보건학석사 학위논문

Comparison between Time Integrated Sampling and Direct Reading Sampling of Nanoparticulate at the Workplace

작업장의 나노입자상 물질에 대한
시간누적 시료채취와 실시간 시료채취 방법 비교

2015 년 2 월

서울대학교 보건대학원

환경보건학과 산업보건전공

김 선 주

Comparison between Time Integrated Sampling and Direct Reading Sampling of Nanoparticulate at the Workplace

작업장의 나노입자상 물질에 대한
시간누적 시료채취와 실시간 시료채취 방법 비교

지도교수 윤 충 식

이 논문을 보건학석사 학위논문으로 제출함

2014 년 10 월

서울대학교 보건대학원

환경보건학과 산업보건전공

김 선 주

김 선 주의 보건학석사 학위논문을 인준함

2014 년 12 월

위 원 장	이 승 묵	(인)
부 위 원 장	최 경 호	(인)
위 원	윤 충 식	(인)

Abstract

Comparison between Time Integrated Sampling and Direct Reading Sampling of Nanoparticulate at the Workplace

Sunju Kim

Department of Environmental Health

Graduate School of Public Health

Seoul National University, Korea

Advisor Chungsik Yoon, Ph.D., CIH

Objective Nanoparticles are generated by engineered and unintended in a variety of workplaces and process. Nanoparticles generation in unintended nanoparticle emitting workplace may originate from hot process, welding process. Number and surface area concentration of nanoparticles is generally assessed by a variety of direct reading instruments unlike traditional method. The purposes of this study were to compare time integrated sampling and direct reading instrument sampling method at nanoparticles generation workplaces, and to compare statistically full time sampling and time interval sampling categorized by time integrated sampling method. As characteristics of a variety of workplaces measured in this study were investigated, this study suggests appropriate sampling method by workplace.

Methods Sampling was used two methods; the way to use a filter which sampled the air of workplace as time integrated sapling method and the way to sample by direct reading instrument such as SMPS, DustTrak, AeroTrak. Each filter was measured the direct reading instrument simultaneously, and for full time sampling compared with time interval, time interval sampling is measured for working time while replacing a filter by predetermined time interval. Analysis is performed for mass, metals, and TEM. Statistical analysis is performed to compare associations between metrics.

Results Concentrations measured at unintended nanoparticle emitting workplaces were higher than those at engineered nanoparticle manufacturing workplaces. CV of concentration is larger as shorter time interval. Full time samples were significantly higher coefficient than time interval samples in spearman's rank test.

Conclusions As $PM_{2.5}$ concentration out of total mass concentration measured at welding workplaces was above 90%, mass concentration is recommended by gravimetric method. Although concentration measured at engineered nanoparticle manufacturing workplaces was relatively low, nanoparticles generation ratio is high. Therefore, the best way of sampling methods are recommended by using together direct reading instrument and gravimetric sampling method.

Keyword: Engineered nanoparticles, Unintended nanoparticles, Direct reading instrument, Time Integrated Sampling, Sampling method

Student number: 2012-21841

Contents

List of Tables

List of Figures

1 Introduction

Aerosol sampling methods have long been in use, from the 19^{th} century, when they were initially developed from sugar tubes, to the invention of time-weighted average (TWA) sampling methods in the 1970s, which are still used today (Spurny, 1998). However, although sampling methods are able to collect smaller-sized particles as newer technology is developed, time-integrated sampling (i.e. gravimetric sampling) is still the reference method used by the National Institute for Occupational Safety and Health (NIOSH), the United States Environmental Protection Agency (EPA), and the Korea Occupational Safety and Health Agency (KOSHA).

With recent developments in nanotechnology, it is possible not only to generate engineered nanoparticles (particles <100 nm in diameter) in a variety of workplaces and processes but also to measure nano-sized particles. However, many toxicity studies have shown that the toxicity of nanoparticles, also known as ultrafine particles (UFPs), is greater than that of the same mass of larger particles of similar chemical composition. Many studies have also shown that exposure to nanoparticles causes respiratory and cardiovascular diseases (NIOSH, 2009).

Workplaces with nanoparticle exposure are categorized as either unintended nanoparticle emitting workplaces or engineered nanoparticle manufacturing workplaces. Nanoparticle generation in unintended nanoparticle emitting workplaces may originate from hot processes, such as welding (Zimmer et al., 2002), and grinding (Maynard et al., 2002). In previous studies, high particulate concentrations have been reported in workplaces where activities such as high-temperature and welding processes take place (Zimmer et al., 2002; Maynard et al., 2002; Elihn et al., 2009).

However, sampling of nanoparticles is limited to assessment by gravimetric sampling methods, which is the traditional method (Heitbrink et al., 2009). A reference method for nanoparticle exposure assessment has not yet been determined; however, assessment methods generally use three metrics: number, surface area, and mass concentration. Instead of using the traditional method, number and surface area concentration are normally assessed by a variety of direct-reading instruments such as a condensation particle counter (CPC), scanning mobility particle sizer (SMPS), or DustTrak aerosol monitor. Mass concentrations of nanoparticles are generally underestimated compared to larger particles (Heitbrink et al., 2009).

Although gravimetric sampling is the reference method, it cannot identify variations in concentration because particles are collected over a long period of time (Morawska et al., 2003). The TWA method over an 8-hour period as a time-integrated sampling method may underestimate particulate exposure in the workplace because the variation in exposure during the work day is large, ranging from background concentrations, such as during break time, to outdoor concentrations and working concentrations. However, unlike direct-reading instruments, with traditional sampling it is possible to identify the chemical composition, morphology, and size of particles. One drawback of direct-reading instruments is that accuracy and reliability are still limited. Few studies have compared measurements from time-integrated sampling methods, such as fine particulate matter ($PM_{2.5}$) concentrations, to those from direct-reading instruments, such as a mass-based DustTrak (Kim et al., 2004; Zhu et al., 2011).

The purposes of this study were to compare time-integrated sampling methods and direct-reading instrument sampling methods at nanoparticle generating workplaces, and to statistically compare direct-reading instrument sampling methods and time-integrated sampling methods. Also, as we investigated the characteristics of a variety of workplaces in this study, we suggest appropriate sampling methods according to workplace type.

2 Methods and materials

2.1 Definition of expression

- Offline monitoring: gravimetric sampling
- Online monitoring: direct reading sampling
- CV (Coefficient of Variation): ratio of the standard deviation to the mean
- "1 min" (1 min for DustTrak; Table 4): 1 min is collected by DustTrak data in the same time periods with gravimetric sample (DustTrak logging time is 1 min).
- "TIS time" (Time Interval Sampling time for DustTrak; Table 4): TIS is selected by DustTrak data that calculated by geometric mean respectively in the same time periods with gravimetric sample time. TIS sample numbers are the same with gravimetric those.

2.2 Study design

This study was conducted at two engineered nanoparticle manufacturing workplaces (workplaces A and B) and at two unintended nanoparticle emitting workplaces (workplaces C and D) where welding processes took place. Measurements were performed for 2 days at each workplace. Sampling was conducted during two full working shifts and once overnight at all workplaces, except for workplace B, which was sampled for one full working shift and once overnight. The complete sampling strategy design is shown in Figure 1.

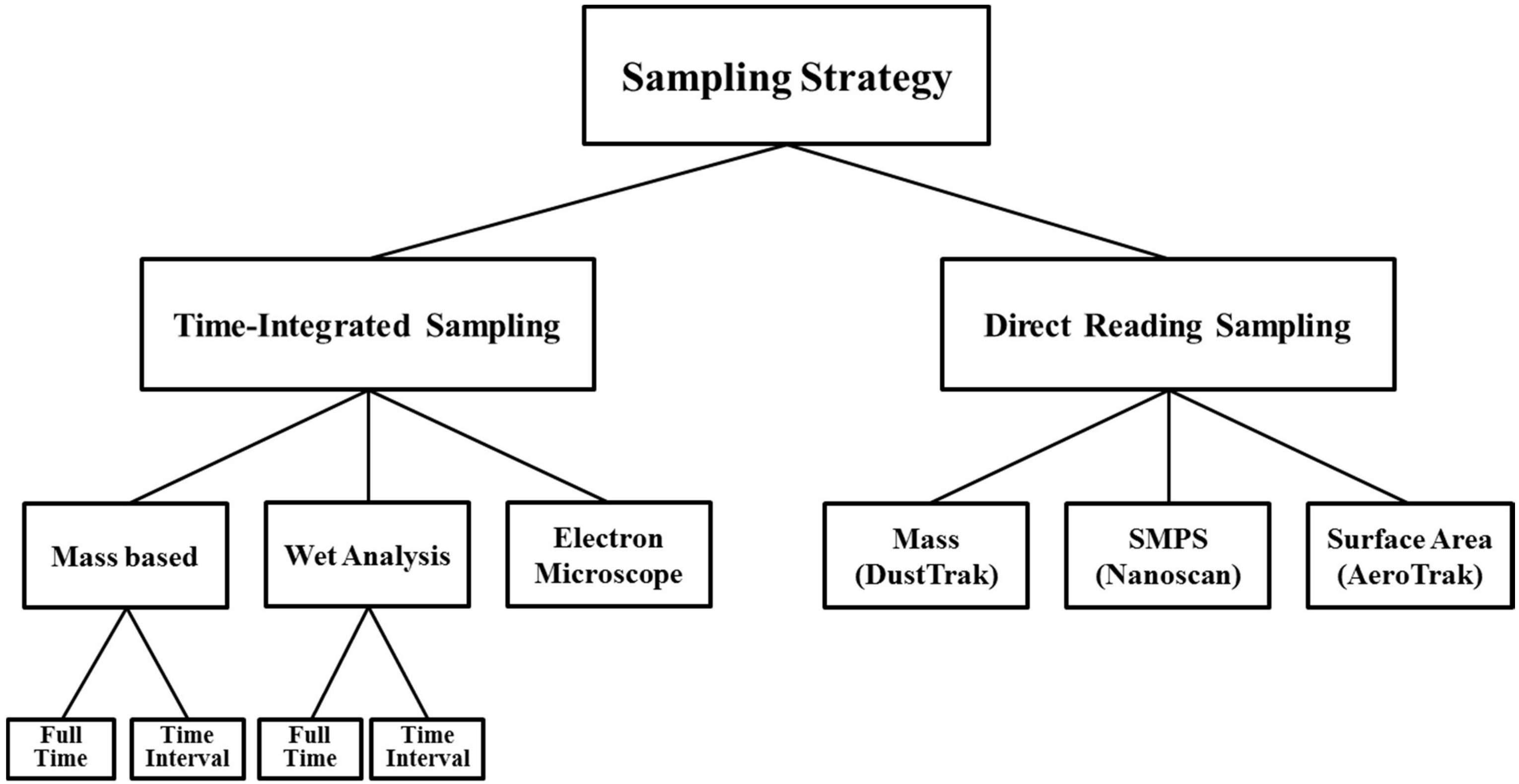


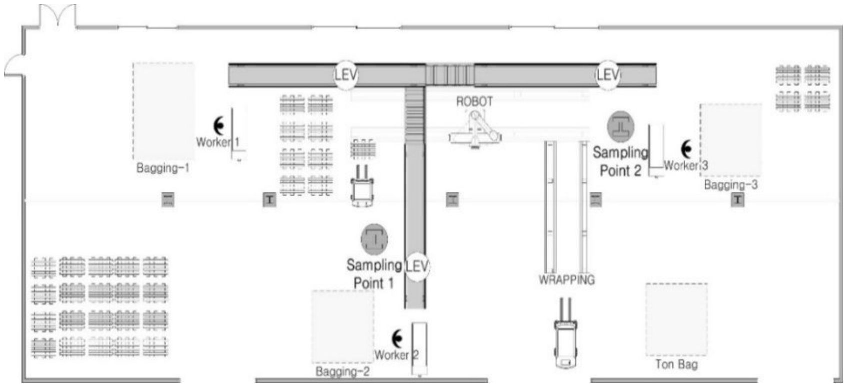
Figure 1. Diagram of sampling strategy in this study.

Workers in workplaces A and B, engineered nanoparticle manufacturing workplaces, were exposed to particles during processes such as bagging and collecting. In workplace A, amorphous silica of 7 - 40 nm average diameter was manufactured, and each process was an automatic system, with the exception of bagging, which was measured in this study. At workplace B, metallic nanopowders such as aluminum, iron, copper, nickel, and silver were manufactured. Nanopowders were produced by the pulsed wire evaporation method, and the main products were copper-nickel and nickel nanopowder.

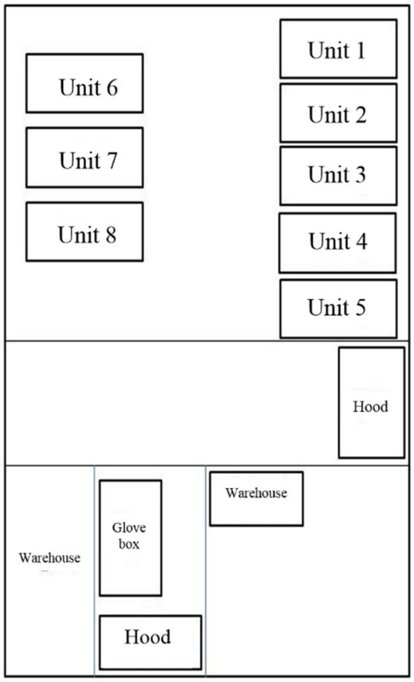
In workplaces C and D, unintended nanoparticle emitting workplaces with high temperatures, particles were generated from fumes generated during welding and melting processes. An automobile engine part was manufactured in workplace C, and sampling was conducted at the melting process on the first day and at the welding process on the second day. Body frames for heavy equipment, such as forklifts, were manufactured in workplace D, which was located at an industrial complex. Sampling was measured at the welding process.

Table 1. Summary of workplace characteristics

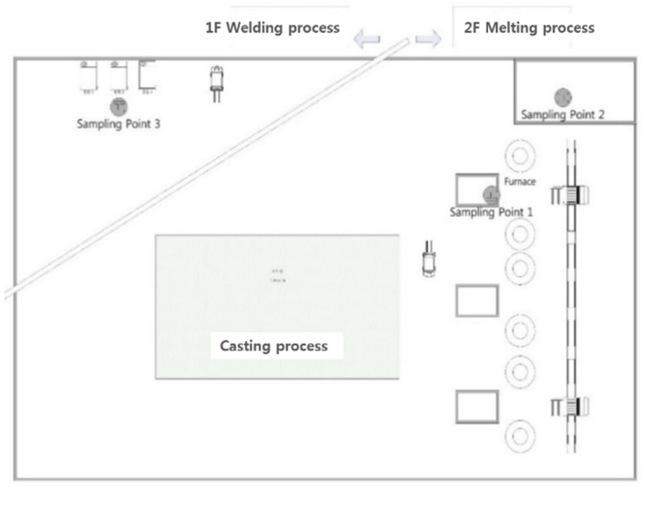
Type of nanoparticle	Workplace	Nanoparticle generation process	Daily production rate	No. of workers exposed to nanoparticles/ Total no. of workers	Work type	Working time per day (hours)	Temperature, humidity
Engineered nanoparticles (ENP)	A	bagging	25 tons	4/1500	semi-automatic	8 (shift work)	31 °C, 57%
	B	sieving, collecting	700 g	6/14	semi-automatic	8	26 °C, 53%
Unintended nanoparticles	C	melting, welding	-	63/178	manual	8 (shift work)	35 °C, 40%
	D	welding	-	30/58	manual	8 (shift work)	41 °C, 32%


LEV
LEV
ROBOT
Worker 1
Bagging-1
Sampling
Point 2
Worker 3
Bagging-3
Sampling
Point 1
LEV
WRAPPING
Worker 2
Bagging-2
Ton Bag

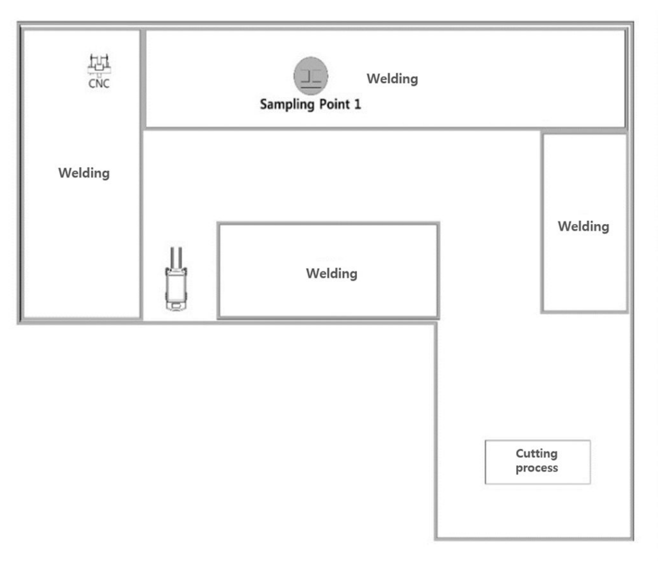
(a)


Unit 1
Unit 6
Unit 2
Unit 7
Unit 3
Unit 8
Unit 4
Unit 5
Hood
Warehouse
Glove box
Warehouse
Hood

(b)



(c)



(d)

Figure 2. The layout of workplaces (a) Workplace A, (b) Workplace B, (c) Workplace C, (d) Workplace D.

2.3 Sampling methods

Sampling was measured using two methods. The first method was time-integrated sampling using filters categorized for mass analysis, metal analysis, and electron microscope analysis. The second method used direct-reading instruments categorized by measurement metrics.

2.3.1 Time integrated sampling

The time-integrated sampling used filters to measure mass concentrations and identify metal contents for quantitative analysis. An electron microscope was used to determine the size, morphology, and aggregation of particles for qualitative analysis. Polyvinyl chloride (PVC Filter, 37 mm, 5 ㎛, Millipore, Germany) was used for gravimetric analysis according to NIOSH method no. 0500, and mixed cellulose ester membrane filters (MCE Filter, 37 mm, 0.45 ㎛, Millipore, Germany) were used for metal analysis according to NIOSH method no. 7300. A transmission electron microscopy (TEM) grid (Q225-CR1, 200 mesh copper, EMS, USA) was used to analyze particle sizes and morphologies with an electron microscope.

Each filter attached to the three-piece cassette sampled using a 2-liter per minute (LPM) pump (Gilian Inc., USA). Measurements with direct-reading instruments were obtained simultaneously with the time-integrated sampling. To compare full shift sampling to time-interval sampling, time-interval sampling was conducted for a working shift while replacing the filter at set time intervals.

The following equation was used to estimate the minimum sampling volume for workplace measurements and evaluations:

$$Ve\ (L) = \frac{LOQ\ (\mu g)}{Q\ (mg/m^3)} \quad \text{(eq. 1)},$$

where *Ve* is the estimated minimum sampling volume, LOQ is the limit of quantification of the measuring device, which is generally threefold the limit of detection (LOD), and Q is the estimated concentration in the workplace.

2.3.2 Direct reading sampling method

Table 2 shows characteristics of the direct-reading instruments. A Nanoscan SMPS (3910, TSI, USA) was used to measure particle number concentrations, a DustTrak aerosol monitor (8533 TSI, USA) was used to measure mass concentrations, and an AeroTrak nanoparticle aerosol monitor (9000, TSI, USA) was used to measure surface concentrations. To confirm the characteristics of the particulates generated during the work, researchers directly recorded in time activity diary (TAD).

Table 2. Characteristics of direct-reading instruments

Metric	Device	Remarks
Mass	DustTrak 8533 (TSI Inc.)	· Particle size range: 0.1 ㎛ to 15 ㎛ · $PM_{1.0}$, $PM_{2.5}$, PM_{10}, Respirable mass
Number	Nanoscan 3910 (TSI Inc.)	· Particle size range: 10 ㎚ to 420 ㎚ · 13 channels · CPC + DMA
Surface Area	Nanoparticle Aerosol monitor 9000 (TSI Inc.)	· Particle size range: 10 ㎚ to 1,000 ㎚ · TPM: 1 $㎛^2$/cc to 2,500 $㎛^2$/cc RPM: 1 $㎛^2$/cc to 10,000 $㎛^2$/cc · Resolution: 0.1 $㎛^2$/cc

2.4 Analysis methods

The PVC filters were stored in a constant temperature/humidity chamber for at least 24 hours (20 °C±5, 55%±5), and then weighed using an analytical balance (Ultra Microbalance XP2U, METTLER TOLEDO, USA) to calculate the mass concentration.

MCE filters were placed into graphite sample decomposition blocks (i.e, vessel; ECOPRE, ODLAB, Korea), 3 ml of ashing acid (nitric acid and perchloric acid 4: 1 mixtures) was added to the vessel, and the temperature was maintained at 130 °C for 30 min. Pretreated samples with a total capacity of 40 ml were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES; Model Optima 3100 DV, Perkin-Elmer, USA). During analysis, the appropriate wavelength for each metal was selected according to NIOSH method no. 7300. The target material in workplace A was silica, but metal content was used as a substitute for mass concentration due to the analysis limitations of ICP. The target materials in workplace B were copper and nickel, and the target materials in workplaces C and D were iron, manganese, chromium, copper, nickel, and zinc. The total metal content was calculated as the sum of the analytical results of each target material.

Electron microscopy was used to identify the morphologies and sizes of particles. The TEM-grid samples from the workplaces were analyzed using high resolution (HR)-TEM (High Resolution - Transmission Electron Microscope, JEM-3010, Japan). The elemental analysis of the particles was performed using energy dispersive spectroscopy (EDS; Energy Dispersive Spectrometer, Oxford, UK).

2.5 Statistical analysis

To compare the time-integrated and direct-reading sampling methods, all direct-reading instruments were placed next to the time-integrated sampling equipment and measurements were obtained simultaneously. A total of 42 paired datasets were collected. Eight pairs were excluded due to incomplete direct-reading or time-integrated measurements. Grubbs' test was used to test for outliers; one sample was excluded as an outlier, leaving a total of 33 samples for further analysis. The direct-reading instrument dataset was compared to the time-integrated sampling dataset using the Kolmogorov-Smirnov test. All data were positively skewed, and therefore all of the direct-reading data were adapted to a log-normal distribution.

The Wilcoxon signed-rank test was used to compare the full shift and time-interval time-integrated sampling methods to the direct-reading sampling method. In addition, Spearman' rank correlation coefficient was used to identify associations between the time-integrated and direct-reading sampling methods. Linear regression modeling was performed to determine the coefficient of determination. All statistical analyses were performed using SPSS version 20.0 (IBM Inc., USA).

3 Results

3.1 Characteristics of workplaces

A summary of the direct-reading sampling and time-integrated sampling is provided in Table 3. The mass concentrations during offline monitoring were generally higher in the unintended nanoparticle emitting workplaces than in the engineered nanoparticle manufacturing workplaces.

Some metal content samples from workplace B were below the limit of detection (LOD) due to the small output. The total metal contents at workplaces C and D were higher than at workplaces A and B. In addition, metal contents measured at the welding process at workplace D were higher than at the welding process at workplace C.

For the online monitoring results, the DustTrak $PM_{2.5}$/total particulate matter (TPM) ratios were >0.9 in workplaces C and D during the welding process, while the ratio was <0.9 during the melting process at workplace C. The highest SMPS measurement of the nanoparticle ratio (> 0.8) was observed at workplace C. The highest surface area concentration was observed at workplace D. As demonstrated by the SMPS measurements of nanoparticle ratios, the engineered nanoparticle manufacturing workplaces generated high nanoparticle number concentrations and high mass concentrations for particles > $PM_{2.5}$.

Table 3. Offline and online concentrations

Workplace	Measurement types	Offline Monitoring: Mass concentration (mg/m^3)	Offline Monitoring: Metal content* (mg/m^3)	Online Monitoring: DustTrak (mg/m^3) PM$_{2.5}$	DustTrak Total	DustTrak PM$_{2.5}$ /Total	SMPS (#/cm^3) <100 nm	SMPS > 100 nm	SMPS Total	SMPS <100 nm /Total	AeroTrak (㎛ ^{2}/cm^3)
A	Full	0.345	0.345	0.096	0.187	0.513	15,450	6,016	21,891	0.706	117
	Full	0.180	0.180	0.075	0.111	0.674	4,832	3,309	8,296	0.582	64
	Full	0.089	0.089	0.055	0.138	0.400	5,652	1,733	7,657	0.738	115
	interval	0.273	0.273	0.070	0.123	0.566	8,201	4,110	12,443	0.659	78
	interval	0.341	0.341	0.129	0.265	0.489	33,612	9,659	44,064	0.763	189
B	Full	0.093	0.003	0.027	0.037	0.732	7,671	1,727	11,383	0.674	39
	Full	0.063	< LOD	0.022	0.023	0.951	5,253	1,809	7,290	0.721	25
	interval	0.044	0.003	0.026	0.038	0.701	9,193	1,797	11,004	0.835	36
	interval	0.165	< LOD	0.029	0.037	0.792	4,749	1,517	6,498	0.731	45
C	Full	1.085	0.042	0.556	0.781	0.712	123,539	12,851	139,492	0.886	429
	Full	0.535	0.044	0.428	0.569	0.753	94,172	12,251	109,450	0.860	307
	Full	2.834	0.012	0.459	0.507	0.906	98,519	18,025	119,325	0.826	374
	interval	1.383	0.116	0.633	0.803	0.788	133,699	20,145	158,434	0.844	547
	interval	0.521	0.086	0.365	0.483	0.755	85,949	8,674	98,330	0.874	302
	interval	0.736	0.157	0.824	1.194	0.690	158,226	14,119	174,926	0.905	531
	interval	0.984	0.120	0.581	0.843	0.689	178,190	17,206	197,217	0.904	512
	interval	1.013	0.101	0.583	0.943	0.618	142,655	14,805	159,319	0.895	233
	interval	0.491	0.079	0.459	0.504	0.910	176,547	22,343	201,689	0.875	515
	interval	0.394	0.122	0.576	0.622	0.926	145,215	22,143	171,250	0.848	495
	interval	0.444	0.097	0.400	0.442	0.904	119,733	15,633	135,694	0.882	374

Workplace	Measurement types	Offline Monitoring		Online Monitoring							
		Mass concentration (mg/m^3)	Metal content* (mg/m^3)	DustTrak (mg/m^3)			SMPS (#/cm^3)				AeroTrak (㎛ ^{2}/cm^3)
				$PM_{2.5}$	Total	$PM_{2.5}$ /Total	<100 nm	> 100 nm	Total	<100 nm /Total	
D	Full	0.423	0.072	0.804	0.818	0.983	81,231	47,950	131,009	0.620	800
	Full	0.217	0.012	0.507	0.528	0.959	41,859	18,932	63,299	0.661	309
	Full	0.363	0.220	0.834	0.871	0.958	72,553	40,986	115,639	0.627	709
	interval	0.830	0.277	1.019	1.054	0.966	138,446	80,369	222,092	0.623	1,374
	interval	0.223	0.136	0.567	0.573	0.991	40,707	21,064	62,550	0.651	352
	interval	1.040	0.155	1.152	1.180	0.976	154,935	92,574	250,216	0.619	1,539
	interval	0.526	0.168	0.944	0.960	0.983	118,916	70,078	192,488	0.618	1,084
	interval	0.637	0.384	1.028	1.089	0.943	121,439	59,093	186,741	0.650	1,122
	interval	0.022	0.165	0.874	0.894	0.978	62,006	47,073	109,598	0.566	847
	interval	0.048	0.086	0.511	0.520	0.983	20,222	9,370	29,810	0.678	135
	interval	1.202	0.376	1.151	1.182	0.974	85,020	56,178	142,662	0.596	1,093
	interval	1.163	0.342	0.909	0.976	0.932	100,286	51,252	155,053	0.647	863
	interval	0.224	0.168	0.624	0.655	0.953	47,655	28,216	76,915	0.620	507

*Sum of target materials: workplace A = Si; workplace B = Cu, Ni; workplaces C and D = Fe, Mn, Cr, Cu, Ni, Zn; LOD (µg/sample): 0.0121 (Cu), 0.0089 (Cr), 0.0102 (Ni), 0.0106 (Mn), 0.0071 (Fe), 0.0080 (Zn).

Figure 3 shows the size distributions of SMPS particle measurements for each workplace. The nanoparticle generation ratio was the highest at workplace C. The graph indicates bimodal distributions of nanoparticles at the unintended nanoparticle emitting workplaces and normal distributions at the engineered nanoparticle manufacturing workplaces.

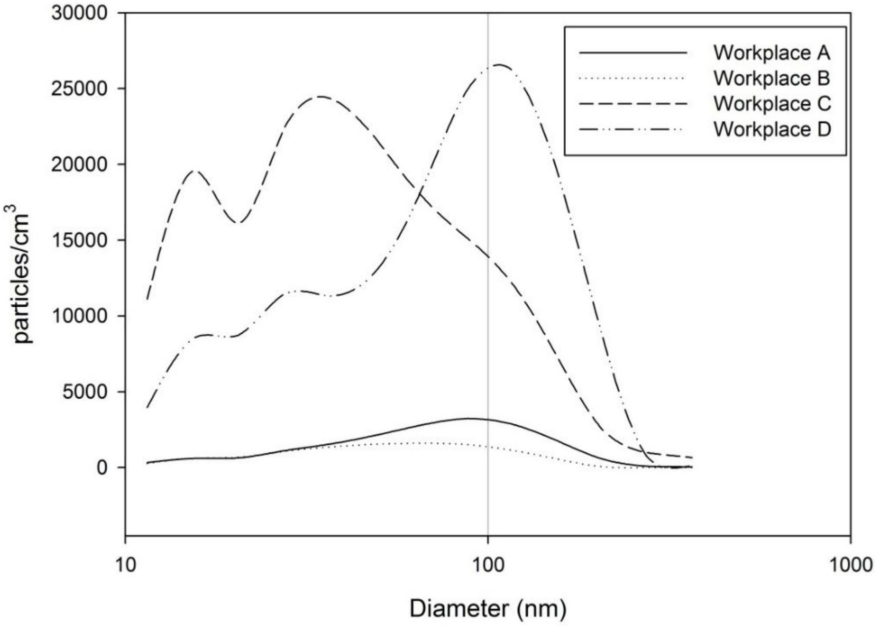
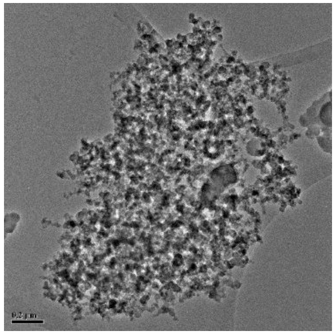
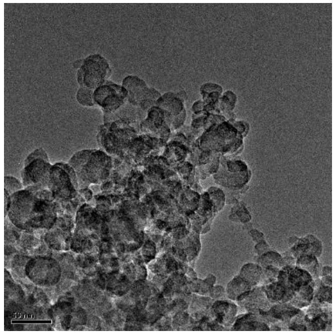


Figure 3. Size distributions from SMPS data from each workplace.

Figure 4 shows a TEM image for particle morphology, size, and aggregation analysis by electron microscopy. Small sized particles formed aggregates at the engineered nanoparticle manufacturing workplaces. There were both nanoparticles and larger particles observed at the melting process in workplace C, while almost all particles were nanoparticles at workplace D.

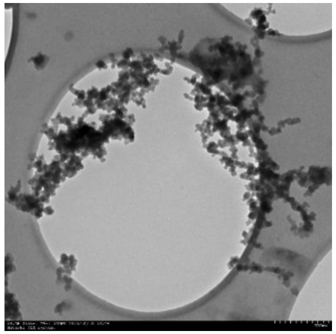


x 10,000

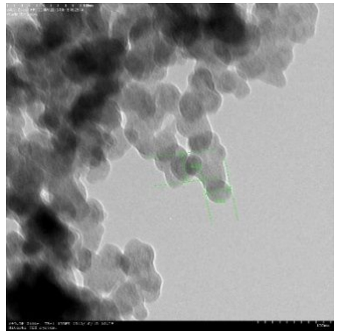


x 50,000

(a)

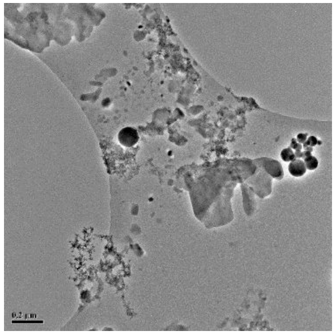


x 10,000

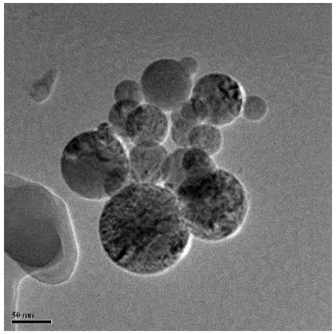


x 50,000

(b)

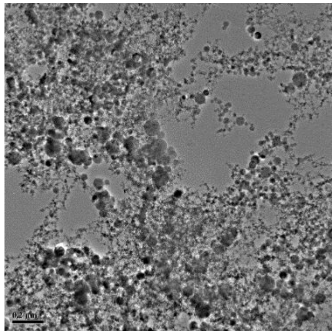


x 10,000

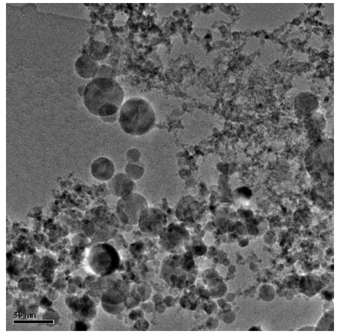


x 50,000

(c)



x 10,000



x 50,000

(d)

Figure 4. TEM images from monitored workplaces (a) workplace A, (b) workplace B, (c) workplace C, (d) workplace D.

3.2 Comparison of time integrated sampling and direct reading sampling method

Figure 5 shows the results of gravimetric sampling and direct-reading sampling with the DustTrak for the entire sampling period. Table 4 shows coefficient of variation (CV) using the results of the time-interval gravimetric sampling and the DustTrak sampling measurements from one day.

Time interval sampling (TIS) was measured only two samples for one day in workplace A and B, and for two days in workplace C and D. “1 min” and “TIS time” are collected by direct reading sample. The reason for classifying direct-reading instrument data in two ways was to compare variation between 1 min and TIS time intervals.

First, gravimetric sampling data was compared to 1 min interval direct-reading data. As shown in Figure 5, CV of gravimetric sampling is observed to lower value compared with 1 min interval data, and the CV of gravimetric sampling compared with 1 min interval in workplace B is higher. CV values of 1 min and TIS time measured by direct reading instrument in workplace A are higher than that of gravimetric sampling. All of direct reading instrument data on the first day in workplace C shows the highest variation compared with the others workplaces because workplace C shows the highest variation on first day measured at melting furnace working for 24 hours (> 1.0). CV of gravimetric sampling is higher than that of “1 min” and “TIS time” measured by DustTrak on the first and second day in workplace D.

Secondly, as compares with “1 min” and “TIS time”, all of “1 min” data shows the higher variation than “TIS time”. There is a significantly difference of variation between 1.3 times (DustTrak $PM_{2.5}$) in workplace D on second day and over 16 times (SMPS > 100 nm) in workplace C on first day.

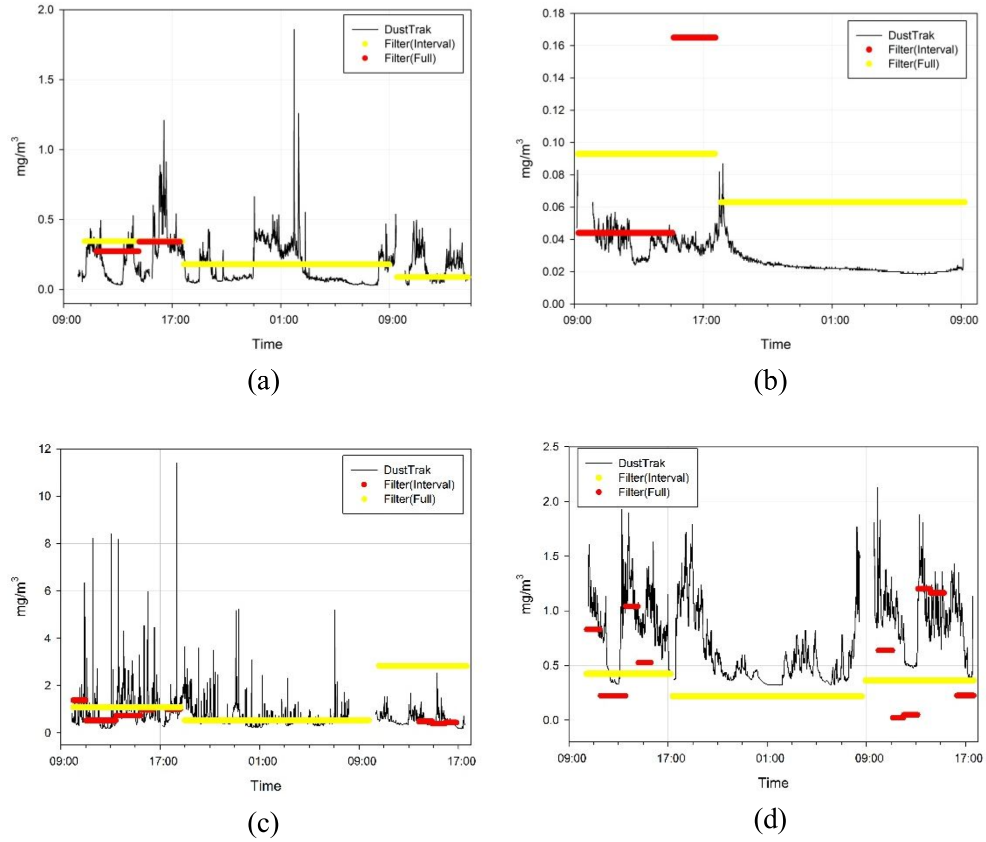


Figure 5. Time-integrated sampling results and DustTrak direct-reading sampling results (a) workplace A, (b) workplace B, (c) workplace C, (d) workplace D.

Table 4. Coefficient of variation (CV) based on the results from time-interval gravimetric sampling and DustTrak direct-reading sampling from one day

Workplace		Gravimetric Sampling	DustTrak $PM_{2.5}$		DustTrak Total		SMPS <100 nm		SMPS Total		AeroTrak	
			1 min*	TIS time**	1 min	TIS time	1 min	TIS time	1 min	TIS time	1 min	TIS time
	A	0.110	0.837	0.328	0.779	0.341	1.591	0.654	1.467	0.610	0.895	0.424
	B	0.577	0.109	0.046	0.182	0.021	0.348	0.150	0.326	0.130	0.206	0.100
C	Day 1	0.313	1.249	0.198	1.028	0.214	1.224	0.131	1.280	0.121	1.523	0.434
	Day 2	0.090	0.470	0.184	0.455	0.174	0.321	0.156	0.346	0.156	0.522	0.167
D	Day 1	0.472	0.381	0.205	0.383	0.210	0.614	0.306	0.552	0.306	0.554	0.319
	Day 2	0.894	0.337	0.255	0.342	0.257	0.879	0.474	0.714	0.432	0.582	0.424

* "1 min" (1 min for DustTrak) is collected by DustTrak data in the same time periods with gravimetric sample (DustTrak logging time is 1 min).
** "TIS time" (Time Interval Sample time for DustTrak; Table 4) is selected by DustTrak data that calculated by geometric mean respectively in the same time periods with gravimetric sample time. TIS sample numbers is the same with gravimetric those.

3.3 Comparison of full time and time interval sampling methods Comparison of the full shift and time-interval sampling methods

Sample volumes were calculated using equation 1, which is described in the methods section. The LOD of the balance used for measurements in this study was 6.9 µg, and the lowest concentration during the full shift was 0.093 mg/m^3. Therefore, the estimated minimum sampling volume was 223 L (the sampling flow rate was 2 L/min), and the minimum sampling time was 1 hour, 55 min. In this study measurements were sampled for a minimum 3 hours at workplaces A and B. At workplaces C and D, the highest concentration during the full shift was 2.834 mg/m^3, and the minimum sampling time was 4 min. At these workplaces, time-interval sampling time was appropriate.

Gravimetric sampling data were categorized as either full shift samples (11 samples), or time-interval samples (22 samples). The 33 samples of direct-reading instrument data, including gravimetric mass concentrations, AeroTrak surface concentrations, DustTrak $PM_{2.5}$/TPM ratios, and SMPS nanoparticle/TPM ratios, were not normally distributed. Therefore, nonparametric methods were used to compare gravimetric sampling measurements and direct-reading instrument sampling measurements.

The Wilcoxon signed-rank test was used to compare gravimetric sampling measurements and direct-reading sampling measurements. The Wilcoxon signed-rank test indicated that there were no differences in $PM_{2.5}$ and TPM concentrations obtained from gravimetric sampling and DustTrak sampling, but differences were detected between gravimetric and AeroTrak (p <0.001) surface concentrations, and between gravimetric and SMPS TPM concentrations (p <0.001).

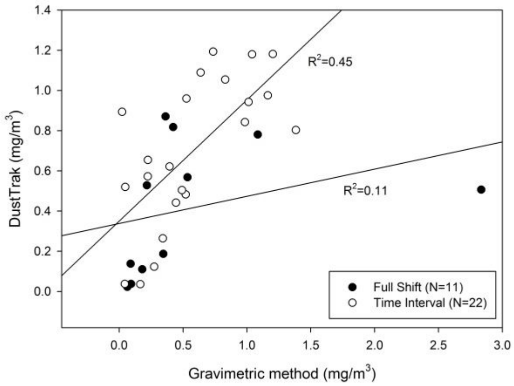
Spearman's rank correlation was used to determine the strength of the association between gravimetric sampling concentrations, categorized as total gravimetric sampling data, full shift samples, and time-interval samples, and direct-reading instrument concentrations. Table 5 shows the Spearman's rank correlation coefficient results. The Spearman's rank correlation coefficients for all data were found to be statistically significant (p <0.01). The Spearman's rank correlation coefficient for full shift gravimetric sampling concentrations and SMPS data was >0.9, indicating a strong positive association between the two measurements.

Table 5. Spearman correlation coefficient result

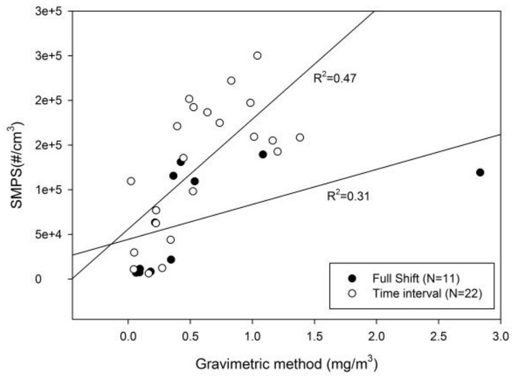
	Total	Full time	Time interval
AeroTrak	0.620*	0.782*	0.634*
DustTrak $PM_{2.5}$	0.584*	0.736*	0.628*
DustTrak Total	0.642*	0.736*	0.675*
SMPS <100 nm	0.769*	0.927*	0.652*
SMPS Total	0.761*	0.918*	0.679*

* p <0.01

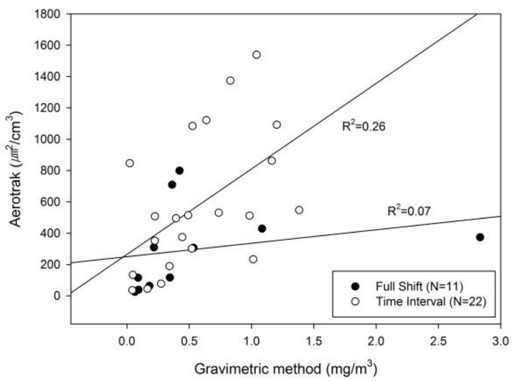
Linear regression analysis was used to determine the coefficient of determination between the full shift and time-interval gravimetric sampling methods. Figure 6 shows regression model graph, including the coefficients of determination. The time-interval samples had higher coefficients than the full shift samples for all metrics.



(a)



(b)



(c)

Figure 6. Regression analysis of full shift and time-interval gravimetric sampling data compared to direct-reading sampling data (a) Gravimetric data compared to DustTrak data, (b) Gravimetric data compared to SMPS data, (c) Gravimetric data compared to AeroTrak data.

4 Discussions

In this study, time-integrated sampling (gravimetric sampling) and direct-reading sampling methods were compared at nanoparticle generating workplaces.

Sampling at engineered nanoparticle manufacturing workplaces was conducted at the bagging process because the processes for producing nanoparticles were conducted at contained facilities. Although the $PM_{2.5}$/TPM ratios (0.4 - 0.7) at these workplaces were lower than that at other workplaces, the nanoparticle (i.e., UFP) ratios were not low. These results suggest that particles were already aggregated at the bagging process. The TEM images showed that nanoparticles were aggregated, and nanoparticles have a natural tendency to agglomerate. In workplace B, one of the two engineered nanoparticle manufacturing workplaces, the $PM_{2.5}$/TPM ratio was >0.7. This is possibly because the sampling point was located in front of a contained facility, and the door was open for bagging after nanopowder production was complete. A study by Tsai et al. (2011) suggested that when conducting exposure assessments at nanopowder-related workplaces, the mass distributions of both submicron (<1 μm) particles and respirable particles should be considered.

Particle concentrations measured at the welding workplaces (workplaces C and D) were higher than at the engineered nanoparticle manufacturing workplaces. $PM_{2.5}$ generation ratios were above 90%, and nanoparticle number concentrations were very high. In this study, we found that particles generated during the welding process were almost all <2.5 μm. A study by Elihn and Berg (2009) also found that the percentage of submicron particles was high at high-temperature processes, but that the number of nanoparticles was not higher than at other processes. Therefore, this suggests that $PM_{2.5}$ sampling at the welding process is appropriate for sampling the greatest concentration of generated particles. The size distributions measured by SMPS exhibited bimodal distributions at the unintended nanoparticle emitting workplaces. In most studies bimodal distributions were reported at the welding process; a bimodal distribution can be caused by the coalescence of nuclei (Vishnyakov et al., 2013). In addition, the size distributions differed between workplaces C and D. Particle sizes may have been affected by different welding methods and materials (Elihn and Berg, 2009).

The metal contents at the unintended nanoparticle emitting workplaces were higher than those at the engineered nanoparticle manufacturing workplaces. Metal contents had lower concentrations compared to the total mass concentrations. In a study conducted by Yoon et al. (2009), metal contents, including Na and K, were analyzed, however we did not include Na and K in this study. Different welding materials can affect the chemical components and concentrations of particles (Yoon et al., 2009).

In addition to processes that occur at the workplace, nanoparticles may also be generated by diesel engines (Vincent et al., 2000). Diesel-fueled forklifts were used in some workplaces for carrying products, and these machines can have a great effect on measurements. It is important to identify nanoparticle emission sources in the workplace. Therefore, Ham et al. (2012) suggest that researchers record activities in TAD.

Other studies that have compared gravimetric and DustTrak $PM_{2.5}$ measurements have shown that the two metrics are well correlated, and that DustTrak concentrations were overestimated by a factor of 2 or more when compared to gravimetric $PM_{2.5}$ concentrations (Kim et al., 2004; Zhu et al., 2011). However, total dust (i.e., TPM) was measured in this study. There were a variety of differences between DustTrak concentrations and gravimetric sampling concentrations. It is estimated that the particle size range of the DustTrak is 1–15 μm, but the size range of the gravimetric sampling method is unlimited.

It was difficult to collect sufficient particles when using time-interval sampling methods. Other studies have reported that short-term gravimetric sampling is difficult, and that the amount particulates in the short term would likely be below the LOD for gravimetric sampling (Kim et al., 2004). The minimum sampling time in low-concentration workplaces was over 2 hours in this study. Therefore, to collect enough mass using gravimetric sampling methods, long-term sampling is generally recommended.

When comparing the time-integrated sampling method and direct-reading instrument sampling methods, the major advantage of direct-reading sampling was the ability to identify concentration variations. Concentration variation cannot be calculated with full shift gravimetric sampling because the sample size is one, however, with direct reading instruments it is possible to identify variation. When comparing the CV of 1 min intervals of direct-reading instrument data to that of time-interval gravimetric sampling, there were no significant differences in variations of sample size, analysis error, or characteristics of workplaces. However, CV of 1 min interval in direct reading instruments was higher than CV of TIS interval in those. This result shows that, unlike gravimetric sampling methods, direct-reading instrument methods are able to identify concentration variations.

Statistical results showed no differences between DustTtrak and gravimetric concentrations. All Spearman's rank test results indicated strong associations between gravimetric sampling and direct-reading sampling. But there are not significantly characteristics between Spearman's rank test and linear regression result. This result is considered small sample size.

Table 6 describes the characteristics of online and offline monitoring according to workplace type. This study had several limitations. First, the workplaces we examined were not representative of all workplaces. Although various processes such as grinding, smelting, welding, and laser cutting can take place at unintended nanoparticle emitting workplaces, the processes we examined were primarily welding processes. Second, we were unable to perform a statistical comparison between the two types of nanoparticle generating workplaces because the engineered nanoparticle manufacturing workplaces had a small sample size. Third, particle concentrations in the workplace can be affected by season, ventilation, and working process. However, in this study we did not consider all of these factors.

Table 6. Characteristics of online and offline monitoring results according to workplace type

	Engineered nanoparticle manufacturing workplace	Unintended nanoparticle emitting workplace
Online monitoring	As particles of various sizes are generated, direct-reading instruments such as SMPS, AeroTrak, or DustTrak are required to determine the particle size distribution	To determine peak concentrations, sampling should be conducted at the welding process
Offline monitoring	As time-interval sampling is not suitable at workplaces with low particle concentrations, full shift gravimetric sampling is recommend for identifying mass concentrations	As most particles generated during the welding process are <2.5 µm, gravimetric sampling should be conducted

5 Conclusions

In this study, concentrations measured at unintended nanoparticle emitting workplaces were higher than those at engineered nanoparticle manufacturing workplaces, and nanoparticle number concentrations were also high. $PM_{2.5}$ concentrations made up >90% of the total mass concentrations measured at welding workplaces, and most particles were <2.5 μm. Therefore, gravimetric methods should be used for sampling mass concentrations. However, mass concentrations measured at engineered nanoparticle manufacturing workplaces were relatively low, but the nanoparticle generation ratios were high. Therefore, both direct-reading instrument methods and gravimetric sampling methods should be used together at engineered nanoparticle manufacturing workplaces.

There are many limitations in assessing short-term exposure and identifying variations in concentration. Although direct-reading instruments have limited accuracy and reliability, these instruments may be necessary to identify variations in concentration. Therefore, when conducting exposure assessments of workplaces we suggest the use of both direct-reading instrument sampling methods and gravimetric sampling methods together.

6 References

Brouwer, D. (2010). Exposure to manufactured nanoparticles in different workplaces. *Toxicology*. 269: 120-127.

Brouwer, D., Berges, M., Virji, M. A., Fransman, W., Bello, D., Hodson, L., Gabriel, S. and Tielemans, E. (2012). Harmonization of measurement strategies for exposure to manufactured nano-objects; report of a workshop. *Ann Occup. Hyg.* 56: 1-9.

Brouwer, D. H., Gijsbers, J. H. J. and Lurvink, M. W. M. (2004). Personal exposure to ultrafine particles in the workplace: exploring sampling techniques and strategies. *Ann. Occup. Hyg*. 48: 439-453.

Conti, J. A., Killpack, K., Gerritzen, G., Huang, L., Mircheva, M., Delmas, M., Harthorn, B. H., Appelbaum, R. P. and Holden, P. A. (2008). Health and Safety Practices in the Nanomaterials Workplace: Results from an International Survey. *Environ. Sci. Technol.* 42: 3155-3162

Elihn, K. and Berg, P. (2009). Ultrafine particle characteristics in seven industrial plants. *Ann Occup. Hyg*. 53: 475-484.

Ham, S., Yoon, C., Lee, E., Lee, K., Park, D., Chung, E., Kim, P. and Lee, B. (2012). Task-based exposure assessment of nanoparticles in the workplace. *Journal of Nanoparticle Research*. 14: 1-17.

Heitbrink, W. A., Evans, D. E., Ku, B. K., Maynard, A. D., Slavin, T. J. and Peters, T. M. (2009). Relationships among particle number, surface area, and respirable mass concentrations in automotive engine manufacturing. *J. Occup. Environ. Hyg*. 6: 19-31.

Kim, J. Y., Magari, S. R., Herrick, R. F., Smith, T. J. and Christiani, D. C. (2004). Comparison of fine particle measurements from a direct-reading instrument and a gravimetric sampling method. *J. Occup. Environ. Hyg*. 1: 707-715.

Maynard, A. D. and Zimmer, A. T. (2002). Evaluation of Grinding Aerosols in Terms of Alveolar Dose: the Significance of Using Mass, Surface Area and Number Metrics. *Ann. occup. Hyg*. 46: 315-319.

Morawska, L., He, C., Hitchins, J., Mengersen, K. and Gilbert, D. (2003). Characteristics of particle number and mass concentrations in residential houses in Brisbane, Australia. *Atmospheric Environment*. 37: 4195-4203.

O'Shaughnessy, P. T. (2013). Occupational health risk to nanoparticulate exposure. *Environmental Science: Processes & Impacts*. 15: 49-62.

Ostiguy, C., Roberge, B., Woods, C. and Soucy, B. (2010). *Current Knowledge about Occupational Health and Safety Risks and Prevention Measures*, Vol. 2, IRSST Press, Montreal

Paik, N.W., Park, D. W., Yoon, C. S. and Shin, Y. C. (2011). Workplace measurement and evaluation, Shinkwang books, Seoul.

Spurny, K. R. (1998). Methods of Aerosol Measurement before the 1960s. *Aerosol Science and Technology*. 29: 329-349.

Tsai, C. J., Huang, C. Y., Chen, S. C., Ho, C. E., Huang, C. H., Chen, C. W., Chang, C. P., Tsai, S. J. and Ellenbecker, M. J. (2011). Exposure assessment of nano-sized and respirable particles at different workplaces. *Journal of Nanoparticle Research*. 13: 4161-4172.

Vincent, J. H. and Clement, C. F. (2000). Ultrafine particles in workplace atmospheres. *The Royal Society*. 358: 2673-2682.

Vishnyakov, V. I., Kiro, S. A., Ennan, A. A. (2014). Bimodal size distribution of primary particles in the plasma of welding fume: Coalescence of nuclei. *Journal of Aerosol Science*. 67: 13-20.

Yoon, C. S., Paik, N. W., Kim, J. H. and Chae, H. B. (2009). Total and Soluble Metal Contents in Flux-Cored Arc Welding Fumes. *Aerosol Science and Technology*. 43: 511-521.

Zhu, Y., Smith, T. J., Davis, M. E., Levy, J. I., Herrick, R., Jiang, H. (2011). Comparing gravimetric and real-time sampling of PM 2.5 concentrations inside truck cabins. *J. Occup. Environ. Hyg*. 8: 662-672.

Zimmer, A. T., Baron, P. A. and Biswas, P. (2002). The influence of operating parameters on number-weighted aerosol size distribution generated from a gas metal arc welding process. *Journal of Aerosol Science.* 33: 519–531.

국문초록

작업장의 나노입자상 물질에 대한 시간누적 시료채취와 실시간 시료채취 방법 비교

김 선 주

서울대학교 보건대학원

환경보건학과 산업보건전공

지도교수 윤 충 식

연구배경: 나노입자는 다양한 분야의 사업장 및 공정에서 의도적, 비의도적으로 발생한다. 기존의 입자상물질의 측정 방법은 중량법을 이용하여 평가하였지만, 나노입자의 경우 독특한 특성 때문에 실시간 기기를 이용하여 수농도 혹은 표면적 농도로 평가한다. 따라서 기존의 측정방법인 시간누적시료채취와 실시간기기를 이용한 시료채취방법을 비교한 연구가 필요하다. 시간누적 측정법인 중량법은 작업시간동안 농도변이를 알 수 없으며, 단시간 측정이 어렵다. 따라서 본 연구의 목적은 나노입자가 발생하는 사업장에서의 입자상 물질을 평가하는 전통적인 방법과 실시간기기를 비교하고, 일반적인 입자평가법인 시간가중평균치방법과 시간간격측정방법을 비교하여 작업장별 적절한 측정법을 제안하는 것이다.

연구방법: 측정은 실시간 기기인 SMPS, DustTrak, AeroTrak 및 필터를 사용하였다. 필터는 실시간 기기와 동시에 측정하였으며, 시간별 비교를 위하여 전체작업시간동안 측정 및 1시간 혹은 일정시간간격마다 교체하였다. 채취 후 분석은 중량분석, 중금속 분석, 전자현미경 분석 및 시간별로 측정한 데이터 비교를 위하여 통계분석을 실시하였다.

결과: 비의도적 나노입자발생 사업장이 의도적 나노입자발생 사업장에 비하여 전체적으로 많은 입자가 발생되었다. 농도의 변이는 시간간격을 짧게 측정할수록 커졌다. 시간별로 측정한 필터와 실시간 기기는 전체시간을 측정한 데이터가 높은 상관관계를 보였다.

결론: 용접 사업장에는 $PM_{2.5}$의 이하의 입자 비율이 높아 필터를 이용한 중량법으로 측정하여 관찰하고, 의도적 나노입자 발생사업장에서는 다양한 입자크기 분포를 보이기 때문에 실시간기기와 함께 사용하는 것이 좋다. 그러나 가장 좋은 방법은 각각의 장단점을 보완하기 위하여 시간누적시료채취법과 실시간기기를 병행하여 측정하는 것을 제안한다.

주요어: 의도적 나노입자, 비의도적 나노입자, 실시간 기기, 시간누적 시료채취, 시료채취방법

학번: 2012-21841