University of Cincinnati

Date: 11/12/2015

I, Konstantinos Zavyos, hereby submit this original work as part of the requirements for the degree of Master of Science in Environmental Engineering.

It is entitled:
Collection And Pre-Concentration of Aerosol for Optical Spectroscopies

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Collection and Pre-Concentration of Aerosol for Optical Spectroscopies

A thesis submitted to the Graduate School of the University of Cincinnati
In partial fulfillment of the requirements for the degree of Master of Science
In the Department of Biomedical, Chemical and Environmental Engineering
College of Engineering & Applied Science by

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B.A. National and Kapodistrian University of Athens 2011

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Abstract

During the last few decades there has been an ever-growing need for aerosol monitoring and measurement. The fields of interest vary, and span from air pollution and public health, to science and nanotechnology and up to medicine and chemicals. Occupational safety demands aerosol monitoring to assure that hazardous aerosols are not present or are at acceptable concentration levels, in public and industrial work areas. Aerosol measurements have also been conducted for the evaluation of their effect on climatic changes. The growing need to regulate aerosol pollution has led to the growth and expansion of the scientific methods used for aerosol monitoring, which are many times very costly and time consuming. A great variety of scientific instruments and approaches have been developed for that cause. These methods range from basic filter-based collection to the use of modern near-real time instrumentation. In this study, the design and performance characteristics of our method for collection and pre-concentration of aerosol sample for optical spectroscopies are discussed. This method can be applied to a portable, near-real time instrument for aerosol monitoring.

We first presented the background and motivation of this study and reviewed some of the literature pertaining to the main focus of our experimental research.

We then determined the electrode size diameter after the introduction of spark discharge. A brief introduction and problem statement are given, followed by an explanation and analysis of the experimental design, including the
appropriate figures. Experimental results are later discussed, focusing on the results obtained for the variation of the coverage in different experimental conditions and the results regarding the footprint size diameter.

In the main body of this thesis we discuss the subject of collection and analysis of aerosol particles in a pre-concentrator system. An introduction and problem statement are given, followed by an explanation and analysis of the design of the pre-concentrator. Schematic diagrams, pictures and tables are used for better understanding of the experimental setup and its key components. Experimental results are then discussed. First, we analyzed the losses in the pre-concentrator inlet nozzle area, and graphically presented the data obtained. Then, the determination of the distance between the electrodes of the pre-concentrator is discussed, followed by an analysis on the optimization for the corona current. Our main experimental analysis follows, presenting the determination of the pre-concentrator collection efficiency. Figures, schematic diagrams and pictures are used for better explanation of the methods and instruments used in this study, followed by figures presenting the data obtained from all of the experiments conducted. An optical analysis of and discussion on the experiments using a scanning electron microscope is then presented. A discussion on the performance characteristics of the Pen-Ray UV Lamp charger follows, and figures of the results regarding this subject are presented.

We summed up all the significant results and conclusions obtained in this study, and made suggestions for future work in this experimental area of interest. Finally, the significant contribution of this thesis was explained.
Acknowledgements

Firstly, I would like to express my deep gratitude to my Masters thesis advisor Prof. Dr. Dionysios D. Dionysiou for his endless support, assistance and encouragement since my first day of acceptance in the University of Cincinnati and for giving me a golden opportunity to fulfill my dream and academic endeavors.

Besides my advisor, I would like to thank my scientific research supervisor at NIOSH/CDC, Dr. Pramod S. Kulkarni for providing me with the unique privilege to be a part of a fully professional and highly productive scientific group and for giving me access to outstanding research facilities and laboratories. His patience, motivation and guidance helped me successfully complete my research and writing this thesis.

I would also like to thank Prof. Dr. George Sorial for his useful suggestions and insightful comments that helped improve this thesis.

My sincere thanks also go to Dr. Gregory Deye for his immense knowledge, support and help on laboratory related matters and theoretical aspects of my research.

Last but not least, I would like to thank my parents Ioannis and Panagiota for their love, support and encouragement throughout the entire process of my post-graduate studies and my life in general. They have always been there for me and always kept me going. This Masters thesis would not have been possible without them.
# Table of Contents

Abstract......................................................................................................................ii  
Acknowledgements..................................................................................................v  
List of Figures.............................................................................................................viii  
List of Tables............................................................................................................x  
List of Symbols.........................................................................................................xi  

## CHAPTER 1: INTRODUCTION

1.1 Background and Literature Review.................................................................1  
1.1.1 Aerosol Particles Collection Mechanisms..................................................2  
1.1.2 Aerosol Particles Charging Mechanisms......................................................7  
1.1.3 Corona Discharge.........................................................................................15  
1.2 Thesis Outline.................................................................................................16  

## CHAPTER 2: DETERMINATION OF THE ELECTRODE SIZE DIAMETER BY THE INTRODUCTION OF SPARK DISCHARGE

2.1 Introduction......................................................................................................18  
2.2 Experimental Design.......................................................................................19  
2.3 Results and Discussion  
  2.3.1 Variation of Coverage in Different Conditions........................................21  
  2.3.2 Size of the Footprint..................................................................................22  
2.4 Conclusions.....................................................................................................23  

## CHAPTER 3: COLLECTION AND ANALYSIS OF AEROSOL PARTICLES IN A PRE-CONCENTRATOR

3.1 Introduction......................................................................................................24  
3.2 Design of Pre-Concentrator............................................................................26  
3.3 Results and Discussion  
  3.3.1 Inlet Nozzle Losses....................................................................................32  
  3.3.2 Determination of the Electrodes Distance and Optimization of Corona Current.........................................................................................................................34  
  3.3.3 Determination of the Pre-Concentrator Collection Efficiency.................36  
  3.3.4 Scanning Electron Microscopy Analysis...................................................54  
  3.3.5 Performance Characteristics of the Pen-Ray UV Lamp Charg...............65  
3.4 Conclusions.....................................................................................................70
CHAPTER 4: CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

4.1 Conclusions and Suggestion for Future Work...........................................71
4.2 Significant Contribution of this Thesis.......................................................74

REFERENCES....................................................................................................75
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig.1</td>
<td>Spark Discharge and Collection Area Experimental setup</td>
<td>20</td>
</tr>
<tr>
<td>Fig.2</td>
<td>Microelectrodes Configuration</td>
<td>21</td>
</tr>
<tr>
<td>Fig.3</td>
<td>Schematic diagram of the pre-concentrator</td>
<td>27</td>
</tr>
<tr>
<td>Fig.4</td>
<td>The sharpened fine tungsten tip of the corona electrode</td>
<td>28</td>
</tr>
<tr>
<td>Fig.5</td>
<td>Schematic diagram of the experimental setup</td>
<td>31</td>
</tr>
<tr>
<td>Fig.6</td>
<td>Pre-concentrator inlet nozzle losses</td>
<td>33</td>
</tr>
<tr>
<td>Fig.7</td>
<td>Relationship between the high voltage and the corona current</td>
<td>35</td>
</tr>
<tr>
<td>Fig.8</td>
<td>Penetration for different experimental parameters</td>
<td>38</td>
</tr>
<tr>
<td>Fig.9</td>
<td>Collection electrode with and without Teflon layer</td>
<td>39</td>
</tr>
<tr>
<td>Fig.10</td>
<td>Schematic diagram of IC setup</td>
<td>42</td>
</tr>
<tr>
<td>Fig.11</td>
<td>Sulfate Calibration curve</td>
<td>44</td>
</tr>
<tr>
<td>Fig.12,13</td>
<td>Collection efficiencies &amp; mass losses for $Q= 5 \text{ l/min and Po}^{210}$</td>
<td>48</td>
</tr>
<tr>
<td>Fig.14,15</td>
<td>Collection efficiencies &amp; mass losses for $Q= 5 \text{ l/min and UV}$</td>
<td>49</td>
</tr>
<tr>
<td>Fig.16,17</td>
<td>Collection efficiencies &amp; mass losses for $Q= 2\text{l/min and Po}^{210}$</td>
<td>50</td>
</tr>
<tr>
<td>Fig.18,19</td>
<td>Collection efficiencies &amp; mass losses for $Q= 2\text{l/min and UV}$</td>
<td>51</td>
</tr>
<tr>
<td>Fig.20,21</td>
<td>Collection efficiencies &amp; mass losses for $Q= 5\text{l/min and Po}^{210}$</td>
<td>52</td>
</tr>
<tr>
<td>Fig.22,23</td>
<td>Collection efficiencies &amp; mass losses for $Q= 5\text{l/min and UV}$</td>
<td>53</td>
</tr>
<tr>
<td>Fig.24</td>
<td>The collection electrode at 0 minutes</td>
<td>55</td>
</tr>
<tr>
<td>Fig.25</td>
<td>The collection electrode after 5 minutes of particle collection</td>
<td>56</td>
</tr>
</tbody>
</table>
Fig. 26  The collection electrode after 10 minutes of particle collection.................................................................57

Fig. 27  The collection electrode after 20 minutes of particle collection.......................................................................58

Fig. 28  The collection electrode after 25 minutes of particle collection.......................................................................59

Fig. 29  The collection electrode after 30 minutes of particle collection........................................................................60

Fig. 30  The collection electrode after 45 minutes of particle collection........................................................................61

Fig. 31  The particle distribution on the flat electrode surface after a collection period of 30 minutes...............................................................63

Fig. 32  The particle distribution on the electrode side walls surface after a collection period of 30 minutes..........................................................64

Fig. 33  Schematic diagram of the UV charger.................................................................................................................66

Fig. 34  Time vs Temperature relationship for UV charger.................................................................................................66

Fig. 35  The UV charger particle loss percentages for different $d_p$.......................................................................................67

Fig. 36  UV charger size-dependent charging efficiency and charge/particle........................................................................69
List of Tables

<table>
<thead>
<tr>
<th>Table 1</th>
<th>DMA Characteristic Values for different Particle Diameters studied ................................................................................................................................................................. 26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2</td>
<td>Key Components of the Experimental Setup.......................................................................................................................................................................................................................... 31</td>
</tr>
</tbody>
</table>
List of Symbols

\( m_p \)  
Particle Mass

\( \eta \)  
Collection Efficiency

\( Q_f \)  
Aerosol Volumetric Flow Rate

\( \rho_p \)  
Particle Density

\( t_c \)  
Collection Time

\( d_p \)  
Number-based Size Distribution of Aerosols

\( N_t \)  
Total Particle Concentration

\( d_{pg} \)  
Mean Diameter

\( N \)  
Particle Concentration

\( D \)  
Particle Diffusion Coefficient

\( L \)  
Tube Length

\( \bar{U} \)  
Average Flow Velocity through Tubing

\( P \)  
Penetration

\( Q \)  
Flow Rate

\( \text{MDL} \)  
Method Detection Limit

\( S \)  
Standard Deviation
CHAPTER 1: INTRODUCTION

1.1 Background and Literature Review

During the last few decades there has been an ever-growing need for aerosol monitoring and measurement. The fields of interest vary, and span from air pollution and public health, to science and nanotechnology and up to medicine and chemicals. Occupational safety demands aerosol monitoring to assure that hazardous aerosols are not present or are at acceptable concentration levels, in public and industrial work areas. Aerosol measurements have also been conducted for the evaluation of their effect on climatic changes. The growing need to regulate aerosol pollution has led to the growth and expansion of the scientific methods used for aerosol monitoring, which are many times very costly and time consuming. A great variety of scientific instruments and approaches have been developed for that cause. These methods range from basic filter-based collection to the use of modern near-real time instrumentation. In this study, the design and performance characteristics of our method for collection and pre-concentration of aerosol sample for optical spectroscopies are discussed. This method can be applied to a portable, near-real time instrument for aerosol monitoring.
1.1.1 Aerosol Particles Collection Mechanisms

Many epidemiological studies show an existing relationship between ambient particulate pollution and detrimental health effects on humans (Schwartz 2001; Samoli et al. 2005). In the last few years, ultrafine aerosol particles have been of great scientific research interest, because of their risk to human health and their ability to enter the lowest part of the human lungs, as well as their great content of toxic organic compounds (Delfino et al. 2005). However, the relationship of their toxic properties with the aerosol particles properties, such as particle size, surface area and chemistry is still rather unknown (Han et al. 2009). For better understanding of the toxicological properties of aerosol particles, the most common method has been the collection of particles on filters, followed by removal using solvents. It might be a widespread and simple technique, but it has many drawbacks concerning the sample analysis, such as extraction, lyophilization and sonication. Filtration techniques are also affected by physical and chemical phenomena during the sampling procedures, such as evaporation of semi-volatile compounds, adsorption of gases on the filter, as well as reactions between the particles collected and the surrounding gaseous compounds (Eatough et al. 2003; Schauer et al. 2003). An alternative method for collection of ambient aerosol particles is the Electrostatic Precipitator (ESP) (Volckens and Leith 2002). Because of the smaller collection surface area of an ESP than the surface area of a filter, vapor adsorption and particle evaporation can be significantly diminished. Nonetheless, sampling techniques using an ESP
are also subject to possible chemical artifacts. Ozone, being a byproduct of corona discharge in air, has the ability to change the chemical balance of the collected particles. High-Voltage fields and corona discharge produce ozone and oxidant ions in ESPs (Arnold et al. 1997), which have the ability to react with particles and vapors entering the plasma area (Seinfeld 2006). The degradation of particle-bound compounds caused from these reactions can narrow and even avert the use of ESPs as a sampling technique for atmospheric aerosols (Han et al, 2009).

The exposure to toxic metals can cause serious health effects such as great risk of cancer and diseases of the respiratory systems (Pope et al. 2002), which makes the measurement and monitoring of aerosol particles in the atmosphere an affair of great importance for safeguarding of human health and the environment. Most particulate metal contaminants are collected in filters in a period of many hours, followed by analysis of the collected samples by the use of analytical methods. These techniques are acceptable for conventional control applications, which target certain regulations. Nonetheless, an increasing number of research operations need additional measurements below already established exposure limits, and measurement times. This brings forth the many deficiencies related to the use of filter-based methods. Measurement times span from a few to many hours, not being able to simulate the high-intensity and short-time exposures, typical of an industrial atmosphere. Analysis turnaround times also span from several days to weeks. This shows the growing need for semi-
continuous or real-time instruments, being able to deliver on site information for aerosol chemical properties for use in indoor, ambient and industrial environments. Especially for occupational and indoor use, the compact size and the portability of the instrument used for the aerosol measurement operation, is of critical importance for the precision of the exposure assessments (Diwakar et al. 2012). Single-particle mass spectrometers will usually produce the most comprehensive real-time information concerning the size and content of the aerosols studied, but they are inadequate for routine measurement utilization, because of their big size, bulkiness and price.

Human exposure to aerosol particles that contain toxic metals produced by industrial activities like mining, welding, cutting, brazing and soldering can cause serious health effects both in ambient and industrial atmospheres (EPA 2011; OSHA 2011). Growing emergence of nanotechnology has raised several concerns regarding possible health effects from inhaling engineered nanoparticles, thus leading to the demand for precise instruments with low detection limits (Oberdorster et al. 2007). These methods are prone to large errors, due to sampling artifacts and operator sampling and testing errors, not providing real-time information for the aerosol composition, thus creating an increasing demand for the development of near-real-time, portable instruments, able to measure multi-elemental aerosol composition and expedite effective exposure measurement and hazard recognition techniques (DREAM 2009). Our aerosol pre-concentration method involves collection of airborne particles on the
tip of two microelectrodes, with diameters of 500 and 1.58 mm respectively, by
the use of electrostatic forces. Particle collection efficiency ($\eta (d_p)$) was
estimated by measuring the particle number concentration upstream and
downstream of the collection unit by the use of a CPC, with and without presence
of an electric field across the two electrodes.

$$\eta(d_p)_\text{HV on} = \frac{N_{\text{in}}^{V=0} - N_{\text{out}}^{HV}}{N_{\text{in}}^{V=0}}$$

$$\eta(d_p)_\text{HV off} = \frac{N_{\text{in}}^{V=0} - N_{\text{out}}^{V=0}}{N_{\text{in}}^{V=0}}$$

Nanotechnology is becoming increasingly important in workplace areas
because of the array of applications it has in broad range of fields of interest,
spanning from medicine to new alternate energy technologies. As a result of
these emerging technological applications comes the hazard of exposure to
airborne nanoparticles of size diameters smaller than 100 nm, for communities
as well as workers at industrial environments (NIOSH 2006). The mass
concentration of airborne particles collected on filters is the most typical method
for monitoring ambient air quality and limits of exposure (Huang and Yang 2006).
The very small size of airborne nanoparticles will often render them mass
collection that is unimportant in comparison to larger particles. Measurements of
airborne nanoparticles expressed as a function of particle number and/or surface
area has been proven to be a more crucial parameter regarding possible health
effects than particle mass (Duffin et al. 2007; Stoeger et al. 2006). The equipment and techniques to measure particle numbers and/or surface area concentrations are available, but are bulky and costly to operate (Brouwer et al. 2004). Capillary pore membrane (CPM) filters have been proven to be an excellent solution for analysis using scanning electron microscopy (SEM), due to their flat collection surface that is optimally designed for particle counting (Gentry et al. 1982). Most of these filters are 10 μm thin polycarbonate films circular pores, perpendicular to the surface. These pores are a product of heavy irradiation and heavy etching, followed by random distribution across the surface. The possibilities when attempting collection of airborne particles on CPM filters are: either collection of particles on the filter surface or deposition in the pores, or the case of particles passing through the filter. A model for CPM overall collection efficiency has been proposed, using different conditions for each of the deposition mechanisms: Diffusion to pore walls, interception and impaction. For the smallest particle size diameters ($d_p<100$ nm), the deposition of particles is governed by diffusion. Larger particles deposition is dominated by interception and inertial impaction (Spurny et al. 1969). Extensive experimental work has been performed so as to determine CPM filters collection efficiency and the aspects influencing it (Spurny et al. 1969; Smith et al. 1976; Liu and Lee 1976; John and Reischl 1978; Gentry et al. 1982), but none of these research attempts has confirmed the theoretical model of deposition of nanoparticles on CPM filters.
1.1.2 Aerosol Particles Charging Mechanisms

During a long period of time, comprehensive analysis on the stationary bipolar charging characteristics of aerosol particles has been performed, including both theoretical and experimental aspects. Both theoretical and experimental approaches have shown that the charge distribution follows Boltzmann’s law in the continuum:

\[ n_p = \frac{\exp\left(-\frac{p^2 e^2}{d_p k T}\right)}{\sum_{p=-\infty}^{\infty} \exp\left(-\frac{p^2 e^2}{d_p k T}\right)} \]

Where \( n_p \) is the number of particles that carry \( p \) elementary units of charge, \( n_T \) is the total number of particles, \( e \) is the elementary unit of charge, \( d_p \) is the particle size diameter, \( k \) is the Boltzmann constant and finally \( T \) is the absolute temperature. Nonetheless, Boltzmann’s law distribution is not globally recognized for particle size diameters below 0.05 μm. This has led to numerous experiments during the last decades, leading to the establishment of various different theories that have been developed (Liu and Pui, 1974; Marlow and Brock, 1975; Kojima, 1978). These theories provide a broad diversity of experimental values, showing the great challenge and difficulties found in the analysis of ultrafine aerosol particles. Large diffusion losses, large electrical mobility of aerosol particles, small charging probability as well as the relative instability in aerosol particles generation are some of the fore-mentioned difficulties faced (Kousaka et al. 1983).
Bipolar diffusion charging is a matter of great importance in many aerosol measurement operations using electrical techniques and requiring a known, predictable charge distribution (Ku et al. 2011). As stated in Boltzmann’s theory, the bipolar charge distribution comes as a consequence of the equilibrium exchange between particles and ions. Diffusion charging of the particles is highly dependent on the ion diffusion to the particulate surface, whereas the diffusion rate of the ions to the particulate surface is dependent on the ion mobility, the Coulombic force between ions and particles and the attractive image force and Van der Waals force. Another model, which includes a Coulomb and image potential for calculating the ion attachment coefficients, has also been developed (Fuchs 1963). The assumption that all particles studied are spherical has been made in both of these proposed models, which have been confirmed by various experimental analyses. The particles shape and structure effects on particle diffusion charging characteristics is a matter of great importance and has grown a lot of experimental interest in the last few decades.

It has been observed that in electrostatic precipitators (ESPs), a high space charge caused by high concentrations of unipolar charged particles can cause corona quenching. The electrical field near the active electrode will decrease and it will increase near the passive electrode. There will be decrease in the discharge current and sparking voltage, as well as in the particle charge and precipitation (McLean 1988). High concentrations of small particles tend to be ambiguous, carrying a high specific surface that determines the particles
charging process (Choi and Fletcher 1997). Corona quenching is a term used for other aerosol effects apart from the description of the altering of electrical fields by space charging, including mechanisms operating at voltages near the corona onset. The number of charges will still be very low at or near the corona onset, so these effects can’t derive from a significantly enlarged space charge. Therefore, we have to examine the interactions of the aerosol with the discharge itself (Stommel et al. 2006). Experimental work on the change of onset voltage by corona quenching has been performed, showing that the change is smaller for positive instead of negative discharge. In case the particle has the same polarity as the discharge in areas near the active electrode, a decrease of the electrostatic field has been observed, providing a potential justification for the onset voltage increase. Moreover, the proposal that particles present in the active region inhibit electron avalanches culpable for creating and maintaining the discharge has been made (Awad and Castle 1974). Lower onset voltages while operating on negative corona for a solid aerosol in the low μm-range have been examined, and are associated to the contact of particles with the active electrode, thus changing the discharge surface roughness. While operating in low voltages, the “Surface roughness factor” has been introduced for useful calculations, while only corona quenching is believed to be a mechanism for voltages higher than the onset voltage (Gallimberti 1998). It has been questionably thought that particles on the active electrode can cause alterations of the onset voltage, while precipitation of particles is through to be caused by turbulence (Huan and Chen 2003). Lawless et al. have shown that a particle on
the discharge electrode could operate as an extension with a greater curvature, thus leading to lower onset voltages. Additional experimental work has shown that electronic avalanches can occur inside porous particles before the onset voltage for electrode geometry can be achieved (Jacobs et al. 1952). When working on fluid aerosols, a shift, depending on the electrode diameter, has been observed for corona onset voltages. Two justifications were given for this shift. First, an uncharged particle near the active electrode could be capable of causing a discharge between the electrode and the particle, due to increased electrical field strength. Second, the particles already deposited on the active electrode could re-depart after charging. Gradient forces or turbulence could lead in particles precipitating on the active electrode, as fluid particles could merge before dispersion (Riebel et al. 2002).

The presence of an ion field combined with the presence of a corona discharge in a highly non-uniform electric field close to a sharp-edge inlet can be responsible for the electric charging of particles entering this field. The aspiration efficiency of particles might be altered by this phenomenon. When those charged particles are aspirated, they tend to become more prone to wall losses in the tubing connecting the sampling and aerosol monitoring instruments areas (Liu et al. 1985). The ability to aspirate and transport particles with a high efficiency, is a matter of great importance for practical aerosol sampling techniques (Vincent 1989). The main reasons for particle losses at the inlet during aspiration are related to the particles size, air stream velocity, apparatus geometry and
sampling flow rates. Aspiration efficiency (the fraction of particles drawn into the inlet) can also be a function of the presence of electrostatic forces at the inlet, notably when particles are charged before, or at the inlet of the sampling apparatus. It is very crucial to examine particle loss mechanisms during transport through the tubing after the particles are aspirated. These losses can be caused by inertial impaction (large fast-moving particles at bends in tubing cross-sections), gravitational settling (large slow-moving particles in horizontal sections) and diffusion (submicron particles). In the case of turbulent tube flows, there might be losses caused by turbulent deposition. Also, losses may be caused by electrical forces in the case of electrical charging of the particles and/or tubing. Image and/or space charge effects are capable of creating this effect, and are dependent on the particle size and charge, as well as the tubing geometrical features. It has been experimentally shown that coiled tubing will create a secondary flow, forcing particles to move close to the tubing walls, thus causing an increase to losses (Romay et al. 1996). Choosing the appropriate tubing material is also significant to electrostatic particle losses. These losses are much larger in polytetrafluoroethylene (Teflon) and polyethylene (Polyflo) tubing than the losses observed while using polyvinylchloride (Tygon) tubing (Liu et al. 1985).

A matter of great importance in aerosol mechanics is the production, detection and charging kinetics mechanisms for ultrafine aerosol particles. Particles of this size range are very challenging in their measurement techniques
applied, since they have to be measured obliquely, using electrical mobility instruments (Knutson 1976) or condensation particle counters (Hogan 1979). For better understanding of the impact of particle size on reaction rates, studies have been performed on developing reactive aerosols of known structure and size. Spurny et al. generated silver aerosol particles by homogeneous condensation, because of their low vapor pressure and reactivity with I₂, O₂ and S₂. Liu and Pui developed an electrical aerosol analyzer (EAA) for aerosol particles concentration measurements and for the determination of the aerosol size distribution. To be able to define the EAA’s results, it was extremely important to know the charge distribution. In studies using larger particles (d_p>1.0 μm) characterized by multiple charges, the results showed agreement between the Boltzmann distribution and charge measurements (Keefe 1959). For ultrafine aerosol particles carrying one or no charges, studies performed showed great inconsistencies between results obtained and the Boltzmann distribution, with much greater fractions of charged ultrafine aerosol particles. The need to explain these discrepancies between the Boltzmann theory and the experimental results led to the development of different charge distributions (Liu and Pui 1974; Kojima 1978; Haaf 1979; Whitby and Cantrell 1979; Liu and Gentry 1982).

Charging of aerosols is very critical in aerosol science and technological applications, due to the fact that electrically charged particles play an important role in many applications, such as characterization of aerosol particles, aerosol particles detection and control technologies (Li and Chen 2011). For particles
spanning in the sub-micrometer range, charging of particles by unipolar ion diffusion has been mainly used, nonetheless current unipolar chargers produce a charging efficiency that reduces while decreasing the particle size diameters (d_p < 20 nm) (Chen and Pui 1999). For improvement on the charging efficiency of ultrafine aerosol particles, many studies have been performed by the use of irradiation techniques such as: i) Ultraviolet (UV) (Burtscher et al. 1982; Jung et al. 1988; Matter et al. 1995; Mohr et al. 1996; Maisels et al. 2003; Hontañon and Kruis 2008) and ii) Soft x-ray irradiation (Kulkarni et al. 2002; Shimada et al. 2002; Jiang et al. 2007). After UV exposure, and once the particles are irradiated, electrons will be emitted from the particle surface. Irradiated particles become positively charged in the case that the incident proton energy surpasses the particle material work function. In this thesis we will be using an aerosol charger utilizing pen-type Hg lamps for UV irradiation based on the model that Li and Chen (2011) developed to examine the aerosol photo-charging process by taking measurements for the charging efficiencies and distributions of ultrafine aerosol particles. In their study they used DMA- classified monodisperse silver (Ag) particles (d_p: 7-30 nm) and observed the effect of light intensity on photo charging. The prototype UV charger operated at a flow rate of 5 l/min and produced higher charging efficiency than corona- based unipolar chargers operating under similar conditions. The UV charging model following the Fowler-Nordheim equation (Fowler 1931) was introduced to calculate the charging performance, and was confirmed by experimental results.
For sub-micron particles, inertial means for transport control are not applicable, so a common practice has been the use of external electrical forces, with the necessity of charged particles. Ambient aerosols at normal temperatures (\(-25 \, ^\circ \text{C}\)) are typically neutral and the use of the Boltzmann equation can provide us with the approximate particle charge distribution (Friedlander 2000). It has been experimentally observed that the particle charging efficiency will significantly decrease as we reach the lower end of the nanoscale range (\(d_p<30 \, \text{nm}\)). ESPs have been extensively used for aerosol particles control in many scientific and industrial applications, capitalizing on the electrical forces on particles for separation from the gas streams, producing mass-based collection efficiencies close to 100%. Nonetheless, when particle size diameters are in the low end of the nanoscale (\(d_p<50 \, \text{nm}\)), the mass-based collection efficiency will decrease as the particle size is being reduced. Ineffective charging of the ultrafine aerosol particles is thought to be the main reason for this phenomenon (Zhuang et al. 2000). Charging of ultrafine aerosol particles has been an objective of broad experimental analysis during the past. Fuchs (1947), established an equation based on the diffusional charging model, which has been experimentally proven to be reasonably accurate for calculating aerosol nanoparticles charging probabilities (Liu and Pui 1997; Hussin et al. 1983; Wiedensohler and Fissan 1991). ESPs charge particles by a corona developed by high DC voltage, which is applied to the two electrodes. For nano-sized
particles, unipolar corona has been proven to be an insufficient charging mechanism, so photoelectric techniques such as UV irradiation have been used.

1.1.3 Corona Discharge

Unipolar ions are governed by high mobilities and mutual repulsion, hence they have a very short lifespan. Radioactive discharge, corona discharge, flames and UV radiation are the mechanisms that are capable of producing ions in air. Though, unipolar ions at high concentrations to be valuable for aerosol charging can only be produced by corona discharge. For the production of corona discharge in this thesis, we established a non-uniform electrostatic field between two tungsten needle electrodes and a tungsten needle and tungsten rod electrodes. Air and other gases are good insulators, but in an area of adequately strong high field, the air will be subjected to electrical breakdown thus becoming conductive. The field geometry will be decisive for this breakdown becoming a corona discharge or an arc. For the area of interest in this thesis (corona region), the electrons will be accelerated up till a velocity adequate to knock an electron from an air molecule after colliding with it, thus creating a free electron and a positive ion. Corona discharge is the thick free electron and positive ions cloud created by a self-sustaining avalanche. This phenomenon is established by ions and electrons that are created by natural radiation. Positive and negative coronas look different and have different properties. In positive coronas the area
surrounding the electrode has a solid and glowing blue/green sheath, while in negative coronas, a glow is present in tufts or brushes that are reminiscent of a dancing motion above the electrode surface region. There will be enough energy for the production of ozone from oxygen in the corona region, with this production of ozone being ten times more for the negative corona, being the reason why indoor ESPs use negative coronas. Gas temperature, pressure and chemical compositions are factors that can alter corona production (Hinds 1982).

1.2 Thesis Outline

The Master’s thesis “Collection and Pre-Concentration of Aerosol for Optical Spectroscopies” has been organized so as for each chapter to be self-contained with an introduction and conclusions. All conclusions are summed up in the final chapter of the thesis (Chapter 4). The references for all chapters are presented at the end of the thesis. All symbols have been defined at the first time of their usage, and a detailed list of symbols, figures and tables has been presented in the front matter of this thesis.

Chapter 1 (this chapter) presents the background and motivation of this study and reviews some of the literature pertaining to the main focus of our experimental research.

Chapter 2 of this thesis determines the electrode size diameter after the introduction of spark discharge. A brief introduction and problem statement are given, followed by an explanation and analysis of the experimental design, including the appropriate figures. Experimental results are later discussed,
focusing on the results obtained for the variation of the coverage in different experimental conditions and the results regarding the footprint size diameter. Finally, a brief presentation of the experimental conclusions is given, summing up all the significant results obtained.

Chapter 3 of this thesis discusses the subject of collection and analysis of aerosol particles in a pre-concentrator system. An introduction and problem statement are given, followed by an explanation and analysis of the design of the pre-concentrator. Schematic diagrams, pictures and tables are used for better understanding of the experimental setup and its key components. Experimental results are then discussed. First, we analyzed the losses in the pre-concentrator inlet nozzle area, and graphically presented the data obtained. Then, the determination of the distance between the electrodes of the pre-concentrator is discussed, followed by an analysis on the optimization for the corona current. Our main experimental analysis follows, presenting the determination of the pre-concentrator collection efficiency. Figures, schematic diagrams and pictures are used for better explanation of the methods and instruments used in this study, followed by figures presenting the data obtained from all of the experiments conducted. An optical analysis of and discussion on the experiments using a scanning electron microscope is then presented. A discussion on the performance characteristics of the Pen-Ray UV Lamp charger follows, and figures of the results regarding this subject are presented. Finally, we summed up all the significant results and conclusions obtained in this study.
In Chapter 4, which is the final chapter of this thesis, we presented all the experimental conclusions obtained in Chapters 2 and 3, and made suggestions for future work in this experimental area of interest. Finally, the significant contribution of this thesis was explained.

CHAPTER 2: DETERMINATION OF THE COLLECTION ELECTRODE SIZE DIAMETER BY THE INTRODUCTION OF SPARK DISCHARGE
2.1 Introduction

A microelectrode system has been used to determine the spark discharge footprint on a PTFE filter substrate (d=25 mm), for several electrode distances, pulse energy setpoints and electrode angles. A pulsed spark discharge was generated across the electrodes with input energy values ranging from 100 to 400 mJ per pulse, and a spark pulse rate of 5000 ms. The spark discharge footprint has been characterized by measuring the coverage percentage for different rotations of the filter coated electrode and the footprint diameter. For a 45° angle between the electrodes and for a number of 10-20 pulses for every 20° and 30° of rotation of the filter coated electrode, coverage ranged from 70%-100%, while the diameter of the footprint was in the range of 3.2-6.4 mm. The pulsed spark discharge generated across the electrodes had input energy values ranging from 100 to 250 mJ per pulse, whereas the electrode distance ranged from 2mm-4mm. For a coaxial placement of the two electrodes and no rotation of the filter coated electrode, we studied the effect of the corona discharge on the
filter substrate by measuring the footprint diameter for 1-10 pulses, pulse energy setpoints ranging from 100 to 400 mJ per pulse and electrode distances ranging from 2mm-4mm. The footprints ranged from 0.3mm-2.4 mm, with very high radius coverage (>85%). The results were very consistent and repeatable, helping us determine the geometry and sizes of the collection electrodes used in our pre-concentrator method design as analyzed in Chapter 3.

2.2 Experimental Design

We designed a system to enable us to introduce spark discharge between a microelectrode and a substrate, while determining the spark footprint on a needle surface. We used a 125 mm long glass tube (d=6 mm, thickness=0.3 mm), with a 135 mm long tungsten rod ideally placed inside it, having a 5 mm long tungsten microelectrode needle (d=0.5 mm) centered at its bottom part as an anode for spark generation. The 10 mm top part of the rod exiting the glass tube was used to make electrical contact with an ARC-2 high power pulse generator (Vtech Engineering Corporation, Andover, MA). The system containing of the glass cylinder, the tungsten rod and microelectrode needle were designed so as to be able to rotate at an angle up till 45° from its vertical axis. Coaxially placed was an aluminum disk (d=25 mm) used as a cathode for spark generation, having a PTFE filter substrate (d=25 mm) coated on its top surface facing the microelectrode needle, in distances ranging from 2mm-4mm. The ARC-2 high power pulse generator was connected to a computer using a RS-232
Serial Data Interface and controlled via HyperTerminal. Schematic diagrams of our system and microelectrodes configuration are shown in Figures 1 and 2.

**Fig. 1** Spark Discharge and Collection Area Experimental setup
2.3 Results and Discussion
2.3.1 Variation of Coverage in Different Experimental Conditions

We first characterized the variation of the footprint radius coverage for different electrodes angles and distances, number of pulses and pulse energy setpoints. For a 45° angle between our electrodes and a spark pulse rate of 5000 ms and 10 pulses for every 20° of rotation of the filter coated electrode and pulse energy setpoints ranging from 100-250 mJ per pulse, we measured a 70% coverage in a 2π rotation for an electrode distance of 4 mm, an almost 100% coverage in a 2π rotation for an electrode distance of 2 mm and a 100% coverage in a 3π rotation for an electrode distance of 4 mm. For a spark pulse
rate of 5000 ms and 15-20 pulses for every $20^\circ$ of rotation, we had 100% coverage in a $2\pi$ rotation for an electrode distance of 2 and 4 mm. Coverage was 100% in both $2\pi$ and $4\pi$ rotations of the filter coated electrode for 10 pulses for every $30^\circ$ of rotation. We then repeated the same procedure without rotation of the filter coated electrode and the two electrodes coaxially placed, with pulses ranging from 1-10 and pulse energy setpoints ranging from 100-400 mJ per pulse. The coverage was 85%-100% for electrode distances of 2-4mm. Filter samples were analyzed using a research microscope (Labophot-2, Nikon) and a digital camera (Moticam 2300, Motic) for characterization of the footprint radius coverage.

2.3.2 Footprint Size

We characterized the footprint size for different electrodes angles and distances, number of pulses and pulse energy setpoints. For a $45^\circ$ angle between our electrodes and a spark pulse rate of 5000 ms and 10 pulses for every $20^\circ$ of rotation of the filter coated electrode and pulse energy setpoints ranging from 100-250 mJ per pulse, we measured a footprint size diameter of 4.7 mm in a $2\pi$ rotation for an electrode distance of 4 mm, a footprint size diameter of 4.5 mm in a $2\pi$ rotation for an electrode distance of 2 mm and a footprint size diameter of 6.4 mm in a $3\pi$ rotation for an electrode distance of 4 mm. For a spark pulse rate of 5000 ms and 15-20 pulses for every $20^\circ$ of rotation, we measured a footprint size diameter ranging from 3.2-4.7 mm in a $2\pi$ rotation for an electrode distance of 2 and 4 mm. The footprint size diameter was measured
to be 3.2 mm for a $2\pi$ rotation of the filter coated electrode, for 10 pulses for every $30^\circ$ of rotation, and 5.6 mm for a $4\pi$ rotation of the filter coated electrode, for 10 pulses for every $30^\circ$ of rotation. We then repeated the same procedure without rotation of the filter coated electrode and the two electrodes coaxially placed, with pulses ranging from 1-10 and pulse energy setpoints ranging from 100-400 mJ per pulse. The footprint size diameter ranged from 0.3-0.65 mm for one pulse, 1.0-1.2 mm for two pulses, 1.50-1.59 mm for five pulses and 1.90-2.40 mm for ten pulses. Filter samples were analyzed using a research microscope (Labophot-2, Nikon) and a digital camera (Moticam 2300, Motic) for characterization of the footprint size.

2.4 Conclusions

A microelectrode system has been effectively used to determine the spark footprint coverage radius percentage and footprint size, after generating a pulsed spark discharge across the electrodes. We studied this problem for different electrode distances, pulse energy setpoints and electrode angles, for better understanding of the effects of the application of pulsed spark discharge across the electrodes, on the footprint characteristics. Overall footprint radius coverage was very high for all experimental parameters, ranging from 70%-100%, being more effective for coaxial placement of the electrodes (85%-100%). The footprint size diameter was measured to be 3.2mm-6.4 mm for an angle of 45° between
the electrodes, for different electrode distances, pulse numbers and energy setpoints, and electrode rotations. The footprint size diameter for the same parameters and a coaxial placement of the electrodes was measured to be 0.3mm-2.4 mm. Reproducibility of the results was excellent, providing us with useful information on the effects of the application of pulsed spark discharge across a microelectrode configuration. This preliminary work clearly provided us with knowledge on the range of electrode size diameters that could be used as collection electrodes in our pre-concentrator apparatus developed. For that purpose, and for coaxial placement of the microelectrodes used in the pre-concentrator, we studied the focused collection of sub-micrometer aerosol particles on electrodes (d=0.5mm and 1.5785mm) after the application of high voltage.

CHAPTER 3: COLLECTION AND ANALYSIS OF AEROSOL PARTICLES IN A PRE-CONCENTRATOR

3.1 Introduction

A new approach has been developed for collection and pre-concentration of aerosol particles for optical spectroscopies. The method includes focused electrostatic deposition and pre-concentration of miniscule particle mass of charged (NH4)2 SO4 particles onto a flat micro-electrode tip for a wide range of particle size diameters (50-1000 nm). The collected material has been quantitatively analyzed using scanning electron microscopy (SEM) and the mass deposited has been analytically determined using ion chromatography (IC).
Count-based collection efficiency has been found to be very consistent and reproducible for both collection electrode sizes (d=0.5 and 1.5785 mm), system flow rates (2-5 l/min), aerosol particle chargers (Po\textsuperscript{210} and Pen-Ray UV Lamp) and collection periods (1-30 min.), with values in the range of 33%-60% with the application of high voltage in our corona electrode, whereas the values ranged from 15%-20% without the application of high voltage. Mass samples were collected for 30 min. and placed in DI water for mass determination of the salt deposited through IC analysis. Mass-based collection efficiency values ranged from 35%-65% with the application of high voltage in our corona electrode, whereas the values ranged from 12%-25% without the application of high voltage. The values obtained from these two methods come to close agreement, while the repeatability of our measurements varied from 1% to 10%. Particle distribution and losses on the side walls of the collection electrodes have been studied using SEM. Distribution of particles was homogeneous throughout the biggest part of the flat electrode tip surface, and losses at the side walls were approximately 8%, in close agreement with the particle loss range of 8%-17% obtained from IC analysis. Our approach proved to be a reliable and consistent method for collection of sub-micron aerosol particles on the flat tip of a micro-electrode, showing its advantages over other substrate and filter-based collection techniques. Further, the pre-concentrator small size, and system low pressure drop, can allow us operate at higher inlet flow rates using micro-pumps, making our apparatus ideal for use at a near-real time field-portable instrument using optical spectroscopies for aerosol measurements.
3.2 Design of Pre-Concentrator

Test aerosols were generated using a six-jet pneumatic atomizer (Model 9306, TSI Inc., Shoreview, MN, USA), powered by a pressure pump (GAST Manufacturing, Benton Harbor, MI, USA) operating at 25 psi, so as to atomize elemental standard solutions. To obtain an ammonium sulfate [(NH₄)₂ SO₄] standard stock solution of 18 g/l, 99.9% pure (NH₄)₂ SO₄ salt was dissolved in in ultrapure DI water (FisherScientific, Pittsburgh, PA, USA). The aerosolized standard was then passed through three sequential diffusion dryers for desolvation (1X Model 30600, TSI Inc., and 2X Model DD250, ATI, Ownings Mills, MD, USA), followed by classification in a differential mobility analyzer (DMA) (Model 3080, TSI Inc.) operating at a sheath flow of 2.4 l/min, for particle size diameters spanning from 50-1000 nm, for obtaining a monodisperse test aerosol. Operational characteristics of the DMA for different particle size diameters are shown in Table 1.

<table>
<thead>
<tr>
<th>d_p (nm)</th>
<th>DMA Voltage (V)</th>
<th>Electrical Mobility (cm²/V s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-110.9</td>
<td>-9.6066×10⁻¹⁰</td>
</tr>
<tr>
<td>100</td>
<td>-388.7</td>
<td>-2.7161×10⁻¹⁰</td>
</tr>
<tr>
<td>200</td>
<td>-1217.4</td>
<td>-8.6723×10⁻¹¹</td>
</tr>
<tr>
<td>300</td>
<td>-2202.2</td>
<td>-4.7941×10⁻¹¹</td>
</tr>
<tr>
<td>400</td>
<td>-3245.8</td>
<td>-3.2527×10⁻¹¹</td>
</tr>
<tr>
<td>500</td>
<td>-4316.2</td>
<td>-2.4460×10⁻¹¹</td>
</tr>
<tr>
<td>600</td>
<td>-5401.6</td>
<td>-1.9545×10⁻¹¹</td>
</tr>
<tr>
<td>700</td>
<td>-6497.4</td>
<td>-1.6249×10⁻¹¹</td>
</tr>
<tr>
<td>800</td>
<td>-7602.1</td>
<td>-1.3887×10⁻¹¹</td>
</tr>
<tr>
<td>900</td>
<td>-8.711.0</td>
<td>-1.2120×10⁻¹¹</td>
</tr>
<tr>
<td>1000</td>
<td>-9823.6</td>
<td>-1.0747×10⁻¹¹</td>
</tr>
</tbody>
</table>
The classified particles were then electrically charged to a steady state by either: (i) a Po\textsuperscript{210} bipolar charger (Amount: 500 mC, Half-life: 02/2010) or (ii) a Pen Type UV lamp charger powered by two power supply units (Model P/N 99-0055-01, UVP, Upland, CA), before entering the pre-concentrator inlet area. Our pre-concentrator apparatus used in this study consists of three sub-areas: (i) the inlet area, (ii) the aerosol collection and analysis chamber and (iii) the outlet area. A schematic diagram of the pre-concentrator is shown in Figure 3.

\begin{center}
\textbf{Fig. 3} Schematic diagram of the pre-concentrator.
\end{center}
The inlet area consists of: (a) the inlet nozzle (Vespel, d=2mm), (b) a sharpened fine tungsten needle centered at the nozzle (d=0.5 mm, Metal Cutting, Cedar Grove, NJ) and (c) a metal mounting on the side of the nozzle used for the application of High Voltage at the needle. The sharpened fine tungsten needle tip can be seen in Figures 4a and 4b.

Fig. 4a, b.  The sharpened fine tungsten tip of the corona electrode.
The aerosol collection and analysis area consists of: (a) the aerosol collection electrode and (b) side glass windows used for optical observation of the corona and electrode distances. The collection area was designed to directly collect particles from the gas phase onto a flat tip of: (a) a 0.5 mm diameter straight tungsten needle (Metal Cutting, Cedar Grove, NJ, USA) or (b) a 1.5785 mm diameter straight tungsten rod (ESPI Metals, Ashland, OR, USA). Tungsten was picked as our substrate collection material because of its superior electrical and thermal properties, as well for the fact that its spectral lines did not intervene with the elemental measurements (Diwakar et al. 2012). The 0.5 mm tungsten needle used was of 99.996% chemical purity, and the 1.5785 tungsten rod used was of 3N8 purity. Both collection electrodes were of very high chemical purity, thus having the minimum interference from trace impurities. The particles were charged using the corona generated from the sharpened fine tungsten needle centered at the nozzle (corona electrode). A high positive potential (4-6 kV) was applied across the corona electrode, by using a High Voltage DC Power Supply (Series 2300, BERTRAN, Hicksville, NY, USA). The aerosol collection electrode was grounded. A constant, but not lasting (1-2 minutes) corona current of an average of 4.8 μA was maintained between the corona and the collection electrodes when using the 0.5 mm collection electrode, while a constant and very stable corona current of an average of 5.1 μA was maintained when using the 1.5785 collection electrode. Both electrodes were always placed coaxially, with a distance of 4 mm between the corona electrode tip and the flat tip surfaces of our
collection electrodes. The corona electrode was 1 mm outside of the Vespel nozzle, while the collection electrode was 1 mm outside of the dielectric sheath placed in the lower part of our pre-concentrator collection area. The diameters of our collection electrodes were chosen to be in the range of 500-2000 mm to approximate the special extent of the spark generated footprint, as analyzed in chapter 2. The aerosol particles entered the collection area through a concentric Vespel nozzle around the corona electrode, obtaining electrical charge from the attachment of ions developed by the corona electrode. Under the impact of the electric field created between the two needles, these ions will be deposited on the flat tips of our collection electrodes. Our experimental system has been optimized for a variety of parameters, including the inlet nozzle losses, the high voltage and corona current between the electrodes, the two electrodes distance and the aerosol samples flow rates. The concentration-based collection efficiency of our pre-concentrator was characterized for a size range of 50-1000 nm. Using a two-way valve before the pre-concentrator inlet area, and by the use of a condensation particle counter (CPC) (Model 3022A, TSI Inc.) operating at a low flow configuration (Q=0.3 l/min), we were able to measure the concentration of particles, upstream and downstream, thus obtaining concentrations of particles entering and exiting the unit. To maximize our ability to control the aerosol flow rates entering the pre-concentrator, we used a vacuum pump (GillAir Plus, Gillian). The pump was operating at 1.7 l/min for a desirable flow rate of 2 l/min entering the pre-concentrator, and at 4.7 l/min for a desirable flow rate of 5 l/min entering the pre-concentrator. A schematic diagram of our experimental setup is
shown in Figure 5. A list of the key components of our experimental setup is shown in Table 2.

**Table 2. Key Components of the Experimental Setup**

<table>
<thead>
<tr>
<th>Component</th>
<th>Model/Brand</th>
</tr>
</thead>
<tbody>
<tr>
<td>HV Power Supply for Aerosol Collection</td>
<td>Bertran S-230</td>
</tr>
<tr>
<td>Condensation Particle Counter</td>
<td>Model 3022A, TSI Inc.</td>
</tr>
<tr>
<td>Differential Mobility Analyzer</td>
<td>Model 3080, TSI Inc.</td>
</tr>
<tr>
<td>Pneumatic Atomizer</td>
<td>Model 9306, TSI Inc.</td>
</tr>
<tr>
<td>Mass Flow Controller</td>
<td>Model 4100, TSI Inc.</td>
</tr>
<tr>
<td>Vacuum Pump</td>
<td>GillAir Plus, Gillian</td>
</tr>
<tr>
<td>Pressure Pump</td>
<td>GAST Manufacturing Inc.</td>
</tr>
<tr>
<td>Chemical Standards</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

**Fig. 5** Schematic diagram of the experimental setup.
These concentrations, with and without the application of high voltage were used to calculate the collection efficiency values. Collection electrode samples where then analyzed in a scanning electron microscope (SEM) (Model S-3000N, Hitachi Science Systems) for the determination of possible particle losses within our pre-concentrator collection and analysis area and the ratio of particles deposited on the collection electrode flat tip, over the particles deposited on its side walls. For the optimization of our ability to determine this ratio more accurately, collected samples for different experimental parameters were analyzed using an ion chromatography (IC) instrument, consisting of a DIONEX Model LC20 chromatography enclosure, a DIONEX Model CD25 conductivity detector and a DIONEX Model GP50 gradient pump (Thermo Fisher Scientific Inc.), connected to a computer using the PeakNet software. The implications of these findings will be discussed later.

3.3 Results and Discussions

3.3.1 Inlet Nozzle Losses
A matter of significant importance in this study was the characterization of losses in our system’s inlet nozzle. It was desirable that we have the minimum losses possible in the inlet nozzle, for particles entering the pre-concentrator chamber. Sub-micrometer (NH₄)₂ SO₄ particles were generated from our standard stock solution using a pneumatic atomizer and classified (50-700 nm) by the DMA, followed by charging from our Po²¹⁰ charger before entering the pre-
concentrator inlet area. The aerosol flow rate entering our system was 5 l/min and the distance between the two electrodes was 4 mm. A high voltage of 5.2 kV was applied to our corona electrode, obtaining a stable corona of 4.8 μA. We then measured the upstream concentrations for several particle size diameters spanning from 50-700 nm through the CPC, with and without the application of high voltage. The losses were proven to be satisfactory low (0-5 %), thus leading us to the assumption that there are no significant losses in our inlet nozzle area. The results obtained can be seen in Figure 6.

Fig. 6 Pre-concentrator inlet nozzle losses.
3.3.2 Determination of the Electrodes Distance and Optimization of Corona Current

The determination of the distance between the corona and collection electrodes has been analyzed in this part of our experiment, while optimizing the corona current stability after the application of high voltage at our corona electrode and operating our system under several aerosol sample flow rates (2-5 l/min). Concentration-based collection efficiency is a function of particle size, operational flow rates, the electrical charges of the particles and the characteristics of the electric field that is developed between the corona and collection electrodes. From previous experiments while developing our pre-concentration system, we had observed very stable corona for electrode distances 3-5 mm, for both 0.5 mm and 1.5785 mm electrodes. Several configurations were tested, but the most stable and promising results were obtained for an electrodes distance of 4mm. As discussed earlier, the corona electrode was 1mm outside of the Vespel nozzle, while the collection electrode was 1 mm outside of the dielectric sheath placed in the lower part of our pre-concentrator collection area, thus providing us with stable corona current, from a few seconds to several minutes of operating the system. For the 0.5 mm flat collection electrode, we observed stable corona current for a range of 1-10 μA, while high voltage of 4- 5.4 kV was applied to the corona electrode. Even though the stability of the corona current has been satisfactory, its duration for this case has been in the range of 1-2 minutes. For the 1.5785 mm flat collection electrode, we observed stable corona current for a range of 1- 19 μA, while high
voltage of 3.1-8 kV was applied to the corona electrode. The corona current in this case has been very stable and manageable for a broader range of high voltage values. The relationship between the high voltage and the corona current, for both 0.5 mm and 1.5785 mm electrodes can be seen in Figure 7.

![Graph showing the relationship between high voltage and corona current.](image)

**Fig. 7** Relationship between the high voltage and the corona current.
3.3.3 Determination of the Pre-Concentrator Collection Efficiency

It was desirable that a large percentage of the particles entering our pre-concentrator collection area be deposited on the flat tip of our collection electrodes. The particle mass that is collected on the collection electrode can be given by:

\[ m_p = Q_f t_c \int_{d_{p\text{min}}}^{d_{p\text{max}}} n(d_p) \left( \frac{\pi}{6} d_p^3 \rho_p \right) n(d_p) \, d d_p \]  

(1)

Where \( \eta(d_p) \) is the size-dependent collection efficiency of particles, \( Q_f \) is the aerosol volumetric flow rate, \( \rho_p \) is the particle density, \( t_c \) is the collection time on the electrode tip and \( n(d_p) \) is the number-based size distribution of the aerosol that can be given by:

\[ n(d_p) = \frac{N_t}{\sqrt{2\pi} d_p \ln \sigma_g} \exp\left(-\frac{(\ln d_p - \ln d_{pg})^2}{2(\ln \sigma_g)^2}\right) \]  

(2)

Where \( N_t \) is the total particle concentration and \( d_{pg} \) is the mean diameter.

As mentioned earlier, the concentration-based collection efficiency is a function of particle size, operational flow rates, electrical charges of the particles and the characteristics of the electric field that is developed between the corona and collection electrodes. Particle concentration-based size-dependent collection efficiencies (\( \eta(d_p) \)) of the collection electrodes were estimated by measuring the particle number concentration upstream and downstream of the collection unit by the use of a CPC, with and without presence of an electric field across the two electrodes. The expressions providing us with these values can be given by:

\[ \eta(d_p)_{\text{HV on}} = \frac{N_{\text{HV in}} - N_{\text{HV out}}}{N_{\text{HV in}}} \]  

(3)
\[ \eta(dp)_{\text{HV off}} = \frac{N_{\text{in}}^{V=0} - N_{\text{out}}^{V=0}}{N_{\text{in}}^{V=0}} \] (4)

Where \( N \) is the particle concentration for each case.

A matter of significant importance is the diffusion of the aerosol particles to the tubing walls. Mathematical solutions have been acquired, assuming laminar flow and circular cross section of the tubing. The dimensionless parameter \( \mu \) can be used as a function of the fraction of entering particles that exit the tubing of diameter \( d_t \):

\[ \mu = \frac{4DL}{\pi d_t^2 \bar{U}} \] (5)

Where \( D \) is the particles diffusion coefficient, \( L \) is the tube length and \( \bar{U} \) is the average flow velocity through the tubing.

The penetration \( P \) (fraction of entering particles that exit through the tubing) can be given as a function of \( \mu \) with an accuracy of 1%, for all \( \mu \) values.

\[ P = \frac{n_{\text{out}}}{n_{\text{in}}} = 1 - 5.5\mu^{2/3} + 3.77\mu \quad \text{for} \ \mu < 0.009 \] (6)

\[ P = 0.819 \exp(-11.5\mu) + 0.0975 \exp(-70.1\mu) \quad \text{for} \ \mu \geq 0.009 \] (7)

The particle losses inside the tubing walls used in our experimental design have been calculated for both operational flow rates (2 and 5 l/min), for both upstream and downstream configurations and have been incorporated to the calculations made for the concentration-based collection efficiency values. The penetration \( P \) for these cases can be seen in Figure 8.
Fig. 8 Penetration for different experimental parameters.

Experimental concentration-based collection efficiencies have been obtained over the size range of 50-1000 nm by the use of DMA-classified particles, under different conditions as described earlier. In most cases studied, the collection efficiency remained stable during the entire duration of particle collection, for the entire particle size range. The collection efficiency with the application of high voltage in the corona electrode ranged from 33%-60%, whereas we still had a collection of particles in the area of 15%-20%, without the application of high voltage in the corona electrode. Our collection and analysis system in this study was designed and optimized for sub-micrometer particles. The experimental results for each case obtained in this study are
shown later in Figures 10-20, as compared to the mass-based collection efficiency values after IC analysis.

It was validated that the corona didn’t generate any extra particles. However, the fore-mentioned results do not include the particle losses to regions outside the flat electrode tips in the electric field presence, or possible losses in the side walls of our collection electrodes. For the determination of the second aspect, we developed a technique to enable us calculating the losses in the side walls of the collection electrodes, as well as to determine the amount of particulate mass deposited on our collection electrodes tips. For different flow rates (2 and 5 l/min) and particle chargers (Po$_{210}$ and Pen-Ray UV Lamp), we collected particulate mass on the tip of our collection electrodes for a time period of 30 minutes. The collection electrodes were firstly placed bare, being 1 mm outside the sheath, and then placed with a thin Teflon layer wrapping around the part exiting the sheath, only leaving their flat tips exposed. The technique used is shown in Figure 9.

![Fig. 9a, b](image)

**Fig. 9a, b** Collection electrode with and without Teflon layer.

This procedure was repeated with and without the application of high voltage on the corona electrode. After the collection of particles on the electrodes, they were very carefully removed from our pre-concentrator collection
and analysis area and placed in a custom made vial system containing of 3 ml of ultrapure DI water (Fisher Scientific), ensuring that only the electrode part being exposed in the collection experiment is in the liquid. The vials containing the samples were then sonicated (Model ME4.6, Mettler Electronics Corp., Anaheim, CA) for a time period of 15 minutes. The electrodes were then removed, and the liquid samples were momentarily stored in a refrigerator operating at 3 °C for about 24 hours. To obtain information about the particulate mass entering and exiting our pre-concentrator chamber, we developed a technique using PTFE filter membranes (Millipore, Billerica, MA). In this study, the filter membranes used had a diameter of 25 mm and 0.5 μm pore size. We installed two 25 mm filter cassettes (Omega Specialty Instrument Co., Chelmsford, MA), containing of a 25 mm cellulose support pad (Omega Specialty Instrument Co.) and the PTFE filter membranes, in-line to the inlet and outlet of the pre-concentration system. We once more generated DMA-classified particles, for a time period of 30 minutes, thus collecting particulate mass in the filters, for the same conditions and experimental design configurations as mentioned. The filter samples were then carefully removed from the cassettes and after being liquidated with 0.1 ml of ethanol, they were placed in 3ml vials containing ultrapure DI water (Fisher Scientific). PTFE filter membranes are hydrophobic, thus demanding addition of small amounts of ethanol or other wetting agents to aid the wetting procedure. The liquid samples containing the filter membranes were sonicated for 15 minutes, followed by stirring for 15 minutes. The filter membranes when then removed from the vials and the liquid samples were stored in a refrigerator
operating at 3 °C for about 24 hours. We also collected three filter samples which have been induced by a NIST traceable standard sulfate (SO₄²⁻) solution (Sigma-Aldrich) of known SO₄²⁻ mass, so as to obtain valuable information about the filter extraction efficiency. These collected samples were analyzed using an IC setup as described earlier. The schematic of the IC operational model is shown in Figure 10.
The objective of this analysis was to determine concentrations of SO$_4^{2-}$ in our liquid samples. Initially, a NIST traceable SO$_4^{2-}$ standard solution for IC...
(Sigma-Aldrich) of 1000 mg/l ± 4 mg/l has been obtained, and five different working standard solutions (0.01 mg/l – 2 mg/l) were prepared from the standard solution and diluted in Milli-Q water (Millipore, Billerica, MA) in 3 ml vials. A second working standard of 5 mg/l has also been prepared in order to perform a standard check evaluation. One litter of 38 mM potassium hydroxide (KOH) eluent solution has been prepared for the IC operation. The working standard of 0.01 mg/l was injected four times, whereas the working standards of 0.05 mg/l – 2 mg/l were each injected once. Each of our liquid samples obtained from the mass collected on the collection electrodes as well as the samples obtained by filtration were then injected thrice. Milli-Q water was used as blank and injected once more, and the 0.1 mg/l working standard was finally injected once to perform a standard check evaluation. When the ions of each sample passed through the detector, a peak formed in each graph obtained from the PeakNet software. The areas under the peaks were proportional to the amount of SO\textsubscript{4}^{2-} ions and were used to generate the instrument calibration curve. The calibration curve for our experiment is shown in Figure 11.
The calibration curve was constructed using five different working standard solutions with concentrations in the range of 0.01 mg/l – 2 mg/l, by plotting the area of peak as a function of the sulfate concentration in our samples. The calibration curve was linear with a regression coefficient of 0.9994 and a slope of 0.393. The method detection limit (MDL) has been calculated by using the standard deviation determined from the lowest standard concentration and is given by:

$$MDL = S \times t^{99\%}, n = 5 \quad (8)$$
Where $S$ is the standard deviation of the lowest standard concentration used (0.01 mg/l) and $t$ is the researcher’s value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

In our case studied, the MDL for $\text{SO}_4^{2-}$ detection was 10.3934 μg/l. After obtaining the values of $\text{SO}_4^{2-}$ mass detected in our liquid samples from the collection electrodes and filters, we were able to calculate the mass-based collection efficiency for each case. The mass-based collection efficiency after the application of high voltage at the corona electrode, can be given by:

$$\eta_m(d_p)_{HV_{on}} = \frac{m_p(\text{in}) - m_p(\text{tip})_{HV_{on}}}{m_p(\text{in})} \quad (9)$$

Where $m_p(\text{in})$ is the mass entering our pre-concentrator system, as collected from the filter sample, and $m_p(\text{tip})_{HV_{on}}$ is the mass deposited on the collection electrode flat tip, after the application of high voltage in the corona electrode. The mass-based collection efficiency without the application of high voltage at the corona electrode, can be given by:

$$\eta_m(d_p)_{V=0} = \frac{m_p(\text{in}) - m_p(\text{tip})_{V=0}}{m_p(\text{in})} \quad (10)$$

Where $m_p(\text{tip})_{V=0}$ is the mass deposited on the collection electrode flat tip, without the application of high voltage at the corona electrode. Another significant area of interest in this study was to calculate the particulate matter loss in the collection electrodes side walls, with and without the application of high voltage at the corona electrode. The mass loss at the side walls after the application of high voltage at the corona electrode can be given by:

$$\text{Loss}(d_p)_{HV_{on}} = \frac{m_p(\text{tip})_{HV_{on}} - m_p(\text{tip})_{HV_{on}(teflon)}}{m_p(\text{tip})_{HV_{on}}}, \quad (11)$$
Where $m_{p}(tip)_{H_{V_{on}}}$(teflon) is the mass collected on the tip of our collection electrode, with the introduction of a Teflon wrapping around it, to ensure the deposition of particulate matter only at the flat electrode tip, when high voltage has been applied at the corona electrode. The mass loss at the side walls without the application of high voltage in the corona electrode can be given by:

$$Loss(d_p)_{V=0} = \frac{m_{p}(tip)_{V=0} - m_{p}(tip)_{V=0}(teflon)}{m_{p}(tip)_{V=0}}$$

(12)

Where $m_{p}(tip)_{V=0}(teflon)$ is the mass collected on the tip of our collection electrode, with the introduction of a Teflon wrapping around it, to ensure the deposition of particulate matter only at the flat electrode tip, without the application of high voltage at the corona electrode. The filter extraction efficiency has proven to be very high (~98%) and the particulate mass loses of ~2% were included in our calculation for the mass-based collection efficiency values.

Experimental mass-based collection efficiencies have been obtained over the size range of 50-1000 nm by the use of DMA-classified particles, under different conditions as described earlier. In most cases studied, the collection efficiency remained stable during the entire duration of particle collection, for the entire particle size range. The collection efficiency with the application of high voltage in the corona electrode ranged from ~35%-65%, whereas we still had a collection of particles in the area of ~12%-25%, without the application of high voltage in the corona electrode. The experimental concentration-based collection efficiency values obtained came to very close agreement to the mass-based collection efficiency values obtained after IC analysis. The particulate mass losses at the side walls of the collection electrode after the application of high voltage at the corona electrode were in the range of 8%-17%, whereas the particulate mass losses at the side walls of the collection electrode without the application of high
voltage at the corona electrode were in the range of 3%-15%. The comparison of the results obtained for the collection efficiency and mass losses for each set of experimental conditions are shown in Figures 12-23.
Charger: Po$^{210}$
Nozzle Diameter: 2 mm
I= 5 µA
HV= 5.1 kV
Electrode Diameter= 1.5785 mm
Q= 5 l/min

Fig. 12,13. Collection efficiencies and mass losses for Q= 5 l/min and Po$^{210}$ charger.
Fig. 14,15. Collection efficiencies and mass losses for Q= 5 l/min and UV charger.
Fig. 16, 17. Collection efficiencies and mass losses for Q= 2 l/min and Po\textsuperscript{210} charger.
Fig. 18, 19. Collection efficiencies and mass losses for Q = 2 l/min and UV charger.
Fig. 20, 21. Collection efficiencies and mass losses for Q= 5 l/min and Po\textsuperscript{210} charger.
Fig. 22, 23. Collection efficiencies and mass losses for Q= 5 l/min and UV charger.
3.3.4 Scanning Electron Microscopy Analysis

After the determination of the concentration and mass-based collection efficiencies of our pre-concentrator, we performed IC analysis to obtain information about the particulate mass losses on the side walls of our collection electrodes. A second quantitative method has been used to verify our results. We first aerosolized green fluorescent polystyrene latex (PSL) particles of known diameter (d=2μm) (Thermo Scientific, Fremont, CA, USA) and used the 1.5785 mm collection electrode, for collection of particles from 0-45 minutes, to obtain information about the particle time-dependent deposition and distribution on the electrode flat tip. The collection electrode samples were analyzed using a SEM (Model S-3000N, Hitachi Science Systems) providing us with an optical representation of the time-dependent particle deposition and distribution on the electrode. The resulting images showed a quantitative relationship of time vs particle deposition, as the density of particles deposited on the tip was increasing for the increase of the collection time period. The distribution of particles was homogeneous throughout the biggest part of the flat electrode tip surface, showing a relatively higher concentration in the central part. The choice of larger particles(d=2μm) and the 1.5785 mm collection electrode was made for better optical analysis, bigger collection surface area and accuracy at our measurements. The images obtained presenting the collection electrode at 0 minutes are shown in Figures 24 a, b:
Fig. 24a, b  The collection electrode at 0 minutes.

The images obtained presenting the particle distribution on the electrode surface after a collecting period of 5 minutes are shown in Figures 25 a, b:
Fig. 25 a, b  The collection electrode after 5 minutes of particle collection.
The images obtained presenting the particle distribution on the electrode surface after a collecting period of 10 minutes are shown in Figures 26 a, b:

**Fig. 26 a, b** The collection electrode after 10 minutes of particle collection.
The images obtained presenting the particle distribution on the electrode surface after a collecting period of 20 minutes are shown in Figures 27 a, b:

![Image of electrode after 20 minutes collection](image1)

**Fig. 27 a, b** The collection electrode after 20 minutes of particle collection.

The images obtained presenting the particle distribution on the electrode surface after a collecting period of 25 minutes are shown in Figures 28 a, b:
**Fig. 28 a, b** The collection electrode after 25 minutes of particle collection.

The images obtained presenting the particle distribution on the electrode surface after a collecting period of 30 minutes are shown in Figures 29 a, b:
The collection electrode after 30 minutes of particle collection.

The images obtained presenting the particle distribution on the electrode surface after a collecting period of 45 minutes are shown in Figures 30 a, b:
We then aerosolized green fluorescent polystyrene latex (PSL) particles of known diameter (d=2μm) (Thermo Scientific, Fremont, CA, USA) and used the 1.5785 mm collection electrode, for collection of particles for a time period of 30 minutes, after the application of high voltage at the corona electrode and with the

Fig. 30 a, b  The collection electrode after 45 minutes of particle collection.
electrode tip being 1 mm outside of the sheath, to obtain information on the ratio of particles deposited on the flat electrode surface over the particles deposited on the electrode side walls. The images were then analyzed using the ImageJ software for better calculation of this ratio. Analysis showed a deposition ratio of 12:1, thus showing that we have a particulate mass loss of 8.3% at the electrode side walls. This value is within the range of the experimental values obtained earlier after IC analysis (8%-17%). The images presenting the particle distribution on the flat electrode surface after a collection period of 30 minutes are shown in Figures 31 a, b, c.
Fig. 31 a, b, c  The particle distribution on the flat electrode surface after a collection period of 30 minutes.

The images presenting the particle distribution on the electrode side walls surface after a collection period of 30 minutes are shown in Figures 32 a, b.
Fig. 32 a, b  The particle distribution on the electrode side walls surface after a collection period of 30 minutes.
3.3.5 Performance Characteristics of the Pen-Ray UV Lamp Charger

In this study as discussed earlier, we used a Pen-Ray UV lamp aerosol charger, for DMA-classified particles entering our pre-concentrator system. The UV charger was designed and built following the specifications proposed by Li and Chen (2011). The quartz tube was about 3 in. long, surrounded by four low pressure Hg lamps with a 0.94 in. lighted length (UVP Model 90-0033-01, Upland, CA, USA). A PTFE 3 in. cuboid case with an 1 in. aluminum ending (outlet area), having an aerosol inlet and outlet at the its ends, was used to enclose the Hg lamps and quartz tube, preventing us from UV light exposure and allowing aerosol transport through the tube, without contacting the Hg lamps, was developed. An ion trap at the outlet area of the quartz tube was used for minimization of the recombination of positively charged particles and negative ions. In this study, the operational flow rates were 2 and 5 l/min, and the ion trap voltage was -10 V. The Pen Type UV lamp charger was powered by two power supply units (Model P/N 99-0055-01, UVP, Upland, CA, USA). A schematic diagram of the UV charger is shown in Figure 33. We first performed a time-dependent temperature check for our charger, to reassure avoiding overheating. The maximum operational time period for this study was 30 minutes and the results obtained are shown in Figure 34. The cool-down time for the charger to go back to room temperature (24.6 °C) was 35 minutes.
Fig. 33  Schematic diagram of the UV charger.

Fig. 34  Time vs Temperature relationship for UV charger.
To characterize the particle losses within the charger, sub-micrometer \((\text{NH}_4)_2 \text{SO}_4\) particles were generated from our standard stock solution, followed by DMA classification (50-700 nm). Two sequentially placed CPCs were used, before the charger inlet and after the charger outlet, so as to measure particle concentrations entering and exiting the charger. The particle percentage lost within the charger was within the acceptable range, with an average of \(5\%\). The particle loss percentages for different particle size diameters is shown in Figure 35.

**Fig. 35** The UV charger particle loss percentages for different particle size diameters
Characterization of the UV charger charging efficiency was a key parameter for the performance of our instrument. We counted the percentage of entering neutral particles acquiring electrical charges in the charger, without regards on the losses within the charger or their exit from it. We used the experimental setup used by Li and Chen (2011), containing a needle valve, the UV charger, two ESPs and a CPC. The aerosol flow rate entering the charger was 5 l/min, while the CPC operated at the low flow configuration of 0.3 l/min. The charging efficiency was calculated using the method of Romay and Pui (1992) given by:

$$\eta = 1 - \frac{N_1}{N_2} \quad (13)$$

Where $N_1$ and $N_2$ were the particle number concentrations measured with the CPC, downstream of the first ESP, with and without the application of high voltage.

For characterization of the UV Charger charge per particle values, we used an aerosol electrometer (Model 3068B, TSI Inc.), that provided us with accurate and sensitive measurements for total net charge of aerosol particles. With known particle charge distribution, we can accurately calculate the particle concentration from the charge measurements. We obtained data for the current vs $d_p$ for DMA-classified particles (100-1000 nm). The electrometer sample flow rate was 1.5 l/min, whereas we had a total flow rate of 5 l/min through the UV
charger. The experimental results obtained for the size-dependent UV charger charging efficiency and charge per particle are shown in Figure 36.

**Fig. 36** UV charger size-dependent charging efficiency and charge per particle.
3.4 Conclusions

A new approach for characterizing the collection efficiency and losses of airborne particles on a tip of a micro-electrode has been developed for aerosol analysis using an aerosol pre-concentration method. That method has been analytically (IC) and quantitatively (SEM) confirmed. Our methodology allows efficient and focused collection of aerosol particles on a fine micro-electrode tip using an electrostatic technique, for a broad range of particle sizes (50-1000 nm) and for collection times from a few to many minutes. The pre-concentrator performance characteristics have been optimized and its collection efficiency has been experimentally evaluated, based both in number particle concentrations and particle mass collected. We found that our method can collect ambient atmospheric particles on the tip of a micro-electrode with high efficiency and uniformity, whereas the reproducibility of the results obtained ranged from 1%-10%. These experimental results indicate that our method can be a promising tool for collecting and sampling of atmospheric aerosols, for various aspects of chemical analysis. The collection of airborne particles using the electrostatic technique allows using higher system operational flow rates, with a minimum pressure drop, while the pre-concentrator chamber can be contained in a volume of a few cm$^3$, makes our pre-concentrator ideal for use in a field-portable aerosol measurement instrument. Our pre-concentrator system for collection of aerosol particles is a simple yet up-and-coming methodology allowing the buildup for a near-real time field-portable instrument using optical spectroscopies for aerosol measurements.
CHAPTER 4: CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

This chapter demonstrates a summary of conclusions from Chapters 2 and 3 and presents some suggestions for future work. The significant contributions of this thesis have also been included.

4.1 Conclusions and Suggestions for Future Work

In Chapter 2, a microelectrode system has been used for characterization of the effects of generation of pulsed spark discharge across the electrodes on the spark footprint coverage radius percentage and footprint size. It was shown that for different electrode distances, pulse energy setpoints and electrode angles, the spark footprint radius coverage percentage was very high, with the experimental results ranging from 70%-100%. Detailed analysis has been also performed to obtain useful information on the spark footprint size diameter, especially for coaxial placement of our electrodes and different electrode distances, and pulse numbers and energy setpoints. For this case, the spark footprint size diameter results obtained ranged from 0.3 mm-2.4 mm. Repeatability of the experimental results were very high, thus providing accuracy and robustness to our method. Characterization of the effects of generation of pulsed spark discharge across the electrodes on the spark footprint coverage radius percentage and footprint size, provided us with an estimation for the collection electrode size used in the development of our pre-concentrator for collection and analysis of sub-micrometer aerosol particles on the tip of a fine microelectrode, after the application of high voltage.
The future work in this area can be aimed at characterizing the effects of generation of pulsed spark discharge across the electrodes on the spark footprint coverage radius percentage and footprint size for a wider variety of electrode angles and numbers of pulses. Optical representation of the footprints could also be used as a dependable method for footprint coverage and size.

Chapter 3 presented a study on the design of a pre-concentrator for the collection and analysis of sub-micrometer aerosol particles. Several experimental characteristics of our apparatus have been analyzed and optimized for further experimental analysis, including the pre-concentrator inlet nozzle losses, the electrodes distance and the corona current behavior after the application of high voltage at the corona needle. The concentration-based particle collection efficiency has been studied, for a broad range of particle sizes (50-1000 nm), different collection electrode sizes and system flow rates, and for collection times from a few to many minutes. A second method using analysis by IC was used to compare our findings. The experimental results between these two methods showed great consistency and their repeatability was very high. We achieved satisfactory collection efficiency values in the range of 35%-65%, after the application of high voltage in the corona electrode, while we still collected 12%-25% of particles entering the chamber, without the application of high voltage in the corona electrode. A two-method approach used to determine the particulate mass losses at the side walls of the collection electrode. After IC analysis, the
particulate mass losses at the side walls of the collection electrode after the application of high voltage at the corona electrode were in the range of 8%-17%, whereas the particulate mass losses at the side walls of the collection electrode without the application of high voltage at the corona electrode were in the range of 3%-15%. SEM optical analysis showed that we have a particulate mass loss of ~8.3% at the electrode side walls, a value within the experimental results range obtained by IC analysis. The methods used showed that our pre-concentrator system for collection of aerosol particles is a simple, robust and reliable technique which allows its introduction in a near-real time field-portable instrument using optical spectroscopies for aerosol measurements.

Future studies can be performed on the stabilization of the corona current after the application of high voltage, for a broader voltage range, after the use of a smaller collection electrode (d<0.5 mm). Further research on the optimization of the collection efficiency can also be conducted, with the minimization of particulate losses within our system to be the main objective. Finally, future studies could be performed on particle size diameters covering a broader range, so as to determine the pre-concentrator performance characteristics from the lower nanoscale to low micrometer particles.
4.2 Significant Contributions of this Thesis

The significant contributions of this thesis can be summarized in the following:

1. The design of the Pre-Concentrator system
2. The experimental evaluation of the Pre-Concentrator system
3. The optimization of the Pre-Concentrator performance characteristics
4. Crosschecking of the Pre-Concentrator performance characteristics using IC analysis
5. Crosschecking of the Pre-Concentrator performance characteristics using SEM analysis
6. The ability for future use of the Pre-Concentrator system in a near-real time and field portable instrument
References


dose for acute lung inflammation in mice. Environmental Health Perspectives, 114:328–333.


