RESEARCH ARTICLE

Particle size selective sampling of airborne arsenic during electroplating operations

Arsenic exposure can be a significant problem among a number of industries, including mining, metal refining, construction, agriculture and health care. Airborne arsenic particles are typically collected using either 37-mm closed-face cassettes (CFCs) for determining the "total" particulate mass, or cassette and cyclone assemblies to determine the respirable particulate mass. Alternatively, the Institute of Occupational Medicine (IOM) sampler can be used to collect the inhalable fraction of particles, which is considered to be more relevant to human health. A total of 69 samples (23 side-by-side comparisons) were collected at an electroplating plant using CFC, IOM, and cyclone samplers to measure airborne arsenic. The CFC and IOM measurements were not statistically significantly different from each other. However, most of the respirable samples measured below the limit of detection. Results from this study will be informative for understanding the relationship between different particle size selective sampling methods used for similar operations.

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INTRODUCTION

Arsenic is a metal that is found naturally within the earth's crust and is used to manufacture or produce a variety of common items, including, car batteries, electronic devices, pesticides, wood preservatives, and medicinal treatments.[1] Arsenic is listed as a known human carcinogen by the American Conference of Governmental Industrial Hygienists (ACGIH) and the International Agency for Research on Cancer (IARC). Additionally, arsenic has been determined to be harmful to the dermatologic, cardiovascular, reproductive, developmental, neurological, respiratory, hepatotoxic, hematologic, renal and gastrointestinal systems in humans.[1,2]

Several industries have the potential to generate arsenic, such as mining, metal refining, construction, agriculture, and health care.[1,2] The primary route of arsenic exposure from an occupational environment is inhalation, although workers can also be exposed through ingestion and skin absorption. The Occupational Health and Safety Administration (OSHA) has established a permissible exposure limit (PEL) for inhalation of arsenic at 10 $\mu g/m^3$ over an eight hour time weighted average (TWA) with an Action Limit (AL) of 5 $\mu g/m^3$. The National Institute for Occupational Safety and Health (NIOSH) has set a Recommended Exposure Limit (REL), and the ACGIH has set a Threshold Limit Value (TLV) at the same concentration as the OSHA PEL. The PEL, REL, and TLV are based on workers developing lung cancer.[3]

A common practice for sampling and analysis of arsenic is the NIOSH Method 7300 "Elements by ICP," which uses a closed-faced cassette (CFC) to collect the airborne particles. The CFC is the most commonly used sampler in the United States, though it has a number of limitations including under-sampling of particles $> 30\ \mu m$, inner wall losses (e.g., from electrostatic attraction of the particulates to the cassette wall), bypass leakage around the filter, non-uniform deposition on the filter, and potentially under sampling when the inlet orifice is facing downward.[4–8] This sampler is also not size-selective for health-based particle fractions (e.g., respirable, thoracic or inhalable). Therefore, given ACGIH's intent to replace all 'total' particulate samples with a size-selective TLV[3] it may be informative to investigate the use of these other sampling techniques alongside the CFC. This is especially true regarding monitoring for arsenic, as only limited data are available from other sampler types.[9–11]

One common alternative to the standard CFC is the Institute of Occupational Medicine (IOM) sampler to

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Table 1. Tested Aerosol Samplers.

	CFC	IOM	Cyclone
Sampling Method	NIOSH 7300	MDHS 14/3	NIOSH 0600
Flow Rate	2 lpm	2 lpm	2.75 lpm
Particulate Mass Fraction	'Total'	Inhalable	Respirable
Size Selectivity (50% cut point)	~30 μm	100 μm	4 μm
Picture			

measure the inhalable particle sizes using the "Methods for the Determination of Hazardous Substances (MDHS) 14/3 method" from the United Kingdom. Another common size selective sampler is the cassette-cyclone method, which is used to measure respirable particle sizes. The cyclone method is described in NIOSH Method 0600 "Particulates Not Otherwise Regulated, Respirable." Both the IOM and cyclone samplers have consistently met the health-based particle size selective criteria established by ACGIH and the International Organization for Standardization (ISO).

The difference in measurements made by these three samplers (i.e., the CFC, IOM, and cyclone) is based on the size distribution of the airborne particles that the samplers are able to collect. The IOM collects a larger range of particle sizes (up to 100 μm) than the CFC, although the CFC is defined by OSHA as collecting 'total' particulates.[12] This is because the IOM was designed to follow the ISO conventions for inhalable particulates.[13] The CFC was initially used as a filter holder and was not necessarily intended to be size-selective. Alternatively, the cyclone collects the smaller respirable size particulates (4 μm median cut point) and the larger particles collect in the sampler's grit pot.

Multiple controlled laboratory and field studies have reported comparisons between these various samplers for hazardous substances other than arsenic.[6,7,14–17] These studies suggest there are many factors which may cause differences among the sampler results. For example, factors include the sampler placement and the sampler orientation (i.e., the direction the inlet is facing), the wind speed, and the shape and density of the particles. Therefore, site-specific comparisons are needed to minimize variations in the outcome of the results.[18]

The purpose of this study was to compare monitoring data from simultaneous side-by-side air sampling for arsenic concentrations, during an industrial electroplating process that has the potential to generate airborne arsenic, to ascertain the comparability of data using different size-elective sampling methods.

METHODS

The sampling for this study was conducted at an industrial plant where electroplating is performed. During the electroplating process, arsenic impurities in the source metal sink to the bottom of the tanks with the electrolytic slurry/slime. It is assumed the arsenic particles in the slimes are then disturbed by the constant flow of solution entering the tanks and draining into the overflow, causing them to become airborne.

Samples were collected in between two rows of tanks, with 18 tanks in each row. The samplers were placed in the aisle of the two rows, on the inlet side of the tanks where the solution enters the tank. In this way, both of the rows of tanks had the inlet side facing the samplers. The same area of the plant was used for all sampling events.

A picture of the sample collection devices used is shown in Table 1. These devices include (1) a 37-mm 0.8 μm pore size mixed cellulose-ester (MCE) filter in a three-piece closed-face cassette (CFC) (SKC Inc., Eighty Four, PA, USA) to collect the 'total' arsenic particulate mass, (2) an Institute of Occupational Medicine (IOM) sampler manufactured with conductive plastic (SKC Inc., Eighty Four, PA, USA) with a 25-mm 0.8 μm pore size MCE filter (SKC Inc., Eighty Four, PA, USA) to collect the inhalable arsenic particulate mass, and (3) a 37-mm 0.8 μm pore size MCE filter in a three-piece cassette attached to a GS-3 conductive plastic cyclone (SKC Inc., Eighty Four, PA, USA) to collect the respirable arsenic particulate mass. The IOM samplers were cleaned and reused for subsequent sampling events by rinsing with distilled water and air drying before use.

The cyclone is a 10-mm plastic attachment to the standard three-piece CFC and is used to collect respirable size particles. It meets the ACGIH criterion for respirable particulate mass with a cut-point of 4 μm at a flow rate of 2.75 L/min. Conductive plastic IOMs and cyclones were used because of the harsh acidic conditions in the electroplating area.

Dedicated precision flow air sampling pumps (GilAir 5 personal pump, Sensidyne Industrial Health & Safety Instrumentation, Clearwater, FL, USA) were used for each type of sampling device to maintain the desired air sampling flow rate. At the beginning of each day, the three sampling devices were calibrated at the appropriate flow rate (see Table 1) using a Bios DryCal Defender 530 (Brandt Instruments, Prairieville, LA, USA). The pump's flow rates were set to 2.0 L/min for the CFC and IOM and 2.75 L/min for the cyclone. The flow rate when calibrating the CFC was tested 10 times consecutively and an average air flow rate was calculated. The same calibration method was used for the IOM sampler with the exception that the IOM calibration adapter was used. The cassette cyclone assembly was calibrated in a one-liter calibration chamber using the Bios DryCal Defender 530. Post calibration was performed in the same manner to ensure the flow rate did not change by more than ±5%. The IOM cover was placed on the internal cassette, which was immediately inserted into the transport clip, after post calibrating and before transporting to the laboratory for analysis.

A total of 23 side-by-side samples with each device ($n = 69$ total samples) were collected. Each sampler was attached with duct tape to a stand that allowed them to be elevated to approximately 1.5 meters (five feet) above floor level so that the particles were collected near the height of an average workers breathing zone. These sampling stands were placed approximately 10 cm (four inches) away from the tank. Three stands were constructed, each holding one set of the three types of sampling devices, which were then placed in the appropriate section of the tank house. The samplers were operated for a minimum of four hours, with a maximum of eight hours. 21 of the 23 side-by-side sampling events had the same sampling time. For the other two groups the CFC had a shorter sampling time than the IOM and cyclone, but all were sampled for more than four hours.

No significant work, including unloading and loading of metal with cranes, was being performed by workers within about 14 meters (45 feet) of sampling. The only workers who were in the area were monitoring for and knocking off nodules that can grow on stainless steel blanks located inside the electrolytic tanks, a task which involved dipping a long bar into the solution to knock off the nodules. A water hose was also sprayed twice a day in the section where sampling was performed, but it was determined that this did not impact the samplers.

All samples were analyzed by an American Industrial Hygiene Association (AIHA) accredited lab for a range of metals using the NIOSH 7300 method. Particles that were deposited on the walls of the IOM's cassette were analyzed along with the filter, as is specifically required for this sampler. Deposits on the inside of the CFC were not included, as it was not specified in the NIOSH method used by the lab.

The correlation between the arsenic measurements obtained by the samplers was examined using a Regression Analysis, Spearman Correlation, and a Kruskal–Wallis test using Stata/SE 11.1 statistical software (StataCorp, College Station, TX, USA). The Kruskal–Wallis test was conducted as the results were not normally distributed (see Figure 3).

RESULTS

The results for all sampling events are shown in Table 2. The limit of detection (LOD) for arsenic from the lab was 1 μg mass. The cyclone results were all under the LOD except for one sample (Sample #17: 0.58 μg/m^3), so the cyclone sampling results were unable to be included in any of the subsequent data analyses. For statistical purposes, the results for the CFC and IOM samplers that were below the LOD were substituted with 0.7 μg/m^3. This value was used as it is a relatively conservative standard practice previously used by the facility which was sampled. The results for the CFC ranged from below the LOD up to 5 μg/m^3 of arsenic, with a standard deviation of 1.40. The range of results for the IOM sampler was below the LOD up to 6.5 μg/m^3, with a standard deviation of 1.68. The overall mean of the 23 samples from the CFC and IOM were 2.3 μg/m^3 and 2.5 μg/m^3, respectively.

The Spearman Correlation Coefficient had an r_s value of 0.755, with a p-value of 0.0001. The regression analyses, shown in Figure 1, were conducted using a general linear model to compare the CFC to the IOM, which resulted in an R^2 of 0.677 (p-value < 0.0001). This indicates that 67.7% of the variation in the IOM's arsenic results was explained by its relationship with the CFC. The Kruskal–Wallis test was also performed, resulting in an H-statistic of 0.0061

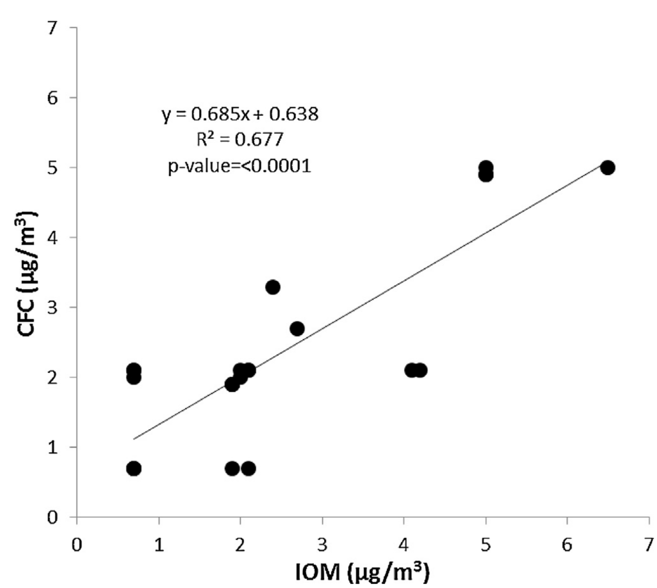

Figure 1. Regression model showing the relationship between the CFC and IOM samplers with all measurements below the LOD substituted with 0.7 μg/m^3.

Table 2. CFC, IOM, and Cyclone Sampling Results.

Sampling Event	Date	CFC[a] (μg/m^3)	IOM[a] (μg/m^3)	Cyclone[a] (μg/m^3)
1	6/8/2011	2.7	2.7	ND
2	6/10/2011	3.3	2.4	ND
3	6/10/2011	5.0	6.5	ND
4	6/22/2011	2.1	2.1	ND
5	6/22/2011	2.1	ND	ND
6	6/22/2011	2.1	ND	ND
7	6/22/2011	2.1	4.1	ND
8	6/22/2011	2.1	2.0	ND
9	6/22/2011	2.1	4.2	ND
10	6/24/2011	2.1	2.1	ND
11	6/24/2011	ND	2.1	ND
12	6/24/2011	1.9	1.9	ND
13	6/28/2011	2.0	2.0	ND
14	6/28/2011	1.9	1.9	ND
15	6/28/2011	2.0	ND	ND
16	7/1/2011	4.9	5.0	ND
17	7/1/2011	4.9	5.0	0.58
18	7/1/2011	5.0	5.0	ND
19	7/6/2011	ND	ND	ND
20	7/6/2011	ND	ND	ND
21	7/6/2011	ND	ND	ND
22	7/7/2011	ND	1.9	ND
23	7/7/2011	1.9	1.9	ND
Average		2.3	2.5	N/A

[a] ND = Non-Detected (<1 μg of mass).

and p-value of 0.9378. This suggests that the relationship between the CFC and IOM was not statistically significant.

Statistical tests were also performed after removing the sampling events that had at least one result below the LOD. That analysis ($n = 15$) produced a Spearman Correlation with r_s of 0.917 (p-value = 0.0001), a regression, shown in Figure 2, with $R^2 = 0.704$ (p-value = 0.0001), and a Kruskal–Willis test, p-value = 0.6897. This supports the previous analysis that showed the relationship between the CFC and IOM was not statistically significant.

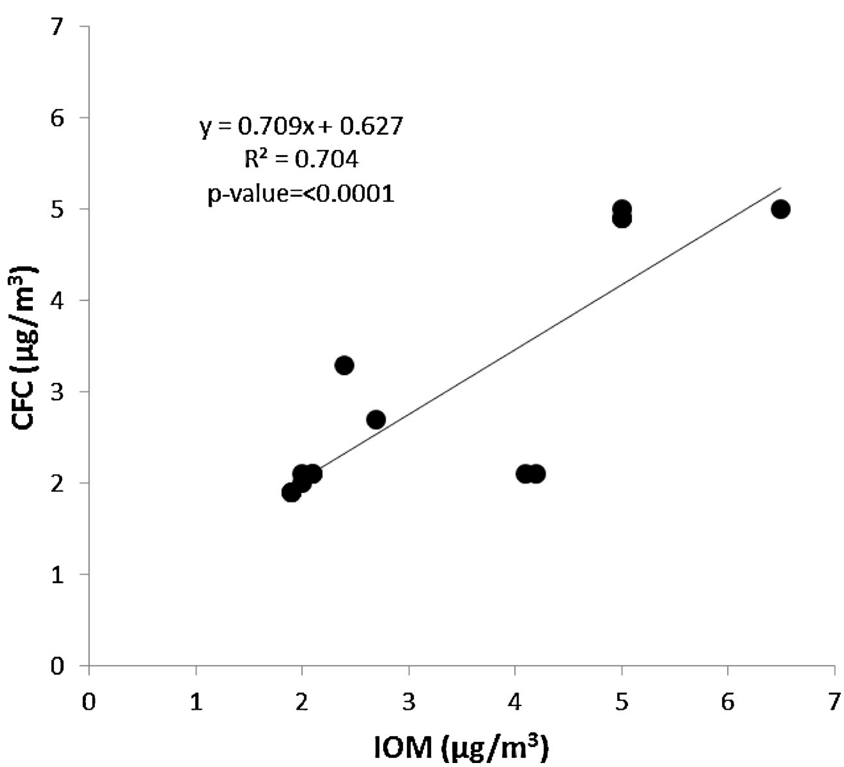

Figure 2. Regression model showing the relationship between the CFC and IOM samplers, with all measurements below the LOD removed from analysis.

DISCUSSION

The CFC and IOM samplers provided similar measurements of arsenic concentrations, although the IOM results were slightly higher on average than the CFC. By contrast, all but one of the cyclone results was measured below the LOD of 1 μg mass. The results imply that the plant should be less concerned about respirable arsenic particulates during this particular electroplating process. However, the similarity in results from the CFC and IOM samplers indicates that the plant may be able to sample with either of these samplers to obtain an accurate measurement of the potential arsenic exposure. Together, these results provide useful information for which size-selective sampling techniques are most appropriate in this type of workplace. Changes in process or materials may require re-evaluation of this, however, in case the particle size distribution of airborne arsenic particulates significantly changes.

A major strength of this study was that all sampling occurred in the same location, and away from any air moving equipment (e.g., fans or other ventilation equipment) that could potentially disturb the dispersion of the airborne particulates. Although personal sampling was not performed, each set of samplers was elevated on stands to a height of about 1.5 meters (five feet) to collect air samples that would be representative of arsenic concentrations in a worker's breathing

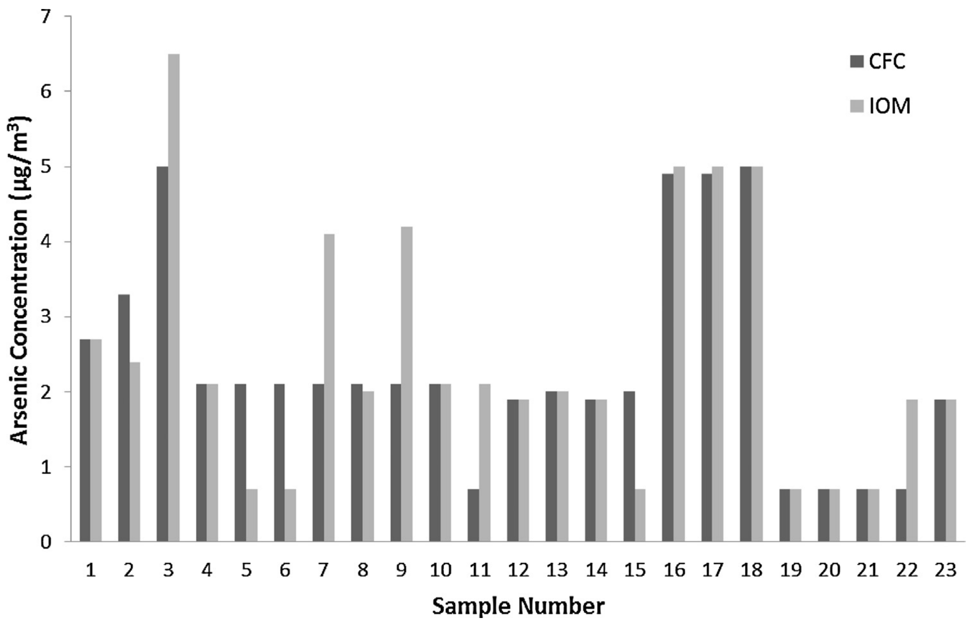

Figure 3. CFC and IOM comparison by sampling event.

zone. Also, the sampling pumps were interchanged between the different sampler types for subsequent sampling events to eliminate the possibility of having a systematic error due to a faulty pump.

Due to the lack of respirable arsenic collected by the cyclone, there could be concerns that perhaps the cyclone was improperly calibrated or malfunctioning. However, it should be noted that the laboratory results included information on other metals besides arsenic, e.g., copper, which were above the LOD. This implies that the cyclones were operating properly and collecting respirable particulates, but there was such a small amount of respirable arsenic that it was only detected in one sampling event.

The results also show that there was a wide range of measured concentrations between sampling events. For example, in Sample #6 the IOM result was below the LOD (substituted with 0.7 $\mu g/m^3$, the default value for non-detected) and yet on the same date in Sample #7 the IOM collected 4.1 $\mu g/m^3$. The arsenic levels are dependent on the concentration in the anode as well as the length of time the anode is in the tank. The more ‘slime’ that falls to the bottom of the tank the longer it is in the electrolytic solution. It is assumed that the electrolytic solution flowing in and out of the tanks disturbs the slimes and allows the arsenic particulates to become airborne. Therefore, it is not surprising that the arsenic levels would change throughout the day.

There were also several sampling events that showed a large difference between the CFC and IOM during single events. For example, Sample #7 had the widest range between the two samplers, collecting 2.1 $\mu g/m^3$ with the CFC and 4.1 $\mu g/m^3$ with the IOM. Several different variables could be the cause of the difference. For example, the particle size may have been too large for the CFC to collect (>30 μm), but still in the size range that the IOM was able to collect. However, some sampling events (e.g., Sample #5) showed the CFC collecting more arsenic particulates than the IOM sampler. One explanation for this could be the slight variation in direction that samplers may have been facing during that sampling event.

One weakness of the study was the number of samples that measured below the LOD. The results show that five CFC, six IOM, and 22 cyclone samples were below the LOD. Disregarding the cyclone sampler’s results, the CFC and IOM results showed that 24% of the samples were below the LOD, including three sampling events in which both the CFC and IOM had results below the LOD. In future studies, sampling should be conducted for a longer period of time and in an area of the tank house where more arsenic particulates are likely to be generated. For example, sampling could be conducted when the flow of the electrolytic solution entering and exiting the tanks is at a maximum. This may allow the samplers to collect more particles so there are fewer results below the LOD. The inclusion of wall deposits in the analysis of the CFC sampler would also be an important methodological improvement for future studies.

CONCLUSION

This study found that the CFC and the IOM were not statistically significantly different for measuring airborne arsenic particulates in this industrial electroplating plant. On the other hand, only minimal respirable arsenic was measured at this facility. Together, this may provide important information for properly selecting a sampling method that will provide a more accurate estimate of airborne arsenic concentrations generated during electroplating.

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REFERENCES

1. Chen, C. J.; Chiou, H. Y.; Chiang, M. H.; Lin, L. J.; Tai, T. Y. *Arterioscler. Thromb. Vasc. Biol.* **1996**, *16*(4), 504.
2. Tchounwou, P. B.; Patlolla, A. K.; Centeno, J. A. *Toxicol. Pathol.* **2003**, *31*(6), 575.
3. ACGIH. *Threshold Limit Values for Chemical Substances and Physical Agents, Biological Exposure Indices*; ACGIH; Cincinnati, OH, 2011.
4. Baron, P. A.; Khanina, A.; Martinez, A. B.; Grinshpun, S. A. *Aerosol Sci. Technol.* **2002**, *36*(8), 857.
5. Demange, M.; Gendre, J. C.; Hervé-Bazin, B.; Carton, B.; Peltier, A. *Ann. Occup. Hyg.* **1990**, *34*(4), 399.
6. Demange, M.; Gorner, P. Elcabache, J.-M., ; Wrobel, R. *Appl. Occup. Environ. Hyg.* **2002**, *17*(3), 200.
7. Kenny, L. C.; Aitken, R.; Chalmers, C.; Fabries, J. F.; Gonzalez-Fernandez, E.; Kromhout, H.; Liden, G.; Mark, D.; Riediger, G.; Prodi, V. *Ann. Occup. Hyg.* **1997**, *41*(2), 135.
8. Puskar, M. A.; Harkins, J. M.; Moomey, J. D.; Hecker, L. H. *Am. Ind. Hyg. Assoc. J.* **1991**, *52*(7), 280.
9. Hetland, S.; Thomassen, Y. *Pure Appl. Chem.* **1993**, *65*(12), 2417.
10. Katchen, M. A.; Puhalovich, V. A.; Swaroop, R.; Culver, B. D. *Biol. Trace Elem. Res.* **1998**, *66*, 59.
11. Thomassen, Y.; Nieboer, E.; Romanova, N.; Nikanov, A.; Hetland, S.; VanSpronsen, E. P.; Odland, J. O.; Chashchin, V. *J. Environ. Monit.* **2004**, *6*(12), 985.
12. O'Shaughnessy, P. T.; Lo, J.; Golla, V.; Nakatsu, J.; Tillery, M. I.; Reynolds, S. *J. Occup. Environ. Hyg.* **2007**, *4*(4), 237.
13. Mark, D.; Vincent, J. H. *Ann. Occup. Hyg.* **1986**, *30*(1), 89.
14. Li, S. N.; Lundgren, D. A.; Rovell-Rixx, D. *Ind. Hyg. Assoc. J.* **2000**, *61*(4), 506.
15. Vaughn, N. P.; Chalmers, C. P.; Botham, R. A. *Ann. Occup. Hyg.* **1990**, *34*(6), 553.
16. Vincent, J. H. *Aerosol Science for Industrial Hygienists*; Elsevier Science Inc.; Tarrytown, NY, 1995.
17. Witschger, O.; Grinshpun, S. A.; Fauvel, S.; Basso, G. *Ann. Occup. Hyg.* **2004**, *48*(4), 351.
18. Reynolds, S. J.; Nakatsu, J.; Tillery, M.; Keefe, T.; Mehaffy, J.; Thorne, P. S.; Donham, K.; Nonnenmann, M.; Golla, V.; O'Shaughnessy, P. *Ann. Occup. Hyg.* **2009**, *53*(6), 585.