Comparing the NIOSH Method 5040 to a Diesel Particulate Matter Meter for Elemental Carbon

David M. Ayers
COMPARING THE NIOSH METHOD 5040 TO A DIESEL PARTICULATE MATTER METER FOR ELEMENTAL CARBON

A Dissertation
Submitted to the School of Graduate Studies and Research
in Partial Fulfillment of the
Requirements for the Degree
Doctor of Philosophy

David Matthew Ayers
Indiana University of Pennsylvania
December 2017
Indiana University of Pennsylvania
School of Graduate Studies and Research
Department of Safety Sciences

We hereby approve the dissertation of

David Matthew Ayers

Candidate for the degree of Doctor of Philosophy

____________________________________
Christopher Janicak, Ph.D., CSP, CEA, ARM
Professor of Safety Sciences, Chair

____________________________________
Tracey Cekada, D.Sc., CSP
Associate Professor of Safety Sciences

____________________________________
Lon Ferguson, Ed.D., CSP, CFPS
Professor of Safety Sciences

ACCEPTED

____________________________________
Randy L. Martin, Ph.D.
Dean
School of Graduate Studies and Research
Title: Comparing the NIOSH Method 5040 to a Diesel Particulate Matter Meter for Elemental Carbon

Author: David Matthew Ayers

Dissertation Chair: Dr. Christopher Janicak

Dissertation Committee Members: Dr. Tracey Cekada
Dr. Lon Ferguson

Introduction: The sampling of elemental carbon has been associated with monitoring exposures in the trucking and mining industries. Recently, in the field of engineered nanomaterials, single wall and multi-wall carbon nanotubes (MWCNTs) are being produced in ever increasing quantities. The only approved atmospheric sampling for multi-wall carbon nanotubes in NIOSH Method 5040. These results are accurate but can take up to 30 days for sample results to be received.

Objectives: Compare the results of elemental carbon sampling from the NIOSH Method 5040 to a Diesel Particulate Matter (DPM) Meter.

Methods: MWCNTs were transferred and weighed between several trays placed on a scale. The NIOSH Method 5040 and DPM sampling train was hung 6 inches above the receiving tray. The transferring and weighing of the MWCNTs created an aerosol containing elemental carbon. Twenty-one total samples using both meters type were collected.

Results: The assumptions for a Two-Way ANOVA were violated therefore, Mann-Whitney U Tests and a Kruskal-Wallis Test were performed. The hypotheses for both research questions were rejected. There was a significant difference in the EC concentrations obtained by the NIOSH Method 5040 and the DPM meter. There were also significant differences in elemental carbon level
concentrations when sampled using a DPM meter versus a sampling pump based upon the three concentration levels (low, medium and high).

Conclusions: The differences in the EC concentrations were statistically significant therefore, the two methods (NIOSH Method 5040 and DPM) are not the same. The NIOSH Method 5040 should continue to be the only authorized method of establishing an EC concentration for MWCNTs until a MWCNT specific method or an instantaneous meter is invented.
ACKNOWLEDGEMENTS

I would like to acknowledge my Committee Chairman, Dr. Janicak not only for his knowledge, wisdom and hard work but for developing the IUP Safety Science doctoral program. I would also like to thank my committee members Dr. Cekada and Dr. Ferguson for their expertise and support with improving my study.

Additionally, I would like to thank safety professionals associated with the NIOSH Nanotechnology Research Center who provided personal interviews as well as perspectives on atmospheric sampling, Dr. Geraci and Matt Dahm. I would also like to thank Dr. Lippy, one of the co-authors of the OSHA grant on Nanotechnology for his guidance.

For the analytics, I would like to thank Dr. Kimberly Warren for making statistics seem fun and interesting along with Stella Hanis of ALS Environmental for expertise in air sampling techniques.

Finally, without the love and support from my family and most importantly my wife Jessica and children Zach and Zoe, I could have never completed the program. Thank you for your understanding and patience.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INTRODUCTION .............................................................. 1</td>
</tr>
<tr>
<td></td>
<td>Background and Significance ............................................ 1</td>
</tr>
<tr>
<td></td>
<td>Problem Statement ......................................................... 6</td>
</tr>
<tr>
<td></td>
<td>Purpose of Research ...................................................... 9</td>
</tr>
<tr>
<td></td>
<td>Objectives ................................................................. 9</td>
</tr>
<tr>
<td></td>
<td>Research Questions ....................................................... 10</td>
</tr>
<tr>
<td></td>
<td>Terms, Acronyms and Definitions ....................................... 10</td>
</tr>
<tr>
<td></td>
<td>Assumptions ............................................................... 12</td>
</tr>
<tr>
<td></td>
<td>Limitations ..................................................................... 13</td>
</tr>
<tr>
<td></td>
<td>Delimitations .................................................................. 13</td>
</tr>
<tr>
<td></td>
<td>Summary .......................................................................... 13</td>
</tr>
<tr>
<td>2</td>
<td>LITERATURE REVIEW ............................................................ 15</td>
</tr>
<tr>
<td></td>
<td>MWCNT Applications .......................................................... 15</td>
</tr>
<tr>
<td></td>
<td>MWCNT Characteristics ...................................................... 16</td>
</tr>
<tr>
<td></td>
<td>OSHA Grant ...................................................................... 17</td>
</tr>
<tr>
<td></td>
<td>GoodNanoGuide .................................................................. 17</td>
</tr>
<tr>
<td></td>
<td>Consumer Product Safety Commission ................................... 18</td>
</tr>
<tr>
<td></td>
<td>American Society for Testing and Materials (ASTM) .................. 18</td>
</tr>
<tr>
<td></td>
<td>Exposure Limits .............................................................. 19</td>
</tr>
<tr>
<td></td>
<td>Medical Surveillance ......................................................... 19</td>
</tr>
<tr>
<td></td>
<td>MWCNT Exposure – Animal Studies ...................................... 22</td>
</tr>
<tr>
<td></td>
<td>NEAT 2.0 .......................................................................... 25</td>
</tr>
<tr>
<td></td>
<td>Cyclones ......................................................................... 26</td>
</tr>
<tr>
<td></td>
<td>Elemental Carbon as a Marker of MWCNT Exposure .................. 26</td>
</tr>
<tr>
<td></td>
<td>Minimum Air Volume for a MWCNT Sample ............................ 27</td>
</tr>
<tr>
<td></td>
<td>NIOSH Method 5040 Lab Analysis ....................................... 28</td>
</tr>
<tr>
<td></td>
<td>Diesel Particulate Matter (DPM) Atmospheric Meter ................ 28</td>
</tr>
<tr>
<td></td>
<td>Particle Counters ............................................................ 31</td>
</tr>
<tr>
<td></td>
<td>Weighing and Transferring MWCNT – Humans ......................... 31</td>
</tr>
<tr>
<td></td>
<td>Control Banding .............................................................. 33</td>
</tr>
<tr>
<td></td>
<td>Conclusion ....................................................................... 36</td>
</tr>
<tr>
<td>3</td>
<td>METHODOLOGY ................................................................... 39</td>
</tr>
<tr>
<td></td>
<td>Research Overview ............................................................ 39</td>
</tr>
<tr>
<td></td>
<td>Weighing and Tranferring MWCNTs ...................................... 39</td>
</tr>
<tr>
<td></td>
<td>Research Design ............................................................... 39</td>
</tr>
<tr>
<td></td>
<td>Research Setting ............................................................. 41</td>
</tr>
<tr>
<td></td>
<td>Equipment Staging ............................................................ 41</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>Sample Totals .................................................</td>
</tr>
<tr>
<td>2</td>
<td>G-Power Two-Way ANOVA Sample Results .........................</td>
</tr>
<tr>
<td>3</td>
<td>Independent Variables Assessing Elemental Carbon ..........</td>
</tr>
<tr>
<td>4</td>
<td>Sample Concentration Groupings ................................</td>
</tr>
<tr>
<td>5</td>
<td>Mann-Whitley U Results Comparing Test Methods ... (\text{Across the Three Concentration Levels} )</td>
</tr>
<tr>
<td>6</td>
<td>Mean Ranks by Meter Types and Concentration Levels ........</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Surface area of nanomaterials</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Minimum air collection volume per sample</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>Mathematical calculation of minimum air volume</td>
<td>42</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

Background and Significance

Engineered Nanomaterials (ENMs) were first envisioned by physicist Richard Feynman in 1959 during his talk “There’s Plenty of Room at the Bottom” in which he described the direct manipulation of atoms (NNI, 2016). From automotive parts, hunting and fishing equipment to computer chips, ENMs are an ever increasing part of our everyday lives.

“The past is rife with examples of emergent technologies that failed to incorporate safeguards against hazards: asbestos insulation, off-road vehicles without rollover protection, airtight buildings, computer keyboard position, and lead in gasoline” (Myers, 2007, p. 1043). However, human health and protection has not always kept up with technology. To address these new challenges, this dissertation will compare the traditional NIOSH Method 5040 that collects a sample with a sampling pump to an alternative diesel particulate matter (DPM) meter as an effective means to sample for elemental carbon. This dissertation is intended to fill a gap between the traditional waiting times for a sample analysis from the lab (as long as 30 days) to the instantaneous results that are obtained from the DPM.

Multi-Walled Carbon Nanotubes (MWCNT) are engineered nanomaterials (ENM). According to NIOSH (2014), “Engineered nanomaterials are materials that are intentionally produced and have at least one primary dimension less than
100 nanometers (nm)” (p. iv). The MWCNTs are added to existing materials, such as plastics and steel, to form composite materials.

MWCNTs by their very nature are chosen for their unique characteristics and cannot be eliminated or substituted for an alternate safer material. Single-walled carbon nanotube (CNT) and multi-walled carbon nanotubes (MWCNT) are very similar (Albanese, Tang, & Chan, 2012). The only difference is MWCNTs are perfect cylinders wrapped around each other. Current research into the potential human health effects of MWCNTs are still in its infancy (Caskey & Kolbash, 2011).

MWCNTs are used extensively in aerospace and defense. There is research on MWCNT exposure at manufacturing facilities but limited MWCNT exposure information is available on the weighing and transferring of the final product (Ding et al., 2016). Ellenbecker & Tsai (2015) Commented, “Nanopowder handling presents the greatest potential for airborne exposure, since dry powders are easily aerosolized by relatively small amounts of energy” (p. 67).

There are conflicting views on the potential hazards posed by nanomaterials. There are no Occupational Safety and Health Administration (OSHA) enforceable Permissible Exposure Limits (PELs) for MWCNTs. With a decrease in particle size, there is an increase in available surface area for the particle to interact with the lungs. Figure 1 illustrates the surface area of a 6 cm²
block in comparison to the same area in which the particles are of nanomaterial size.

Figure 1. Surface area of nanomaterials. (National Nanotechnology Initiative, 2016) – Reprinted with Permission from National Nanotechnology Initiative (NNI)

The lungs have a massive surface area and filter out larger particles, but nanoparticles and particles in the respirable range (< 10.0 μm) can enter the lungs (Brown, Gordon, Price, & Asgharian, 2013). Not all particles are deposited in the lungs. At 4 μm about 50% of the particles can be deposited in the lungs. The other half never settle and are expelled with the next exhale. MWCNT particle sizes can range from nanometer (nm) to micrometer size (μm) and can be deposited deep into the lungs (Methner, Hodson, Dames, & Geraci, 2010b).

Nanotoxicology is a branch of toxicology concerned with the study of the toxicity of nanomaterials, which can be divided into those derived from combustion processes (like diesel soot), manufacturing processes (such as spray drying or grinding) and naturally occurring processes (such as volcanic eruptions or atmospheric reactions) (Nature, 2017).
Nanomaterials have a much larger surface area than their conventional chemical cousins. The National Institute of Occupational Safety and Health (NIOSH) has published Recommended Exposure Limits (RELs) for unbound carbon nanotubes (CNTs) and CNFs (Franco, 2011; Kuempel, Geraci, & Schulte, 2012a; Kuempel, Castranova, Geraci, & Schulte, 2012b; Maynard, 2009; NIOSH, 2016b). The NIOSH REL for MWCNT is $< 1 \mu g/m^3$ (NIOSH, 2013a). The Mine Safety and Health Administration (MSHA) limit for atmospheric exposure in underground mines is $160 \mu g/m^3$ as total carbon, which is the total from the sum of elemental carbon (EC) and organic carbon (OC). Additionally, the American Conference of Governmental Industrial Hygienists (ACGIH) has proposed a threshold limit value (TLV) of $20 \mu g/m^3$ for elemental carbon (EC) associated with diesel exhaust/diesel particulate matter. Diesel exhaust/diesel particulate matter was the subject of a joint Hazard Alert in 2012 from both OSHA and MSHA (OSHA, 2013; OSHA, 2014). In June 2012, the International Agency for Cancer Research (IARC) classified diesel exhaust/diesel particulate matter as a known human carcinogen (group 1) (OSHA, 2013). Diesel exhaust primarily consists of elemental carbon (Ashley, 2015; Evans, Ku, Birch, & Dunn, 2010).

The current NIOSH Method 5040 for elemental carbon which uses a sampling pump and cassette to determine exposure to MWCNTs (NIOSH, 2013a). NIOSH Method 5040 is currently the only approved sampling method for determining exposure to MWCNTs (NIOSH, 2013a).

With so many unknown health risks, many MWCNT manufacturers have chosen the ALARA principle, or in other words, keep the potential exposure as
low as reasonably achievable (Balshaw, Philbert, & Suk, 2005; Bergamaschi, 2009; Boverhof & David, 2010; Boverhof et al., 2015; Ono-Ogasawara, Serita, & Takaya, 2009). MWCNTs are typically grown to be in the 5 – 50 nm size range. To a lesser extent, absorption through skin, injection, and ingestion contribute to MWCNT exposure (Logan, Ramachandran, Mulhausen, Banerjee, & Hewett, 2011; Monteiro-Riviere & Tran, 2007; Borm et al., 2006; Methner, Hodson, & Geraci, 2010a). NIOSH additionally recommends medical surveillance for employees who handle engineered nanomaterials (ENMs), although health outcomes have not been determined (NIOSH, 2009a; NIOSH, 2009b; NIOSH, 2013a; NIOSH, 2016b). MWCNTs are unquestionably moving towards larger production volumes every year which poses a problem for the protection of employee safety and health (Invernizzi, 2011).

It’s important to understand how particles behave so effective engineering controls can be properly applied. Traditional engineering controls such as local exhaust ventilation works well at capturing MWCNTs. Local exhaust ventilation is an engineering control used in many industries which captures the contaminants at the source. Due to the small size of these particles they can be easily captured by local exhaust ventilation systems. It is important to verify the capture of contaminants after engineering controls are applied because they can be expelled out of the local exhaust ventilation system capture area from activities such as weighing and packaging MWCNTs.

Diesel particulate matter (DPM) meters have recently become small and affordable enough for employees to wear. The FLIR Systems (2015) Airtec DPM
meter claims to be just as accurate as the NIOSH Method 5040, which utilizes a sampling pump and cassettes without the time to wait for the lab analysis results before the operator/user implements controls to reduce or eliminate their EC exposure. The DPM calculates and graphs both elemental and total carbon.

The Airtec Diesel Particulate Monitor is a commercial product manufactured and available from FLIR Systems to display elemental carbon levels in real-time, taking the measurement out of the laboratory and placing it in the hands of mine operators and ventilation engineers. Sensitive, rugged and easy to use, the Airtec monitor provides results that are time-and space-resolved. This capability enables rapid modification of vehicle use, personnel placement and mine or building ventilation. The monitor uses technology developed by the diesel particulate group at the NIOSH Pittsburgh Research Laboratory and has been determined to precisely replicate results from their method 5040 test (FLIR Systems DPM Manual, 2015, p. 4).

**Problem Statement**

This dissertation will compare the traditional NIOSH Method 5040, which utilizes a sampling pump with cassettes to a DPM meter for elemental carbon during the weighing and transferring of MWCNTs. The weighing and transferring of MWCNTs will result in the generation of elemental carbon. When taking samples using the NIOSH Method 5040 sampling pump and filter, the analysis can take as long as 30 days. This time lag allows potential exposure to EC during the sampling analysis phase.
NIOSH has established that elemental carbon exposure can be linked to MWCNT exposure (NIOSH, 2013a). In Current Intelligence Bulletin (CIB) 65 Occupational Exposure to Carbon Nanotubes and Nanofibers, NIOSH commented, “Occupational exposure to all types of CNT and CNF can be quantified using NIOSH Method 5040” (NIOSH, 2013a, p. xi).

The study of ENMs is still in its infancy and MWCNTs have unknown health effects (Broekhuizen, Broekhuizen, Cornelissen, & Reijnders, 2012). Naturally occurring nanomaterials (sea spray from waves, volcanoes, etc.) as well as ENMs from combustion byproducts (gasoline engines, diesel engines, propane heaters, etc.) complicate MWCNT sampling making an accurate EC analysis very challenging. Particle counters only count the particles present in the desired size range and are not able to distinguish between the different types of particles (i.e., MWCNT, dust, pollen, road dust, CO from diesel exhaust, etc.). Lam (2006) found exposure to MWCNTs produced lung fibrosis that progressed quicker than quartz or carbon black. Armed with this information, safety professionals can make proactive determinations based on available controls to ensure exposure does not occur. This is a case where the regulations and science has not kept up with technology.

It is generally agreed that the size of respirable particles is less than 10 μm (Birch, 2016; NIOSH, 2013a; OSHA, 2013; (Sampling Train - Cyclones, 2017). Every day, humans breathe millions of naturally occurring respirable sized particles. Particles in the μm and nm range can deposit deep in the lungs and can interfere with the gas exchange system (Bergamaschi, Poland, Canu, &
Once in the bloodstream, these particles travel throughout the body. Some are caught in the body’s filters such as the liver and kidney while others will be excreted via urine and feces (Monteiro-Riviere & Tran, 2007). MWCNT particles can be small enough to cross the blood-brain barrier.

The researcher found a need for this type of research. The National Institute for Occupational Safety and Health (NIOSH) is expressly looking for this kind of research due to a lack of methods available to sample for EC (NIOSH, 2013b). As such, this dissertation will directly support NIOSH “Research Need #2 – Develop measurement tools for detection and monitoring of ENMs in realistic exposure media and conditions during the life cycles of ENMs and NEPs” (NNI Research Strategy, 2011, p. 13).

The primary benefit of the DPM method over the NIOSH Method 5040 is the time it takes to receive the lab analysis. The DPM meter will provide instantaneous results on the operators EC concentration levels. The operator can then take corrective action immediately to minimize their EC exposure.

This dissertation involved the weighing and transferring of MWCNTs over a 15-minute time period. This scenario will monitor EC concentration levels in a realistic exposure scenario.

In addition to the literature review and examining NIOSH research needs, the researcher interviewed the NIOSH Associate Director for Nanotechnology, Dr. Geraci (personal communication, February 2, 2016), to ensure this research was not actively being pursued. It was verified that comparing the NIOSH Method 5040 to a DPM is not being actively pursued by NIOSH.
The researcher also interviewed Matthew Dahm, CIH, MS of NIOSH. Mr. Dahm has conducted many on site exposure assessments involving the monitoring of elemental carbon to examine MWCNT exposure. Mr. Dahm believes this dissertation would be a good comparison between the traditional NIOSH Method 5040 and the DPM meter (personal communication, November 28, 2016).

**Purpose of Research**

This dissertation is a comparison between the traditional NIOSH Method 5040 and a DPM meter for elemental carbon. The NIOSH Method 5040 uses a sampling pump along with a cassette to gather a sample for analysis. The purpose of the comparison is to give employers an alternate method of sampling that will provide an option to gather instantaneous results and make proactive adjustments to the workplace thus limiting their EC exposure.

**Objectives**

The primary purpose of this design and experiment/exploration dissertation is to investigate if a DPM meter for elemental carbon is equally effective as a sampling method to the traditional NIOSH Method 5040 for determining MWCNT (EC) exposure. Monitoring equipment to be used includes:

- FLIR AirTec DPM (9.0 – 600 μg) (for elemental carbon)
- Sampling Pump, 25-mm cassettes for NIOSH 5040 (current test for elemental carbon)
Research Questions

The researcher wishes to answer the following questions:

1. Are there significant differences in elemental carbon level concentrations when sampled using a FLIR AirTec DPM versus a NIOSH Method 5040 sampling pump?

2. Are there significant differences in elemental carbon level concentrations when sampled using a FLIR AirTec DPM versus a sampling pump based upon the three concentration levels described in this study?

Terms, Acronyms and Definitions

The following terms, acronyms and associated definitions are used throughout this document:

ACGIH: American Conference of Governmental Industrial Hygienists. This is an independent non-governing body of IH professionals dedicated to the safety of health of employees.

ALARA: as low as reasonably achievable. The maximum effort a company can do to reduce a chemical or physical exposure within reason.

BZ: breathing zone.

Carcinogen: “Substances and exposures that can lead to cancer are called carcinogens” (American Cancer Society, 2016).

CNF: Carbon nanofiber

CNT: Carbon nanotube

Elemental carbon (EC): “refers to the inorganic forms of carbon which can be found in crystalline and amorphous forms” (WiseGeek, 2016).
*Engineered nanomaterial (ENM)*: “Engineered nanomaterials are materials that are intentionally produced and have at least one primary dimension less than 100 nanometers (nm)” (NIOSH, 2014, p. iv).

**HEPA**: high-efficiency particulate air.

**LEV**: local exhaust ventilation.

**LOD**: limit of detection. “LOD is the lowest analyte concentration likely to be reliably distinguished from the LoB and at which detection is feasible.” (Armbruster & Pry, 2008, p. S49).

**LOQ**: limit of quantification. “LOQ is the lowest concentration at which the analyte can not only be reliably detected but at which some predefined goals for bias and imprecision are met.” (Armbruster & Pry, 2008, p. S49).

**LPM**: liters per minute.

**Macrophages**: a white blood cell that digests foreign substances (Medicinenet, 2017).

**MWCNT**: Multi-walled carbon nanotubes

**μg**: microgram.

**μm**: micrometer.

**NM**: Nanomaterial (naturally occurring) a few examples include dust, pollen, particles from volcanoes, and particles from forest fires and sea spray from ocean wave action.

**nm**: nanometer.
**NOAEL**: No adverse effects level. “The greatest known concentration of a substance that, after testing, has failed to harm plants or animals” (Medical Dictionary, 2002).

**OEL**: Occupational Exposure Level.

**PEL**: “PELs, or Permissible Exposure Limits, are regulations that establish the acceptable amount or concentration of a substance in the air in the workplace. They are intended to protect workers from adverse health effects related to hazardous chemical exposure” (OSHA, 2016).

**Respirable particulates**: particles that are less than 10 μm.

**TC**: Total carbon.

**TEM**: Transmission electron microscope.

**TLV**: Threshold Limit Value (American Conference of Governmental Industrial Hygienists, 2017).

**TWA**: time weighted average.

**Assumptions**

The researcher will assume the following:

1. The MWCNT powder used for this dissertation contains particles in the respirable range as outlined in the materials specification found on the Vendor’s website.

2. The transfer and weighing of the MWCNT powder will generate an aerosol containing EC.
Limitations

The following limitations will apply to this study:

1. Results from this study are limited to the equipment under study and cannot be applied to other types of monitoring equipment.

2. Results from this study cannot be applied to other types of tasks that result in elemental carbon exposures.

3. Results from this study cannot be applied to MWCNTs from other manufacturers.

4. Results from this study that indicate an increase of EC in the sample concentration cannot be determined to be 100% MWCNTs.

Delimitations

The following delimitations will apply to this study:

1. This study is delimited to comparing exposure levels obtained from an FLIR AirTec DPM and NIOSH Method 5040, which utilizes a sampling pump and cassettes.

2. This study is delimited to measuring elemental carbon levels produced in a defined task.

3. This study is delimited to the amount of specific time of sampling (15 minutes).

Summary

NIOSH has established that elemental carbon exposure can be linked to MWCNT exposure (NIOSH, 2013a). In Current Intelligence Bulletin (CIB) 65 Occupational Exposure to Carbon Nanotubes and Nanofibers, NIOSH
commented, “Occupational exposure to all types of CNT and CNF can be quantified using NIOSH Method 5040” (NIOSH, 2013a, p. xi).

Exposure to MWCNTs and their health effects are still unknown (Hassellöv, Readman, Ranville, & Tiede, 2008; Bergamaschi, 2009; Dobrovolskaia, Shurin, & Shvedova, 2016). As discussed in detail in Chapter 2, MWCNT exposure potential has been extensively researched in the MWCNT manufacturing environments but limited in the weighing and packaging operations (NIOSH, 2016b).

There has been considerable research and technical progress regarding the manufacturing process for MWCNTs, but far less research on safety and health consequences after MWCNTs are released into the workplace during the weighing and transferring operations (Petersen et al., 2011).

MWCNTs are specifically used to increase the strength of the material while decreasing the weight. The MWCNT (once liberated) will agglomerate to other particles in the area such as dust, pollen and/or other pollutants. Lam (2006) found exposure to MWCNTs produced lung fibrosis that progressed quicker than quartz or carbon black.

The results of this study are intended to compare the traditional NIOSH Method 5040 to a sampling method that utilizes a DPM meter for measuring elemental carbon exposure.
CHAPTER 2
LITERATURE REVIEW

MWCNT Applications

Multi-walled carbon nanotubes (MWCNTs) are used primarily in commercial applications and increasingly in consumer products (Piccinno, Gottschalk, Seeger, & Nowack, 2012). The global forecast for CNTs were dominated by MWCNTs with a 95% market share that rose to $700 million in 2015 and, “is expected rise at 16.8% over the 2016 - 2022 timeframe with an estimated $2,070.5 million dollars” (Research and Markets, 2017). Commercial applications of MWCNTs are primarily used as an additive to make conductive plastics, lithium battery and hydrogen storage cells to name a few. The MWCNT composite materials give strength and flexibility. MWCNTs are also added to paint to create electrostatic spray paint which is applied primarily to cars and airplanes. In modern airplanes, many of the parts have MWCNTs integrated into the plastics. A relatively new application is as wastewater filter media to increase the capture and surface area of the filters.

MWCNTs are also being introduced into consumer products. Kessler (2011) stated, “Nanotechnology-enabled products are quietly proliferating on U.S. store shelves, despite nagging questions about the safety of synthetic nanoparticles and the products that contain them” (p. 2). MWCNTs are being integrated into consumer items such as tennis racquets, golf club shafts, road and mountain bike frame.
There are no regulations for labeling the contents of materials containing MWCNTs. Additionally, there is no recycling code for materials containing MWCNTs (Vance et al., 2015). An employee of a recycling center would not know how or if to take any special precautions when handling materials containing MWCNTs. The actual number of consumer products containing MWCNTs is unknown. Despite the unknown hazards, MWCNTs continue to be introduced to the consumer.

**MWCNT Characteristics**

MWCNTs have high tensile strength, elastic modulus and high thermal conductivity, respectively (Burton, Lake, & Palmer, 2017). “Ultimate tensile strength is the capacity of a material can withstand while being stretched or pulled” (Corrosionpedia, 2017). Elastic modulus is the substance's resistance to being deformed. The definition of elastic modulus is, “Ratio of pressure (stress) applied to a body to the resistance (strain) produced by the body” (Businessdictionary, 2016). High thermal conductivity is the ability to conduct heat. This high tensile strength along with high elastic modulus and high thermal conductivity contribute to the growing use of MWCNT manufacturing. After manufacturing, the MWCNTs are added to a commercial application or other consumer product.

MWCNTs are ENMs. According to NIOSH (2014), “Engineered nanomaterials are materials that are intentionally produced and have at least one primary dimension less than 100 nanometers (nm)” (pg. iv).
OSHA Grant

The US Occupational Safety and Health Administration (OSHA) sponsored a Susan Harwood grant in 2010 to educate personnel in the nanotechnology field. The grant was executed by William Marsh Rice University (William Marsh Rice University, 2010). The objective of the grant was to educate the emerging workforce in the nanotechnology sector. ENMs are intentionally made for a specific form and function. There is no long term data on the health effects of these new materials.

The grant does reference NIOSH Method 5040 to sample for elemental carbon as an indication of MWCNT exposure. The grant training materials recommended using a 37-mm quartz fiber filter and setting the flow rate at 2-4 liters per minute in accordance with NIOSH Method 5040 (William Marsh Rice University, 2010). In CIB 65 Occupational Exposure to Carbon Nanotubes and Nanofibers, NIOSH commented, “Occupational exposure to all types of CNT and CNF can be quantified using NIOSH Method 5040” (NIOSH, 2013a, p. xi). The grant does not mention using a DPM meter to monitor for elemental carbon.

GoodNanoGuide

The GoodNanoGuide is sponsored by NIOSH, Oregon Nanoscience and Microelectronics Institute (ONAMI) and Oregon State University (OSU). The GoodNanoGuide is where researchers and industry come together to share methods and processes to minimize employee exposure to nanomaterials (GoodNanoGuide, 2016). The main purpose of the group is to share methods for injury reduction in the ENM Manufacturing plants. There are a number of
small startup companies that depend on these posted injury reduction methods since they do not have the resources for a dedicated safety professional. The GoodNanoGuide website has extensive language on the use of ventilation and control banding. After these are applied, the GoodNanoGuide recommends confirming control measures by atmospheric sampling. Additionally, NIOSH Method 5040 with a 25-mm quartz fiber cassette is mentioned for sampling for MWCNT exposure but there is no mention of using a DPM meter.

The researcher conducted an extensive search of the GoodNanoGuide and there are no specific general or operational protocols for transferring and weighing MWCNTs and the safety measures that must be followed.

**Consumer Product Safety Commission**

The researcher was unable to identify any statutory regulations involving the use of MWCNTs added to items intended for commercial applications or consumer products. MWCNTs are primarily found in commercial applications and only limited applications are available to the everyday consumer (Vance et al., 2015; Thomas et al., 2006). The researcher has been unable to find any mention of using NIOSH Method 5040 or a DPM meter for determining potential MWCNT exposure in consumer products.

**American Society for Testing and Materials (ASTM)**

The researcher was unable to identify any ASTM standards for the use of MWCNT added to items intended for commercial or consumer products. ASTM contains more than 140 technical committees, some deal directly with safety and health standards such as safety glasses, hardhats and safety boots (steel toe
and composite). Additionally, the use of NIOSH Method 5040 or the use of a DPM meter was not mentioned as a method for sampling for MWCNT exposure.

**Exposure Limits**

Currently, OSHA does not have a Permissible Exposure Limit (PEL) for MWCNTs. NIOSH has a REL for MWCNTs which is < 1 μg/m³. The researcher investigated regulatory agencies and MWCNT manufacturers to see which exposure level and which form of carbon was used and documented on their SDS (Cheap Tubes, 2015; DropSens, 2008; Nanoshell, 2014; Sigma-Aldrich, 2015). The researcher was unable to find any MWCNT manufacturer that has adopted the NIOSH REL of < 1 μm/m³. Instead, it appears that only Cheap Tubes, Inc. adopted the OSHA PEL of 5 mg/m³ (respirable fraction) and 15 mg/m³ (total dust) as an exposure guideline. Another recommendation from Cheap Tubes, Inc. was to follow the ACGIH TLV for particulates not otherwise specified as nuisance dust at 3 mg/m³.

Additionally, there was inconsistent language when it came to warnings about ventilation (natural, local or mechanical) and personal protective equipment (PPE) use, along with if the MWCNTs are combustible. The education of employees and the public is difficult when inconsistent, ineffective warnings and exposure levels are applied.

**Medical Surveillance**

NIOSH published the “Current Intelligence Bulletin 60 Interim Guidance for Medical Screening and Hazard Surveillance for Workers Potentially Exposed to Engineered Nanoparticles” in 2009 (NIOSH, 2009a). While no specific guidance
is offered, a general review of the employee’s health along with the type of work performed will help form definitive tests for future nanomaterial workers (Nasterlack, 2008; Crosera, 2009; Franco, 2011).

When the degree of hazard has not been ascertained, the general guidance of government agencies is to treat candidate nanomaterials in their workplaces as if they are potential hazards until a higher level of certainty about the presence or degree of hazard is available. (Schulte et al., 2014, p. 6)

The general elements of a medical surveillance program for engineered nanomaterials are recommended by NIOSH (2009a). Endpoints for a nanomaterial medical surveillance program have not been established. Biomarkers can be used until more data is gathered and can be analyzed to look at long term health effects (Iavicoli, Leso, Manno, & Schulte, 2014).

In occupational health practice, biomarkers of exposure play a highly relevant role since they make it possible to assess exposure by all routes, taking also into account the inter-individual variabilities in absorption, metabolism, and excretion; and the individual workload, as well as the recent versus past exposure. (Iavicoli, Leso, Manno, & Schulte, 2014, pp. 2-3)

Since there are currently no biomarkers or recommended medical surveillance guidelines for nanomaterials, a general health effects model could be used. For example, if the employee under medical surveillance is being checked for interstitial lung function on a regular basis (every 6 months) and
results indicated degraded lung function from previous examination results then this would be a case of early disease detection. All factors would then have to be determined to include diet, nutrition, exercise, smoking and an examination of exposures from previous professions (Dobrovolskaia, Shurin, & Shvedova, 2016; Monteiro-Riviere & Tran, 2007; Trout & Schulte, 2010; Schulte, Murashov, Zumwalde, & Kuempel, 2010; NIOSH, 2009a).

The initiation of a nanomaterials exposure registry is discussed as part of a medical surveillance program. The nanomaterials exposure registry would follow the nanomaterial exposures of the employee throughout their working life. In an ideal world, the exposure registry would follow and collect nanomaterial samples as the employee progressed through the different jobs at the nanomaterial company. Additional difficulty arises when the employee switches jobs and/or moves throughout the country. A nanomaterials exposure registry would be especially useful due to the uncertain future health effects from exposure to the vast myriad of nanomaterials currently on the market (Trout & Schulte, 2010; Brouwer, 2010; Balshaw, Philbert, & Suk, 2005).

When there is uncertainty about the nature, degree, and extent of hazards of nanomaterials, it is incumbent on employers to know what nanomaterials are in their workplaces, to identify processes where exposures can occur, and to support studies to determine the bioactivity of the nanomaterials. (Schulte et al., 2014, p. 2152)
MWCNT Exposure – Animal Studies

Inhalation of MWCNTs present the largest source of potential MWCNT exposure in the workplace. NMs are unseen to the human eye. Once the MWCNTs have been inhaled they can easily pass through the lung-gas exchange region and travel throughout the body.

The role of the MWCNTs as a health hazard potential is not well understood. NIOSH (2013a) noted that MWCNTs have high aspect ratios and the ability to persist in human lungs. Sanchez (2009) remarked biopersistence along with the body’s ability to expel the fibers is difficult to account for when modeling animal studies for inhalation exposure studies. MWCNTs tend to agglomerate and are difficult to inject into the test animal with any consistency. The long biopersistant fibers of asbestos trigger inflammation in the lungs along with the macrophages. Macrophages are a type of white blood cell (Medicinenet, 2017). The macrophages are very efficient at attacking foreign material but can be overwhelmed. Inflammation and granulomas soon appear in the lungs once the macrophages are overwhelmed. Sanchez (2009) commented, “Given the similarities in high aspect ratio between manufactured carbon nanomaterials and asbestos fibers and their projected widespread use, considerable effort is being devoted to identify the physical and chemical parameters responsible for their potential toxicity” (p. 8).

It is estimated that roughly 10 - 20% of insoluble nanoparticles entering the lungs are never cleared and are permanently retained. This is especially true and sometimes higher in some individuals who smoke or have some other
diminished lung function which results in retaining a greater amount of insoluble nanoparticles (Geiser & Kreyling, 2010). From NIOSH (2013a),

A number of research studies with rodents have shown adverse lung effects at relatively low-mass doses of CNT and CNF, including pulmonary inflammation and rapidly developing, persistent fibrosis. Although it is not known whether similar adverse health effects occur in humans after exposure to CNT and CNF, the results from animal research studies indicate the need to minimize worker exposure (p. 2).

Murray (2012) devised a study using mice, “Because the effects of airborne CNF have not been previously addressed, we designed a comparative study assessing pulmonary inflammation, fibrosis, and systemic immune responses to respirable CNF, SWCNT, and asbestos” (p. 2). Murray (2012) used the theory that since ENMs look exactly like asbestos under a microscope, they would have the same or very similar health effects on humans. There is widely reported exposure results for asbestos and CNTs but limited data is available on MWCNT exposure. In the Murray (2012) study, the mice were fed SWCNT, CNFs and asbestos in a one-time feeding via pharyngeal aspiration. In the Murray (2012) study, there was inflammation and general lung stress via different proteins throughout the study. Murray (2012) defined inflammation for this study as, “inflammation was evaluated by total cell counts, cell differentials, and accumulation of cytokines in the bronchoalveolar lavage (BAL) fluid” (p. 14). The mice were fed SWCNT, CNF and asbestos at 1, 7 and 28 days. A post exposure survey was also conducted to look at how the animals expelled or retained the
SWNT, CNF or asbestos and generally their health after exposure. Murray (2012) commented, “Overall, SWCNT, CNF, and asbestos were all capable of inducing acute pulmonary cell damage with the potency as follows: the SWCNTs are more hazardous than CNFs which is more hazardous than asbestos” (Murray et al., 2012, p. 4 - 5).

Lam (2004) devised an experiment using mice to examine the potential toxic effects of CNTs, “Mice were intratracheally instilled with 0, 0.1, or 0.5 mg of carbon nanotubes, a carbon black negative control, or a quartz positive control and euthanized 7 days or 90 days after the single treatment for histopathological study of the lungs” (p. 1). All the mice that were treated with the low dose of CNT (0.1 mg) had no adverse clinical signs of exposure. Of the mice treated in the high dose group, 2 of the 4 mice died in the 7 day group and 3 of the 5 mice died in the 90 day group. For both groups, each mouse died within 3 - 5 days.

Poland et al., (2008) Conducted a study where mice were fed one of the four different MWCNTs chosen by the study team. Two of the four samples were considered long MWCNTs and two were considered short MWCNT. The theory was that MWCNTs have the general appearance of asbestos and should act in the same manner. Additionally, the study was looking at exposure of short vs. long MWCNT to see if there was any difference. The mice were fed a saline solution of 0.5 ml of a 50 μg dose. Half of the mice were killed at 24-hours and the other half at 7 days to examine for granulomatous lesions. Granulomas were present in all the mice.
Kisin (2011) also performed a study to look at the toxicology comparing SWCNTs to CNFs to asbestos, “Since CNFs have a high aspect ratio and biodurability that are characteristic features of amphibole asbestos (crocidolite), we hypothesize that CNF may behave like asbestos” (p. 7). The Kisin (2011) study used Chinese dwarf hamsters. The lung cells were exposed to CNF, asbestos or SWCNT (0, 3, 12, or 48 μg/cm²) for 24 hours. After the exposure, the lung cells were removed and put into a medium and allowed to continue growing. This would show the progression of the exposure after it continued for greater than 24 hours and allow the micronuclei to grow. Kisin (2011) concluded, “In our study, significant DNA damage was induced as early as 3 hours of exposure at 48 μg/cm² while 3 μg/cm² of CNF caused significant DNA damage after 24 hours of treatment” (p. 8). The end result was that SWCNTs were more harmful than CNFs which were more harmful than asbestos.

**NEAT 2.0**

NEAT stands for Nanomaterial Exposure Assessment Technique. NEAT 2.0 reflects the learning from NEAT 1.0 and is more focused on assessing the exposure of nanomaterials as opposed to emission assessment. NEAT 2.0 is focused on finding the jobs in which nanomaterial exposure occurs and using engineering controls to confirm results. NEAT 2.0 places more emphasis on time integrated and filter based (NIOSH Method 5040) sampling techniques. Eastlake et al., (2016) comments, “The goal of NEAT 2.0 is to assist users in performing a comprehensive exposure assessment and in making educated decisions to decrease the potential for occupational exposure using the hierarchy of controls
(elimination, substitution, engineering controls, administrative controls, and personal protective equipment)” (p. 11).

When this dissertation was started NEAT 1.0 was in effect and recommended the use of a 37-mm cassette for NIOSH Method 5040 for elemental carbon. NEAT 2.0 recommends the use of a 25-mm cassette for NIOSH Method 5040 for elemental carbon. This dissertation is using the 25-mm cassette as indicated in the most updated research on EC.

**Cyclones**

Cyclones play a major role in measuring the amount of respirable material present in the sample. A cyclone is used to help with the size selective characteristics of sampling respirable sized particles. The larger particles are collected in the grit pot while the respirable sized particles are collected on the paper filter (Sampling Train – Cyclones, 2017). Both of the sampling methods utilize a cyclone. With the NIOSH Method 5040 and the cyclone attached, the particles have an even disbursement over the quartz filter.

**Elemental Carbon as a Marker of MWCNT Exposure**

Elemental carbon (EC) is the main ingredient of graphite which is where the MWCNT is produced. MWCNT is typically over 95% EC. Depending upon any further refining, other metals are also present such as iron and nickel.

Erdeley (2013) commented in his study, “Overall, the measurement of EC is a more specific and sensitive marker of exposure which provides a more realistic workplace exposure concentration when compared to gravimetric sampling” (p. 2). EC provides a more realistic exposure concentration because it
does not evaporate away from the cassette such as OC will do. The longer it takes to analyze the cassette, the more OC has evaporated away. EC is stable and does not change regardless of the amount of time before analysis.

**Minimum Air Volume for a MWCNT Sample**

Birch (1996) established NIOSH Method 5040 in 1996 for the analysis of diesel exhaust but discovered it could be used to measure for elemental carbon and not just for total carbon. NIOSH Method 5040 has a level of detection (LOD) of 0.3 μg (Birch, 2003, p. 1). The limit of detection was based upon 10 samples taken from NIOSH scientists sampling for MWCNT using NIOSH Method 5040 (NIOSH, 2013a). The “LOD is the lowest analyte concentration likely to be reliably distinguished from the LoB and at which detection is feasible” (Armbruster & Pry, 2008, p. S49). The researcher investigated and conducted interviews to determine the minimum air volume needed to be collected to ensure the sample can be analyzed by a lab for elemental carbon and count as a valid sample (Dr. Schaal, personal communication, March 5, 2017; Dr. Lippy, personal communication, March 9, 2017; Dr. Guffey, personal communication, March 6, 2017; Dr. Geraci, personal communication, March 14, 2017). The LOQ for a 25-mm cassette is 0.09 μg/m³ and the LOD is 0.30μg/m³ (NIOSH, 2013a, p. 56). The “LOQ is the lowest concentration at which the analyte can not only be reliably detected but at which some predefined goals for bias and imprecision are met” (Armbruster & Pry, 2008, p. S49). The formula for measuring minimum air collection volume (in L) below as Figure 2.
Volume (in L) \[= \frac{RL}{E \cdot F}\]
Where:
- RL = Analytical Reporting Limit (micrograms (μg))
- E = Exposure Limit (milligram per cubic meter (mg/m\(^3\))
- F = Estimate of the Exposure Limit in the Sampling Environment expressed as a percent (in decimal form) of the Standard TLV or PEL parameter. For example, if it is estimated that the sampling environment is 10 percent of the TLV, “0.1” would be used. (US Army, 2012, pp. 7-8)

Figure 2. Minimum air collection volume per sample

The US Army minimum air collection volume per sample equation was verified by several industrial hygienists as the correct formula to use for a short term sample of 15 minutes (Dr. Schaal, personal communication, March 5, 2017; Dr. Lippy, personal communication, March 9, 2017; Dr. Guffey, personal communication, March 6, 2017; Dr. Geraci, personal communication, March 14, 2017).

NIOSH Method 5040 Lab Analysis

To analyze a 25-mm quartz cassette for EC, the entire cassette is then placed inside an oven above 850°C. Helium and oxygen are introduced to the oven chamber in several steps. The EC then forms a char. The char is then reduced to CH\(_4\) (methane) where it is then analyzed using a flame ionization detector (FID). The detector converts the flame increase to an EC concentration.

The final report will have a breakdown of the sample and report on OC, EC and TC. To determine MWCNT exposure, a manual split of the EC/OC must occur since graphite is difficult to measure (Birch, 2016).

Diesel Particulate Matter (DPM) Atmospheric Meter

Only recently have DPMs become small enough to be handheld models and wearable by employees (FLIR Systems DPM Manual, 2015). The operation
of the DPM starts with an internal pump pulling a sample through the cyclone. This is where the particles are segregated by size. The cyclone captures respirable particles while at the same time, discards the larger non-respirable particles to the grit pot. A laser is then applied to the internal filter and the resulting scatter is captured on the photodetector. The photodetector takes the image and converts the signal to a corresponding EC concentration. The EC concentration is then shown on the DPM display (Fallon & Takiff, 2016). The DPM uses laser transmittance to measure the amount of laser absorbed along with sensor voltage drop. This value is then compared to the calibration curve to give a final output as an equivalent measurement of elemental carbon in the μg/M³ range. Per the researcher’s interview with FLIR, the DPM filter must be changed after every sample to ensure accuracy (FLIR Systems, 2015; Hyde, 2016).

The FLIR Airtec DPM was developed by the NIOSH diesel particulate group to replicate NIOSH Method 5040 for elemental carbon (FLIR Systems, 2015). The DPM was developed for underground miners to wear on their belt and is equipped with a sampling tube that extends to the operators breathing zone. The DPM LCD display makes the unit easy for miners to reference as they are working and take corrective action immediately to eliminate or reduce their exposure to elemental carbon.

The DPM Operations manual has a warning on its use: “WARNING: The Airtec is for testing purposes only. It should not be used to establish that an environment is safe, and the user should only use it in parallel with established
methods of air sampling” (FLIR Systems DPM Manual, 2015, p. 4). This study will measure elemental carbon via the FLIR Airtec DPM and the traditional NIOSH Method 5040.

The prefilter will alarm at 1/3 of capacity remaining. When the prefilter is nearly full, an error message of Change Filter will appear. After the change filter error appears, further data acquisition will not be valid (FLIR Systems, 2015). With the unknown EC concentration to be sampled with the DPM, there is a concern that the prefilter will exceed capacity during the sampling period.

Care must be exercised if the unit is brought from a cold environment into a warm environment; the user must wait 5 – 10 minutes for the unit to stabilize before continuing the sample (FLIR Systems, 2015).

Noll and Janisko worked for NIOSH at the diesel particulate group and invented the first DPM meter, which would later be transferred from NIOSH to private industry. Noll and Janisko (2007) tested their DPM unit at an underground stone mine against the NIOSH Method 5040. Noll and Janisko (2007) stated, “the difference between the two methods was less than or equal to 17% for 90% of the samples and less than or equal to 10 % for over 70% of the samples. Two samples showed a difference between 20-25%” (p. 6). All of the sample results were 8-hour samples to represent a full shift. The results were acceptable under the NIOSH/OSHA agreed upon +/-25% accuracy rate when comparing sampling methods (NIOSH, 1995).
Particle Counters

Particle counters are commonly used in the investigation of EC exposure. Particle counters are portable, light and used to help determine an elevated particle count during operations (Ono-Ogasawara, Serita, & Takaya, 2009; Kuempel, Castranova, Geraci, & Schulte, 2012b; Hallock, Greenley, DiBerardinis, & Kallin, 2009; Dahm, Evans, Schubauer-Berigan, Birch, & Fernback, 2011; Wohlleben, Kuhlbusch, Schnekenburger, & Lehr, 2014; Hull & Bowman, 2014). One of the problems with a particle counter is it cannot differentiate background naturally occurring nanomaterials from anthropomorphic sources (EC) (Johnson, Methner, Kennedy, & Stevens, 2010; Boverhof & David, 2010; Peters et al., 2008). The particle counter only counts size and amount of particles present at that point in time. A particle counter cannot discriminate the different particle types, only that an increase in the particle range has occurred. A particle counter was not chosen for this study due to this fact.

Weighing and Transferring MWCNT – Humans

The weighing and transferring operation is the last step before shipping the product to the customer. This operation is usually conducted under a fume with the fume hood turned off. The MWCNTs are very light and in powder form take very little energy to create an aerosol. This aerosol would quickly be expelled through the fume hood to the outside air. A recommendation from (NIOSH, 2013a) is, “Use light-colored gloves, lab coats, and workbench surfaces to make contamination by dark CNT and CNF easier to see” (NIOSH, 2013a, p. XIII).
The majority of exposure data for the weighing and transferring of MWCNTs are in the form of particle counters. During these operations a significant rise in particles is attributed to the MWCNTs becoming aerosolized (TSI, 2017; NIOSH, 2009b; Brouwer, van Duuren-Stuurman, Berges, Bard, & Mark, 2009; Asbach et al., 2017; Tsai, 2013; Tsai, 2009) Natural gas is a major component of the MWCNT production and process. The emissions from the MWCNT industrial sources make the sampling for MWCNT very challenging. Methner, Hodson, Dames, & Geraci (2010b) describes a situation in where NIOSH was performing a field investigation and identified an increase in particle count when an electric arc welder elevated the particles to 84,600 particles per cm$^3$ and in another case a propane forklift elevated the particles to 45,000 particles per cm$^3$.

Johnson, Methner, Kennedy, & Stevens (2010) performed a study at the US Army Corp of engineers Laboratory in Vicksburg, MS. This experiment was to weigh and transfer MWCNT in a fume hood with the ventilation system turned off. Background particle readings were established to examine the particle rise with this associated operation. The background particles averaged 13,694 and the measured particles were 137,037. The difference between the background and measured was 123,403 (Johnson, Methner, Kennedy, & Stevens, 2010, p. 23). This was the amount of additional particles added to the room from this operation. There was significant particle generation in the smaller of the particle sizes measured. A particle counter can only count the number of particle sizes
and cannot definitively conclude that it was 100% MWCNT particles that added to the particle load.

Hedmer et al. (2015) Conducted air and surface sampling at a small scale MWCNT producer. The exact results were not noted except that samples in excess of 1 μg/M³ were detected in several samples. The weighing and transfer operations was sampled during this study. Hedmer et al. (2015) Also used a novel adhesive tape application to investigate surface sampling for MWCNT. MWCNTs were found in four of the eight samples and the researchers were trying to find a method of surface sampling that was less costly than a scanning electron microscope (SEM) or a transmission electron microscope (TEM).

Han et al. (2008) Investigated a MWCNT manufacturing plant in South Korea. The researchers used NIOSH Method 7902 (modified from asbestos) to sample for MWCNT. Before engineering controls were applied, the weighing and transfer operation had an EC concentration of 113.3 μg/M³, after engineering controls were applied the EC concentration was non-detectable (ND). The engineering controls included a few simple fans, rearrangement of the work flow along with moving a chiller (that caused a lot of vibration) to an outside location.

Control Banding

Control banding (CB) is a technique in which similar hazards and exposures to chemicals can be put into a band of control measures. In keeping the MWCNT exposure ALARA, CB techniques are just starting to be used by ENM manufacturers (Paik, Zalk, & Swuste, 2008; Beaudrie & Kandlikar, 2011). There have been conceptual models put forward for the assessment of ENM
exposure in the workplace (Tielemans et al., 2008; Schneider et al., 2011; Maynard & Kuempel, 2005; Mazzuckelli et al., 2007; Woskie, Bello, & Virji, 2010; Foss Hansen, Larsen, Olsen, & Baun, 2007).

CB alone cannot be used as a surrogate for proper safety processes and procedures. Elimination of the hazard is the best method to ensure that employees are not exposed to the hazard whereas PPE is the least preferred method.

NIOSH, ACGIH and the American Industrial Hygiene Association (AIHA) have partnered to get the CB initiative into mainstream occupational safety circles (Zalk & Nelson, 2008). Many safety professionals have a difficult time with the CB process when there are so many unknowns associated with the potential chemical exposure to nanomaterials (Zalk et al., 2010).

The CB principle is built around using a generic model in order to satisfy multiple industries (Schulte, Murashov, Zumwalde, & Kuempel, 2010; Methner, Hodson, & Geraci, 2010a; Methner, Hodson, Dames, & Geraci, 2010b; Broekhuizen, Broekhuizen, Cornelissen, & Reijnders, 2012). A few researchers have tried to create a nanomaterial specific CB process. A nanomaterial specific CB process would be of great value given the unknown health effects and a lack of research to indicate an effective contaminant controls.

Zalk and Paik have worked together extensively at the Lawrence Livermore Laboratory to create a nanomaterial specific control banding process. Their nanomaterial CB asked more extensive questions such as mutagenicity, toxicity and reproductive hazards. A pilot nanomaterial CB (Paik, Zalk, &
Swuste, 2008) was run and a few of the areas and scores were adjusted after exposure to real world scenarios (Zalk & Nelson, 2008; Zalk, Paik, & Swuste, 2009).

The Zalk and Paik CB model uses a severity factor (SF) and a probability factor (PB) to mathematically calculate a score. When determining the Severity Factor (SF), a few of the categories ask about a low, medium or high potential and some are just a simple yes/no. The low, medium and high question have a gradient score depending on the exposure. A yes/no score is all points awarded to the category (yes answer) or zero points for a no answer.

When determining the Probability Factor (PF), there are several levels to answer and the points are determined upon the exposure probability. Both the SV and PF also have an answer for unknown with a predetermined amount of points awarded. Once the SF and PF are calculated, the risk level (RL) is calculated. The score range from 0 – 100. The scoring ranges are:

- 0 – 25 Low
- 26 – 50 Medium
- 51 – 75 High
- 76 – 100 Very High

The blocks have an additional risk level (RL) rating. The RL levels range from 1 to 4. For an RL 1 score, general ventilation is required for the workplace. An RL 2 score means the MWCNT must be handled under a fume hood or with local exhaust ventilation. An RL 3 score calls for containment of the process to
ensure a human cannot be exposed while a RL 4 basically says for the company to seek the advice from a specialist.

For example a process is assessed where MWCNT powder is harvested from the synthesis reactor. The SF was calculated to be 75 and the PF was 70. Both scores meet at a RL3 block which calls for containment of the process to ensure the MWCNT powder cannot enter the work area.

Another example could be a process where MWCNT powder is transferred and weighed into 5 gram bags. The SF was calculated to a 70 and the PF was calculated to a 45. Both scores converge on a RL2 block. In this case, a fume hood or local exhaust ventilation would be required. This operation is taking place on the shop floor and a local exhaust ventilation system trunk can be run right to the source of generation of the MWCNT aerosol.

Other scores could equal an RL1 where general ventilation must be used. The highest score of a RL4 is when a specialist must be used to ensure the carbon fibers are controlled and not entering work zone.

Conclusion

The results of the literature search indicate there is little research on the effects of MWCNT exposure. The researcher was unable to find any MWCNT manufacturer that has adopted the NIOSH REL of < 1 μm/m³. One MWCNT manufacturer is using either the OSHA PEL of 5 mg/m³ (respirable fraction) and/or 15 mg/m³ (total dust-nuisance dust) as an exposure guideline. Additionally, the TLV for particulates not otherwise specified as dust was at 3 mg/m³.
Animal studies conclude there are harmful effects from exposure to MWCNT but the results vary. Some of the variation in exposure measurement is from the different testing animals along with the method of how the MWCNTs were introduced to the test animal's lungs. Many of the studies attempted to compare CNT and MWCNT exposure to asbestos since asbestos exposure has been widely studied and accepted as a known human carcinogen. The theory behind many of the studies is that MWCNTs look exactly the same as asbestos and thus should behave the same way.

Various operations can contribute to exposure to MWCNTs. The majority of the scientific literature on MWCNT is focused on the manufacturing process whereas this dissertation focuses on the weighing and transferring of MWCNTs. Several studies have been performed at MWCNT manufacturers. These studies used the NIOSH 5040 for elemental carbon but did not attempt to use a DPM meter.

The literature search discovered OSHA grant material from 2010 that was very good at looking at MWCNT exposure at the manufacturing facility. Additionally control banding (CB) was researched. There are no OSHA standards along with PELs for MWCNTs and control banding offers a solution while safety standards are catching up with technology. The researcher investigated different nanomaterial specific CB methods available and while it appears to be a stop-gap approach, they are very difficult and cumbersome to use.
Finally, the researcher has been unable to find any studies where MWCNTs were weighed and transferred to investigate employee EC exposure by comparing the NIOSH 5040 for elemental carbon to a DPM meter.
CHAPTER 3

METHODOLOGY

Research Overview

The researcher in this study weighed and transferred MWCNTs to generate an aerosol to measure for elemental carbon. The researcher compared the air monitoring results obtained using a traditional sampling pump for the NIOSH Method 5040 to a DPM meter. The researcher hypothesized there would be no significant difference between the two methods when comparing atmospheric concentration measurements of elemental carbon. If this was true, the two sampling methods could be considered comparable.

Weighing and Tranferring MWCNTs

The researcher expected when the MWCNT powder is weighed and transferred, an aerosol containing EC would be generated. The DPM meter was chosen to compare exposures which can exceed the NIOSH REL of \(<1 \mu g/m^3\). NIOSH (2013a) remarked, “Carbon nanofibers and CNT have negligible (if any) OC content, making EC a good indicator of these materials” (p. 154).

Research Design

The experiment was designed to purposefully generate aerosol MWCNT to measure. This experiment involved a short term sample involving a task where an employee will weigh and transfer MWCNTs as part of the packaging and shipping operation. The researcher used a scale and several transfer trays. The start weight was 5.0 grams and MWCNTs were added to keep the transfer amount at 5.0 grams. The sampling train including the cyclone will be placed on
a stand 6 inches over the scale and receiving tray. This experiment is a realistic scenario seen by many NIOSH researchers (Dr. Geraci, personal communication, March 14, 2017). There was a minimum of 21 samples in this study with each being measured using the two sampling techniques; the NIOSH Method 5040 and a DPM meter for EC exposure. Table 1 below lists the sample totals.

Table 1

<table>
<thead>
<tr>
<th>MWCNT Concentration</th>
<th>DPM</th>
<th>NIOSH 5040</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Medium</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Large</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>21</strong></td>
<td><strong>21</strong></td>
</tr>
</tbody>
</table>

There will be a minimum total of 21 samples collected in this research.

Mauch & Park (2003) describes this type of dissertation as a *Design and Demonstration* along with elements of the *exploratory type*. This dissertation compared the sampling method in NIOSH Method 5040 with a DPM meter for EC exposure during the weighing and transferring of MWCNTs. All of the data collected in this dissertation supported of this dissertation.

The literature review did identify a few studies involving MWCNT exposure by sampling for elemental carbon, although no study used a DPM meter. The previous study considerations have been incorporated into this dissertation.
Research Setting

This research took place in a room in which all doors remained closed to the room to limit access and not to impact the air flow of the room. The researcher wore a disposable Tyvek suit, gloves, a full-face respirator with P100 cartridge, and shoe covers. Both meters were placed on the table with the sample train extending over the receiving transfer container and scale.

Equipment Staging

All equipment was staged at least one hour before use. The DPM manual contains a warning about moving the meter from a cold to a warm atmosphere too quickly as this will fog the optics and cause an inaccurate EC result.

MWCNT Powder

The MWCNT powder chosen for the experiment is small enough to be considered respirable. The technical specifications for the MWCNT (short length) powder are:

- Outer Diameter: <8 nm
- Length: 0.5-2.0 μm
- Purity: >95%
- Ash: <1.5 wt%

Sampling Volume

The sampling volume for NIOSH Method 5040 was 960 liters. For this dissertation, this sample volume was not realistic given that the weighing and transferring of MWCNTs is a relatively short term duration process. For comparison purposes to the DPM, the flow rate was set at 1.7 LPM for both
meters. The DPM was set on the high flow level of 1.7 LPM. The NIOSH Method 5040 recommends the sampling rate be set at 2 – 4 LPM. A sample was included if it has reached the minimum air collection volume for NIOSH Method 5040 via the US Army Public Health Command Technical Guide 141, Industrial Hygiene Sampling. The analytical reporting limit (RL) for EC is 0.3 μg. The exposure limit for EC is from the NIOSH REL of 1.0 μg. The estimate of exposure was a conservative 100 μg. The minimum volume of air needed for a sample was determined to be 3 liters of sampled air (See Figure 3). Therefore, at 1.7 liters per minute, the minimum sample time was 1.8 minutes.

\[
\text{Volume (in L)} = \frac{\text{RL}}{E \times F} \\
\text{Volume (in L)} = \frac{0.3 \, \mu g \times \frac{1 \, \text{mg}}{1000 \, \mu g}}{0.01 \, \text{mg} \times 100 \times \frac{1 \, \text{m}^3}{1000 \, \text{m}^3} \times \frac{1 \, \text{L}}{1000 \, \text{L}}} \\
= \text{SUM(0.3*(1/1000)/(0.01/1000)*100*(1/1000))} = 3 \text{ liters of sampled air or 1.8 minutes of sample time @ 1.7LPM}
\]

*Figure 3. Mathematical calculation of minimum air volume*

The sample time was set at 15 minutes per device as the minimum required sample volume to equal a short term exposure scenario. The US Army minimum air collection volume per sample equation was verified by several industrial hygienists as the correct formula to use for a short term sample of 15 minutes (Dr. Schaal, personal communication, March 5, 2017; Dr. Lippy, personal
communication, March 9, 2017; Dr. Guffey, personal communication, March 6, 2017; Dr. Geraci, personal communication, March 14, 2017).

**FLIR AirTec DPM Data Collection**

The researcher followed the manufacturer’s instructions outlined in the operations manual (FLIR Systems DPM Manual, 2015). Each sample’s data was transferred to a PC data file and had a documented sample number. The captured data include sample time, EC exposure and sample volume. The researcher recorded the results of the DPM as a backup. The monitor was set to measure at one 15-minute interval at high flow rate of 1.7 LPM to equal the sampling pump used for the NIOSH Method 5040 comparison. The DPM performs an auto calibration to keep the flow level at the high rate of 1.7 LPM. The FLIR Airtec uses software in order to help visually examine the data. A new filter was used for each sample to give a true elemental carbon exposure.

**NIOSH Method 5040 Data Collection**

The researcher followed the manufacturer’s instructions for equipment as outlined in the operations manual. A pre and post calibration occurred on the sample pump. The flow rate of the sampling pump was set to equal the flowrate of the DPM at 1.7 LPM. A new filter (2) was used for each 15 minute sample. To help minimize the effect of OC on the sample, two filters were used, a top and the bottom filter. The sampling cassettes come preloaded with two filters and have been performance validated at 1.7 and 2.0 L/min (SKC Inc., 2016). Each sample had a documented sample number. These samples were sent to ALS Environmental and analyzed for elemental carbon. These samples were
expected to have a maximum 30-day turnaround time. The ALS Environmental lab report contained a detailed breakdown for each sample as OC, EC and TC. The EC is the important value for this investigation.

**Sample Collection and Documentation**

All samples were documented with a start and stop time along with the meter type. The FLIR DPM data was documented via paper after each sample and documented on paper for a backup. The samples from the traditional NIOSH Method 5040 was documented via paper and sent to an ALS Environmental lab for analysis. A sample number was used for tracking purposes.

**Sample Exclusion/Inclusion Criteria**

Samples were excluded if there is a breakdown/malfunction of equipment or the sampling time does not meet the 15-minute criteria. Samples were also excluded if the post sampling calibration of the sampling pump is greater than +/- 5% of 1.7 LPM (1.62 – 1.78).

**Research Questions and Variables**

The dependent variable under examination in this study was the airborne concentration of elemental carbon measured using the two different methods. The independent variables were the concentration levels of the samples along with the type of method.
The research questions under examination in this study are:

1. Are there significant differences in elemental carbon level concentrations when sampled using a FLIR AirTec DPM versus a NIOSH Method 5040 sampling pump?

2. Are there significant differences in elemental carbon level concentrations when sampled using a FLIR AirTec DPM versus a sampling pump based upon the three concentration levels?

Statistical Analysis

The statistical analysis consisted of a descriptive analysis and an inferential analysis. IBM SPSS, version 24 was used as the statistics software for this investigation. A Two-Way Analysis of Variance (ANOVA) was used to identify significant differences in the dependent variable based upon the independent variables. If the hypotheses proposed by the researcher are true, there should be no significant differences of elemental carbon concentration levels when comparing the two different test methods. This would mean the two methods obtained similar results. An alpha level of .05 will be used to determine significance. A descriptive analysis was performed to determine if the concentrations of elemental carbon obtained using the two different test methods are comparable.

Study Power

The researcher used G*Power (Faul, Erdfelder, Buchner, & Lang, 2013) to compute the minimum power to be used for this type of investigation. An ANOVA was used with three different groups (Low, Medium, and High). The
experiment had an Alpha of 0.05 and Power of 80%. A large effect is envisioned so an effect of 0.80 was chosen. The computed minimum sample size is 20 while the experiment will contain a minimum of 21 samples. See Appendix A – C for A Priori Power Analysis, Appendix A for Methods, Appendix B for Sample Concentration, and Appendix C for Methods multiplied by Sample Concentration. Table 2 below is the results of the G-Power Analysis to perform a Two-Way ANOVA.

Table 2

<table>
<thead>
<tr>
<th>G-Power Two-Way ANOVA Sample Results</th>
<th>Source of Variation</th>
<th>df</th>
<th>Two-Way ANOVA Sample Size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methods</td>
<td>(2-1) = 1</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>Concentration</td>
<td>(3-1) = 2</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Methods X Concentration</td>
<td>(2-1)(3-1) = 2</td>
<td>20</td>
</tr>
</tbody>
</table>

Two-Way ANOVA

In order to perform a Two-Way ANOVA, the following set of assumptions must be tested for and met (Laerd Statistics, 2013)

1. Dependent variable should be measured at the continuous level (i.e., they are interval or ratio variables) – Elemental Carbon
2. The two independent variables should each consist of two or more categorical, independent groups.
3. Observations are independent – no relationship in groups or between groups
4. There should be no significant outliers. This is tested using the residuals with box plots.
5. The dependent variable should be approximately normally distributed for each combination of the groups of the two independent variables. This is tested using Shapiro-Wilk’s Test on the residuals.

6. There needs to be homogeneity of variances for each combination of the groups of the two independent variables. This is tested using Levene’s Test Homogeneity.

Because the data did not meet the assumptions of the ANOVA, three Mann-Whitney U tests were performed along with the Kruskal-Wallace Test. These tests compared the median airborne concentration levels based upon test method for each of the three concentration levels. Table 3 shows the two independent variables along with the different values for statistical comparison.

Table 3

<table>
<thead>
<tr>
<th>Independent Variables Assessing Elemental Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable Description</td>
</tr>
<tr>
<td>Type</td>
</tr>
<tr>
<td>Value</td>
</tr>
<tr>
<td>Analytical Method</td>
</tr>
<tr>
<td>Sample Concentration</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Atmospheric Meter</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 4

RESULTS

Background

The research objectives were investigated by analyzing descriptive statistics of the data and using the Two-Way Analysis of Variance (ANOVA), Kruskal-Wallis non-parametric test, and Mann-Whitney U Post Hoc nonparametric test. Results of these analyses are summarized in this chapter. SPSS version 24 was used for all the statistical analysis.

The researcher compared the air monitoring results obtained using a traditional sampling pump for the NIOSH Method 5040 to a DPM meter. The researcher hypothesized there would no significant difference between the two methods when comparing atmospheric concentration measurements of elemental carbon.

Sample Inclusion/Exclusion

There were no mechanical breakdowns of equipment or sample time less than 15 minutes (See Appendix E). All post-sampling calibrations were within the +/- 5% of the sample calibration results (See Appendix D). All samples were included in the study.

Sample Results

This study was performed on September 1 – 2, 2017. The temperature was 65 degrees Fahrenheit and rainy. The goal of the dissertation was to create an aerosol during the transfer and weighing of the MWCNT. The results of the sampling data are listed in Appendix F.
Sample period 17 and 23 (NIOSH 5040) have been bolded to indicate that they were outliers when compared to the entire data set. The sample data was further broken down into the three EC concentration groups; low, medium and high. The results of the concentrations groups are shown in Table 4 below.

Table 4

*Sample Concentration Groupings*

<table>
<thead>
<tr>
<th>EC Concentration Group</th>
<th>DPM (μg)</th>
<th>NIOSH 5040 (μg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>2.12 – 5.03</td>
<td>14 - 29</td>
</tr>
<tr>
<td>Medium</td>
<td>5.06 – 8.47</td>
<td>31 – 49</td>
</tr>
<tr>
<td>High</td>
<td>9.63 – 16.96</td>
<td>57 - 160</td>
</tr>
</tbody>
</table>

**NIOSH-OSHA Sampling Method Comparability Results**

NIOSH/OSHA agreed upon +/-25% accuracy rate when comparing sampling methods (NIOSH, 1995). See Appendix G for a sample by sample comparison.

An examination of the data in Appendix G indicates that zero samples have an overlapping value and thus no sampling point is considered compatible of determining EC exposure when transferring and weighing MWCNTs within +/-25%.

**Descriptive Statistics**

There were a total of 48 samples with the lowest EC concentration at 2.12 μg and the highest EC concentration at 160 μg. The mean EC concentration was 28.876 μg with a Standard Deviation of 34.105.
Two-Way Analysis of Variance

An examination of the assumptions for a Two-Way ANOVA indicated the study met assumptions 1 – 3 as outlined in Chapter 3 but failed to meet assumptions 4 – 6 which deal with outliers, normality of residuals, and homogeneity of variances. Boxplots were run to identify outliers across the measurement methods and the three EC Concentration bands. An examination of the Boxplots indicated there were a number of outliers.

The assumption of normality was also violated, because the Shapiro-Wilks significance level was less than 0.05 for Low concentrations (Shapiro-Wilks = .947, df = 16, p = .442), Medium concentrations (Shapiro-Wilks = .901, df = 16, p = .082), High concentrations (Shapiro-Wilks = .828, df = 16, p = .007), the test method DPM (Shapiro-Wilks = .944, df = 24, p = .199), and the test method NIOSH Method 5040 (Shapiro-Wilks = .799, df = 24, p = .000).

The assumption of homogeneity of variances was violated because the result of Levene’s Test was less than 0.05. (Levene’s Test = 16.280, df = 5, 42, p < .001) Because the assumptions for a Two-Way ANOVA procedure were violated, the researcher ran three Mann-Whitney U tests along with a Kruskal-Wallis Test.

Mann-Whitney U Tests

Laerd Statistics (2013b) states, “The Mann-Whitney U test is used to compare differences between two independent groups when the dependent variable is either ordinal or continuous, but not normally distributed.”
The results from the Mann-Whitney U test indicated the mean ranks across all concentration levels of EC were significantly different based upon the type of meter (Mann-Whitney U = 575, n = 48, p = .000). The mean rank for the DPM method was 12.54 and the mean rank for the NIOSH Method 5040 was 36.46.

Next, Mann-Whitney U Tests were then run for the three separate concentration levels are shown below in Table 5. These results indicate that based upon concentration levels, there again were significant differences in EC levels when comparing test method. A summary of the mean ranks appears in Table 6.

Table 5

*Mann-Whitney U Results Comparing Test Methods Across the Three Concentration Levels*

<table>
<thead>
<tr>
<th>Concentration Level</th>
<th>Mann-Whitney U</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>64.00</td>
<td>.000</td>
</tr>
<tr>
<td>Medium</td>
<td>64.00</td>
<td>.000</td>
</tr>
<tr>
<td>High</td>
<td>64.00</td>
<td>.000</td>
</tr>
</tbody>
</table>
Table 6

<table>
<thead>
<tr>
<th>Concentration</th>
<th>DPM</th>
<th>NIOSH 5040</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>4.50</td>
<td>12.50</td>
</tr>
<tr>
<td>Medium</td>
<td>4.50</td>
<td>12.50</td>
</tr>
<tr>
<td>High</td>
<td>4.50</td>
<td>12.50</td>
</tr>
</tbody>
</table>

**Kruskal-Wallis Non-Parametric Test**

The Kruskal-Wallis test is an extension of the Mann-Whitney U Test. The Kruskal-Wallis test is rank based and meant to look for significant differences between the independent variables (Method and Concentration) and the dependent variable (EC). The Kruskal-Wallis test was used to compare EC levels across the three levels defined by the researcher. The mean rank for the Low concentration was 16.44, the mean rank for the Medium concentration was 24.5 and the mean rank for the High concentration was 32.56. The Kruskal-Wallis test indicated significant differences in distributions ($K$-$W = 10.614$, $df = 2$, $p = .005$). Dunn-Bonferroni Post-Hoc tests were run to examine the pairwise differences between the EC Concentration levels. The Low-Medium EC Concentration is ($p = .310$). The Low-High EC Concentration is ($p = .003$) and the Medium to High EC Concentration is ($p = .310$). The significance level is <.05 so the Low-High EC Concentration group has significant differences while the Low-Medium and Medium-High EC Concentration groups are not significantly different. This indicates that dividing the samples obtained in this study into
these three groups does result in a significant range of concentration levels for which to compare test method results.
CHAPTER 5
CONCLUSIONS

Discussion

An analysis of the data indicated there was a statistically significant difference in the in EC levels obtained from the DPM meter as compared to the NIOSH Method 5040 for EC. The results also indicated these significant differences in elemental carbon level concentrations when sampled using a DPM meter as compared to a sampling pump occurred across all of the concentration levels used in this study.

The EC results of the DPM and the NIOSH Method 5040 are statistically significantly different and the NIOSH Method 5040 should continue to be the only validated measure of EC exposure for MWCNT transferring and weighing operations. The Researcher contacted FLIR Technical support to help understand why the experiment did not work. According to FLIR Technical Support the DPM was made and only tested with diesel exhaust and no other substances. Diesel exhaust is a very round particle as compared to MWCNT, which is extremely thin and long. The rounder particle has a larger surface area for the laser to reflect off and thus be counted more easily.

A proposed theory from FLIR Technical Support was that the DPM uses the reflected laser along with software to analyze the EC concentration. Because the MWCNT particles are extremely thin and long, the laser is reflecting in a different manner than the software can compute and is thus underreporting the EC concentration. The Researcher is trying to work with FLIR on either a
software or laser change in order to make the DPM work for ENMs. There were many makes and models of ENMs so it is envisioned that only tested ENMs will have an exposure model (a factor) in where the user might have to multiply the EC concentration by a factor (ex. 1.5) to get a true instantaneous EC concentration result.

A DPM meter was chosen for this comparison to eliminate the wait time for results from an analytical lab allowing the operator take immediate proactive measures and reduce/eliminate their EC exposure. Obtaining lab results can take as long as 30 days. During this time frame, EC exposure is taking place.

**Comparision of Results with Past Studies**

The researcher is unaware of any studies involving the comparison of DPM meter to the NIOSH Method 5040 for EC while transferring and weighing MWCNTs. EC has been studied extensively in the mining and trucking industries. MWCNTs are still relatively new and not studied extensively. An EC comparison is made more difficult by the small number of studies which EC is sampled during the transferring and weighing operation.

(Ono-Ogasaware, Takaya, & Yamada, 2015) Performed a short term sample (less than 15 minutes) with the transferring and weighing of MWCNT powder with an EC concentration of 15 μg/M$^3$ (no engineering controls) which is consistent with the researchers low exposure group of 14 – 29 μg/M$^3$ using the NIOSH Method 5040. Additionally, Ono-Ogasaware, Takaya, & Yamada (2015) deployed a sampling meter to capture a far field (about 5 feet away) analysis with an EC concentration of 5 μg/M$^3$.  

55
Dahm, Evans, Schubauer-Berigan, Birch, & Fernback (2011) performed EC sampling at several primary and secondary manufactures of MWCNT and noted, “Very little personal exposure information is available for exposures among downstream, secondary manufactures, or manufacturers above the research and development phase” (pg. 3). Sampling of several sites with the transferring and weighing of MWCNTs indicated that MWCNTs are escaping the capture of engineering controls. Two sites (operation in fume hood) had EC concentration readings of 7.54 and 7.86 μg/M³.

The majority of the articles found by the Researcher involved sampling for MWCNT exposure with a particle counter. Ding et al. (2016) performed a summary of all the ENMs (including MWCNTs) studies that could be located. Particle counters indicated that some form of a particle is present but cannot ascertain the exact particle type (TSI, 2017). A review of (Ding et al., 2016) indicates that the use of particle counters is still prevalent when trying to determine MWCNT (EC) exposure.

Methner, Hodson, Dames, & Geraci (2010b) performed a particle counter survey on the transferring and weighing operations that resulted in a baseline of background particles at 14,992 p/cm³ that rose to a range of 57,000 – 157,800 p/cm³ with a sampling range of 10 – 1000 NM. Johnson, Methner, Kennedy, & Stevens (2010) performed a particle counter survey on the transferring and weighing operations that resulted in a baseline of 14,922 p/cm³ that rose to a range 18,782 – 177,155 p/cm³. Another proven technique to help employees see the MWCNT exposure is to purposefully use light colored PPE to help see
the dark black MWCNT that is present on the PPE. This is also a great exercise to show employees how contamination can spread if proper chemical hygiene is not followed.

**Study Strengths**

The researcher identified two strengths of this study. Based on the researcher’s knowledge, this is the first known study to directly compare a DPM meter to the NIOSH Method 5040 for EC. More specifically, during the transferring and weighing operation. MWCNTs can be easily aerosolized in the powder form. Another strength of the study is that weighing and transferring MWCNTs are real world operations and these findings have real world applicability. Transferring and weighing MWCNTs in powder form is an activity that happens to varying degrees every day at the MWCNT producer facility.

**Study Limitations**

There are many study limitations. In addition to the limitations outlined in Chapter 1, additional limitations include the fact that the samples were not taken in the operators breathing zone, which would provide a more true representation of worker exposure. The primary objective of the study was to generate an aerosol to study the DPM meter and NIOSH Method 5040 and compare their results to EC. The sampling filters were placed directly (six inches) over the weighing and transfer operation to ensure that particles in the respirable size (< 10 μm) were part of the aerosol. MWCNTs can bind to other particles and may exceed the respirable size (> 10 μm). Another limitation is that the study took place in a non-temperature and humidity controlled environment. It will be
difficult to replicate this study again in where the temperature is 65 degrees Fahrenheit, raining outside with 85% humid in the study area. Finally, a limitation was the agglomerating of the MWCNT. MWCNT particles clump and agglomerate more with an increase in humidity. Trying to unclump and move the powder probably caused the researcher to use more energy to move the MWCNT powder and this in turn had an increase in the aerosolized MWCNT.

**Recommendations for Future Research**

Even though the DPM meter and NIOSH Method 5040 were not compatible, there are opportunities for future research. There are many options to work with companies to better understand the MWCNT particle characteristics and to build a meter to factor in those unique characteristics of the MWCNT particles.

There are many recommendations for future research involving EC concentration exposure (not in priority order):

1. Perform the same experiment in a cleanroom environment so the likelihood of the MWCNT binding to any other particles is greatly reduced.

2. Perform the same experiment but with MWCNT powder from different manufacturers to ensure different dimensions of MWCNTs are sampled.

   The researcher chose MWCNTs that had an outer diameter less than 8 nm, length 0.5-2.0 μm, a purity level of 95%. Different grades of MWCNTs and lesser grades purity can be used to look at EC exposure.
These are just a few of the examples of future research into the ability to accurately sample and determine EC exposures.

**Conclusions**

This study indicates that there is a statistically significant difference in the EC measurement concentration between the DPM meter and the NIOSH Method 5040 for EC. The study also indicates that there are significant differences in elemental carbon level concentrations when sampled using a DPM meter as compared to a sampling pump based upon the three concentration levels (low, medium and high). This study failed to support the research questions posed, there were significant differences in EC concentration results based upon the measurement method. With that said, the world of wearable atmospheric meters is ever expanding. Current atmospheric meters factor in that the particle is very round (such as diesel exhaust or most chemical contaminants). ENMs by their nature are mostly very long and thin.

Until an accurate and reliable EC concentration meter can be developed, ENM users should focus on engineering controls, PPE and medical surveillance. Engineering controls can be in the form of process isolation, glove boxes and fume hoods. Process isolation can include building an exhausted enclosure around the process and ensuring a human cannot be exposed to EC. A glove box would also enclose the operation on a smaller scale, allowing the MWCNT powder to easily be weighed and transferred without exposing the human to EC. A fume hood could also be used but might be less effective. The operator’s body, arm and hand movements effect the airflow and EC could be dragged out
via the operator's actions. Other activities in the room can also affect airflow patterns within the hood potentially exposing the worker.

When all engineering options have been exhausted and as a last line of defense, employees can wear PPE in the form of respiratory protection with a minimum N-95 rating for particulates, a Tyvek suit with hood and shoe covers along with gloves. It is very important to seal the gloves to the Tyvek suit or a gap might be created in where the MWCNT could contact the employee. The researcher wore this same PPE for the experiment and additionally used a P-100 rating as respiratory protection.
REFERENCES


http://www.businessdictionary.com/definition/elastic-modulus.html


DropSens:


http://www.ncbi.nlm.nih.gov/pmc/articles/PMC4707963/


doi:10.1093/annhyg/mev036


http://www.nature.com/subjects/nanotoxicology


https://www.osha.gov/dts/hazardalerts/diesel_exhaust_hazard_alert.html


OSHA. (2016, March 26). "Air contaminants". Retrieved from OSHA:

OSHA. (2016, August 28). *Preventing occupational illnesses through safer chemical management*. Retrieved from OSHA:
https://www.osha.gov/chemicalmanagement/index.html


Appendix A

A Priori Power Analysis For Methods

An A priori was run to establish there were enough samples to run the experiment. The results are shown below for the Methods (degrees of freedom (DF) = 1):

<table>
<thead>
<tr>
<th>Analysis:</th>
<th>A priori: Compute required sample size</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input:</strong></td>
<td>Effect size f = 0.8</td>
</tr>
<tr>
<td></td>
<td>α err prob = 0.05</td>
</tr>
<tr>
<td></td>
<td>Power (1 - β err prob) = 0.8</td>
</tr>
<tr>
<td></td>
<td>Numerator df = 1</td>
</tr>
<tr>
<td></td>
<td>Number of groups = 6</td>
</tr>
<tr>
<td><strong>Output:</strong></td>
<td>Noncentrality parameter λ = 10.2400000</td>
</tr>
<tr>
<td></td>
<td>Critical F = 4.9646027</td>
</tr>
<tr>
<td></td>
<td>Denominator df = 10</td>
</tr>
<tr>
<td></td>
<td>Total sample size = 16</td>
</tr>
<tr>
<td></td>
<td>Actual power = 0.8217176</td>
</tr>
</tbody>
</table>


*F tests* – ANOVA: Fixed effects, special, main effects and interactions
Appendix B

A Priori Power Analysis for Concentration

An A priori was run to establish there were enough samples to run the experiment. The results are shown below for the Concentration (DF = 2):

\[ F \text{ tests – ANOVA: Fixed effects, special, main effects and interactions} \]

\begin{align*}
\text{Analysis:} & \quad \text{A priori: Compute required sample size} \\
\text{Input:} & \quad \text{Effect size } f = 0.8 \\
& \quad \alpha \text{ err prob} = 0.05 \\
& \quad \text{Power (1-}\beta \text{ err prob)} = 0.8 \\
& \quad \text{Numerator df} = 2 \\
& \quad \text{Number of groups} = 6 \\
\text{Output:} & \quad \text{Noncentrality parameter } \lambda = 12.8000000 \\
& \quad \text{Critical F} = 3.7388918 \\
& \quad \text{Denominator df} = 14 \\
& \quad \text{Total sample size} = 20 \\
& \quad \text{Actual power} = 0.8252111
\end{align*}
Appendix C

A Priori Power Analysis for Methods Multiplied by Concentration

An A priori was run to establish there were enough samples to run the experiment. Finally, the results for the shown below for the Methods Multiplied by Concentration (DF = 2):


**F tests** – ANOVA: Fixed effects, special, main effects and interactions

**Analysis:**
- A priori: Compute required sample size

**Input:**
- Effect size f = 0.8
- α err prob = 0.05
- Power (1−β err prob) = 0.8
- Numerator df = 2
- Number of groups = 6

**Output:**
- Noncentrality parameter λ = 12.800000
- Critical F = 3.7388918
- Denominator df = 14
- Total sample size = 20
- Actual power = 0.825211
# Appendix D

## Sampling Pump Pre/Post Calibration

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Sampling Pump Pre</th>
<th>Sampling Pump Post</th>
<th>Difference (greater than +/-5%)</th>
<th>Include Sample in Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Sept. 2017</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>2</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>3</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>4</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>5</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>6</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>7</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>8</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>9</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>10</td>
<td>1.7 lpm</td>
<td>1.69 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>2 Sept. 2017</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>12</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>13</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>14</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>15</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>16</td>
<td>1.7 lpm</td>
<td>1.69 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>17</td>
<td>1.7 lpm</td>
<td>1.68 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>18</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>19</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>20</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>21</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>22</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>23</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>24</td>
<td>1.7 lpm</td>
<td>1.7 lpm</td>
<td>N</td>
<td>Y</td>
</tr>
</tbody>
</table>
## Appendix E

### Meter Start/Stop Data

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>DPM Start Time</th>
<th>DPM End Time</th>
<th>Sampling Pump Start Time</th>
<th>Sampling Pump End Time</th>
<th>Include Samples in Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Sept. 2017</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1704</td>
<td>1719</td>
<td>1704</td>
<td>1719</td>
<td>Y</td>
</tr>
<tr>
<td>2</td>
<td>1731</td>
<td>1746</td>
<td>1731</td>
<td>1746</td>
<td>Y</td>
</tr>
<tr>
<td>3</td>
<td>1755</td>
<td>1810</td>
<td>1755</td>
<td>1810</td>
<td>Y</td>
</tr>
<tr>
<td>4</td>
<td>1851</td>
<td>1906</td>
<td>1851</td>
<td>1906</td>
<td>Y</td>
</tr>
<tr>
<td>5</td>
<td>1914</td>
<td>1929</td>
<td>1914</td>
<td>1929</td>
<td>Y</td>
</tr>
<tr>
<td>6</td>
<td>1939</td>
<td>1954</td>
<td>1939</td>
<td>1954</td>
<td>Y</td>
</tr>
<tr>
<td>7</td>
<td>2003</td>
<td>2018</td>
<td>2003</td>
<td>2018</td>
<td>Y</td>
</tr>
<tr>
<td>8</td>
<td>2027</td>
<td>2042</td>
<td>2027</td>
<td>2042</td>
<td>Y</td>
</tr>
<tr>
<td>9</td>
<td>2050</td>
<td>2105</td>
<td>2050</td>
<td>2105</td>
<td>Y</td>
</tr>
<tr>
<td>10</td>
<td>2115</td>
<td>2130</td>
<td>2115</td>
<td>2130</td>
<td>Y</td>
</tr>
<tr>
<td>2 Sept. 2017</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0535</td>
<td>0550</td>
<td>0535</td>
<td>0550</td>
<td>Y</td>
</tr>
<tr>
<td>12</td>
<td>0600</td>
<td>0615</td>
<td>0600</td>
<td>0615</td>
<td>Y</td>
</tr>
<tr>
<td>13</td>
<td>0624</td>
<td>0639</td>
<td>0624</td>
<td>0639</td>
<td>Y</td>
</tr>
<tr>
<td>14</td>
<td>0647</td>
<td>0702</td>
<td>0647</td>
<td>0702</td>
<td>Y</td>
</tr>
<tr>
<td>15</td>
<td>0711</td>
<td>0726</td>
<td>0711</td>
<td>0726</td>
<td>Y</td>
</tr>
<tr>
<td>16</td>
<td>0740</td>
<td>0755</td>
<td>0740</td>
<td>0755</td>
<td>Y</td>
</tr>
<tr>
<td>17</td>
<td>0804</td>
<td>0819</td>
<td>0804</td>
<td>0819</td>
<td>Y</td>
</tr>
<tr>
<td>18</td>
<td>0826</td>
<td>0841</td>
<td>0826</td>
<td>0841</td>
<td>Y</td>
</tr>
<tr>
<td>19</td>
<td>0851</td>
<td>0904</td>
<td>0851</td>
<td>0904</td>
<td>Y</td>
</tr>
<tr>
<td>20</td>
<td>0911</td>
<td>0926</td>
<td>0911</td>
<td>0926</td>
<td>Y</td>
</tr>
<tr>
<td>21</td>
<td>0935</td>
<td>0950</td>
<td>0935</td>
<td>0950</td>
<td>Y</td>
</tr>
<tr>
<td>22</td>
<td>0958</td>
<td>1013</td>
<td>0958</td>
<td>1013</td>
<td>Y</td>
</tr>
<tr>
<td>23</td>
<td>1021</td>
<td>1036</td>
<td>1021</td>
<td>1036</td>
<td>Y</td>
</tr>
<tr>
<td>24</td>
<td>1043</td>
<td>1058</td>
<td>1043</td>
<td>1058</td>
<td>Y</td>
</tr>
</tbody>
</table>
Appendix F

Dissertation Sample Results

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>1 Sept. 2017</th>
<th>2 Sept. 2017</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DPM (EC) – 15 min. sample (ug)</td>
<td>NIOSH 5040 (EC) – 15 min. sample (ug)</td>
</tr>
<tr>
<td>1</td>
<td>3.34</td>
<td>62</td>
</tr>
<tr>
<td>2</td>
<td>5.06</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>2.12</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>4.70</td>
<td>29</td>
</tr>
<tr>
<td>5</td>
<td>3.64</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>10.76</td>
<td>62</td>
</tr>
<tr>
<td>7</td>
<td>5.03</td>
<td>31</td>
</tr>
<tr>
<td>8</td>
<td>8.01</td>
<td>49</td>
</tr>
<tr>
<td>9</td>
<td>4.64</td>
<td>39</td>
</tr>
<tr>
<td>10</td>
<td>7.33</td>
<td>34</td>
</tr>
<tr>
<td>11</td>
<td>12.24</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>11.26</td>
<td>21</td>
</tr>
<tr>
<td>13</td>
<td>5.92</td>
<td>22</td>
</tr>
<tr>
<td>14</td>
<td>8.47</td>
<td>17</td>
</tr>
<tr>
<td>15</td>
<td>11.86</td>
<td>37</td>
</tr>
<tr>
<td>16</td>
<td>16.96</td>
<td>84</td>
</tr>
<tr>
<td>17</td>
<td>12.79</td>
<td>160</td>
</tr>
<tr>
<td>18</td>
<td>7.13</td>
<td>57</td>
</tr>
<tr>
<td>19</td>
<td>6.92</td>
<td>14</td>
</tr>
<tr>
<td>20</td>
<td>4.41</td>
<td>25</td>
</tr>
<tr>
<td>21</td>
<td>9.63</td>
<td>18</td>
</tr>
<tr>
<td>22</td>
<td>9.99</td>
<td>32</td>
</tr>
<tr>
<td>23</td>
<td>3.44</td>
<td>140</td>
</tr>
<tr>
<td>24</td>
<td>5.39</td>
<td>24</td>
</tr>
</tbody>
</table>
## Appendix G

### Sample by Sample Comparison for Sample Method Comparability

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>DPM (μg)</th>
<th>DPM Range</th>
<th>NIOSH 5040 Range</th>
<th>NIOSH 5040 (μg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.34</td>
<td>2.51 - 4.18</td>
<td>46.5 - 77.5</td>
<td>62</td>
</tr>
<tr>
<td>2</td>
<td>5.06</td>
<td>3.80 - 6.33</td>
<td>47.25 - 78.75</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>2.12</td>
<td>1.59 - 2.65</td>
<td>34.5 - 57.5</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>4.70</td>
<td>3.53 - 5.88</td>
<td>21.75 - 36.25</td>
<td>29</td>
</tr>
<tr>
<td>5</td>
<td>3.64</td>
<td>2.73 - 4.55</td>
<td>29.25 - 48.75</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>10.76</td>
<td>8.07 - 13.45</td>
<td>46.5 - 77.5</td>
<td>62</td>
</tr>
<tr>
<td>7</td>
<td>5.03</td>
<td>3.77 - 6.29</td>
<td>23.25 - 38.75</td>
<td>31</td>
</tr>
<tr>
<td>8</td>
<td>8.01</td>
<td>6.01 - 10.01</td>
<td>36.75 - 61.25</td>
<td>49</td>
</tr>
<tr>
<td>9</td>
<td>4.64</td>
<td>3.48 - 5.80</td>
<td>29.25 - 48.75</td>
<td>39</td>
</tr>
<tr>
<td>10</td>
<td>7.33</td>
<td>5.50 - 9.16</td>
<td>25.5 - 42.5</td>
<td>34</td>
</tr>
<tr>
<td>11</td>
<td>12.24</td>
<td>9.18 - 15.3</td>
<td>75.00 – 125.</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>11.26</td>
<td>8.45 - 14.08</td>
<td>15.75 - 26.25</td>
<td>21</td>
</tr>
<tr>
<td>13</td>
<td>5.92</td>
<td>4.44 - 7.40</td>
<td>16.5 - 27.5</td>
<td>22</td>
</tr>
<tr>
<td>14</td>
<td>8.47</td>
<td>6.35 - 10.59</td>
<td>12.75 - 21.25</td>
<td>17</td>
</tr>
<tr>
<td>15</td>
<td>11.86</td>
<td>8.90 - 14.83</td>
<td>27.75 - 46.25</td>
<td>37</td>
</tr>
<tr>
<td>16</td>
<td>16.96</td>
<td>12.72 - 21.2</td>
<td>63 - 105</td>
<td>84</td>
</tr>
<tr>
<td>18</td>
<td>7.13</td>
<td>5.35 - 8.91</td>
<td>42.75 - 71.25</td>
<td>57</td>
</tr>
<tr>
<td>19</td>
<td>6.92</td>
<td>5.19 - 8.65</td>
<td>10.5 - 17.5</td>
<td>14</td>
</tr>
<tr>
<td>20</td>
<td>4.41</td>
<td>3.31 - 5.51</td>
<td>18.75 - 31.25</td>
<td>25</td>
</tr>
<tr>
<td>21</td>
<td>9.63</td>
<td>7.22 - 12.04</td>
<td>13.5 - 22.5</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>-----</td>
<td>------------</td>
<td>------------</td>
<td>----------</td>
</tr>
<tr>
<td>22</td>
<td>9.99</td>
<td>7.49 - 12.49</td>
<td>24 - 40</td>
<td>32</td>
</tr>
<tr>
<td>23</td>
<td>3.44</td>
<td>2.58 - 4.30</td>
<td>105 - 175</td>
<td>140</td>
</tr>
<tr>
<td>24</td>
<td>5.39</td>
<td>4.04 - 6.74</td>
<td>18 - 30</td>
<td>24</td>
</tr>
</tbody>
</table>