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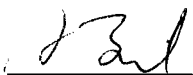
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Walter Reed National Military Medical Center"

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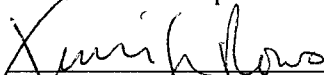
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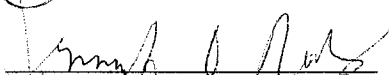
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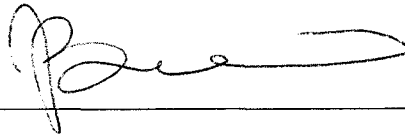
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A handwritten signature in black ink, appearing to read 'Korami Dembele', is written over a horizontal line.

CAPT KORAMI DEMBELE

Determining Nanoparticle Inhalation Exposure in the Prosthetics Laboratory at Walter
Reed National Military Medical Center

by

CPT Korami Dembele

Thesis submitted to the faculty of the
Preventive Medicine and Biometrics Graduate Program
Uniformed Services University of the Health Sciences
In partial fulfillment of the requirements for the degree of
Master of Science in Public Health 2013

Thesis submitted to the Faculty of the Graduate School of the Uniformed Services
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of Master of Science in Public Health

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DEDICATION

To Batouré Yacouba and Marie Chantal

ABSTRACT

Title of Thesis: Determining Nanoparticle Inhalation Exposure in the Prosthetics

Laboratory at Walter Reed National Military Medical Center

CAPT Korami Dembele, Master of Science in Public Health, 2013

Thesis directed by: CDR A Biles, Assistant Professor, Preventive Medicine and
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The increase of wounded warriors has amplified dramatically the need for prosthetics. Generation of particle matter occurred during the four steps of the prostheses manufacturing processes (lamination, plasterization, thermoforming, and grinding). Particle matter from these manufacturing processes are hazardous to human health and suspicion exists that nano-sized aerosols generated during the process will increase this hazard. The author designed a gravimetric and direct reading research study to measure sub-micron particle size distributions in the Walter Reed National Military Medical Center (WRNMMC) prosthetics laboratory. The gravimetric reading consisted of a weight-based measurement, and direct reading used a particle count procedure. Weight analysis did not detect any dust, but X-ray diffraction revealed the presence of quartz, tridymite, and cristobalite. The result obtained from Nanoparticle Emission Assessment Technique showed that each process generated dominantly one type of particle. For particle sizes from 0.3 to 10 μ m, no difference was identified between lamination and

thermoforming ($p=0.189$). For nanoparticles, two groups emerged, namely, lamination and plasterization ($p=1$), as well as grinding and thermoforming, which generated many more nanoparticles ($p=1$). Plasterization generated the largest particle number concentration for particles between five and ten μm . Grinding and thermoforming generated most of the smaller particle number concentrations, and lamination was the least productive of particle number concentration. Although results were below occupational exposure levels, increases in particle numbers demonstrated additional exposures.

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CHAPTER 1: Introduction

From historical times to the industrial revolution, human activities have generated dust, fume, smoke, mist, haze, and smog. All the materials cited above are aerosols, i.e., suspension of solid or liquid particle matter. This particle matter (PM) is small replicates of parent materiel in diverse sizes, shapes, and compositions (52). An increase of particle matter in the air, usually known as pollution, strongly correlates with an increase of mortality and health burden (11; 50). For example, the estimated mortality attributable to landscape fire smoke is more than 300,000 deaths/year with the majority occurring in sub-Saharan countries (23). Particulates are present in many workplaces and commonly called particle matter (PM) in industrial hygiene (occupational-related PM exposures). The most frequently named are $PM_{2.5}$ and PM_{10} (14) because these are PM with a diameter size of 2.5 μm and 10 μm respectively. According to Riest (1984), smaller components of an aerosol are the most reactive with their surroundings and therefore, more toxic (52).

Physical characteristic such as diameter size, shape helped to classify particle as coarse, respirable or nanoparticles. Particles also can be named according to the place of deposit in the respiratory system. Table 1 shows the particle repartition according to size.

Table 1. Particle classification according to their size

Name	Size in Nanometer
Total	particle size ≥ 100000
Respirable	particle size ≤ 4000
Fine	particle size ≥ 2500
Nanoparticle	1-100

Regardless of respiration rate, age, and health condition, PM will enter the respiratory system. Generally, an increase of breathing rate will also increase the amount of particle number deposition in the respiratory system. However, the particle size determines the place of deposition. The respiratory system cavity area decreases from the nose to the alveoli. As particle matter deposits according to their size, coarse particles exit the respiratory system (e.g., sneezing) or stay in the thoracic zone whereas nanoparticles move to the alveoli in the lungs. All particle sizes have potentially negative health effects. The effect of larger particles includes sleep disorder, asthma exacerbation, cardiovascular, and metabolic disorders (50; 66).

1-1 NANOPARTICLE ORIGINS

The original Greek word “nanos,” which signifies “dwarf,” was used subsequent to the current prefix of “nano” (10). The nanometer is one subdivision of a meter breakdown into a billion parts. Convention accepts that PM with a diameter smaller than

100nm be called nanoparticles. Nanoparticle materials can be organic or inorganic, regardless of the origin.

1-1-1 Natural origins

Along with anthropogenic origins, nanoparticles occurs naturally. Dust storms, volcanic eruptions, and forest fires are natural events, both accidental and non-accidental, which generate a significant amount of nanoparticles. Dust storms appear to produce various size of particles, it mostly comprise in a range from 100 nm to several microns. Concentrations up to 1500 particles/m³ can be reached in the 100-200nm range (5). Natural habitat, such as bush and forest undergo renew cycle most the year by human labor or by nature activity such lightning strikes that induce forest and grass fires all that together generate nanoparticles from ash and smoke. The amount of particles, especially nanoparticles, released when a volcano erupts is huge. In addition to lava, vapor condensation droplets, gases, and up to 30 million tons of ash are generate and accelerated into the atmosphere, reaching heights at times of more than 18,000m (5).

1-1-2 Anthropogenic origin

Nanoparticles have been part of the human beings' living environment and consummation of products for centuries. Historically Egyptians consumed cosmetic product components that included black soot and mineral powders long before the industrial revolution (29). More recently, tobacco smoke has been part of the lifestyle of billions of people, and the exposure of smokers to particles from an approximate six nm to 700nm range is well established. Studies found that the average diameter size of tobacco smoke is around 150 nm (62). Although the Industrial Revolution greatly has improved human indoor activities, there are large parts of the world, in third word and

developing countries where daily occupations and activities exposed people to nanoparticles. Daily occupations and activities (e.g., cooking, cleaning, smoking, fireplaces, insect repellent, etc) expose people to nanoparticles. In contemporary lifestyles, a large source of nanoparticles comes from automobile exhaust. Most particles from fossil combustion in vehicle engine are in the size range of 20-130 nm for diesel engines even the clearer engine such gasoline generated particle of the size between 20-60 nm (5).

As industry needs new materials, such as carbon fibers, these new materials are becoming major sources of nanoparticles. Carbon fibers are a breed of high-strength materials discovered in 1879. As mass-production created requirements for better and more efficient material for the aerospace industry that can support heavy duty and the transportation of materials required less energy. That type of need applies eminently to military aircraft. The use of carbon fiber to the above application has made it to become of paramount importance. In recent decades, as carbon fibers strength, resistance to fatigue and stiffness in addition to light weight remain the main properties sought by industries, its energy saving potentially during the movement in comparison to heavy material has created a great interest in commercial and civilian aircraft as well as recreational and industries.

Carbon fiber application is widespread in technology; however, specialized technologies (e.g., aerospace and nuclear engineering, general engineering, and transportation) are where carbon fiber application is mainly used for parts susceptible to fatigue over time. Those parts include bearings, gears, fans, and blades. Recently, some new applications of carbon fibers have emerged in military application other than

aviation indeed rehabilitation and orthopedic prosthesis construction industries have become is great user of carbon fiber.

1-2 PARTICLE MATTER HEALTH EFFECTS

Since the London pollution study of 1952, it has been shown that increases of PM in the air increase total mortality and morbidity. It is well established PM, specifically PM_{2.5}, increases heart failure (61) and increases mortality by 10.9 to 20.8% (13). In addition, PM_{2.5} particles are more harmful than coarse particles. Dominici, et al. (12) have shown that there is direct link between acute and chronic exposures to airborne particles and the increase of morbidity and mortality (12). The American Cancer Society (ACS) conducted a prospective study on long-term PM exposure has shown that children and adults were affected differently by PM exposure. Children have predominantly an increase in respiratory illness while adults experience an increase in cardiopulmonary mortality. Particle pollution was associated with increased public health system burden by increasing hospitalizations and respiratory disease incidences and fatality case (49). In the same extensive review, Pope and Dockery have suggested that the trend of mortality count was parallel to concentrations of PM₁₀. Also locations with higher PM_{2.5}/PM₁₀ ratios had higher mortality, suggesting that smaller particles are most detrimental to human health than bigger particle as highlighted by Riest (52).

Respirable particulate matter can initiate body reaction that manifested as coughing, wheezing, and shortness of breath, the more PM are in the environment the higher these symptoms increase (63). There are few studies, however, that show a relation between nanoparticles and health adverse health effects in the literature compared to the literature on PM₂₅ and PM₁₀ (63). Among the few that link nanoparticle and health effects,

Pekkamen, et al. (48) have demonstrated an association between nanoparticle levels and cardiovascular symptoms (48).

Exposure of workers to nanoparticles can occur by several means, including inhalation, dermal contact, and ingestion (56; 65). According to Tinkle, et. al. (58), inhalation dominates routes of exposure for chemicals and airborne particles, including nanoparticles concerning exposure. Once in the body, the deposition of PM triggers a cascade of physiological responses, including oxidative stress-related inflammatory reactions. More interestingly, recent analysis of historical data from the 1952 London pollution study using modern microscopy technology showed the observation of nanoparticles in great numbers in autopsy tissue, suggesting that nanoparticles played a substantial role in this large-scale death event (20).

Nanoparticles, because of their small size and agglomeration capacity, have more interactions points with biological materials. As the reactivity of nanoparticles is proportional to the interactions points, they exhibit greater biological activities than particles of larger size. Local inflammatory and fibrogenic responses are induced in the lung tissues, accompanied by modified systemic immunity *ex vivo* (25; 35).

Like respirable particles, nanoparticles can induce various diseases. In fact, their small size allows them to go deeper into the human body, overcoming the immune system, degenerating the nervous system and inducing failure in major organs such as the heart, kidney, spleen, and lung (4). Clinical diagnosis of exposure to nanoparticles can vary from respiratory diseases (e.g., asthma, bronchitis, emphysema, and lung cancer), degenerative diseases like Parkinson's and Alzheimer's, and other pathology such as Crohn's disease, colon cancer, and autoimmune disorders (e.g., systemic lupus

erythematosus, scleroderma, and rheumatoid arthritis) (15).

1-3 LACK OF EFFICIENT FILTERS AGAINST NANOPARTICLES

In the workplace, the main personal protective equipment (PPE) available to protect against particle exposure is the respirator filter. The National Institute for Occupational Safety and Health (NIOSH) and the European Union certified the N95 and P100, FFP2, and FFP3 face shields, however, the expected level of protection is not provided in regard to nanoparticles (41). The efficiency varied between five to 10 percent (53). Breath rate and the filter material dictate the magnitude of nanoparticle breakthrough. The majority of the nanoparticles that cannot be filtered out by the N95 and P100 are those 50 nm or lesser. Performance from static material filters is less efficient than filters pre-treated with ionic surfactants (3). An experimental performance test of the N95 at simulated flow rates of 30 and 85 l/min showed that an increase in the flow rate increases the filtration efficiency for large particles ($>1\ \mu\text{m}$) because of the inertia effect but decreases the filtration efficiency for small particles ($<1\ \mu\text{m}$) due to the diffusion and electrostatic effects (36). As the smaller particles are the most toxic, it can therefore be concluded that workers' protection decreases with higher breathing rates (3; 53).

1-4 PROBLEM STATEMENT

Current research has established that nanoparticles has adverse health effect on human, especially to the respiratory system, but there is no universal method of characterizing these particles. With the development of materials capable of producing nanoparticles in the prosthetics business, and the forecast of an increasing number of prosthetics needed in the future, it is important to fill the gap of knowledge of potential

PM exposures in the nanoparticle range. For this reason, small-scale manufacturing facilities are very good locations to characterize the exposures to nanoparticles.

Currently, traditional gravimetric methods is used to assess the exposure to dust during orthopedic prosthesis fabrication at Water Reed National Military Medical Center (WRNMMC). These methods cannot detect nor quantify nanoparticles. This gap needs to be filled to achieve a better understanding of the exposure in prosthesis laboratory and improved protection of workers. Worker health is essential to ensure prosthesis manufacturing. As military personnel require more prosthetics for wounded warriors, it becomes critical to protect prosthetics technicians from nanoparticle exposure.

Currently PPEs in use in the WRNMMC prosthetics laboratory for respiration protection is mainly the N95 mask. It is important to determine if any of the current controls in place are effective in reducing the exposure of nanoparticles to prosthetics technicians. The nanoparticles of interest will be carbon fiber, talc, and vitreous fibers because of the amount generated during orthopedic prosthesis processing.

1-5 MILITARY RELEVANCE

With the current high operational tempo, there is an increase of wounded warriors. According to statistic more than 4,000 American men and women and 158 Canadian have died in Iraq and Afghanistan. In addition, many more were injured of which some have become permanently disabled. According to a survey from a British 34th field hospital during the first Iraq war, the rate of amputation was 16% of the wounded warriors (51). To increase wounded warriors' life quality, it is important to provide them with excellent orthopedic material.

WRNMMC's prosthetic laboratory is part of a three-centers network that the Department of Defense has organized in response to the wounded warriors' special care needs. In addition to WRNMMC, the network includes the Center for the Intrepid at the San Antonio Military Medical Center, and the Complex Casualty Care Center at the Naval Medical Center, San Diego. The WRNMMC amputee center's prosthetic laboratory as well as the other two centers designs custom prosthetic limbs for service members using the latest technology available in the field. Those prosthetics are made of carbon fiber and other diverse chemicals. Workers making prostheses need to be protected against excess exposure to carbon fibers and other nanoparticles because while the toxicity of nanoparticles are known, there is no current regulation establishing exposure limits.

This study can serve as a good pilot study in determining the quantity of nanoparticles generated in the WRNMMC prostheses laboratory. This body of knowledge will also be extendable to other military operations, for example mishap investigation and aircraft maintenance exposure surveys. There is always a possibility of mishaps occurring during military operations. In the near future, Royal Canadian air forces and US air forces are projected to buy several F-35s. The F-35 will be composed of nearly 38% to 40% composite materials. If a F-35 is involved in any type of mishap in which the material is broken down, exposure of investigators to a significant amount of nanoparticles can occur. To prevent health hazards to these individuals, it is important to discover how to prevent overexposure to nanoparticles.

1-6 PUBLIC HEALTH RELEVANCE

Prosthetics technicians whose clients are in the civilian general population need to be protected against nanoparticle exposure as well. The World Health Organization is projecting that there will be as many as 57 million amputees from diabetes complications alone by 2030. In addition land mines and civilian war victims in African countries are contributable factors to increase prosthesis demand. Most of these amputees will need prosthetics with strong and resistance composite material such as carbon fibers, which means additional exposure to nanoparticles for prosthetics technicians if the exposure amount is not adequately assessed and prevented.

This exposure is of concern as carbon nanoparticles can be in a roll form with a diameter on the order of 1.5 nm for single-walled carbon nanotubes (32; 60). This structure is comparable to crocidolite asbestos, a fiber and respiratory toxicant that is associated with asbestosis and mesothelioma. This morphological similarity to asbestos (AB) strongly suggests the toxicological importance in pulmonary disease and structural alteration such as inflammation, granuloma formation, and fibrosis. The increase of these diseases will increase the burden on the public health system.

CHAPTER 2: Literature review

The following review will provide insight into the nanoparticle mechanisms of toxicity and exposure assessment. The exposure assessment metrics will be reviewed and contrasted. Finally, optical and condensation particle counters operational methodology will be discussed.

A nanoparticle is PM with a diameter less than 100nm. When compared to familiar material, a nanoparticle is 50,000 times smaller than an ant, 1000 times smaller than the width of a sheet of paper, 800 times smaller than human hair and has a similar size to the influenza and HIV viruses. Another important physical characteristic of nanoparticles is the great surface area to mass ratio in comparison to larger particles comprised of similar chemical components. Nanoparticles have surface areas volume ratio always greater than $60 \text{ m}^2/\text{cm}^3$.

A nanoparticle can be formed in two ways. The formation can be small to large, where nanoparticle formation begins with a nucleus. Once a particle nucleus is formed, its size increases to become a nanoparticle. Nanoparticles will agglomerate per shape and size. Alternately, it can be formed from top down, where bigger particles generate smaller elements as a consequence of manufacturing processes such as grinding, heating, sanding, etc.

2-1 NANOPARTICLE TOXICITY

The mechanism of toxicity is mainly caused by oxidative stress. Oxidative stress can trigger mitochondrial perturbation, inflammation, protein denaturation, and lipids peroxidation as already proved in different types of cells (9). Cell exposure to a nanoparticle has been shown to modify cell function via DNA and other organic damage

and increase cell apoptosis via reactive oxygen (ROS) production and lowering cell antioxidant defense (superoxide dismutase and glutathione) (18; 28; 37). Superoxide dismutase and glutathione are two mechanisms of cell defense against oxidative stress. In addition to lowering cell defense, nanoparticles increase cell death by deregulating transcription factors like c-Jun N-terminal Kinases (JNK) and Nuclear Factor kappaB (NF-kappaB) (6). This deregulation triggers apoptotic or necrotic pathways (16; 34).

2-2 NANOPARTICLE EXPOSURE ROUTES

Workers can be exposed to nanoparticles by several means such as oral, inhalation, and dermal, including the eye (58; 65). From the first points of contact, nanoparticles can move in the body to the target organs through the lymphatic system, the mucosal layer of the gastrointestinal tract, the circulation system (blood) or the optical nerve (65).

Nanoparticle bigger surface area increases the contact point with biological material, inducing more biological activity. In addition to inducing oxidative stress injuries in the tissues, nanoparticles increase pro-inflammatory interleukins that are accompanied by modified systemic immunity *ex vivo*, which triggers fibrogenic responses (25; 35). Nanoparticles can cause histotoxicity that can lead to vital organs damage such as liver, kidney, heart, spleen, accompanied by physiological impairment of the gas exchange within the lungs (24).

The structural analogy to asbestos strongly has suggested the toxicological importance in pulmonary inflammation, granuloma formation, and fibrosis. Experimental research undertaken to compare asbestos and nanoparticles has shown that a single-wall carbon nanoparticle has more severity than asbestos in inflammatory and fibrotic

responses (57). Relevant data in literature support that nanoparticle exposure may cause multiple negative health effects, to include pulmonary diseases, cardiovascular failure effects and decrease of the immune system protection efficiency (49). To prevent nanoparticle toxicity, it is important to assess how people are exposed to them.

Particle toxicity is related to where in the body they can be deposited. When inhaled, bigger particles from 0.1 to 10 μ m enter in the body and can remain in the nose and trachea portion of the transportation area of the respiratory system. Smaller particles, less than 0.10 μ m, are deposited by diffusion in the respiratory tract and can reach the alveoli where they can cross the endothelial cells layer to enter the bloodstream. Once deposited, a cascade of activities occurs, including oxidative stress-related inflammatory reactions. During inhalation, nanoparticle translocation into the system circulation occurs. There is a lack of evidence, however, in the extent of this translocation (4).

Nanoparticles will agglomerate per shape and size, not by chemical composition similarity. As stated in Chapter 1, nanoparticle shape and size will drive the deposition site within the respiratory tract (43; 45). To regulate exposure to nanoparticles, conventionally accepted monitoring devices and exposure metrics must be used to measure and evaluate occupational exposures. There is a lack of enough data for regulatory purposes with the use of these monitoring devices.

2-3 NANOPARTICLE EXPOSURE ASSESSMENT AND EXPOSURE METRICS

Exposure to nanoparticles can be assessed in two ways. The first method is simulation of nanoparticle production. Laboratory simulation is ideal methodology to distinguish nanoparticle release from the investigated process, from nanoparticle from to background naturally present in the environment. To simulate nanoparticle production,

all the activities have to be well characterized so that the emission can be anticipated. To be applicable, this method has to make the assumption that the activity is constant and non-variable, which is not true for most workplace environments. It must also be noted that background aerosols may be a contamination from other work and the work tools. The second method is the direct workplace measurement. The major advantage of this approach is that data from real-work conditions are obtained, but this method barely discriminates particles of concern from the generic background concentration. Therefore, it is very important to assess that background to have an interpretable result. To make a reliable correlation between exposure and health effect, it is important to find the best reporting metric system. For the purpose of risk evaluation, toxicity, and exposure duration should be aligned to determine the potential health effect endpoint for workers.

Apart from chemical composition, there are several other conventional approaches to express exposure to nanoparticles (e.g., number concentration, mass concentration, surface area and particle morphology) (44). The relevancy of their use must be based on suitability, accuracy, and instrumentation availability.

The **mass concentration** method gives the mass of exposure; although it can indicate a real-time exposure it is not suitable for aerosol contains volatile components and smaller particle of 0.5 μ m in diameter as their lesser mass induce great amount of errors (67). Alternately, there is the gravimetric filter base measurement; an example of which is a low-pressure cascade impactor. Experimental design results have shown that this method is poor when differentiating of low and high concentrations of nanoparticles (47). Based on the assumption of smaller particle toxicity, this is not the best suitable method for nanoparticles, as it only detects larger particles (0.5 μ m and greater in

diameter) (30; 67).

Second, **size distribution** can be applied to assess material exposure for those particles where physio-chemical properties are known (64) (e.g., shape and the density of the particle are known). Examples of this kind of measurement are Transmission Electron Microscopy (TEM) or Differential Mobility Analysis. However, these methods are expensive and time consuming.

Characterization of the **surface area** is good metric of nanoparticle exposure assessment as it can be directly related to the surface area of the tracheobronchial surface of the respiratory system. This method is very sensitive to particle solubility. It is well suited for nanoparticles but not acceptable respirable and bigger particles. Some examples of measurement devices are the Electrical Aerosol Detector (EAD) and the Nanoparticle Surface Area Monitor (NSAM). They measure the unipolar ion chemical bond formation rate to the surface area of the particles. This is an indirect measurement that may be more susceptible to environmental conditions (30; 31; 64).

The **number concentration** is the measurement of the number of particles per unit volume. This method is simple, using instruments, such as the Scanning Mobility Particle Sizer (SMPS), Optical Particle Counters (OPC), and Condensation Particle Counters (CPC), which can track temporal changes in exposure and are also able to determine exposure to particles from 10 to 100nm. This method is not specific to the nanoparticle size and therefore, assumption of the size must be made when using these devices. According to studies results, it is possible to correlate, nanoparticle number concentration and their toxicity (44; 45). OPCs and CPCs are available in a portable size and are battery operated; therefore, they can be used for personal monitoring in the

worksite (30).

2-4 INSTRUMENTATION

Workplace exposure assessment for aerosol is well documented and widely uses the gravimetric method (27). This method is not suitable for nanoparticles as the particle number is more biologically significant for their toxicity. To ensure a good risk assessment of nanoparticle exposure, a number of concentration-measuring instrument must be used. New technologies that combine ease of use and number concentration determination for nanoparticles have opened a new era in routine monitoring of occupational exposure to nanoparticle. OPCs and CPCs are suitable as static as well mobile monitors.

2-4-1 Optical Particle Counters

OPCs are particle detection and counting instruments that use light diffraction technology and detection to count particles in specific size ranges (17). Particles pass into the instrument and are directed one at a time through a light beam. When the particles pass through the light, energy is reflected to a detector. The detector converts this reflected light to an electrical signal. The electrical signal strength is used to determine a particle number and determines which of the instrument's size channels the particle falls (Figure 1).

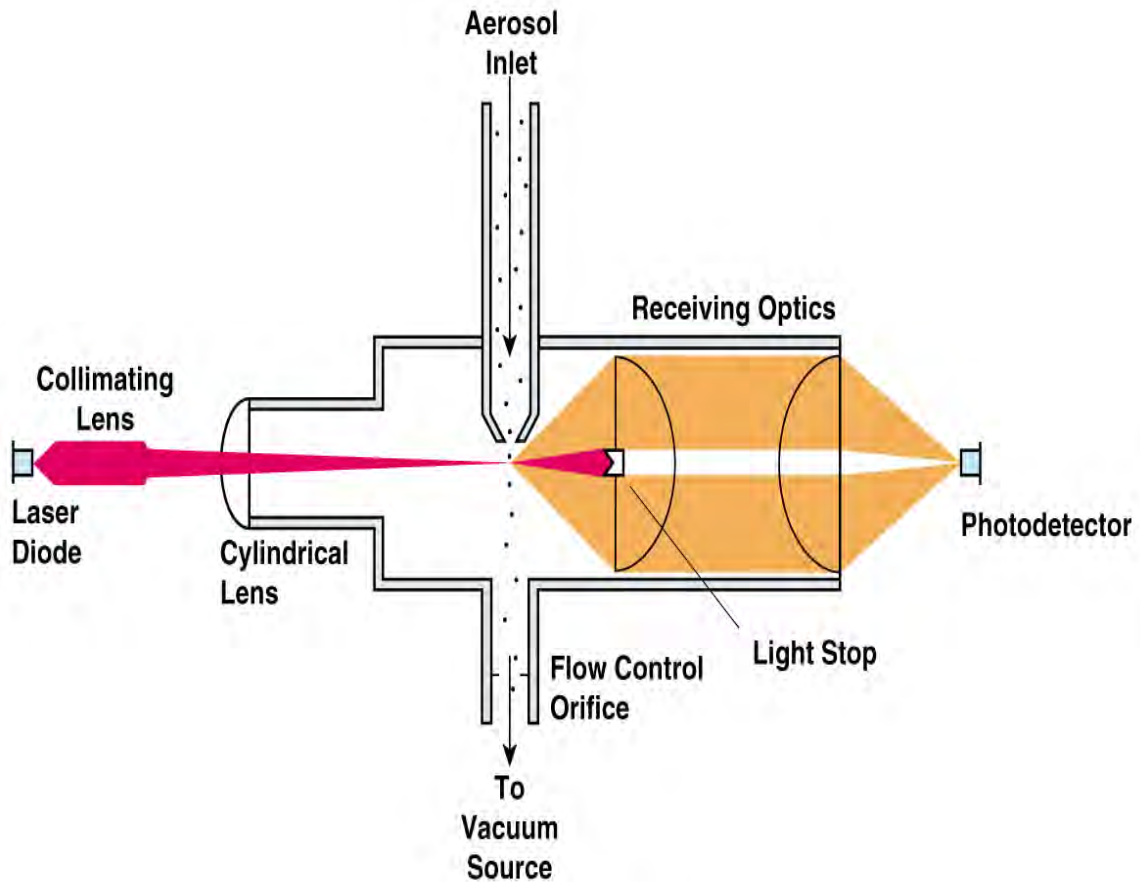


Figure 1. Principle of functioning of an OPC (TSI)

OPCs have several limitations. The major limitations are that the detector can be overwhelmed and that the refracted light is not monotonic for particles sized between 500 and 1500 nm. There is also a response error for different refractive indexes of particles (59). In addition, all particles may not be detected because overlapping particle may rush at the same time through the light beam. When this occurs, these particles can be interpreted as one particle. Reducing the flow through the detector or diluting the incoming aerosol with filtered air without particles can overcome this misinterpretation. The monotonic limitation is due to the signal returned by the detector not being unique to

a particular particle size. That same level of signal is sometimes associated with a range of particle sizes. Another limitation is that the instrument loses accuracy when a range of refractive indexes is present. Detector response error ranges from 50-100%, depending on the refractive index present (17).

2-4-2 Condensation Particle Counters

CPCs are particle detection and counting instruments that employ technology to grow particles in a supersaturated environment (59). This environment allows the particles to be more easily counted. Particles are introduced into the instrument and are sent through a supersaturated isopropyl alcohol solution, in which they are grown. The exposure time and concentration are both closely controlled, and particles are grown to 10 μ m in diameter. Particles grow to the same 10 μ m size regardless of their original diameter. These 10 μ m particles can be easily counted via a calibrated light transmission detector. Due to the growth of the particle, counts for particles within the detection range can be performed, but particle size cannot be determined (Figure 2).

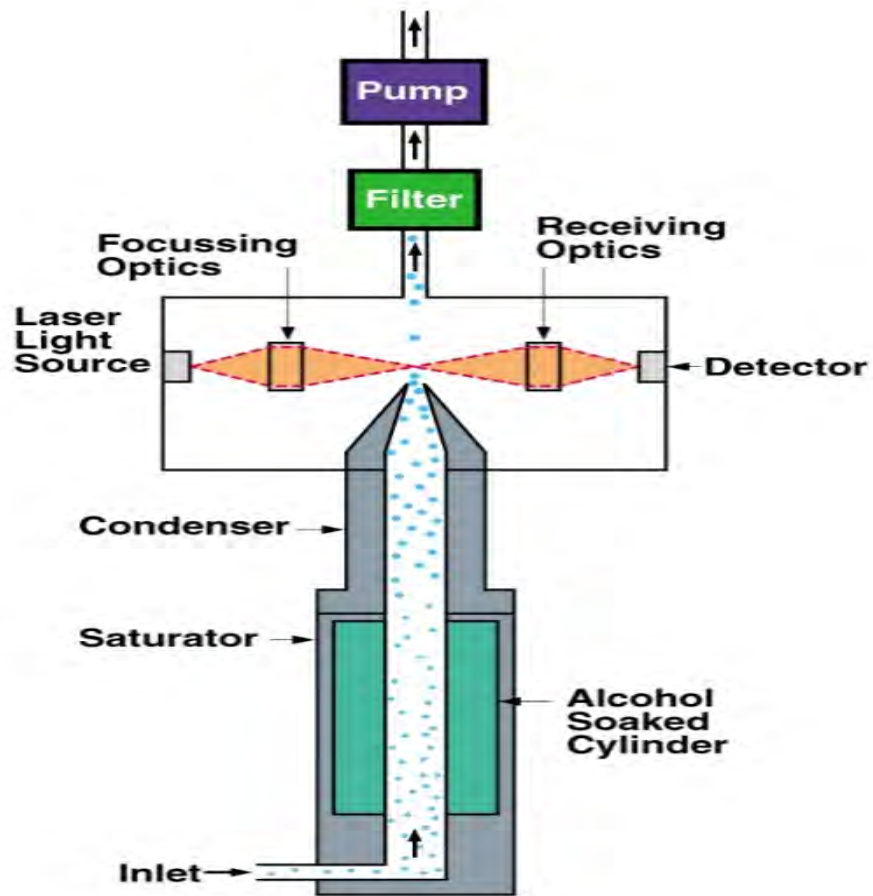


Figure 2. Principle of functioning of a CPC (TSI)

CPCs are limited in two ways. CPCs have a maximum concentration of particles that they can detect, and an inability to differentiate between particles of different sizes. Because particles grow to the same diameter regardless of their original diameter, the meter can not differentiate between particles sizes and reports only a raw particle count/cc measurement. As the CPC cannot accurately distinguish particle type to which worker may be exposed they can be classified as personal sampler device, but the result generated can well characterize particles emitting sources. Usually particle exposure assessment is used in environments which there are obvious evidence of exposure to ensure that this exposure does not exceed the regulatory limit.

CHAPTER 3: Materials and Methods

The WRNMMC prosthetic laboratory was divided between office activity area. A main floor for storage area where various activities took place such as minor paperwork, some prosthetics trial and fitting and also some finishing work and a prosthetic and finally manufacturing area with four rooms (Appendix A). The office area contains management and administration spaces and is physically connected to the second area, which is the main area where there is storage of prostheses, tools, and minor workbenches. The main area is separated from the manufacturing areas that include: 1) a room for lamination, which is accomplished at four stations installed around a workbench equipped with local exhaust ventilation (LEV), 2) a plasterization room equipped with a sink that provides hot and cold water, 3) a thermoforming room equipped with two ovens to heat plastic sheets up to 330°F, a vertical rotating saw to cut the plastic sheets, and two benches with a vacuum system under the benches, 4) a grinding room with two cutting stations, the first with a hand operated rotating saw and the second with a mechanically operated cutting saw. Grinding was conducted on three stations of high speed mechanical grinding devices, each equipped with its own LEV. The LEV hoods had sloping fronts positioned approximately five cm on the side of the grinding roll. Each of these four rooms was ventilated by a 2x2 exhaust and 2x2 supply located in the ceiling.

During prosthesis manufacturing, there are four steps. The first step is plasterization in which the prosthetist evaluates and makes a mold of the limb. The mold is reproduced with the plaster material. During this step, gypsum powder is mixed in

water, and used to mold the stump. From the mold, a positive model that is an exact duplicate of the limb is created.

The second step is thermoforming in which the socket (consisting of a liner that acts as a sort soft contact between the movable soft tissue of the residual limb) is made by collapsing a heated sheet of clear thermoplastic around the mold. To do so, the plastic sheet is heated in a large oven at 330°F and vacuum-formed around the positive model of the limb. The air between the sheet and the mold is sucked out of the chamber.

The third step is the lamination. During this step, the socket is surrounded by tube carbon fiber in a vacuum chamber. To collapse the tube carbon fiber around the socket, a mix of solvent glue and hardener is applied to the top of the carbon fiber tube and expended all-around it. Once the mix is dry, the excess is cut off.

During the fourth and last step, the socket is ground in the appropriate places to produce the final form, according to patient input and the successive tries based on the prosthetist's observations. PM generated by these processes have the potential to pose a health hazard to prosthesis workers who cut, coat, sand, and grind carbon fiber in the prosthesis manufacturing plant. The objective of this study is to evaluate the extent to which workers in the WRNMMC prosthetic laboratory are exposed to particulate matter of various sizes while performing tasks associated with prosthetic production. The study will test three related hypotheses as detailed in following section.

3-1 RESEARCH HYPOTHESES

This study will address one main hypothesis as well as three subsequent more specific hypotheses.

3-1-1 Main Hypothesis

Null Hypothesis, H_{01} :

Prosthesis manufacturing at WRNMMC does not cause overexposure of workers when compared to OSHA Permissible Exposure Limit (PEL) for Particulates Not Otherwise Regulated (PNOR) of $15\text{mg}/\text{m}^3$ (46).

Alternate Hypothesis, H_{A1} :

Prosthesis manufacturing at WRNMMC does cause overexposure of workers above the permissible exposure limit (PEL) of $15\text{mg}/\text{m}^3$ (46).

3-1-2 Specific Hypothesis #2

Null Hypothesis, H_{02} :

There is no difference in the respirable particle matter number concentration (number per liter) between different tasks of prosthesis manufacturing.

Alternate Hypothesis, H_{A2} :

There is a difference in the respirable particle matter number concentration (number per liter) between different tasks of prosthesis manufacturing.

Experiment #1

This experiment was performed by monitoring total dust concentration via a filter cassette hung in the shop for the four steps of prosthesis manufacturing. Sampling was conducted using the Safety NIOSH method 0500 (40). The goal of this methodology was to collect an 8-hour Time Weighted Average (TWA) total particle matter weight. Sampling was conducted using the NIOSH method 0500 (40). The goal of this methodology was to collect an 8-hour Time Weighted Average (TWA) total particle matter mass weight.

Manufacturer pre-calibrated and calibrated daily before and after experiment, a GILAIR 5 pump was used to create vacuum through 37mm PVC cassette filter. As the air goes through the filter it collects particle matter with a diameter below $4\text{ }\mu\text{m}$. The pump attached to a cassette filter was localized one foot near the workstation and three

feet above the ground. For each workstation, 12 samples (the intent was to collect 30 but the sample was stopped at 12 the detection limits could not be reached) were collected. Results from cassette sampling were compared to the OSHA standards, which is $15\text{mg}/\text{m}^3$ for particulates not otherwise regulated (PNOR). No personal sampling was made because the focus was on task-dust generation. After the sampling, the particulate matter weight was determined by weighting filters.

3-1-3 Specific Hypothesis #3

Null Hypothesis, H_{03} :

There is not a statistically significant difference in the number concentration of nanoparticles (number per liter) among the tasks during prosthesis manufacturing.

Alternate Hypothesis, H_{A3} :

There is a statistically significant difference in the number concentration of nanoparticles (number per liter) among the tasks during prosthesis manufacturing.

3-1-4 Specific Hypothesis #4

Null Hypothesis, H_{04} :

There is no difference in the coarse particle matter number concentration (number per liter) between different tasks of prosthesis manufacturing.

Alternate Hypothesis, H_{A4} :

There is a difference in the coarse particle matter number concentration (number per liter) between different tasks of prosthesis manufacturing.

Experiment #2

This experiment will help to answer hypothesis #1. The method used was NIOSH 0600 (39). The device used was an aluminum Cyclone. This experiment was performed for the four steps of prosthesis manufacturing. This experiment collected particle matter with diameter size below $4\text{ }\mu\text{m}$ using a cyclone device as described as follows.

A cyclone is a device that separates particles according to their inertia as they are under vortex force effect. As particles are close to their inertia point they are taken off the stream. Inside the body of the device, under centrifugal force heavier particles fall off the stream as lighter ones remain and are directed to the filter. The flow of particles enters the cyclone and due to the centrifugal forces of the air rotation inside the cyclone body, larger particles are accelerated toward the outside of the cylinder where they descend and collect at the bottom. Smaller particles are not affected by the centrifugal forces and therefore remain within the air current rotation. The upward movement of the rotation ascends the smaller particles toward the medium where they are collected for measurement.

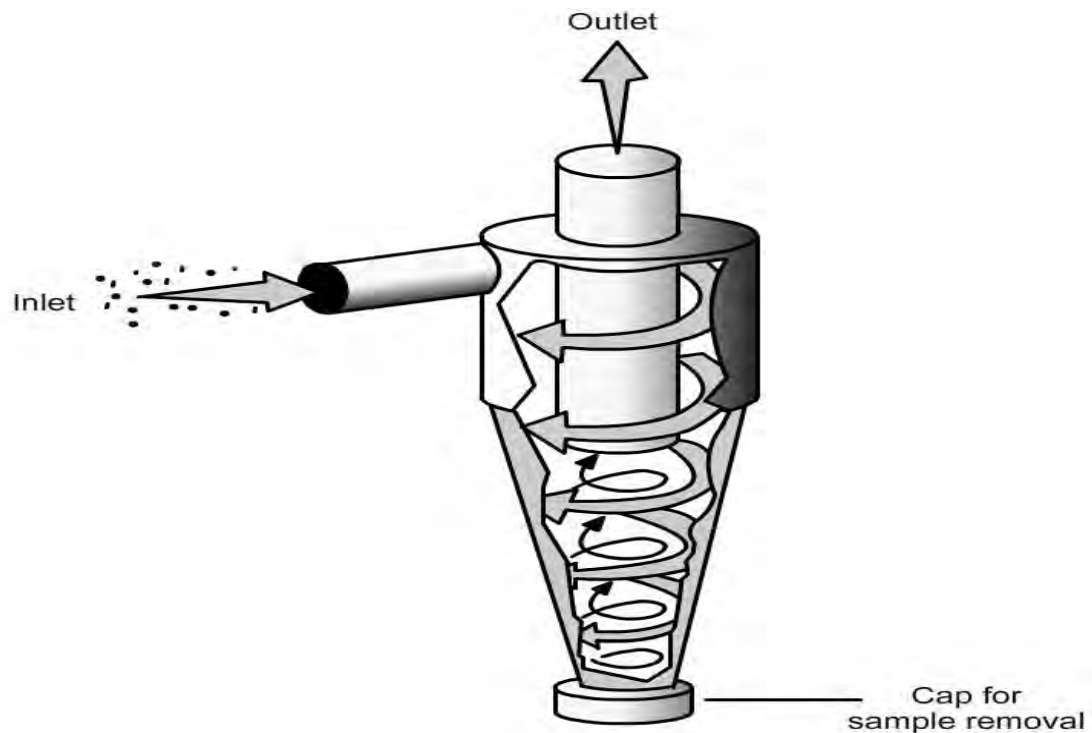


Figure 3. Schematic of the cyclone functioning principle

The aluminum cyclones employed in this study were connected to a high velocity vacuum pump GILAIR 5, set at 2.5 l/min for 480 minutes to ensure that the required flow rate through the cyclone body and in-line filter would be met. The pump was manufacturer pre-calibrated before the commencement of the experiment and also calibrated daily before and after the measurements at 2.5 l/min. Particles exiting the vortex toward the filter were collected onto pre-weighed PVC fiber filters. The Galson Laboratory in East Syracuse, New York, completed the post-test weighing of the filters.

After monitoring, the filters were weighed and the amount of particle matter with a diameter less than 4 μm was quantified by using the NIOSH method 0600 (39). The pump was localized one foot near the workstations and three feet above the ground level. For each workstation, 12 samples were taken. The mean particle matter weight was compared to the OSHA standard of five mg/m^3 using a t-test with a five percent level of significance. X-ray diffraction was conducted on filters by NIOSH method 7500 (42) in order to determine qualitatively the presence of quartz, tridymite, and cristobalite in the samples.

Experiment #3

This experiment helped to answer the three others hypothesis from #2 to #4. The NIOSH Nanoparticle Emission Assessment Technique (NEAT) method for characterizing operations that utilize nanoparticles was used to access the quantity of nanoparticles. This method used direct reading methodology with two counters devices OPC and CPC. OPC's limit of detection at a size of 300nm, therefore the device is not able to determine nanoparticles. The CPC with a lower limit of detection at a size of 20nm could detect nanoparticles but could not distinguish these particles from those in

the upper range of its detection limit of 1000nm. NEAT consists of running in parallel the two particle counters with overlapping detection limits. The reading of one was subtracted from the other so that the overlapping portion could be excluded.

For this experiment, a portable OPC (model fluke 983) was used to measure the number concentration from 300-10000nm in five size channels. The OPC was set with the default channel size of 300nm, 500nm, 1000nm, 5000nm, and 100000 nm. The OPC outputted samples as a raw count in each size range. The OPC is similar to the CPC in that it counts particle number; however, in contrast, the OPC classifies each of the counted particles into a diameter channel according to the light scattered when passing through the light source. Raw data from the OPC and the CPC was used to determine particle fractions, according to computed equations as used in previous studies (19; 55).

NIOSH has suggested building detection of particles on the strengths of the OPC and the CPC by running the detectors in parallel. The OPC data should be used to determine which portion of the CPC data is below the limit of the OPC (43). Heitbrink et al. proposed a method to make that determination (19). Utilizing the fact that the detectable sizes for the two meters overlap, the size channels of the OPC that are below the 1000nm upper detection limit of the CPC are subtracted from the OPC's count. The remaining value represents particles with diameters below the OPC detection limit of 300nm. Heitbrink et al. defined this value as the number of particles with diameters smaller than 300nm particles and calculated as shown in Equation (1).

Equation 1

$$Nufp = Ncpc - \sum_{i=1}^3 Ci$$

Where N_{cpc} is the CPC count. The number 3 is the OPC channel for which the upper limit is 1000nm for the meter used by Heitbrink et al. (19). As the lowest limit from the OPC's first channel is 300nm and the upper limit of the third channel is 1000nm, N_{ufp} is solely the 20nm to 200nm particle count range (19; 55).

For data collection, the OPC and the CPC were manually initiated simultaneously as lamination, plastering, thermoforming, and grinding started and placed within one foot of the process and three and a half feet above the ground. Measurements were done throughout the day. Duration of each measurement was one minute, and each device stopped after recirculation of one liter of air. Statistical analysis of the data will be based on the analysis of variance and descriptive statistics. This method was used on the results of the pilot research data shown in log normal and unimodal distribution. Particle concentration number were directly taken from direct reading was used to calculate mass concentration from each channel of OPC and CPC and the average coarse, respirable, and nanoparticle mass concentration were calculated based on ACGIH criteria (2) and fixing the fraction collection at 50% fraction collection as this fraction corresponds to particles with aerodynamic diameter of 4 μm and below. The diameter of interest is arbitrarily fixed at 100nm for nanoparticles (55).

Particle number concentration were converted to mass concentration by slightly modifying the method used by Sarwar et al. as an OPC diameter was retrieved from the technical manual (54). We assumed that all the particles were spherical with a diameter equal to the channel they came through and used known mathematical formula that determine volume, according to geometrical diameter to determine the volume. Total particle mass, as shown in Equation (2), was determined by first calculating the mass of

one particle. Single particle mass was computed by obtaining the density from the appropriate Material Safety Data Sheet (MSDS) and multiplying it to the volume formula for spheres. Second, the calculated single particle mass was multiplied by the total particle count to determine the total particle mass (54). The study assumed that only one material was predominant in each room (54). The study assumed that only one material was predominant in each room. In the lamination and grinding rooms, carbon fibers with a density of 1.78 was used; in plasterization, plaster with a density of 0.97 was used; and in thermoforming, plastic with a density of 0.87 was used.

Equation (2)

$$M = \pi \rho \left(\frac{d^3}{6}\right) N_i$$

d = diameter of each channel

N_i = count for each channel

ρ = density of material sample

The diameter of the channel was obtained from OPC specifications. This method completed the fraction obtained from the count-difference method (19). The geometric mean was used because of decrease sensitivity to outliers. Based on average standard deviation and the number concentration of particles that can permit detection of a significant difference among measure. The determination was made that 40 samples was an adequate sample number to achieve the power for this study. This number of samples

had an 80% power to detect a difference of standard deviation of 0.4 between tasks using a two-tailed t-test with 5% significance.

3-2 ANALYTICAL SUPPORT

The United States Army Public Health Command (USAPHC) analyzed the samples using approved NIOSH methods for the testing of air samples. The methods used were NIOSH 0600 and NIOSH 7500. Briefly, NIOSH 0600 is a weight base methodology. The collection filter is weighed before and after sampling using a balance with a sensitivity of 0.001mg and a limit of detection of 0.03mg. The difference of weight is considered as the collected particles' weight. NIOSH 7500 is a crystallographic method. Briefly sampling filter was dissolved by sonication in tetrahydrofuran (THF) by and the mixture is analyzed by X-ray diffraction. That method has a detection limit of five μg for quartz and 10 μg cristobalite. This method used crystalline physical properties to differentiate chemical composition and crystallographic structure of natural and manufactured materials.

3-3 STATISTICAL ANALYSES

The number concentrations were measured prior to task performance. These concentrations represented the background particle matter levels. A post-hoc Tukey HSD multiple comparisons was performed to identify significant differences of particle number concentration among rooms. Once number concentration was measured during task performance, these results were first compared to background by oneway ANOVA followed by a Dunnet t-test that compares a single mean to multiple other means.

The number concentrations detected in the lamination, plasterization, thermoforming, and grinding rooms were log-transformed for statistical comparisons so

that outlying values did not significantly affect the means (8). Consecutive measurements obtained from the same room exhibited a large variability. A post-hoc Tukey HSD multiple comparison test was used to identify, which, if any, of the rooms' particle number concentrations were statistically different. The mean and standard error of the particle number concentrations were determined and calculated for each room from the repeated one-minute measurements in that room. These values were used to represent the room particle concentration when determining which task performed in each room significantly influenced total exposure to particle matter in the associated room in the prosthetics laboratory. ANOVA was used to test if particle concentrations were equal across the four rooms with a post hoc Tukey HSD multiple comparisons test to identify which groups had different particle concentrations. Statistical significance for all tests was evaluated at a critical p value of 0.05. Analyses were carried out using the Statistical Product and Service Solutions software (SPSS) version 19 (21).

CHAPTER 4: Results

The findings of this study are presented as gravimetric evaluation and direct reading results. The direct reading results' data is shown in two categories: first, the particle number concentration retrieved from the direct reading instruments and second, the mass concentration as determined from a calculation based on the particle concentration number, particle diameter, and particle density. Density and sphere volume are mathematically depicted in the following Equations (3) and (4).

Equation 3

$$D=m/v$$

Where

$$D=\text{density (kg/cm}^3\text{)}$$

$$m=\text{mass (kg)}$$

$$V=\text{volume (cm}^3\text{)}$$

Equation (4)

$$V= \pi d^3/6$$

Where

$$V=\text{volume (cm}^3\text{)}$$

$$d=\text{diameter (cm)}$$

By substituting the volume formula and rearranging to become Equation (5), the mass can be determined. This calculation was important, as mass is the standard way of evaluating exposure to dust in the workplace (40). Particle number concentration and particle mass concentration are presented in respirable, coarse, and nanoparticle size fractions.

Equation (5)

$$m = Dx(\pi d^3/6)$$

4-1 GRAVIMETRIC RESULTS

As discussed in Chapter 3, OSHA, Environment Canada, and other regulatory agencies use traditional gravimetric methodology to quantify workplace dust exposures in terms of mass concentration. This project at the WRNMMC prosthetic laboratory incorporated the use of that gravimetric methodology. Results from that methodology did not reach the limit of detection (LOD) of 0.010mg/m³. That was an indication that all areas were exposed to lower dust mass concentrations than the Permissible Exposure Limit (PEL) of 15mg/m³. X-ray diffraction analysis conducted by the NIOSH method 7500 revealed the presence of quartz, tridymite, and cristobalite in representative samples from all the prosthetic laboratory areas. Detailed results reported by the laboratory on particle weighting showed that weights were below 0.01 mg/m³ for quartz, 0.02mg/m³ for tridymite and 0.15mg/m³ for dust (see Appendix B). Although significance level was not tested, this result was in concordance with hypothesis #1.

4-2 PARTICLE NUMBER CONCENTRATION

Particle number concentration is the measure of particles per unit volume. Table 2 summarizes the background particle number concentration for each of the four tasks in the WRNMMC prosthetic laboratory. Background particle number concentration was similar in all four rooms prior to the tasks of lamination, plasterization, thermoforming, and grinding. The geometrical mean (MEAN) of the particle number concentration for the background of all areas combined was 3451±225 particles/liter. Statistical analysis

using one-way ANOVA showed no difference ($p=1$) among the background particle number concentrations when the rooms were compared to each other. When the background particle number concentration was compared to the particle number concentrations of the performing period of all four tasks by one-way ANOVA followed by a Dunnet t-test, the difference became significant ($p=0.004$) for lamination and plasterization and ($p=0.0001$) for thermoforming and grinding. The difference of the background from grinding and thermoforming was greater than the difference of the background from lamination and plasterization. At this point, the sampling results could not lead to the acceptance or rejection of null hypothesis # 1, which stated that workers were overexposed to dust in the WRNMMC prosthetics laboratory; however, it demonstrated that workers were exposed to an unspecified level of particles.

Table 2. Background particle number concentration for the four task processing rooms in the WRNMMC prosthetic laboratory

Task	Particle Number Concentration (Mean $\pm$ Standard Error)
Lamination	3764 $\pm$ 784
Plasterization	3336 $\pm$ 270
Thermoforming	3598 $\pm$ 44
Grinding	3105 $\pm$ 197

Table 3 summarizes the coarse particle number concentrations for the four tasks in the WRNMMC prosthetic laboratory. Comparison of coarse particle number concentration by one-way ANOVA followed by post hoc Tukey HSD analysis showed that the tasks generated significantly different particle number concentrations ($p=0.00001$) for all the comparisons except lamination compared to thermoforming ($p=0.189$). Figure 4 represents coarse particle number concentration comparison among

tasks. This resulted in the rejection of null hypothesis #4 that stated that tasks generated similar particle number concentration.

Table 3. Coarse particle number concentrations for the four task processing rooms in the WRNMMC prosthetic laboratory

Task	Coarse Particle Number Concentration (Mean $\pm$ Standard Error)
Lamination	2,116 $\pm$ 219
Plasterization	25,397 $\pm$ 8,640
Thermoforming	4,209 $\pm$ 927
Grinding	15,360 $\pm$ 2,970

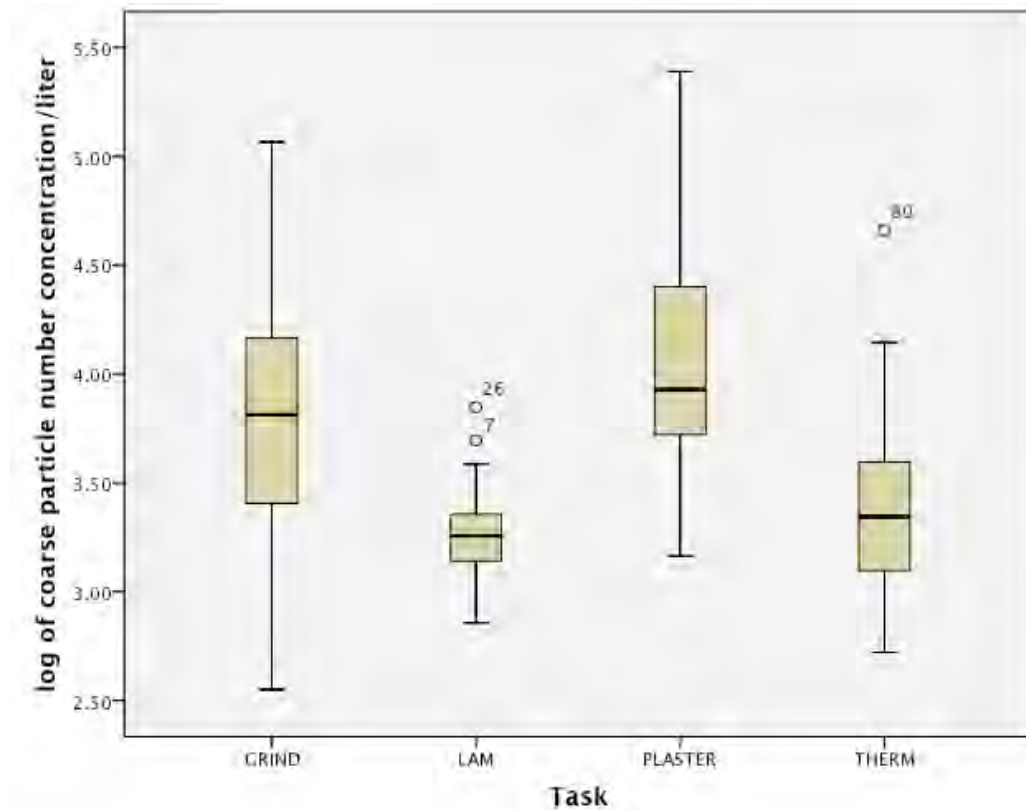


Figure 4. Particle number concentrations/task demonstrating differences among tasks for particle size 5 and 10 μ m

Table 4 summarizes the respirable particle number concentrations for the four tasks in the WRNMMC prosthetic laboratory. Comparison of respirable particle number

concentrations by one-way ANOVA followed by post hoc Tukey HSD analysis showed that tasks generated significantly different particle number concentrations ($p=0.00001$) for all the comparisons except lamination compared to thermoforming ($p=1$). Figure 5 represents respirable particle concentration comparison among tasks. Similar to the results of the coarse particle number concentration comparison among tasks, this resulted in the rejection of null hypothesis #2, which stated that tasks generated similar respirable particle number concentrations.

Table 4. Respirable particle number concentrations for the four task processing rooms in the WRNMMC prosthetic laboratory

Task	Coarse Particle Number Concentration (Mean $\pm$ Standard Error)
Lamination	13,109 $\pm$ 2,537
Plasterization	14,145 $\pm$ 2430
Thermoforming	72,203 $\pm$ 8,893
Grinding	186,890 $\pm$ 80,033

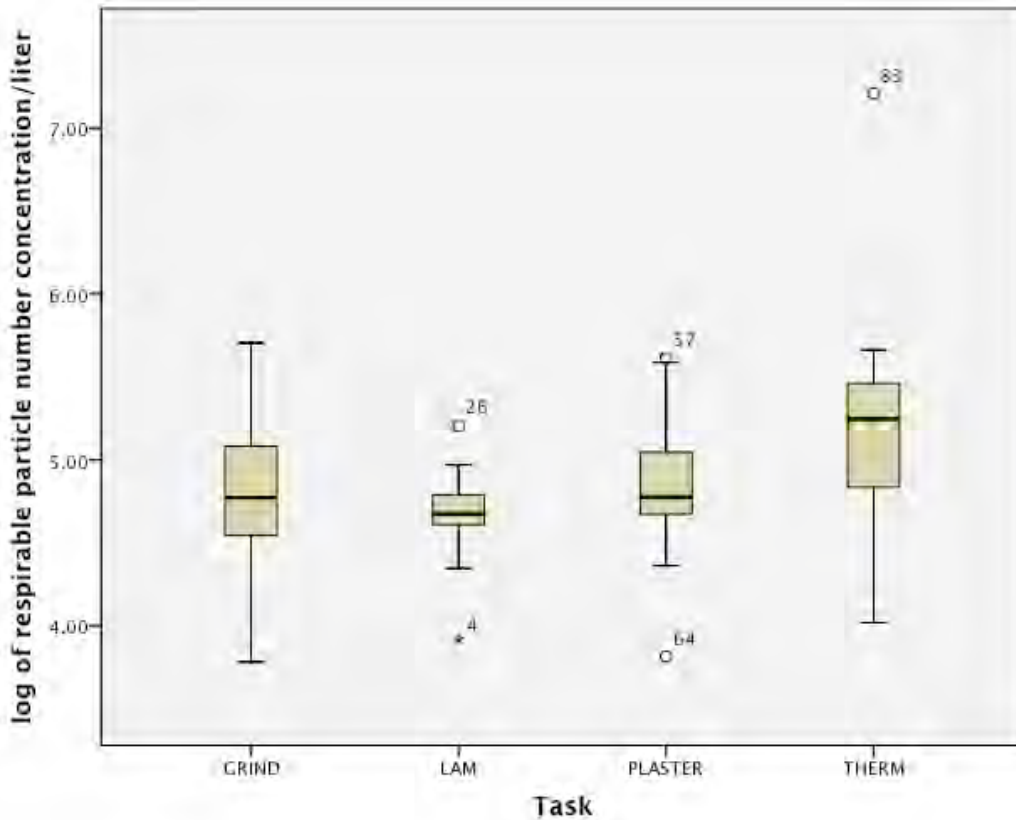


Figure 5 Particle number concentrations/task demonstrating differences among task for size .3 to 2.5 μ m

For better representation of the contribution of each particle size to exposure, the results were computed as cumulative frequencies and percentages. These calculations are summarized in Table 5 and Figure 6. For all four tasks, cumulative frequencies computation of particle number concentrations showed that the respirable size (diameter < 5 μ m) represented more than 90% and the coarse particle size (diameter >5 μ m) represented <10%. For similar size of particles, there were different cumulative frequencies and different percentages of contribution to particle number exposure among tasks. Particle number concentrations were at least 50 times greater in all the rooms during task performance when compared to the background particle number concentration prior to task performance. The difference in frequency distribution for all

particle sizes and particle number concentrations, supported null hypothesis #2 and 4 rejection.

Table 5. Frequency distribution of particle number concentrations by task in the WRNMMC prosthetic laboratory

Task	Particle Size	Percent	Cumulative Percent
Grinding	0.3	48.9	48.9
	0.5	21.6	70.5
	1.0	13.5	84.0
	2.5	10.0	94.0
	5.0	4.2	98.2
	10.0	1.8	100
	Total	100	
Lamination	0.3	75.6	75.6
	0.5	14.0	89.6
	1.0	5.9	95.5
	2.5	3.7	99.2
	5.0	0.6	99.9
	10.0	0.1	100
	Total	100	
Plasterization	0.3	35.9	35.9
	0.5	24.0	59.8
	1.0	18.5	78.3
	2.5	13.9	92.2
	5.0	5.6	97.7
	10.0	2.3	100
	Total	100	
Thermoforming	0.3	93.9	93.9
	0.5	4.1	98.0
	1.0	1.0	99.1
	2.5	0.7	99.7
	5.0	0.2	99.9
	10.0	0.1	100
	Total	100	

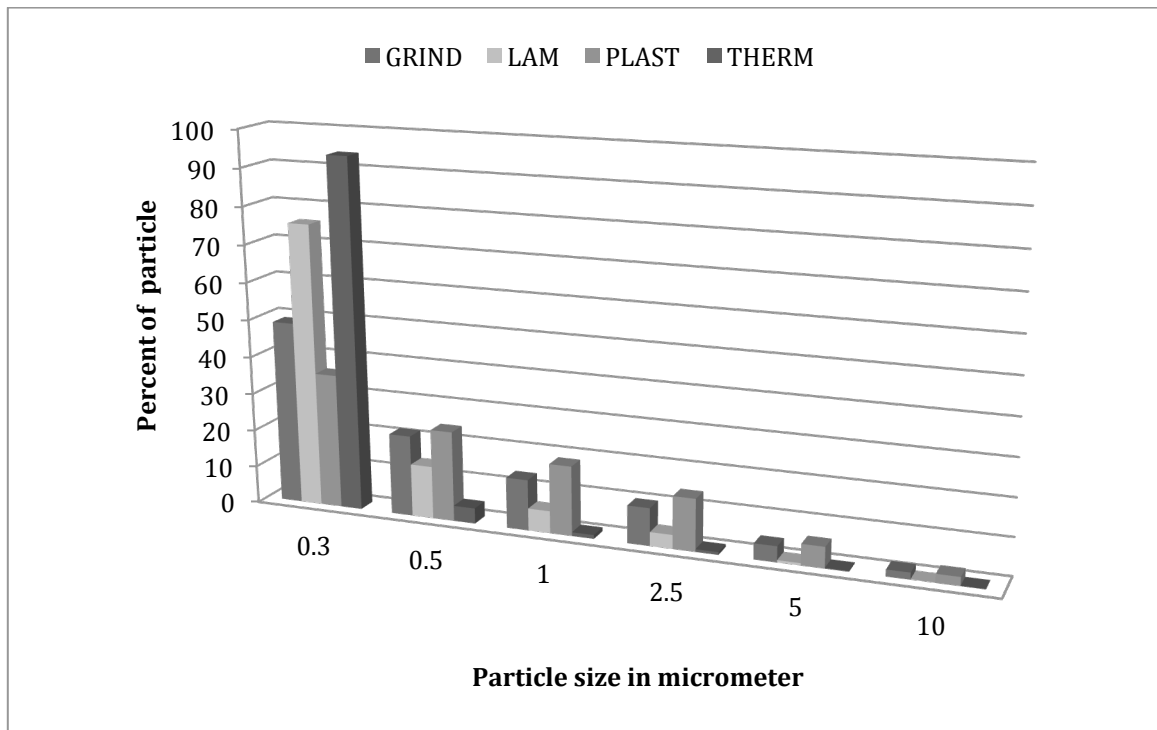


Figure 6. Particle number concentration/task demonstrating size differential distribution between .3 to 10 μm

4-3 NANOPARTICLE NUMBER CONCENTRATION

Table 6 summarizes the nanoparticle number concentrations for the four tasks in the WRNMMC prosthetic laboratory. Particle number concentrations comparison by one-way ANOVA followed by post hoc Tukey HSD analysis showed no significant difference ($p=1$) between plasterization and lamination. No difference between grinding and thermoforming ($p=0.68$) was found. However, the same statistical analysis demonstrated that both grinding and thermoforming were significantly different ($p=0.00001$) from lamination and plasterization (Figure 7). This finding resulted in rejecting null hypothesis #3, that stated that nanoparticle concentration number was the same throughout the WRNMMC prosthetics laboratory.

When examining just the nanoparticle number concentrations, the overall background concentration average was 3275 ± 149 nanoparticles/liter. The lamination process had the least concentration of nanoparticles (40068 ± 46 nanoparticles/liter) and was 12 times greater than the background. Plasterization generated a slightly greater nanoparticle concentration number than the background. Both lamination and plasterization nanoparticle number concentrations were statistically different ($p=0.00001$) from the background. Thermoforming and grinding yielded 14.3 (46871 ± 55 nanoparticles/liter) and 13.9 (45664 ± 92 nanoparticles/liter) times greater nanoparticle concentration numbers than the background respectively (Table 6).

Table 6. Nanoparticle number concentrations by task in WRNMMC prosthetic laboratory

Task	Nanoparticle Concentration (number/liter) (Mean $\pm$ Standard Error)
Lamination	40068 ± 46
Plasterization	40152 ± 50
Thermoforming	46871 ± 55
Grinding	45664 ± 92

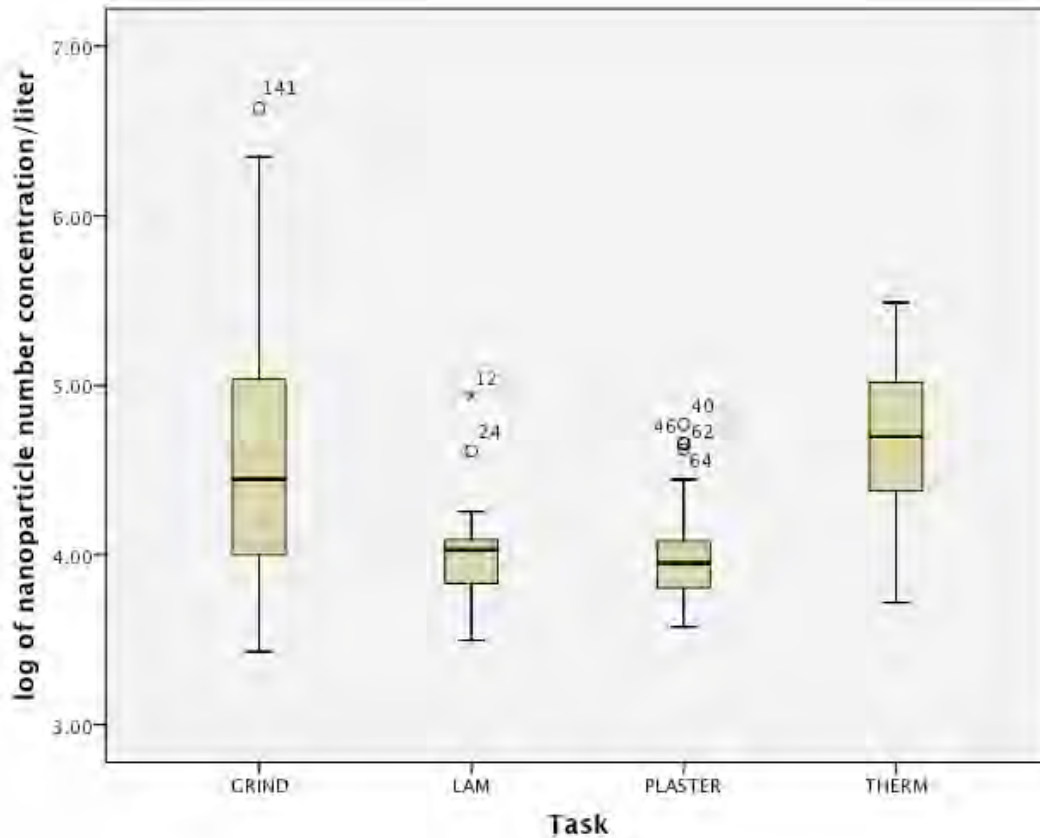


Figure 7. Nanoparticle number concentrations/task demonstrating differences among task

4-4 MASS CONCENTRATION

Although particle number concentration can be a good indication of exposure to dust, it is not commonly used by regulatory agencies such as OSHA and Environment Canada. These agencies use mass concentration as the standard method to report and compare workplace exposure to dust. Therefore, mass concentration from this research was compared to the OSHA PEL to evaluate exposures related to regulatory requirements.

Mass concentration, as explained in Chapter 3, was obtained by multiplying the particle number concentration by the particle density and volume. Particle density was

the density of the component material and that density was found on material data sheet or from providers website. The diameter was the diameter of the channel from the OPC and 100nm was chosen as nanoparticle diameter as by definition nanoparticle have diameter of 100nm less. Table 7 summarizes the coarse particle mass concentration for the four tasks in the WRNMMC prosthetic laboratory. These results were significantly below the OSHA PEL of 15 mg/m³. Although no statistical analysis was made in comparison to OSHA PEL, null hypothesis #1 was rejected based on the calculated results.

Table 7. Coarse Particle mass concentrations in the WRNMMC prosthetic laboratory.

Task	Coarse Particle mass Concentration (µg/cm ³) (Mean ± Standard Error)
Lamination	20.81 ± 1.5
Plasterization	664.77 ± 28
Thermoforming	30.34 ± 3.5
Grinding	204.63 ± 33.3

Table 8 summarizes respirable particle mass concentrations for the four tasks in the WRNMMC prosthetic laboratory. These results were indirectly related to hypothesis #2. Although no statistical analysis was made in comparison of each task to each other, there was enough of a difference in the data of the comparisons that seemed to suggest rejecting hypothesis #2 would be appropriate.

Table 8. Respirable Particle mass concentrations in the WRNMMC prosthetic laboratory

Task	Coarse Particle mass Concentration ($\mu\text{g}/\text{cm}^3$) (Mean $\pm$ Standard Error)
Lamination	22.22 ± 0.0
Plasterization	174.82 ± 26
Thermoforming	22.63 ± 4.2
Grinding	56.06 ± 0.6

The results of the nanoparticle mass concentrations are summarized in Table 9. These results, similar to the Table 8 results, were indirectly related to hypothesis #3. Although no statistical analysis was made in comparison of each task to the others, the results in Table 9 were considerably distinct enough from each other that rejecting null hypothesis #3 was implied as being congruous. The specific details of the particle mass concentrations by size is elucidated and summarized in Table 10.

Table 9. Nanoparticle mass concentrations in the WRNMMC prosthetic laboratory

Task	Coarse Particle mass Concentration ($\mu\text{g}/\text{cm}^3$) (Mean $\pm$ Standard Error)
Lamination	0.00064 ± 0.000
Plasterization	0.00068 ± 0.000
Thermoforming	0.00332 ± 0.000
Grinding	0.00859 ± 0.0002

Table 10. Coarse and respirable mass concentrations in the WRNMMC prosthetic laboratory/size

Particle size	Grinding	Thermoforming	Plasterization	Lamination
0.3	0.24 ± 0.05	3.77 ± 2.8	0.41 ± 0.08	0.49 ± 0.15
0.5	0.93 ± 0.24	0.89 ± 0.23	2.23 ± 0.51	0.68 ± 0.25
1	7.33 ± 1.74	4.02 ± 1.32	27.55 ± 742	3.41 ± 85
2.5	47.56 ± 10.34	13.95 ± 7.02	144.63 ± 43.66	17.64 ± 4.33
Coarse particle				
5	119.6 ± 44.20	16.82 ± 4.02	569.74 ± 23.09	18.24 ± 2.23
10	85.03 ± 22.6	13.52 ± 3.37	95.03 ± 34.30	2.57 ± 0.79

Particle weight in $\mu\text{g}/\text{cm}^3$

Table 11 presents the percent of mass concentration contribution to dust exposure throughout the WRNMMC prosthesis laboratory by particle fraction. For better visualization, total mass concentration was calculated from Table 4, and the ratio of each concentration by task was calculated, as explained in Chapter 3, to determine the percent of contribution summarized as percent of contribution to dust exposure in Table 11. Grinding contributed for 65% of the nanoparticle mass concentration, while the other three tasks contributed less than 25% as evidenced in Table 11. For respirable and coarse particle mass concentrations, the largest contributor was plasterization with 63% and 72% respectively. These results support rejection of both hypothesis #2 and 3. This finding was visible given that nanoparticles nearly composed the entirety of the aerosol. Nanoparticles are characterized by the small mass and big ratio of surface to volume, therefore, despite the high number concentrations, little mass is contributed.

Table 11. Percent of mass concentration contribution to dust exposure in the WRNMMC prosthetic laboratory.

	Respirable particle	Coarse particle	Nanoparticle
Grinding	20	22.2	65
Thermoforming	8.2	3.2	25
Plasterization	63	72.2	5.1
Lamination	8	2.2	4.8

CHAPTER 5: Discussion

5-1 GRAVIMETRIC METHODOLOGY FINDING

The gravimetric method sampling and analysis was discontinued after 12 samples because the methodology did not allow the ($0.01\text{mg}/\text{m}^3$) detection limit to be reached. The gravimetric methodology result was consistent with those obtained with direct reading methodology, as mass concentrations (Table 7 and 8) were very small compared to OSHA PEL ($15\text{ mg}/\text{m}^3$). On the basis that all of the gravimetric results were below the detection limit, and the finding confirmed by secondary methodology, the results seem to be in favor of rejection null hypothesis #1, which led to the study failing to accept that workers were overexposed to dust at the WRNMMC prosthetic laboratory. However, the true outcome may have been limited by the distance between the sampling stations with the devices and results that would be found using personal sampling devices. The reason this distance may result in a different outcome is because as one moves farther from a dust source, there is a gradient of dust concentration and the further the location the less dust can be captured. Because personal sampling is usually closer than one foot to the breathing zone, this difference in location could affect results.

Second, the assumptions made when determining mass concentrations from number concentrations may be explained by the fact this prosthetics laboratory is located in a relatively newly constructed and renovated facility with installed ventilation, including local exhaust systems. General mechanical ventilation in all rooms exceeds six air exchanges per hour, which is the requirement by ASHREA (38). In addition to the mechanical ventilation, the grinding devices are coupled with local exhaust ventilation (LEV) with a capture velocity above 3000fpm , exceeding the ACGIH recommended

2000fpm (1). This explanation can be further justified by the presence of the small amount of minerals in the X-ray diffraction analysis results. This is proof that dust exposure does exist in the WRNMMC prosthetics laboratory, but at small concentrations compared to OSHA PELs.

5-2 DIRECT READING FINDING

The variability between consecutive readings was very high and was the source of multiple outlying values. The background particle number concentration, however, was similar throughout the WRNMMC prosthetics laboratory. Similarity of the background values was a very important determinant for hypotheses #2 and #3, as it ensured that any discrepancies between rooms during task performances would be solely the effect of the tasks.

First, results reflected that particle number concentrations in all rooms during the task performing periods were very high and significantly different from the background. Secondary, results of measurement of particle number concentrations delineated by tasks showed significant difference between tasks regardless of the size of the particles. In addition to particle number concentrations, the results of mass concentration calculation showed different mass concentrations produced by each task, which supports the conclusion that the particle numbers generated was different for each task. In particular, plasterization was the task that generated the highest coarse particle fraction, contributing 63% of the mass (Table 6), whereas, the task contributing the least was lamination with 8% contribution to the total mass. Task performance particle number concentrations were different from the background because there was no spontaneous generation of particles. All particles counted can be related to a task. By being able to show that particle number

and mass concentrations were different for each task, the study rejected hypotheses #2, #3 and #4.

For the coarse fraction, particle number concentrations of the lamination room and thermoforming room were similar and both were significantly smaller from the particle number concentrations of the plasterization and grinding rooms, as shown in Chapter 4. Plasterization induced suspension of larger particles in the air as the workers removed the plaster mixing material from the plaster bag and mixed it in water to fabricate the plaster for the molds. The translocation from the bag to the container dispersed material large enough to fall into the coarse particle category. This plaster mixing material was not crushed, so fewer smaller particles were discharged in the room. Also contributing to the coarse particle fraction finding was the grinding of the edges of the molds. The strength and duration of effort applied to the raw material during grinding determined the size of the byproduct. The coarse fraction is obviously the result of depressed strength and shorter grinding times as those most influential factors in producing coarse particles during the grinding process (68).

Respirable mass concentration in the plasterization room was three times greater than the mass concentration in the grinding room and eight times greater than the mass concentration in the lamination and thermoforming rooms. Overall mass generated by these tasks were small and under the detection limit of the gravimetric method. With direct reading and mass concentration results both showing differences between particle numbers for the tasks, the study rejected hypothesis # 2.

Specifically, for respirable particles, tasks can be aggregated into three groups by the similarity of the particle number concentrations. The highest number concentration

group was found in the grinding room. The medium number concentration groups were in thermoforming, and plasterization. Lamination fell into the lowest respirable particle number concentration group.

Inversely, although thermoforming had a lower respirable particle number concentration, it had the highest mass concentration. The source of the higher respirable particle number concentrations was attributed to the high speed mechanical crushing that occurs during grinding. The grinding task was a high-energy mechanical process, which was anticipated to generate high nanoparticle numbers. According to Zimmer and Maynard (68), when material with a high melting point is ground in the grinding task, the process can generate a large amount of nanoparticles (33; 66).

Nanoparticle mass concentration in the grinding room was two times greater than the mass concentration in the thermoforming room and 125 times greater than the mass concentration in the lamination and plasterization rooms. Nanoparticle generated by grinding were solid particle with higher density therefore they have higher mass. Overall mass generated by these tasks were small and under the detection limit of the gravimetric method as it was generated by high speed mechanical grinding, which is known to generate nanoparticles, which are known to have very small weight. With the results of direct reading and mass concentration both showing differences between particle numbers for the tasks, this study rejected hypothesis # 3.

Specifically for nanoparticles, tasks can be aggregated into two groups by the similarity of the nanoparticle number concentrations. This differed from the nanoparticle mass concentration as, lamination and plasterization exhibited lower number concentrations compared to grinding and thermoforming. Thermoforming had the highest

nanoparticle number concentration amongst the four. Thermoforming in this particular setting included heating the plastic sheets at 330°F and putting it above a freshly wet cast, as explained in Chapter 3. This process generated vapor that condensed to droplets which then was counted by direct reading instruments (26). The source of the two higher nanoparticle number concentrations was attributed to the heat process involved during thermoforming and the high speed mechanical crushing that occurs during grinding. The grinding task is a high-energy mechanical process, which is anticipated to generate high nanoparticle numbers (33; 66).

5-3 CONCLUSIONS

Overall, health hazards to lungs are based on particle size and/or location of deposition: 1) Particles inhaled when deposited at any location within the respiratory track; the PEL is 15mg/m³; 2) coarse particles deposited within the lung and gas-exchange region; and 3) respirable particles deposited solely in the gas-exchange region. The PEL of that fraction for PNORS is 5mg/m³ (2; 46).

The findings of this research were the first assessment of worker exposure in the WRNMMC prosthetics laboratory with two different methodologies that reached the same conclusion. This is also the first time nanoparticles were assessed at WRNMMC. It is important to highlight that the particles of concern at WRNMMC are not those that can be monitored by the traditional gravimetric method, as they are below the threshold of the method. More important, this study showed that nanoparticles, not yet regulated in the occupational environment, represented more than 90% of the particles these results identified for worker exposure. That is of major importance as the literature review showed that these nanoparticles might have negative health effects. Currently, there are

no regulatory standards for nanoparticle number concentration partially because there is no standard measurement methodology to conduct an analysis. This research employed a methodology that might meet this gap and can be used to characterize nanoparticle number concentration so the level of nanoparticle exposure can be measured and quantified.

This study demonstrated that using only a local exhaust ventilation system during prosthesis manufacturing was not adequate to capture the nanoparticles generated by the grinding and thermoforming processes. This conclusion can be conjectured for several reasons based on this study's results. Specifically, the mean nanoparticle number concentration recorded was 57 times greater than the background in the grinding room during task performance. General mechanical ventilation in the thermoforming room was limited for controlling nanoparticles, as evidenced by the particle number being 22 times greater than the background during the task performance. This explanation may also be found in one of the physical properties of particles. When particle matter diameter is below $0.5\mu\text{m}$, the movement is guided by diffusion in opposition to gravity. Even in the presence of an acceptable ventilation system, these smaller particles remain dispersed in the air for a greater time and are not adequately captured (22).

One specific immediate health concern that was determined by this research was that the findings showed that heated plastic produced vapor droplet of plastic byproducts. It has been shown in literature that these byproducts obtained in similar settings can be styrene and polyurethanes, which were not detected by gravimetric methodology but could have been by NIOSH method 2549. Sorbent tubes could have been used, but the methodology employed provided instantaneous single values that were easy to interpret.

This research showed that almost all of the particle exposure in the thermoforming room was potentially plastic byproduct vapor condensation droplet base on other studies, which has been established may alter olfactory senses (7). This alteration may lead to additional health concerns for the worker in the future. One recommendation is that workers at WRNMMC should wear appropriate respiratory protection to minimize or prevent these risks when performing the thermoforming tasks. Currently prosthetic workers at WRNMMC do not wear respiratory protection, which may be due to a false sense of security that they are being minimally exposed due to the decrease in their olfaction caused by the plastic byproducts. Direct reading instruments are appropriate for measuring solid particles and vapor condensation droplets as the detection is based on light scattering. The assessment can be made because both solids and droplets are able to scatter light and be counted.

Worker exposures are generally evaluated according to OSHA standards, but OSHA currently has no PEL or standards for nanoparticles unless the nanoparticle is a controlled material under specific standard regulations. Rather, NIOSH suggests a REL of $7\mu\text{g}/\text{m}^3$. Mass concentration calculations based on particle number concentrations and particle densities were smaller in all the tasks compared to the above-recommended NIOSH REL. However, that REL is solely for carbon nanoparticles. There are different PEL based on particle type. For example, the PEL for titanium dioxide (TiO_2) is fixed at $3\mu\text{g}/\text{m}^3$. The methodology used in this research has the potential to provide a quantifiable level and can be supportive in establishing a nanoparticle REL, as it can be used to assess exposure to various chemical nanoparticles.

Due to the negligible mass of nanoparticles, the results reflected that gravimetric analysis is not an effective way to measure samples for nanoparticle exposure. Particle number concentration direct-reading instruments, as shown in this research and confirmed by others (54; 55) are a more sensitive measurement tool for airborne nanoparticles. Evidence presented in Chapter 4 supports the idea that substantial nanoparticle concentrations are produced by thermogenic and grinding actions.

5-4 LIMITATIONS

A major limitation of this research was the lack of a regulatory standard to which nanoparticle exposure can be compared. In the absence of a regulatory worker exposure standard, the study considered one recognized recommendation, the National Ambient Air Quality Standard (NAAQS), as the standard for comparison to answer hypotheses #3. Although workers are protected by OSHA standards, rather than NAAQS while at work, NAAQS was chosen for comparison as this was the only available and well-known standard or recommendation found in the literature review.

Results of this study are higher than allowable 24-hour concentrations identified by US EPA NAAQS for PM. The assumption was made that indoor air quality, as defined by EPA NAAQS could be an indication for increased protective measures. The US EPA's NAAQS requirement for 24 hour exposure for airborne PM less than 2.5 μm is to be at or below $35\mu\text{g}/\text{m}^3$. This requirement also states that annual mean of respirable particle exposure may not exceed $15\mu\text{g}/\text{m}^3$. The values obtained in this study and reported in Table 4 are above this standard.

OSHA standards allow a much higher exposure than NAAQS. This is because OSHA standard for exposure is eight hours for five days, whereas, the NAAQS

recommendation is for a 24- hour period every day. Although not required by regulatory agencies, efforts to move beyond simple compliance are viewed as consistent with the proper practice of industrial hygiene and general protection of public health and well-being.

The cyclone pump was also a limitation in this study. The highest mass concentration obtained for nanoparticles was 0.0085mg/m^3 . This mass is almost 600 times smaller than the OSHA PEL of 5 mg/m^3 for respirable particles. In gravimetric methodology, the cyclone pump was set at 2.5l/min , which clearly was insufficient to pull enough air volume to accumulate a detectable mass of particles. At this flow rate, it would have taken 600 times the volume pulled during the experiments or a more powerful pump such as the SKC PCXR8, which can deliver a flow rate range from $1000\text{-}5000\text{l/min}$ to approach the LOD for mass. However, this sampling methodology provides general area sampling and conflicts with evaluation of individual exposures through personal sampling.

The mass concentration calculation was made with many assumptions, which also can be limitations. Among these was the assumption that the entire particle was spherical and would have the same diameter by channel. According to the environment temperature, vapor condensation droplet can have different shapes and diameters. Vapor condensation droplet volume changes widely with heating in contrast to solid particles' reaction to heat. Another factor is that according to the environment saturation, smaller droplet can transverse through larger channel diameters without being counted. This can induce droplet count underestimation. Although the vapor droplet counter can be an indicator of the presence of gas particles, vapor more specific monitoring should be used.

To have a better understanding of the exposure to workers in the thermoforming and lamination rooms, a Photo Ionization Detector (PID) should be added as a separate measurement device for particle count. PIDs can accurately assess volatile compounds.

The methodology used within this study cannot distinguish mixture or gas vapors nor true solid particles; this is important as the WRNMMC prosthetic laboratory rooms can be used simultaneously for different tasks. The CPC and OPC cannot assess harm caused by particles to the individuals performing tasks, although the bottom line of exposure assessment is the health protection of the worker.

5-5 FUTURE STUDIES

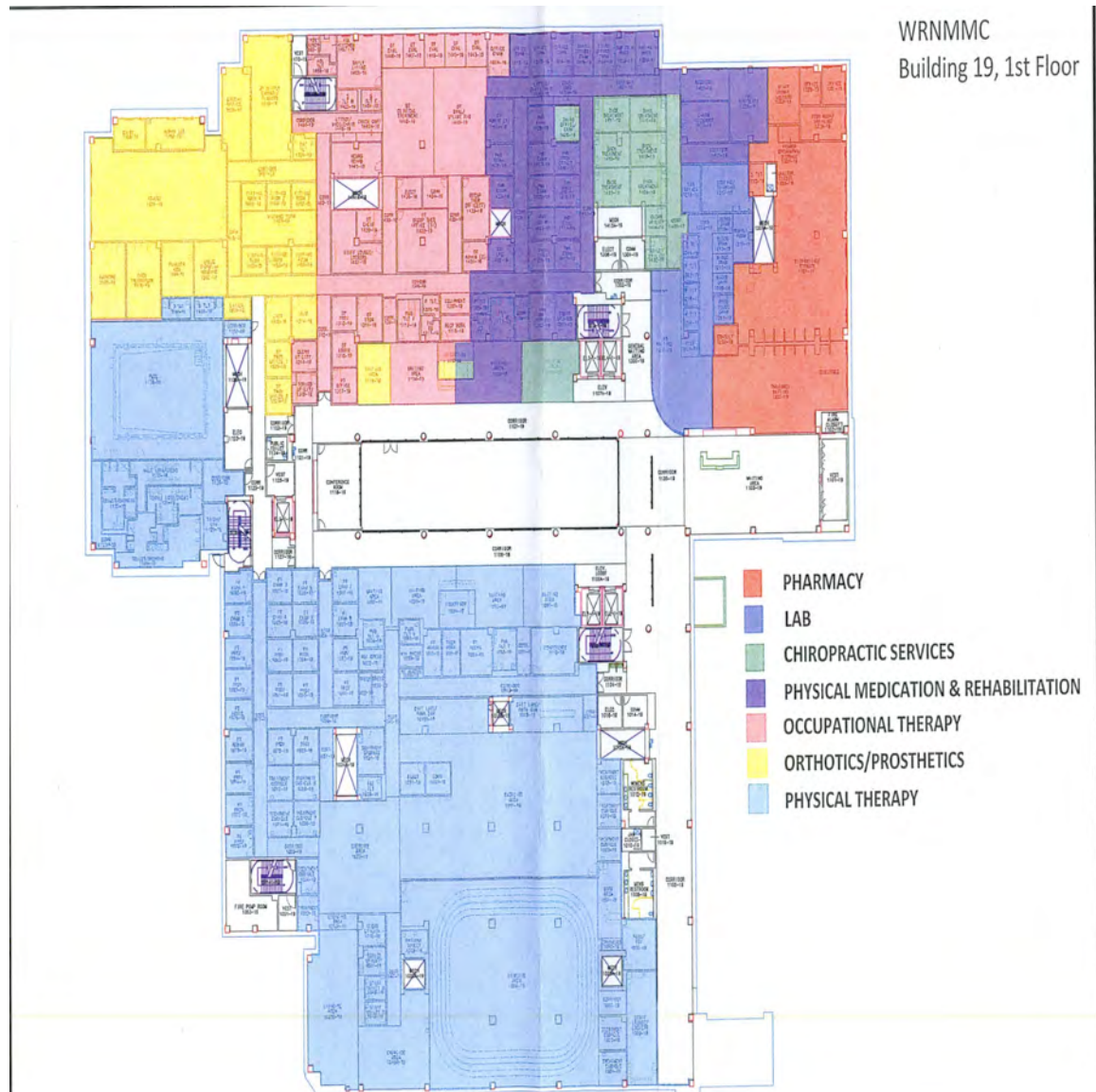
During the thermoforming tasks, measurements of PIDs and sorbent tubes should be examined while running in parallel to compare those results to a direct reading similar to what was used in this research. If the results are in concurrence with the findings of this study, the results can be recommended in support of establishment of a PEL. Additionally, the methodology used in this study is relatively easy and fast and could provide useful quantification methodology in support.

Three more future studies should be undertaken to expand on the work presented in this study. First, gravimetric methodology should be performed with personal sampling devices to reduce the distance from the source to the breathing zone. This will provide more accurate personal exposure results for comparison to the exposure standards. Second, the reactivity of nanoparticles generated in this facility should be determined to assess the toxicity of the particle because smaller numbers do not necessarily mean safer exposures. This measurement is possible by using a Scanning Mobility Particle Sizer (SPMS), which is a particle mass spectrometry that has been used to study nanoparticle

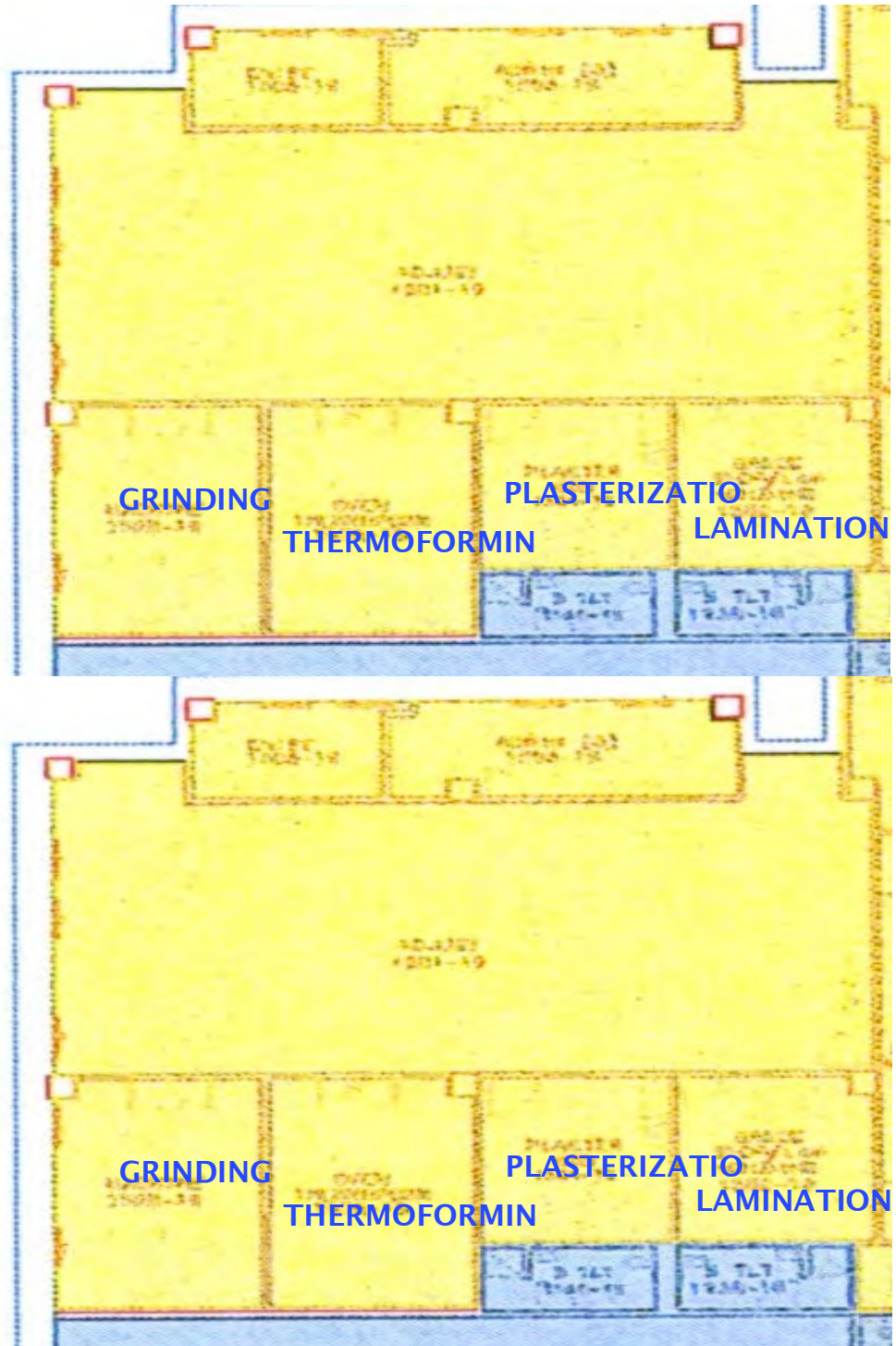
reactivity and ionization ability. This reactivity can be related to the reaction of the nanoparticles with the matter surrounding them. The movement and vibration caused by tasks in the prostheses laboratory should be examined for any physical limitations of the CPC (Ptrap 8525) and the OPC (Fluke 983). This analysis would be valuable because of the significant amount of cutting, hammering, and grinding that occurs during the prosthesis manufacturing process and the effect that could have on air circulation. These limitations may impact negatively the accuracy of the readings used for comparison.

APPENDIX A: Laboratory location and detail

ORTHOPEDIC LABORATORY LOCATION AT WRNMMC (1)



DETAIL OF LABORATORY LAYOUT (2)



APPENDIX B Gravimetric laboratory analysis report for prosthetics laboratory



LABORATORY ANALYSIS REPORT

6601 Kirkville Road
East Syracuse, NY 13057
(315) 432-5227
FAX: (315) 437-0571
www.galsionlabs.com

Client : US Army Public Health Command
Site : WRNMMC
Project No. : 6279
Date Sampled : 24-JUL-12 - 27-JUL-12 Account No.: 13322
Date Received : 24-AUG-12 Login No. : L272371
Date Analyzed : 27-AUG-12 - 28-AUG-12
Report ID : 749518
Contract Number: 09P1478 Pickup/Delivery Order: 1138/1

Respirable Dust and Crystalline Silica: Quartz, Cristobalite, Tridymite

Sample ID	Lab ID	Analyte	Air Vol		mg	%	mg/m3	Dust P E L
			l					mg/m3
62790001 328	L272371-1	Dust	754.2		<0.15		<0.20	5.0
		Quartz	754.2		<0.010	ND	<0.013	
		Cristobalite	754.2		<0.010	ND	<0.013	
		Tridymite	754.2		<0.020	ND	<0.027	
62790002 329	L272371-2	Dust	1073		<0.15		<0.14	5.0
		Quartz	1073		<0.010	ND	<0.0093	
		Cristobalite	1073		<0.010	ND	<0.0093	
		Tridymite	1073		<0.020	ND	<0.019	
62790003 332	L272371-3	Dust	1050		<0.15		<0.14	5.0
		Quartz	1050		<0.010	ND	<0.0095	
		Cristobalite	1050		<0.010	ND	<0.0095	
		Tridymite	1050		<0.020	ND	<0.019	
62790004 334	L272371-4	Dust	1050		<0.15		<0.14	5.0
		Quartz	1050		<0.010	ND	<0.0095	
		Cristobalite	1050		<0.010	ND	<0.0095	
		Tridymite	1050		<0.020	ND	<0.019	

COMMENTS: Please see attached lab footnote report for any applicable footnotes.

Level of quantitation: Dust 0.15mg Q:0.010mg C:0.010mg T:0.020mg Submitted by: LCC/AJD
Analytical Method : mod. NIOSH 0600/7500/mod. OSHA ID-142; Gr Approved by : AEC/KRK
OSHA PEL (TWA) : see 1910.1000 (Table Z-3) Date : 29-AUG-12 NYS DOH # : 11626
Collection Media : PVC MW QC by: Joe Mancuso

< -Less Than mg -Milligrams m3 -Cubic Meters kg -Kilograms
> -Greater Than ug -Micrograms l -Liters NS -Not Specified
NA -Not Applicable ND -Not Detected ppm -Parts per Million
mppcf -Million Particles per Cubic Foot

Page 3 of 26 Report Reference:1 Generated:31-AUG-12 17:14

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Report ID: 6279
Report Ser#: 33954

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LABORATORY ANALYSIS REPORT

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Client : US Army Public Health Command
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Contract Number: 09P1478 Pickup/Delivery Order: 1138/1

Respirable Dust and Crystalline Silica: Quartz, Cristobalite, Tridymite

Sample ID	Lab ID	Analyte	Air Vol l	mg	%	mg/m3	Dust P E L mg/m3
62790001 328	L272371-1	Dust	754.2	<0.15		<0.20	5.0
		Quartz	754.2	<0.010	ND	<0.013	
		Cristobalite	754.2	<0.010	ND	<0.013	
		Tridymite	754.2	<0.020	ND	<0.027	
62790002 329	L272371-2	Dust	1073	<0.15		<0.14	5.0
		Quartz	1073	<0.010	ND	<0.0093	
		Cristobalite	1073	<0.010	ND	<0.0093	
		Tridymite	1073	<0.020	ND	<0.019	
62790003 332	L272371-3	Dust	1050	<0.15		<0.14	5.0
		Quartz	1050	<0.010	ND	<0.0095	
		Cristobalite	1050	<0.010	ND	<0.0095	
		Tridymite	1050	<0.020	ND	<0.019	
62790004 334	L272371-4	Dust	1050	<0.15		<0.14	5.0
		Quartz	1050	<0.010	ND	<0.0095	
		Cristobalite	1050	<0.010	ND	<0.0095	
		Tridymite	1050	<0.020	ND	<0.019	

COMMENTS: Please see attached lab footnote report for any applicable footnotes.

Level of quantitation: Dust 0.15mg Q:0.010mg C:0.010mg T:0.020mg Submitted by: LCC/AJD
Analytical Method : mod, NIOSH 0600/7500/mod. OSHA ID-142; Gr Approved by : AEC/KRK
OSHA PEL (TWA) : see 1910.1000 (Table Z-3) Date : 29-AUG-12 NYS DOH # : 11626
Collection Media : PVC MW QC by: Joe Mancuso

< -Less Than mg -Milligrams m3 -Cubic Meters kg -Kilograms
> -Greater Than ug -Micrograms l -Liters NS -Not Specified
NA -Not Applicable ND -Not Detected ppm -Parts per Million
mppcf -Million Particles per Cubic Foot

CERTIFICATE OF ANALYSIS

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XRD QC SUMMARY REPORT

Login: L272371

Matrix: 57 PVC MW

Instrument: Cubix XRD Pro

Method: mod. NIOSH 7500/mod. OSHA ID-142; XRD

Reporting Level (primary angle): Cristobalite 10 ug, Quartz 10 ug, Tridymite 20 ug

Type	Sample #	Analysis Date	Parameter	True Value ug	Found Value ug	Recovery %	RPD %	Control Limits Recovery	RPD
CCV angle1	WG232698-1	08/28/12 08:55	Cristobalite	50.0	45.9	91.7		85.0-103.	
			Quartz	50.0	53.2	106.		85.4-111.	
CCV angle2	WG232698-2	08/28/12 09:09	Tridymite	50.0	46.2	92.3		71.0-122.	
DLS angle1	WG232698-3	08/28/12 09:23	Cristobalite	10.0	10.8	108.		70.0-130.	
			Quartz	10.0	10.4	104.		70.0-130.	
DLS angle2	WG232698-4	08/28/12 09:37	Tridymite	20.0	16.2	81.1		70.0-130.	
DLS2 angle2	WG232698-5	08/28/12 09:51	Quartz	25.0	19.2	76.9		70.0-130.	
CCV angle1	WG232698-7	08/28/12 13:59	Cristobalite	50.0	46.7	93.4		85.0-103.	
			Quartz	50.0	51.6	103.		85.4-111.	
CCV angle2	WG232698-8	08/28/12 14:12	Tridymite	50.0	42.9	85.7		71.0-122.	
BS angle1	WG232688-2	08/28/12 14:54	Cristobalite	99.9	90.6	90.7		79.2-110.	
			Quartz	100.	104.	104.		84.1-125.	
BSD angle1	WG232688-3	08/28/12 15:08	Cristobalite	99.9	88.7	88.7	2.14	79.2-110.	15.7
			Quartz	100.	102.	102.	1.30	84.1-125.	12.7
BS angle2	WG232688-4	08/28/12 15:21	Tridymite	100.	87.8	87.8		64.1-150.	
BSD angle2	WG232688-5	08/28/12 15:35	Tridymite	100.	93.5	93.5	6.33	64.1-150.	22.7
CCV angle1	WG232698-9	08/28/12 15:49	Cristobalite	50.0	46.9	93.9		85.0-103.	
			Quartz	50.0	51.8	104.		85.4-111.	
CCV angle2	WG232698-10	08/28/12 16:03	Tridymite	50.0	42.4	84.8		71.0-122.	
CCV angle1	WG232698-11	08/28/12 18:35	Cristobalite	50.0	46.2	92.3		85.0-103.	
			Quartz	50.0	52.5	105.		85.4-111.	
CCV angle2	WG232698-12	08/28/12 18:49	Tridymite	50.0	44.7	89.4		71.0-122.	
CCV angle1	WG232698-13	08/28/12 21:20	Cristobalite	50.0	46.5	93.1		85.0-103.	
			Quartz	50.0	52.4	105.		85.4-111.	
CCV angle2	WG232698-14	08/28/12 21:34	Tridymite	50.0	42.7	85.4		71.0-122.	

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