the larger particles that are collected with regulatory-approved, mass-based samplers.[7] Moreover, particle number or surface area concentrations rather than mass concentrations have been shown to scale more closely with the toxic effects of nanoparticle inhalation.[8,9]

Several portable, affordable, and easy to operate instruments are available to measure particle number concentrations. Condensation particle counters (CPCs) provide particle number concentrations between 10 and 1000 nm. Optical particle counters/sizers (OPCs) provide particle number concentrations by size in multiple channels. The lower detection limit of many commercially available, portable OPCs that utilize a laser diode light source is approximately

300 nm with upper limits ranging from 10,000 to 20,000 nm, whereas OPCs that utilize a laser as the light source can measure particles >100 nm but are expensive and not easily portable.[10]

Given a low-end size constraint of 300 nm, researchers have calculated particle number concentrations <300 nm (referred to here as "very fine" particles) by subtracting OPC-measured number concentrations associated with particles in channels ranging between 300 and 1000 nm from all CPC-measured number concentrations. The resulting counts of very fine particles have been measured in a variety of workplaces, such as automotive engine production and engineered nanoparticle production.[11–13]

Likewise, without a currently available field-portable instrument capable of sizing and counting particles <100 nm, NIOSH has suggested determining very fine particle number concentrations using this combined OPC and CPC measurement method, which we refer to as the count-difference method, as one of several nanoparticle exposure assessment techniques explored by that agency.[14] Therefore, this technique has been established as a proxy for assessing nanoparticle exposures. Given that NIOSH suggests measuring nanoparticle number concentrations to assess nanoparticle exposure, we are presenting this research under the assumption that exposure guidelines based on count, rather than mass, will be developed in the future.

There are several possible errors associated with use of the count-difference method to estimate nanoparticle (<100 nm) number concentrations. First, the response of an OPC is strongly dependent on particle refractive index (RI) and shape. Thus, incorrect estimates of particle number concentration by size can result when the shape and RI of measured particles differ from that of calibration particles. Particles with lower RIs than the calibration particles will scatter less light than the amount of light scattered by a calibration particle of the same diameter, and therefore, the OPC will report the particles as having a smaller than actual diameter.[15] The magnitude of the error introduced for different types of engineered nanoparticles is unknown.

More importantly, since most OPCs are unable to detect particles smaller than 300 nm, number concentrations measured with this method are not true estimates of nanoparticle concentrations but actually very fine number concentrations, which are necessarily higher. However, other data reduction approaches might be used to leverage the additional size distribution data provided by an OPC to estimate nanoparticle number concentrations. For example, data simultaneously collected by a CPC and OPC could be used to produce a particle size distribution based on several channels in the nanometer size range from which nanoparticle number concentration can be estimated.

Thus, the goals of this research were to (1) determine the percent error in estimates of very fine particle number concentrations made with the count-difference method for engineered nanoparticles, and (2) evaluate the use of a size distribution method to estimate nanoparticle number concentrations from data obtained by dual use of a CPC and OPC.

MATERIALS AND METHODS

Instruments

Test aerosols were measured with a portable CPC (model 3007, TSI Inc., Shoreview, Minn.), an OPC (model 1.108, GRIMM Technologies Inc., Douglasville, Ga.), and a scanning mobility particle sizer (SMPS, model 3071A electrostatic classifier and model 3010 CPC, TSI). The TSI 3007 and 3010 CPCs both count particles through optical detection and do not differentiate between size. In CPCs, alcohol is condensed onto sampled particles to grow them to a size that they can be detected so that their number concentration may be measured optically. Hämeri et al. showed that the 3007 CPC detects particles from 10–1000 nm.[16] According to manufacturer's specifications, this CPC has a concentration accuracy of ±20%, and the 3010 CPC has a concentration accuracy of ±10%. The GRIMM 1.108 is a laser diode-based, portable OPC that measures number concentration from 300–20,000 nm in 15 size channels. Similar to the CPC, the OPC optically counts particles. However, unlike the CPC, it classifies each particle counted into diameter channels according to the proportion of light scattered in the forward direction by the particle. According to the manufacturer's specifications, it has a reproducibility of ±2%. The manufacturer does not report the counting efficiency relative to channel size. However, an instrument with a similar laser diode light system for sizing particles has a reported efficiency of 50% for 0.3 μm particles, and 100% for all particles >0.45 μm (Aerotrak, model 9306, TSI).

The TSI 3071A/3010 SMPS was used as a reference instrument for evaluating the accuracy of both the very fine and nanoparticle number concentrations determined by the two estimation methods analyzed during this study: count difference and size distribution analysis. Depending on its configuration, the SMPS is capable of measuring particle size distributions from 2–1000 nm. However, it is not easily portable, is fairly complex to operate, and is much more expensive than the other instruments previously described.

Experimental Protocol

Three tests aerosols were produced from engineered nanoparticle bulk powders and included 21-nm primary particle size titanium dioxide (TiO_2, Nanostructured and Amorphous Materials, Inc., Houston, Texas), 20-nm primary particle size silicon dioxide (SiO_2, Evonik Degussa Corporation, Parsippany, N.J.), and iron oxide (Fe_2O_3, Nanostructured and Amorphous Materials) with primary particle sizes of 20–50 nm. These materials were chosen because they all have different refractive indices and therefore may be measured differently by the OPC. A NaCl aerosol was also used because it has a refractive index similar to the materials used to calibrate the OPC.

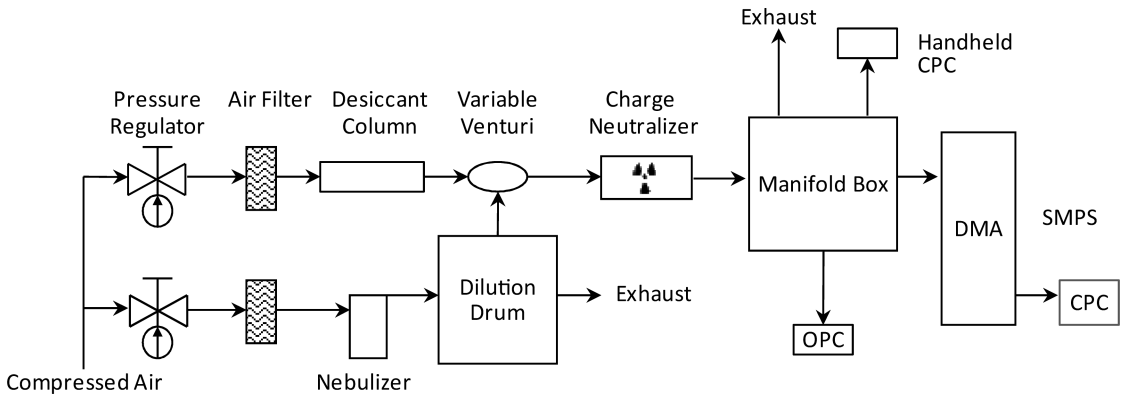

FIGURE 1. Schematic of experimental setup.

Tests were conducted using the experimental setup illustrated in Figure 1. A suspension of engineered nanoparticles in ultrapure water was nebulized with a Collison nebulizer (BGI Inc., Waltham, Mass.). Following nebulization, the aerosol was passed to a dilution drum with an exhaust port. A variable Venturi (Ortho Dial-N-Spray, Marysville, Ohio) was used to reduce particle concentrations. The aerosol was then charge neutralized with a 20-mCi ^{63}Ni source before entering a manifold box to which the instruments were connected. The instruments sampled aerosols simultaneously from a single port with a three-way adapter. To minimize particle losses, the stainless steel sample lines were kept as short as possible (3 cm). To determine particle morphology, a point-to-plane electrostatic precipitator (Intox Products, Albuquerque, N.M.) was used to collect aerosolized particles directly on to a stub used for photographing by transmission electron microscopy (TEM).

The CPC and OPC were set to record a sample every 60 sec, whereas the SMPS was set to sample every 4 min, of which 3 min was required to scan all 105 channels ranging between 7.37 nm to 311 nm. Five separate runs were conducted for each of the four nanoparticle types tested (Table I). One run consisted of measurements over a period of 20 min at stable aerosol concentration conditions that were averaged for each instrument. A 20-min time period was selected so that the SMPS could collect at least five samples. The SMPS distributions and CPC number concentration were monitored throughout the experiment to ensure that distributions were similar and number concentrations remained stable for the 20-min data collecting period.

TABLE I. Characteristics of Test Aerosols

Nanoparticle Aerosol	Primary Particle Diameter (nm)	Refractive Index
Sodium chloride (NaCl)	—	1.54[17]
Titanium dioxide (TiO_2)	21	2.62[18]
Silicon dioxide (SiO_2)	20	1.46[19]
Iron oxide (Fe_2O_3)	2050	3.01[20]

Computation of Number Concentration

Count-Difference Method

Very fine particle number concentration ($N_{CPC-OPC}$) was calculated as the OPC-measured number concentration from five channels collectively ranging between 300 and 1000 nm subtracted from the CPC-measured number concentration. Percent error between the estimated very fine number concentration, as calculated by the OPC and CPC, and the actual very fine number concentration (N_{SMPS}), as measured by the SMPS, was determined using Eq. 1. To make this comparison, the mobility diameter of 300 nm reported by the SMPS was assumed to be equivalent to the same optical diameter reported by the OPC.

$$PercentError = \left(\frac{N_{CPC-OPC} - N_{SMPS}}{N_{SMPS}}\right) 100 \qquad \textbf{(1)}$$

Figure 2 is a theoretical aerosol size distribution with the different instrument particle size limits delineated.

Ratios of the estimated number concentration to the actual number concentration derived from the SMPS of very fine particles were also calculated for each of the five replicates for each aerosol measured. A one-way analysis of variance (ANOVA) was performed at a 95% confidence was conducted with a Tukey pair-wise comparison to determine whether the average ratios differed by nanopowder type. Statistical analysis was performed using Minitab (Release 15, Minitab Inc., State College, Pa.).

Size-Distribution Methods

Two methods, weighted-average and log-probit, for determining the particle size distribution from data obtained with the CPC and OPC were evaluated for estimating nanoparticle number concentrations. The weighted-average method was based on a numerical procedure, and the log-probit method involved a graphical procedure.[21,22] Number concentrations

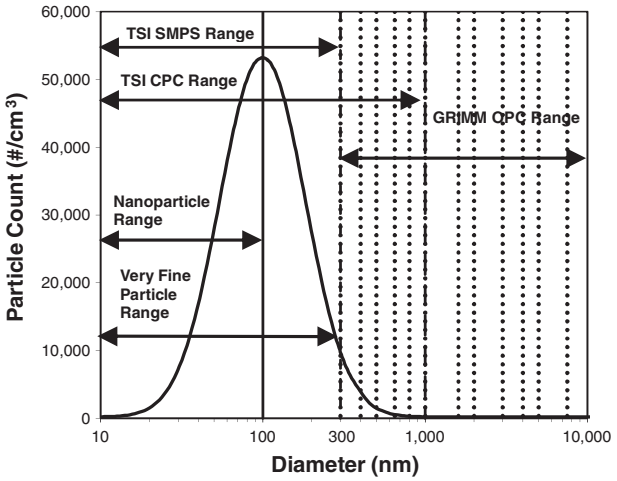

FIGURE 2. Theoretical aerosol size distribution with the OPC, CPC, and SMPS particle size limits.

estimated with these methods were then compared with the actual concentration measured by the SMPS and expressed in percent error. These methods were applied under the assumption the particle size distribution was lognormal and unimodal. Given these assumptions, both methods were used to determine a count median diameter (CMD) and geometric standard deviation (GSD). The lognormal cumulative distribution at a particle diameter, $\Phi_L(d)$, is related to the standard normal cumulative distribution function, Φ_S, by:

$$\Phi_L(d) = \Phi_S\left(\frac{\ln(d) - \mu}{\sigma}\right) \quad \textbf{(2)}$$

where

d = particle diameter of interest
μ = location parameter or ln(CMD)
σ = scale parameter or ln(GSD).

For our purposes, the diameter of interest in Eq. 2 is 100 nm, and the value of $\Phi_L(d)$ obtained would give the fraction of particles smaller than 100 nm. By multiplying the lognormal cumulative probability for particles <100 nm by the actual total number concentration, the estimated number concentration <100 nm was determined. This value was compared with the actual number concentration measured by the SMPS by determining the percent error of the estimated concentration to the measured concentration.

Weighted-Average Method

The weighted-average method for determining the CMD and GSD of a unimodal aerosol distribution uses a weighted average of particle counts over a variety of particle size bins. The CMD is calculated, in part, by multiplying the count for each particle size bin by the geometric mean diameter, d_g, of each bin (Eq. 3).

$$CMD = \exp\left(\frac{\sum d_g \ln(n_i)}{N}\right) \quad \textbf{(3)}$$

where

d_g = geometric mean diameter of each bin
n_i = count for each bin
N = total number of particles counted in all bins.

The number of bins used was based on OPC specifications and included the 15 bins provided by the OPC used for this study, in addition to the one channel between 10 and 300 nm obtained by utilization of the count-difference method. Furthermore, as given by Hinds,[21] the following expression was used for determining the GSD:

$$GSD = \exp\left(\left(\frac{\sum n_i \left(\ln\left(d_{\text{midpoint}}\right) - \ln(CMD)\right)^2}{N-1}\right)^{1/2}\right) \quad \textbf{(4)}$$

Log-Probit Method

The log-probit method calculates the CMD and GSD by first plotting cumulative count fraction or percent on a y-axis with probability scale against particle diameter on a logarithmic x-axis. This was accomplished using Microsoft Excel by first transforming cumulative count probability fractions into their related probit, or "z" values. Probit values can be calculated using the Excel function NORMSINV. To use this function, the frequency for each bin is initially calculated and from which the cumulative probability for each bin is determined and applied to the NORMSINV function to determine the associated z-value. Size bins that had cumulative probabilities greater than 99.9999% were not included in the calculations. After plotting the z-value and corresponding $\log_{10}(d_g)$ value for each bin, the CMD and GSD are calculated by taking the inverse log of the intercept and slope, respectively, as given in Eqs. 5 and 6:

$$CMD = 10^{intercept} \quad \textbf{(5)}$$

$$GSD = 10^{slope} \quad \textbf{(6)}$$

where the slope and intercept are determined by utilizing Excel's regression analysis features.

A limitation of this method is that it required there be at least two points to evaluate a slope and intercept. This would not be the case, for example, when the distribution was narrow and centered on smaller diameters (<300 nm) so that nearly the entire fraction of particles would be contained in the smallest-sized bin with diameters between 10 and 300 nm. As an extreme example, a theoretical aerosol with a CMD of 50 nm and GSD of 1.2 would have counts that would be detected only in the lowest sized bin, and as a result, there would only be one data point to use for calculating slope and intercept, which is impossible.

Comparison of CMD and GSD Determination

The accuracy of the weighted-average and log-probit methods for determining the CMDs and GSDs for particle size distributions in the size range of 10–1000 nm was evaluated by mathematically producing theoretically ideal aerosol size

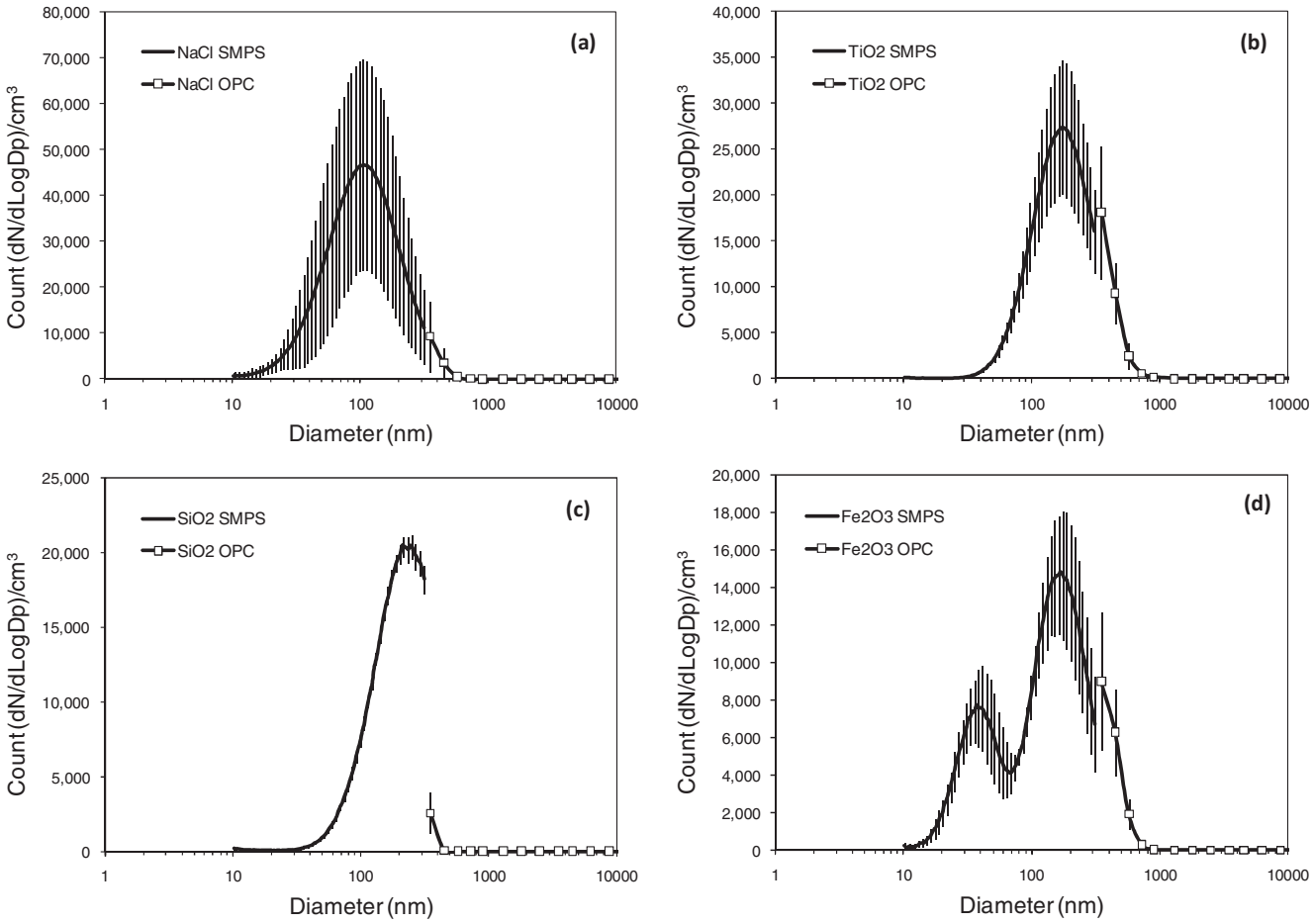

FIGURE 3. Aerosol particle size distributions measured by SMPS and OPC instruments for (a) NaCl, (b) TiO_2, (c) SiO_2, and (d) Fe_2O_3 aerosols.

distributions that are lognormal and unimodal over a range of CMDs and GSDs. The CMDs evaluated ranged from 50–1000 nm and the GSDs ranged from 1.2–2.5. A particle diameter size range was selected that ranged from the lower limit of the CPC to the upper limit of the OPC. The evaluation was performed in Excel with the same number of bins and bin sizes as used for the weighted-average and log-probit methods. An arbitrary total particle number concentration of 1000 was selected and used along with the CMD, GSD, and lognormal distribution function in Microsoft Excel to calculate a cumulative distribution from which counts per channel were obtained. Using counts per channel, the CMD and GSD were recalculated using the weighted-average and log-probit methods. Percent error between the originally assigned CMD and GSD and the calculated CMD and GSD was computed.

RESULTS

Particle Size Distributions

Particle count size distributions were determined for the four aerosols tested using the SMPS and OPC data (Figure 3). The peak diameters of the distributions were greater than the primary particle sizes for all of the engineered nanoparticle aerosols. Representative transmission electronic micrographs of the aerosolized particles are provided in Figure 4 where it can be seen that the particles analyzed were composed of loose agglomerates.

The Fe_2O_3 aerosol was the only aerosol to produce a bimodal distribution with the maximum peak diameter occurring at approximately 150 nm and the smaller peak occurring at about 30 nm. The transition between the SMPS and OPC data was smooth for the NaCl aerosol, but it was disjointed for the TiO_2, SiO_2, and Fe_2O_3 aerosols. The SiO_2 aerosol had little variability in counts per channel between each of the five runs, whereas the other aerosols showed increased variability based on the difficulty associated with consistently generating aerosols from a suspension.

Count-Difference Method

Table II summarizes the percent errors observed using the count-difference method to calculate the very fine number concentration relative to number concentration obtained between 10 and 300 nm by the SMPS. The percent error ranged from

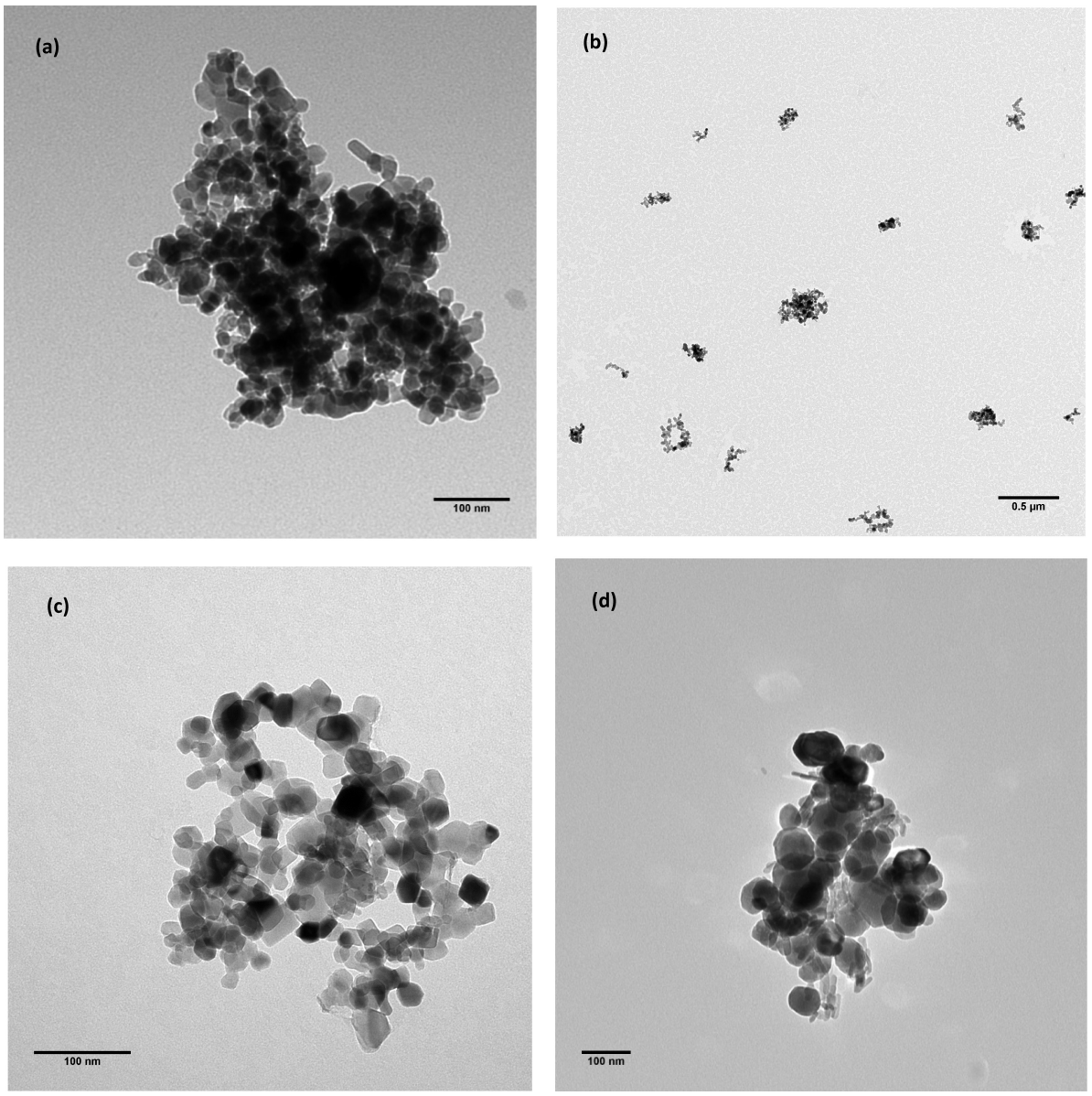

FIGURE 4. Transmission electron micrographs showing a single TiO_2 agglomerate (a), TiO_2 of various sizes (b), an SiO_2 agglomerate (c), and an Fe_2O_3 agglomerate (d).

–10.9% for the TiO_2 aerosol (signifying an underestimation relative to the SMPS) to 58.4% for the SiO_2 aerosol.

Average ratios of the estimated number concentration to the actual number concentration derived from the SMPS are given in Table II. A one-way ANOVA analysis performed at a 95% confidence level indicated a significant difference in the average ratio between aerosol types ($p < 0.001$). Furthermore, a Tukey pair-wise comparison demonstrated that all ratios were significantly different except for those for NaCl and TiO_2. These ratios were closest to unity.

Size-Distribution Methods

There was an overestimation for number concentration of particles smaller than 100 nm for all aerosols using the weighted-average method (Table III). Percent error ranged between 121% for NaCl and 1093.4% for SiO_2. For estimating number concentration <100 nm, the percent error for Fe_2O_3 was 214% and for TiO_2 was 407%.

The log-probit method to determine number concentration <100 nm showed an overestimation of number concentration for all aerosols tested except for Fe_2O_3 (Table III). For NaCl, the percent error was fairly low at –9.6%. The percent error observed for the other aerosols was much greater, with values for TiO_2, SiO_2, and Fe_2O_3 of 115%, 1023%, and –42%, respectively.

Given the CMDs and GSDs calculated from the weighted-average and log-probit methods, theoretical lognormal distributions were determined to compare with those obtained

TABLE II. Summary of the Count-Difference Method (mean ±SD) to Determine Counts <300 nm Relative to SMPS Counts

Aerosol Type	SMPS (<300 nm) #/cm^3	CPC-OPC #/cm^3	% Error <300 nm	<300 nm Ratio (CPC-OPC)/SMPS
NaCl	31,900 ± 15,500	32,500 ± 15,000	3.7 ± 7.5	1.04 ± 0.08
TiO_2	13,700 ± 3500	12,000 ± 2000	–10.9 ± 12.8	0.89 ± 0.13
SiO_2	9200 ± 300	14,600 ± 500	58.4 ± 7.8	1.58 ± 0.08
Fe_2O_3	10,000 ± 1200	12,600 ± 800	27.0 ± 18.6	1.27 ± 0.19

from a combination of OPC and SMPS data (Figure 5). The distributions reproduced by the log-probit method for NaCl and TiO_2 more closely resembled the actual distributions than the weighted-average method; however, the TiO_2 log-probit distribution did not appear as similar as for the NaCl aerosol. For both the NaCl and TiO_2, the weighted-average method shifted the distributions to a smaller size range. Neither the weighted-average nor the log-probit methods were able to reproduce a distribution similar to the actual distributions for SiO_2. In the case of the log-probit, the reproduced distribution was greatly shifted to smaller diameters and had a much larger GSD. The weighted-average method also shifted the distribution to smaller sizes, but the GSD is much narrower.

The actual Fe_2O_3 distribution was bimodal, whereas neither method for determining CMD and GSD accounted for aerosols with modes greater than one. Therefore, both reproduced distributions were unimodal and did not appear to be similar to the actual. For the weighted-average method, the distribution was shifted to smaller diameters and appears to give more weighting to the mode in the smaller size range of the actual distribution. The log-probit method placed most of the distribution in the second Fe_2O_3 mode.

Comparison of CMD and GSD Determination

The percent error for determining CMD using the weighted-average method ranged from approximately –80% to 90% with the least error (< ±10%) observed when the CMD was larger than 500 nm and even lower when the GSD was small. The greatest percent error (> ±50%) occurred between CMDs of approximately 100 nm to 200 nm with GSDs of 1.2 to 2.5. The percent error for determining GSD ranged from –55% to 130% with the least error (< ±10%) observed when the CMD was larger than 500 nm and the GSD less than 1.8 and smaller than 200 nm for GSDs between 1.4 and 2.5. The greatest percent error (> ±50%) occurred between CMDs of approximately 200 nm to 500 nm with GSDs of 1.2 to 2.5.

The accuracy of the log-probit method for determining CMD and GSD was much greater than for the weighted-average method. Percent errors for determining CMDs using the log-probit method ranged from –5% to 25% for CMDs between 50 and 1000 nm and GSDs between 1.2 and 2.5. The highest percent error, 25%, occurred at a CMD of 50 nm and GSD of 1.9. As CMD and GSD increased, the percent error decreased. For CMDs between 100 and 1000 nm, the percent error never exceeded ±10%, and for CMDs between 200 and 1000 nm, the percent error never exceeded ±3%. Percent errors for determining GSDs ranged from −8% to 3% for CMDs between 50 and 1000 nm and GSDs between 1.2 and 2.5. The highest percent error, –8%, occurred at a CMD of 50 nm and GSD of 1.9. As CMD and GSD increased, the percent error decreased. For CMDs between 550 and 1000 nm, the percent error never exceeded ±1%.

TABLE III. Summary of the Weighted-Average and Log-Probit Methods (mean ±SD) to Determine Counts <100 nm Relative to SMPS Counts

		Weighted-Average Method			
Aerosol Type	SMPS <100	Estimated <100	% Error <100	CMD (nm)	GSD
NaCl	16,200 ± 8,700	33,300 ± 15400	121.0 ± 52.4	50.7 ± 2.2	1.46 ± 0.17
TiO_2	2500 ± 500	12,800 ± 2400	407.0 ± 52.9	68.9 ± 5.4	2.25 ± 0.16
SiO_2	1300 ± 100	15,000 ± 500	1093.4 ± 68.4	49.1 ± 1.1	1.33 ± 0.09
Fe_2O_3	4200 ± 800	12,700 ± 700	214.0 ± 50.4	60.7 ± 5.2	1.99 ± 0.21
			Log-Probit Method		
NaCl		14,700 ± 8900	–9.6 ± 28.5	109.0 ± 24.1	1.69 ± 0.20
TiO_2		4900 ± 1600	115.4 ± 52.7	137.5 ± 25.1	1.94 ± 0.11
SiO_2		14,200 ± 800	1022.9 ± 64.5	22.1 ± 11.8	2.89 ± 0.56
Fe_2O_3		2000 ± 2100	–42.0 ± 71.9	177.6 ± 30.3	1.60 ± 0.17

DISCUSSION

Count-Difference Method

The percent error observed using the count-difference method for all aerosols ranged from –10.9% to 58.4%. All estimated number concentrations of very fine particles were overestimated in comparison with the actual number concentrations as measured by the SMPS, except for the TiO_2 aerosol, which was underestimated by –10.9%. With respect to monitoring for occupational exposure, the overestimation of particle number concentration gives a protective assessment of exposure. These results indicate that the count-difference method is effective in determining the presence of very fine particles in a workplace atmosphere, especially one that has a mixture of aerosol types with different particle sizes.

All aerosols in this study had size distributions that did not include a significant number of particles larger than 1000 nm, and therefore, the CPC was able to measure all aerosol particles. The lower particle size limit of the OPC (300 nm) is known, and so it was expected that the percent error for the estimated counts of very fine particles would be very low and within the limits of the instrument's measurability. Deviation from limits of the instrument's measurability could therefore be attributed to OPC performance when measuring particles with different chemical and physical properties than what the OPC is calibrated to measure.

The ability of the OPC to accurately size particles is affected by the refractive index of the particle it is measuring. Ratios of calculate-to-actual very fine number concentrations using the count-difference method were statistically different from each other except for NaCl and TiO_2, the two nanoparticle types with ratios closest to unity. This suggests that the OPC distribution for NaCl and TiO_2 was not as strongly affected by refractive index or other factors that could influence particle light scattering, and the discontinuity between the SMPS and OPC distributions was therefore not as significant. This also suggests that, for NaCl and TiO_2 aerosols, this method is a relatively accurate way to determine very fine particle number concentrations.

Greater percent errors using the count-difference method were observed for SiO_2 and Fe_2O_3, for which the SMPS and OPC distributions did not merge together as well as the NaCl and TiO_2 distributions, indicating increased optical effects on OPC sizing and measurement. SiO_2 has a smaller RI (1.46) than PSL spheres (1.6), and as a result, particles scatter less light and are measured by the OPC as smaller than actual. This was seen as a shift of the OPC distribution to smaller diameters and a gap between the OPC and SMPS distributions. As a result, there was a lower than actual OPC count and subsequently greater error and overestimation. The percent error estimated by the OPC and CPC for the Fe_2O_3 aerosol was 27%, which is an overestimation compared with the SMPS very fine number concentration. This can be explained by the fact that Fe_2O_3 has a RI of 3.01 which is greater than that for PSL spheres. Whereas, the RI of NaCl is approximately 1.54, which is similar to the RI of the PSL spheres, and therefore, the SMPS-to-OPC merger was almost perfect.

The effect of RI on particle sizing by OPCs has been noted by others.[23–27] Many studies have been conducted in relation to how RI affects OPC design and function as well as how to model and correct for the effect through experimental and theoretical approaches.[26,28,29] To confirm the effect of a particle's RI on OPC response, more research is needed, such as providing a definitive determination of the material's RI including the real (scattering effect) and imaginary (absorption effect) components. Given this information, the counts originally assigned to size channels associated with an OPC can be shifted by the number of channels and direction required to accurately place counts in the correct channel.[30] Such an approach would greatly enhance the accuracy of the methods described here. However, correcting an OPC for the RI of a particular material is not necessarily useful if one is measuring aerosols in an environment where there are aerosols composed of multiple materials with potentially multiple RIs.

Nonspherical particles can also cause variability in light scattering that can affect OPC particle sizing. The aerosol particles measured in our research had varying degrees of agglomeration, as witnessed in TEM images, and therefore were not perfect spheres. In addition, the agglomeration observed in this research may differ from that which occurs in the workplace. For example, fresh nanoparticles produced from a high-temperature production process may have a different agglomerate structure and degree of agglomeration than nanoparticle aerosols produced from nebulizing bulk nanoparticle powders.

The sizing mechanism of most OPCs is based on the assumption that particles are spherical; however, there has been research conducted over the years that models light scattering by irregularly shaped particles.[31–33] It has been observed in some cases that scattered light intensity from nonspherical small particles is within approximately 4% of that of an equivalent volume sphere.[34,35] However, it was beyond the scope of this research to quantify the exact effect of particle shape on OPC sizing and differentiate its effect from the effect of RI on OPC sizing, but it is an aspect that affects OPC performance that should be noted.

Size-Distribution Method

In evaluating the accuracy of the size-distribution methods used to estimate number concentration of aerosol particles with diameters <100 nm, the log-probit method was more accurate than the weighted-average method, but the percent error was greater for both these two methods than that observed for the count-difference method used to determine counts of particles <300 nm. As with the count-difference method, for most of the aerosols, both the weighted-average and log-probit methods overestimated number concentration, which implies a protective result in terms of occupational exposure because it errs on the side of caution.

The largest deviations from actual number concentration using the log-probit method appeared to be when the RI

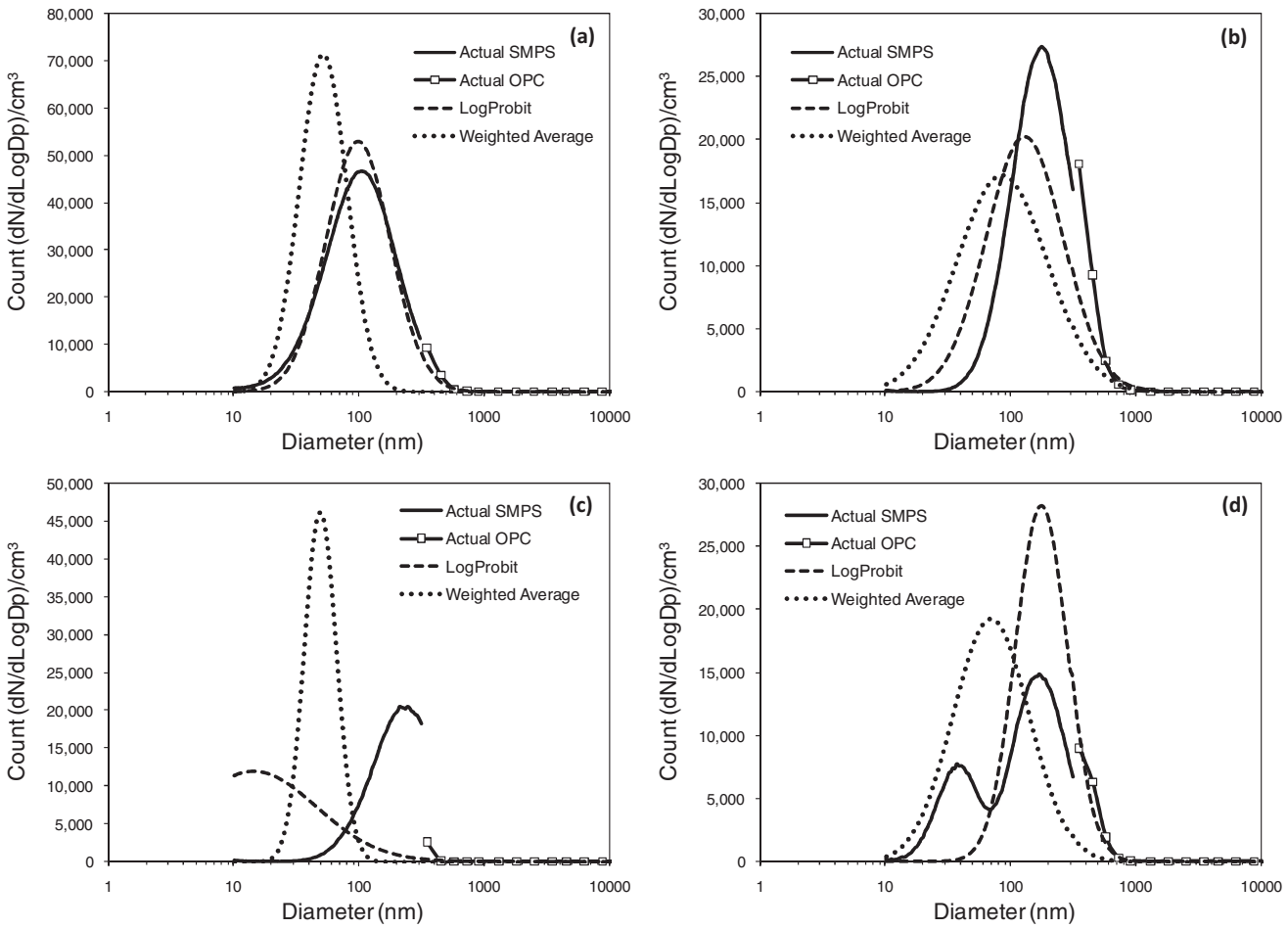

FIGURE 5. Aerosol size distributions from SMPS and OPC measurements, weighted-average method, and log-probit method for (a) NaCl, (b) TiO_2, (c) SiO_2, and (d) Fe_2O_3 aerosols.

of the test aerosol began to differ from the RI of the OPC calibration material. A low percent error was observed for the NaCl and TiO_2 using the count-difference method; however, the percent error for TiO_2 increased from –10.9% for the count-difference method to over 100% for the log-probit method. As for NaCl, the percent error only slightly changed from 3.7% for the count-difference method to –9.6% for the log-probit method, indicating that when optical effects are minimal the log-probit method can be used to estimate nanoparticles within the manufacturer-reported instrument accuracy. The concentration accuracy of the CPC reported by the manufacturer is ±20%, and the reproducibility of the OPC reported by the manufacturer is ±2%.

When measuring TiO_2 particles, even though it was not shown to be significantly different from that of NaCl particles, the OPC distribution was slightly shifted to larger diameters that resulted in a decreased estimation of the CMD by the log-probit method and magnified the overcounting by 115% (Figure 5). This shift may be attributed to the difference between the TiO_2 RI of 2.62 and the RI of the OPC calibration material. Estimations of number concentrations smaller than 100 nm for SiO_2 aerosols using the log-probit method were overestimated by 1023% and were much greater than the instrument percent error range. Optical effects were much more pronounced for SiO_2 than for any of the other aerosols. The smaller RI of SiO_2 caused the OPC distribution to shift to smaller diameters by more than one size bin, resulting in a reduced count for diameters between 300 and 1000 nm. The reduced number concentration led to fewer particles subtracted from the CPC and therefore an overestimation of particle number concentration with diameters smaller than 100 nm.

The log-probit method underestimated Fe_2O_3 particle number concentration smaller than 100 nm by 42%. However, this result was confounded by the formation of a bimodal Fe_2O_3 particle distribution that was not accounted for by either size distribution method (Figure 4). The reproduced distribution was therefore unimodal, with a CMD located in the actual larger-diameter mode, and did not include a significant portion of the other mode in the actual distribution that had a smaller diameter, and as a result, an underestimation of number concentration was observed.

It is unknown why the Fe_2O_3 aerosol was bimodal, but it may be attributed to the primary particle size of the bulk powder, which ranged from 20–50 nm. Also, contaminants in the ultrapure water used for nebulizing the bulk powder may have added to the additional mode. LaFranchi et al.[36] observed a similar occurrence while nebulizing deionized water and found that leaching from water storage containers is a component of the impurities. Schmoll et al.[37] demonstrated that the smaller peak of the bimodal distribution is a result of salts created by elements in the ultrapure water used to create the nanopowder suspension added to the nebulizer.

Percent error for estimating number concentration using the weighted-average method was 121% for NaCl and much greater for the other aerosols. The high overestimation of number concentration may be attributed to the lack of size resolution for lower sizes in the method. This method, as its name implies, applies a weighted-average, consisting of the counts in that bin, to the mid-diameter of a size bin. There were 16 size bins evaluated with one bin containing particle counts for diameters between 10 and 300 nm and the other 15 bins being the original bins the OPC reports. As a result, if a large percentage of particles is placed in the lower size bin, a greater weighting will be placed on that bin, which results in a CMD with smaller than actual diameter.

Figure 5 shows the reproduced size distribution for NaCl using the weighted-average method as well as the original SMPS and OPC distributions. The weighted-average distribution is shifted to a smaller size range, and therefore, the number concentration for particles with diameters smaller than 100 nm was much higher than measured by the SMPS, and in fact, that was the case for all of the different aerosols. Although not given here, it can be demonstrated that the weighted-average method for determining the CMD and GSD becomes more accurate as the bin widths decrease, with the result of having more bins over the entire diameter range analyzed. For example, this method is used by the software supplied by the SMPS used for this research—an instrument capable of separating counts into 64 bins per decade.

Limitations

A variety of types of nano-sized aerosol distributions from unimodal to multimodal of varying size ranges can be observed in workplaces.[11,13,38,39] However, the count-difference method for calculating counts of very fine particles is useful, especially if the particle material type is known, such as industrial operations with known particle source types.[11,38,39] The log-probit method appears to give a good estimate of number concentration of particles <100 nm but is also affected by OPC mismeasurement from particle physical properties as well as when the particles exhibit multimodal distributions. Characterization of nano-size aerosols may therefore require a variety of techniques, depending on field conditions.

CONCLUSIONS

This study evaluated methods to estimate very fine and nanoparticle number concentration from laboratory-produced nanoparticle aerosol data collected from two instruments, an OPC and a CPC, that can be used in assessments of occupational exposure to nanoparticles. It was observed that the very fine particle number concentration can be accurately determined by subtracting OPC number concentration between 300 and 1000 nm from CPC number concentration. This very fine number concentration can be used as an additional channel of particle counts in the 10–300 nm range for estimating nanoparticle number concentration.

However, particle optical properties can seriously affect OPC measurement accuracy. Therefore, further characterization of the aerosol's properties and/or calibration of the OPC for a specific aerosol may be required to mitigate these effects. The log-probit probability method was able to estimate number concentration of particles with diameters smaller than 100 nm with minimal error. However, the percent error of this estimate relative to number concentration made with a SMPS increased when the aerosol RI differed from OPC calibration standards and distributions were multi-modal. In summary, although a workplace assessment utilizing data combined from CPC-OPC measurements is attractive from the standpoint of portability and ease of use, the results should be evaluated on a site-specific basis given changes in OPC response to different aerosols.

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