



October 11, 2007

Brendan McKenney
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Subject: Final Report of the NIOSH Nanotechnology Field Research Team Study at QuantumSphere, Inc. (July 2007).

Dear Mr. McKenney:

Thank you for partnering with NIOSH and providing our Nanotechnology Field Team with the opportunity to collaborate with you to observe and characterize the work practices and processes at your nano-scale metal oxide production facility. Our July 16-18, 2007, site visit and local exhaust ventilation (LEV) effectiveness study was highly successful. The collaborative nature of this program demonstrates how entities engaged in nanotechnology-related enterprises can proactively manage human and environmental health and safety issues, based on the circumstances of their particular operations.

Contained in this final report are the results of the LEV effectiveness study. If you have any questions about the results of the study, please contact me via e-mail at: mmm5@cdc.gov or by phone at (513) 841-4325.

Sincerely,

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**National Institute for Occupational Safety and Health
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U.S. Department of Health and Human Services**

Preface

The National Institute for Occupational Safety and Health (NIOSH) is the federal agency that conducts research and makes recommendations for preventing work-related injuries, illnesses, and deaths. The NIOSH Nanotechnology Research Center coordinates the Institute's laboratory, field, and information dissemination activities on the development of tools, practices, and recommendations for the guidance document "Approaches to Safe Nanotechnology". (<http://www.cdc.gov/niosh/topics/nanotech/safenano/>). A key input to the development of that document is field research studies. The NIOSH nanotechnology field research team has the objective of characterizing processes where nanomaterials are produced or used. To do this, the field team:

- Evaluates the entire material flow of a process and identifies points of potential material emission that can result in worker exposure.
- Uses an array of instruments and conventional air sampling methods to characterize exposures.
- Evaluates engineering controls and their effectiveness in reducing emissions and exposures.
- Evaluates work practices used during the production or use of nanomaterials.
- Evaluates the use of Personal Protective Equipment in use, if any, including respiratory protection.

This report summarizes the evaluation of recently implemented Local Exhaust Ventilation (LEV) engineering control at QuantumSphere Inc.

Background

In 2002, QuantumSphere, Inc. (QSI), was founded in Santa Ana, California, and is engaged primarily in the production of high quality engineered nano-scale materials (ENM's) consisting of metal catalytic materials such as manganese, iron, silver, nickel and cobalt. These ENM's are produced inside stainless steel reactors via a process known as gas-phase condensation. The ENM's are used in the production of energy efficient batteries, fuel cells and photovoltaic devices, to name a few. Currently, the process used by QSI for creating the ENM's is in the research and process development phase, with a long term goal of large-scale commercialization of the both the process and equipment. The 7,500 square foot facility consists of a production area, two laboratories and an office area. The production area houses four gas-phase condensation reactors that produce approximately one kilogram of ENM per reactor per day. Two production technicians operate the reactors, with each technician working an 8 hour shift, 5 days a week.

In January 2007, The National Institute for Occupational Safety and Health (NIOSH) received a request from the management of QSI to be a volunteer participant in a field research study to evaluate process-specific emissions during the production of ENM's (metal and alloy spheres of approximately 15-50 nanometers [nm] in diameter). An initial baseline assessment of work practices, existing engineering controls, personal protective equipment (PPE), and potential sources of nano-scale emissions was conducted in February, 2007, with an interim report of the results issued to QSI in May, 2007.

According to the results obtained during the initial baseline assessment, it was determined that, during specific work practices and procedures (reactor cleanout), ENM's were released to the production area atmosphere and, in turn, could result in potential worker exposure. This finding prompted a request from QSI for NIOSH to provide consultative guidance on engineering control(s) and procedures that could be implemented to reduce/eliminate such releases. In June 2007, QSI purchased a portable fume extractor typically used in the welding industry, to control ENM releases during reactor cleanout procedures. In July 2007, NIOSH returned to QSI and used real-time, direct-reading instrumentation and filter-based air samples to determine the effectiveness of the implemented control technology.

Survey Overview

During the initial baseline assessment, it was determined that the reactor cleanout process emitted a substantial amount of ENM's. To control such an emission, NIOSH suggested using a portable, High Efficiency Particulate Air (HEPA) filtered Local Exhaust Ventilation (LEV) unit commonly used during welding processes to capture fumes (Figure 1). The unit selected for use by the QSI Project Manager consisted of a 6 inch, flexible, flanged duct attached to a HEPA filtered air handler equipped with a carbon pre-filter. This unit is designed to create a maximum exhaust flow rate of 1,000 cubic feet per minute (cfm), which was confirmed using a thermoanemometer. In addition to the use of LEV, personal protective equipment (PPE) remained identical to that used during the initial baseline assessment (full-body Tyvek™ suit, nitrile gloves, wrist-to-elbow cotton arm covers, and a 3M L-122 full-face, positive pressure airline respirator).

On July 17, 2007, the NIOSH nanotechnology field research team representative arrived at the facility and held an initial meeting with the company management and production

staff. During the meeting, the NIOSH representative discussed the proposed effort to evaluate the effectiveness of the newly-acquired LEV control technology and also observed a demonstration of the LEV system.

Methods:

To evaluate the effectiveness of the LEV system in controlling the release of ENM's, area air samples were collected with and without LEV for the duration of the reactor cleanout process (Figures 2,3). All air samplers (filter-based and direct-reading instruments) were positioned at the rim of the opening of the reactor (see Figure 2) and opposite the inlet of the LEV (Figure 3). Additionally, a general area air sample was collected (in the center of the production area before any ENM-generating activities began) to serve as an indicator of background concentrations not related to the reactor cleanout process. Filter-based samples were collected using AirChek™ 2000 (SKC Inc., Eighty Four, PA) pumps at a sampling rate of 7.0 liters per minute (lpm). Pumps were calibrated before and after each day of sampling. Air samples to determine mass concentration of ENM's were collected on 37-millimeter (mm) diameter; 0.8 micrometer (µm) pore size, open-face mixed cellulose ester (MCE) membrane filters and analyzed according to NIOSH Manual of Analytical Methods (NMAM) Method 7302. A duplicate set of air samples was collected alongside the mass-based air samples and analyzed using transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS) capability. TEM with EDS allows the microscopist the ability to identify particles in the nanometer size range, morphology of the particles (size, shape, degree of agglomeration), and elemental composition. Filter-based sampling times ranged from 10 minutes to 30 minutes (volume of air sampled ranged from 70 liters to 210 liters) and was dependent on the time necessary to complete the reactor cleanout process.

In addition to the filter-based air sampling, two direct-reading, real-time instruments were used to characterize emissions, with and without LEV, during the reactor cleanout process. To maintain consistency with the filter-based air sampling effort, the sampling inlet of each direct-reading instrument was positioned adjacent to the filter-based air sampling media.

The first instrument was a TSI model 3007 (TSI, Inc, Shoreview, MN) handheld condensation particle counter (CPC). The CPC operates by drawing air through a size-selective inlet, passing it through a heated saturator filled with isopropyl alcohol, and then cooling the air stream via a condenser chamber. In the condenser, the alcohol vapors condense on the particles and are passed through an optical detector where they are counted. The CPC unit measures particles in the size range of 10 to 1000 nm. The data output is expressed as total number of particles per cubic centimeter of sampled air with an upper dynamic range limit of approximately 100,000 particles per cubic centimeter of air. The value of this instrument for evaluating ENM emissions is its ability to detect particles in the 10 to 100 nm range, even though it will respond to the presence of larger particles.

A second direct-reading, real-time instrument was used to determine the concentration of particulates based on optical counting principles using laser light scattering (HHPC-6,

ART Instruments, Grants Pass, Oregon). This instrument can measure the total number of particles per liter of air within 6 specific size ranges: 300 - 500 nm; 500 - 1,000 nm; 1,000 - 3,000 nm; 3,000 - 5,000 nm; 5,000 - 10,000 nm, and > 10,000 nm.

Since the size of singular and agglomerated ENM's often vary, it was determined that using these particle sizing and counting instruments would provide a qualitative indication of the concentration of both species. For example, a high particle count on the CPC, in combination with a high particle count in the small size range (300-500 nm) on the HHPC, would indicate the possible presence of ENM's. Conversely, a low CPC count, in combination with a high HHPC count in the larger size range (> 1,000 nm) would indicate the presence of larger, agglomerated ENM's.

Since these two instruments cannot distinguish between specific types of particulate matter (e.g. road dust versus manganese oxide spheres), background particle number concentration measurements were made before and after the work shift in the reactor area. The "before and after" background particle number concentration data were averaged and then subtracted from the measurements to calculate an "adjusted concentration". The adjusted concentration will serve as an indicator of particulate matter emitted during reactor cleanout.

Results

The ENM's manufactured during this site visit consisted of oxides of manganese, cobalt, and silver, each in a separate reactor. Three filter-based pairs of area air samples (Mass and TEM) were collected during reactor cleanout processes. Additionally, one set of filters was collected in the production area (near the reactors) prior to commencing the cleanout process and serve as an indicator of background concentrations. None of the metal oxides in production were detected on the background sample.

Air concentrations for the three metal oxides when no LEV was used during reactor cleanout ranged from 714 micrograms per cubic meter of air ($\mu\text{g}/\text{m}^3$) to 6,667 $\mu\text{g}/\text{m}^3$. However, air concentrations measured when the LEV was operating were substantially lower and ranged from 41 $\mu\text{g}/\text{m}^3$ to 1714 $\mu\text{g}/\text{m}^3$ (Table 1). To determine the percent reduction in emissions when using LEV during reactor cleanout, the following formula was used:

$$\frac{(\text{Concentration **without** LEV} - \text{Concentration **with** LEV})}{\text{Concentration **without** LEV}} \times 100 = \% \text{ Reduction}$$

This formula was applied to both filter-based samples as well as particle number concentrations measured with the direct-reading instrumentation. The percent reduction values for three filter-based samples ranged from 74 % to 96 %, with an average (mean) value of 88% (Table 1). In addition to the filter-based air samples, emission of ENM's was measured, with and without LEV, using direct-reading, real-time instrumentation. Similar to the filter-based air samples, the use of LEV reduced particle number concentrations substantially across the entire size range of both instruments (10 nanometers to 10 micrometers). Percent reduction values ranged from 78% to 100%, with an average (mean) value of 96% (Table 2).

Additional confirmation of the effectiveness of LEV in controlling emissions was noted by examining the TEM images. Filters collected during reactor cleanout while the LEV was operating showed a noticeable decrease in ENM when compared to those collected without the use of LEV (Figure 4). All TEM images, regardless of the use of LEV, indicated that the majority of ENM's are emitted as agglomerates.

Conclusions

Based on the analysis of the filter-based air samples and the direct reading instrumentation, it is clear that LEV plays a substantial role in reducing ENM emissions during reactor cleanout operations. This finding, coupled with the current use of PPE appears to be an acceptable method of reducing the potential for worker exposure.

Recommendations

Since the air sampling data indicate that LEV is effective in controlling ENM emissions, and appropriate PPE is worn when conducting reactor cleanout operations, no additional protective measures are necessary.

References:

NIOSH Manual of Analytical Methods (*NMAM*) [2006]. Method 7302. Elements. In: NIOSH Method of Analytical Methods 4th ed., Issue 1. Cincinnati, OH: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication 94-113.

**Table 1: Effectiveness of LEV in Reducing Release of Aerosol during Reactor Cleanout Operations: Air concentrations of Metal Oxides With/Without LEV
Micrograms/cubic meter ($\mu\text{g}/\text{m}^3$)**

**QSI, Inc.
Santa Ana, California**

Operation	Air Concentration “Without” LEV	Air Concentration “With” LEV	Percent Reduction in air concentration due to use of LEV (%)*
Manganese (Mn) Reactor cleanout	3,619	150	96
Silver (Ag) Reactor cleanout	6,667	1,714	74
Iron (Fe) Reactor cleanout	714	41	94
Background (Reactor area Prior to cleanout)	ND	ND	N/A

Mean (+/- S.D.) 88 (+/- 12)

Analytical Limit of Detection = 1.0 $\mu\text{g}/\text{sample}$.

ND = None detected

N/A = Not applicable

S.D. = Standard Deviation

* Percent reduction was calculated as follows: $[(\text{Without LEV} - \text{With LEV}) / \text{Without LEV}] \times 100$

Table 2: Effectiveness of LEV in Reducing Release of Aerosol during Reactor Cleanout Operations: Particle number concentrations and Percent Reduction due to LEV

QSI, Inc., Santa Ana, California

Material	Particle size (nm)	Measured Concentration (Without LEV)	Average Background Concentration	Adjusted Concentration (Without LEV) (subtraction of background)*	Measured Concentration (With LEV)	Average Background Concentration	Adjusted Concentration (With LEV) (subtraction of background)*	Percent Reduction** (%)
Silver (Ag)	300	150,684	104,708	45,976	90,909	104,708	0	100
	500	88,872	14,813	74,059	13,721	14,813	0	100
	1,000	58,561	4,009	54,553	6,113	4,009	2,105	96
	3,000	45,108	2,097	43,012	4,253	2,097	2,157	95
	5,000	28,699	851	27,849	2,431	851	1,581	94
	10,000	4,597	64	4,534	388	64	325	93
	(10 - 1000)	18,196	12,146	6,050	10,556	12,146	0	100
Manganese (Mn)	300	152,058	104,708	47,350	107,766	104,708	3,058	94
	500	77,068	14,813	62,255	13,637	14,813	0	100
	1,000	62,866	4,009	58,858	3,738	4,009	0	100
	3,000	9,153	2,097	7,057	2,045	2,097	0	100
	5,000	9,461	851	8,611	869	851	19	100
	10,000	88,328	64	88,265	73	64	10	100
	(10 - 1000)	29,063	12,146	16,917	13,144	12,146	998	94
Cobalt (Co)	300	189,525	104,708	84,817	93,040	104,708	0	100
	500	80,892	14,813	66,079	13,520	14,813	0	100
	1,000	45,114	4,009	41,106	5,709	4,009	1,701	96
	3,000	32,032	2,097	29,936	3,914	2,097	1,818	94
	5,000	17,646	851	16,796	2,287	851	1,437	91
	10,000	1,827	64	1,764	449	64	386	78
	(10 - 1000)	25,097	12,146	12,951	14,071	12,146	1,925	85

Mean (+/- S.D.)

96 (+/- 6)

* Adjusted Concentration = Measured Concentration - Average Background Concentration. If Average Background Concentration exceeds the Measured Concentration, the Adjusted Concentration value is considered to be zero when calculating percent reduction.

** Percent reduction was calculated as follows: [(Adjusted "Without" LEV - Adjusted "With" LEV)/ Adjusted "Without" LEV] x 100.

Note: The number concentration of particles in the size range (300 nm - 10,000 nm) was measured with an ARTI model HHPC-6 optical particle counter and is presented as total particles per liter of air (P/liter) for a specific size range. The number concentration of particles in the size range (10 nm - 1000 nm) was measured with a TSI Model 3007 condensation particle counter and is presented as total particles per cubic centimeter of air (P/cc).

S.D. = Standard Deviation

Figure 1: Photo of fume extractor used during reactor cleanout procedure.



Figure 2: Reactor cleanout process with no fume extractor (LEV)



Figure 3: Typical location of fume extractor and production operator during reactor cleanout activities (filter-based air sampling devices located in upper left corner of photo on left)

