DEVELOPMENT AND TESTING OF A NOVEL SIZE-SELECTIVE PERSONAL SAMPLER
FOR INORGANIC ACIDIC MISTS AND GASES

By

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To my family, friends, and advisors
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Abstract of Dissertation Presented to the Graduate School
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DEVELOPMENT AND TESTING OF A NOVEL SIZE-SELECTIVE PERSONAL SAMPLER
FOR INORGANIC ACIDIC MISTS AND GASES

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Strong inorganic acid mists containing sulfuric acid have been identified as human
carcinogen, and sulfuric acid mists have adverse health effect on the thoracic region. The NIOSH
Method 7908 open-faced sampler, which replaces the conventional NIOSH Method 7903 glass
tube sampler due to chemical interference, is the current standard method for sulfuric acid mists
in the workplace. However, the NIOSH Method 7908 sampler does not follow the
ISO/CEN/ACGIH defined thoracic convention; thus, the real exposure to the sulfuric acid mists
(i.e. thoracic mass) is unknown. In addition, this sampler cannot sample sulfur dioxide gas which
widely co-exists with sulfuric acidic mists in phosphate fertilizer manufacturing facilities.
Therefore, the goal of this dissertation was to develop a new personal sampler system to
simultaneously sample sulfuric acidic mists and sulfur dioxide gas.

Three sets of studies were conducted to achieve the goal. First, before evaluating the
penetration curve of the new sampler, the calibration of optical diameter measured by an Optical
Particle Counter (OPC) to its aerodynamic diameter was carried out. Second, the feasibility of
cellulose filters to sample sulfuric acid mists in order to minimize the cost without sacrificing
performance was evaluated. Third, the personal sampler system was designed, and its
performance was experimentally evaluated in a laboratory chamber and compared with standard
methods. Consistency of the penetration curve to ISO/CEN/ACGIH thoracic curve and capacity for collecting SO$_2$ were assessed.

The assumption that the optical diameter equals the volume equivalent diameter is only valid if the aerosol has the same optical properties as standard polystyrene (PSL) particles used for OPC calibration. For oleic acid aerosol, the optical diameter was illustrated to be less than the derived volume equivalent diameter because its refractive index ($m = 1.46$) is less than that of PSL ($m = 1.60$). While the refractive index of sodium chloride ($m = 1.54$) is close to that of PSL, a much larger optical diameter of sodium chloride than its volume equivalent diameter was observed due to its irregular crystallography. Therefore, experimental regression equations were developed to convert an optical diameter to its aerodynamic diameter.

Cellulose filters such as Whatman grade 540, 541, and 542 filters were investigated for their feasibility to sample sulfuric acid mists. 30-minute collection efficiency tests showed low collection efficiency for Whatman grade 540 and 541 filters while Whatman grade 542 filter exhibited 95% collection efficiency over eight hours because of its smaller pore size. The high collection efficiency was at the expense of a high pressure drop; however, the pressure drop was still under the backpressure limit for most personal pumps. The integrity test showed the hardened cellulose filters can maintain integrity for more than seven days.

A size-selective sampler system was designed to follow the thoracic convention for sampling sulfuric acid with minimum interferences in an occupational environment. This sampler system consists of (1) a parallel impactor for classifying aerosol by size following the ISO/CEN/ACGIH defined human thoracic fraction, (2) a cellulose filter to collect the residual acid mist but allowing penetration of sulfur dioxide gas, and (3) an accordion-shaped porous membrane denuder (aPMD) for adsorbing the penetrating sulfur dioxide gas. The laboratory
testing demonstrated the penetration curve of the sampler agreed well with the defined thoracic fraction. The aPMDs maintained a gas collection efficiency greater than 95% for 4 hours when sampling 8.6 ppm of sulfur dioxide gas. Testing of the entire sampler with a mixture of sulfuric acid mist and sulfur dioxide gas showed the system could sample both with negligible interference.
CHAPTER 1
INTRODUCTION

Emission of Sulfuric Acid Mists and Sulfur Dioxide in Fertilizer Manufacturing Facilities

About 200 million tons of sulfuric acid (H$_2$SO$_4$) are used each year in the world, mostly by the steel, fertilizer, and petroleum industries (King et al. 2013). The production of H$_2$SO$_4$ requires oxidation and hydration of sulfur dioxide (SO$_2$). Take phosphate industries for example, the key reaction to produce fertilizer (e.g., superphosphate) from “phosphate rock” (fluorapatite, Ca$_5$(PO$_4$)$_3$F) is

\[
2\text{Ca}_5(\text{PO}_4)_3\text{F} + 7\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O} \rightarrow 7\text{CaSO}_4 + 3\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + 2\text{HF}
\] (1-1)

Sulfuric acid is manufactured by the following processes:

A-1) Production of sulfur dioxide:

\[\text{S} + \text{O}_2 \rightarrow \text{SO}_2 \quad \Delta H = -300 \text{ kJ mol}^{-1} \] (1-2)

Elemental sulfur is melted to remove the impurity. The melted sulfur is burnt in excess air to produce 8 – 9% sulfur dioxide in a sulfur burner (Figure 1-1).

A-2) Conversion to sulfur trioxide:

\[\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 \quad \Delta H = -100 \text{ kJ mol}^{-1} \] (1-3)

SO$_3$ is generated by reacting SO$_2$ with oxygen over a catalyst (e.g., vanadium pentoxide on a base support) as shown in Figure 1-1. This process is operated in a four-stage converter. Because this reaction is exothermic, temperature decreases in favor of the SO$_3$ production. However, the reaction rate depends on the temperature, and a minimum temperature is required. Thus, the operating temperature is maintained between 400 – 500 °C.

A-3) Absorption of SO$_3$ to form sulfuric acid:
\[ SO_3 + H_2O \rightarrow H_2SO_4 \quad \Delta H = -200 \text{ kJ mol}^{-1} \]  \hfill (1-4)

The reaction occurs in an absorption tower (Figure 1-1). The \( H_2SO_4 \) concentration is maintained at 98% because 98% \( H_2SO_4 \) has the lowest vapor pressure and acid mist does not escape to the atmosphere. The 98% \( H_2SO_4 \) is produced on site at phosphate processing plants in the U.S.

Hsu et al. (2007a) reported high aerosol mass concentration but low sulfate concentration observed in the attack tank area, belt or rotating table filter floor, and sulfuric acid truck loading/unloading station in phosphate fertilizer manufacturing facilities in Florida. However, only in \( H_2SO_4 \) pump tank areas, \( H_2SO_4 \) accounts for the major aerosol mass concentration. The most likely cause for the high \( H_2SO_4 \) concentrations is the leakage of \( SO_3 \). \( SO_3 \) quickly reacts with water in air to form \( H_2SO_4 \) mist in 2 milliseconds \((k = 1.2 \times 10^{-15}, \text{Reiner and Arnold (1994)})\) with 50% RH in ambient environment. Another process with possible higher concentration of \( H_2SO_4 \) and \( SO_2 \) is the area close to the \( SO_2 \) converter. In step A-2 (Conversion to sulfur trioxide), 69% – 81% conversion is achieved in a \( SO_2 \) converter (Fogler 2010). \( SO_2 \) and \( SO_3 \) gas leak from the system may result in a mixture of \( SO_2 \) and \( H_2SO_4 \) mists.

**Health Effects of Sulfuric Acid Mists and Sulfur Dioxide**

\( H_2SO_4 \) mists and \( SO_2 \) incidentally released into the air during the manufacturing processes irritate people’s skin and eyes and damage their respiratory system. Strong inorganic acid mists containing sulfuric acid are identified as “human carcinogens” by the National Toxicology Program. The health effects of \( H_2SO_4 \) mist in the human respiratory tract is particle size dependent. Thoracic fraction (the mass fraction of inhaled particles penetrating beyond the larynx) matters for the human health risk assessment of \( H_2SO_4 \) mist. This is because the time for \( H_2SO_4 \) aerosol to reach its equilibrium size is shorter than the traveling time of an aerosol in the
upper respiratory system, indicating the acidic aerosol likely deposits in the upper respiratory tract, rather than the deeper alveolar region in a high RH environment. Also, H2SO4 mists are associated with larynx cancer but little association with nasal or lung cancer (Sathiakumar et al. 1997). Hence, the amount of H2SO4 deposited at the site of toxic action, the thorax, is of importance.

SO2 is readily soluble in the wet airways; thus, the exposure to SO2 is highly associated with adverse effects on the upper airways. The exposure to SO2 through nose leads to nasal symptoms and its resistance to the air flow increases. A study by Koenig (2010) showed 30-minute exposure to 2.5 – 12.5 ppm SO2 adversely alters mucociliary clearance as cigarette smoke and H2SO4 aerosol do. At 5 ppm, studies by Amdur et al. (1953) reported most people complained of dryness in the throat and the upper respiratory airways. The smell of 6 – 8 ppm of SO2 is perceptible (Amdur et al. 1953). The effects of SO2 on the lower airways are of substantial concern for people with asthma, and SO2 is related to increased risk of mortality. Adult subjects with asthma and/or allergy have decrements in lung functions during moderate exercise under 10-minute exposure to 1 or 0.5 ppm SO2. Mortality rate in SO2-polluted areas is higher than in non-polluted area in Japan (Koenig 2010).

The interaction of SO2 to metal oxide or the combination of SO2 and H2SO4 has negative effects on the lungs of animals. The fresh metal oxides from combustion may interact with SO2 to form sulfuric acid on the surface of metal oxides, which has strong effects on the physiology and structural integrity of guinea pigs’ lungs. The combination of SO2 and H2SO4 has more negative effects on breathing for guinea pigs while either SO2 or H2SO4 mist alone at the same amount has negligible effect (Amdur 1954).
National and International Regulations for Sulfuric Acid Mists and Sulfur Dioxide

To minimize workers’ exposure to H$_2$SO$_4$ mists, the Occupational Safety & Health Administration (OSHA) has established a Permissible Exposure Limit (PEL) – 8-hour Time Weighted Average (TWA) of 1 mg/m$^3$ for H$_2$SO$_4$ mist (OSHA 1989). Thus, the inhalable fraction of sulfuric mists is sampled based on this standard. However, the thoracic fraction is a better size-selective penetration curve for assessing the human exposure to H$_2$SO$_4$. In order to accurately measure the exposure, measurement methods should follow the thoracic convention.

The American Conference of Governmental Industrial Hygienists (ACGIH) has suggested a Threshold Limit Value (TLV) TWA of 0.2 mg/m$^3$ for thoracic fraction; in comparison, the European Union has a more stringent standard of 0.05 mg/m$^3$. Also, exposure limits for sulfuric acid mists in US, Canada, Brazil, and European Union (EU) have been standardized as thoracic mass (McGinnity and Nicol 2014).

For exposure in such a SO$_2$-rich environment, OSHA PEL for SO$_2$ is set as 5 ppm to protect workers from adverse health effects. NIOSH’s Recommended Exposure Limit (REL) is 2 ppm. ACGIH suggests a TLV of 2.5 ppm. Also, SO$_2$ is one of the six criteria air pollutants regulated by the Environmental Protection Agency.

Sampling Methods for H$_2$SO$_4$

Table 1-1 summarizes the key components of NIOSH Methods 7903 and 7908, OSHA ID 113, and OSHA ID 165SG which are the standard methods for sulfuric mist sampling (NIOSH 1994). These methods have limitations due to their sampler design. NIOSH Method 7903 was widely applied to sample inorganic acid including HF, HBr, HCl, HNO$_3$, H$_2$SO$_4$, and H$_3$PO$_4$. The sampler is made of a glass fiber plug as its front part to collect aerosols and silica gel at the back to adsorb acidic gases. However, this method has the following drawbacks: 1) its sampling efficiency decreases as aerosol size increases due to its tube inlet design, and it does not follow
the inhalable convention; 2) acidic gas, SO₂ for example, reacts with the glass fiber plug. If the acid on the plug is overlooked and discarded, acidic gas concentration is underestimated. If the plug is kept, it is impossible to distinguish whether the sulfur concentration comes from SO₂ gas or sulfate aerosol (Hsu et al. 2007b); 3) particles collected on the glass fiber plug may react with acidic gases, resulting in negative interference of the volatile acidic gases; 4) positive interference of mists may occur when acid mist and its corresponding salt (ex. H₂SO₄ vs. sulfate) co-exist and are analyzed for non-volatile acid; and 5) the residual sulfate in impure silica gel increases the background concentration, resulting in positive interference of sulfuric acid (Hsu et al. 2007b; Breuer and Howe 2006).

Due to the above-mentioned limitations, NIOSH Methods 7906, 7907, and 7908 have replaced NIOSH Method 7903 for different target pollutants. The new NIOSH Method 7908 focuses on merely sulfuric acid and phosphoric acid, while Method 7906 is for sampling particulate fluorides and hydrofluoric acid, and Method 7907 is for volatile acids including hydrochloric, nitric and hydrobromic acids. The NIOSH Method 7908 sampler uses only one 37-mm diameter quartz fiber or PTFE filter to collect H₂SO₄ or H₃PO₄ in workplaces. Collection efficiency > 95% over the range of 0.5 to 10 mg/m³ on PTFE filters and > 95% recovery over 4 weeks were reported (Breuer and Ashley 2014). The inhalable fraction of sulfuric and phosphoric acid aerosol can be collected by means of a pre-filter housed within an optional inhalable mist sampler. Also, SO₂ interference due to the reaction with sampling aerosol media should be negligible in phosphate fertilizer manufacturing facilities because glass fiber plugs are replaced by inert quartz or PTFE filters. Note that, like NIOSH Method 7903, particulate sulfate still gives positive interference when acid mist and corresponding salt co-exist (Breuer and
Ashley 2014). Inhalable mass can be collected by this method with an inhalable sampler inlet, but the health-related thoracic mass is still unknown.

Several thoracic samplers are available in the market. Maynard (1999) compared the penetration performance of six personal thoracic samplers under calm air conditions and concluded BGI GK 2.69 and modified SIMPEDS thoracic cyclone agree well with the thoracic convention. However, all of them are made by metal, which may suffer from acidic corrosion.

**Mist Sizing by an Optical Particle Counter**

Particle penetration to the thoracic region depends on particle size, which is commonly determined by a particle sizer. Because instant information of particle size greatly streamline the experiment, real-time particle sizers such as the Aerodynamic Particle Sizer (APS) and the Optical Particle Counter (OPC) are good candidates. APS measures the particles’ time-of-flight and determines the aerodynamic diameter accordingly, while OPC detects the magnitude of scattering light intensity and calibrates with reference particles to give the optical diameter.

Particle size in the thoracic convention refers to aerodynamic diameter. While the APS is a conventional method to give real-time particle counts and aerodynamic size (Peters et al. 2006), the OPC is an affordable alternative if the optical diameter could be converted to aerodynamic diameter. No theoretical approaches can satisfactorily convert optical diameter to aerodynamic diameter. Therefore, before evaluating samplers’ performance using an OPC, experimental calibration of the OPC is needed.

**Collection Medium for Sulfuric Acid Mists**

To overcome the chemical interference issue in the previous NIOSH Method 7903 that is currently abandoned, NIOSH Method 7908 specifies 37-mm diameter quartz fiber filter or 0.45 µm pore size PTFE filter to sample sulfuric acid mists (Breuer and Ashley 2014). The new method ensures the negligible chemical interference from sulfuric acid on PTFE or quartz filters.
However, for large-scale or long-term sampling programs, the expensive quartz and PTFE filters can add up to a significant cost compared to the cost of the glass fiber filter in NIOSH Method 7903. Thus, the alternative filters are expected to be inexpensive and the material is negligibly interfered by H₂SO₄. Cellulose filters might be a good candidate. The evaluation of their feasibility for H₂SO₄ mist sampling is needed.

**Sulfur Dioxide Sampling Methods for SO₂**

Liquid absorbers are the conventional and common method used by industrial hygienists to sample SO₂. By applying suction at the sampler outlet using a pump, air is drawn through a liquid absorber such as a bubbler, wherein SO₂ gas contacts with an alkaline solution and gets absorbed by chemical reaction. Absorption of gas by chemical reaction depends on the size of the air produced in the bubbler, the interaction of contaminants with reagent molecules, the rate of the reaction, and a sufficient excess of reagent solution (Brown and Monteith 2001). In most cases, the solution is sufficient and SO₂ rapidly reacts with alkali. Thus, complete collection can be achieved during the sampling. However, the method was questioned for its inconvenience and safety issues (Balya 1991).

Na₂CO₃ treated filters as a “dry” sampling technique is a common method to absorb SO₂ (NIOSH Method 6004). This method assumes that gases quickly dissolve to give a perfect solution by the chemical reaction (Brown and Monteith 2001). Such an impregnated filter works as an absorber wherein a small amount of liquid is distributed on a solid support (i.e., filter) with the help of a humectant (i.e., glycerol). Then, the SO₂ drawn through the treated filter is collected in the liquid as the impinger does. Because the liquid amount in the glycerol is in equilibrium with RH, RH influences the performance of the method. Huygen (1963) suggested that the RH should be > 30% for good collection efficiency. However, the outdoor RH > 30% is not always
the case in some dry places such as Arizona and New Mexico. RH also considerably drops if the indoor air becomes warmer before filtration (Huygen 1963).

Annular or honeycomb denuders are commercial samplers that are popular for multi-pollutant collection such as SO₂ and volatile nitric acid in the ambient environment. High efficiency and absorptive capacity are the advantages, and the denuder can readily be incorporated into an aerosol-gas sampling system. However, its bulky design and fragile glass of these denuders restrict their portability, which is an important concern for personal sampler design.

**Research Objectives**

The overall goal of this dissertation was to design and evaluate a novel personal sampler system to accurately measure the H₂SO₄ mists as thoracic mass and SO₂ gas simultaneously. First, before evaluating the penetration curve of the sampler, the calibration of optical diameter measured by OPC to its aerodynamic diameter is needed. The second objective was to evaluate the feasibility of cellulose filters to sample H₂SO₄ mists in order to minimize the cost without sacrificing performance. The third objective was to design the personal sampler system, and its performance was experimentally evaluated in a laboratory chamber and compared with standard methods. Consistency of the penetration curve to ISO/ACGIH/CEN thoracic curve and capacity for collecting SO₂ were assessed.
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</thead>
<tbody>
<tr>
<td>OSHA ID 113</td>
<td>Filter cassette</td>
<td>37mm, 0.8 µm mixed cellulose ester filter membrane</td>
<td>2</td>
<td>sulfate by IC</td>
<td>Underestimated sulfate by cassette inlet (Vincent 2007)</td>
</tr>
<tr>
<td>OSHA ID 165SG</td>
<td>Glass tube filled with sorbent</td>
<td>Silica gel</td>
<td>0.2</td>
<td>sulfate by IC</td>
<td>1. Decreasing sampling efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2. Sulfate artifact due to SO2 interference</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3. Co-existed particulate sulfate will give positive interference</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4. Residual sulfate in silica gel</td>
</tr>
<tr>
<td>NIOSH Method 7903</td>
<td>Glass tube filled with sorbent</td>
<td>Silica gel</td>
<td>0.45</td>
<td>sulfate by IC</td>
<td></td>
</tr>
<tr>
<td>NIOSH Method 7908</td>
<td>Filter cassette</td>
<td>Quartz or PTFE filter with 0.45 µm pore size</td>
<td>1 to 5</td>
<td>sulfate by IC</td>
<td>1. Inhalable fraction</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2. Co-existed particulate sulfate will give positive interference</td>
</tr>
</tbody>
</table>
Figure 1-1. Process flows of a sulfuric acid plant (Simpson and Petherick 2006).
CHAPTER 2
UPON CORRELATING DIAMETERS MEASURED BY OPTICAL PARTICLE COUNTERS
AND AERODYNAMIC PARTICLE SIZER

Background

Aerodynamic Particle Sizer (APS) is a commonly used real-time instrument due to its rapid, precise, and accurate measurement of aerodynamic particle size distribution, which is determined by quantifying the time-of-flight of particles traveling through a laser velocimeter (Baron 1986). While several problems in APS measurement have been reported, including error sizing in high Reynolds number, size shifting for liquid aerosol, and low aspiration efficiency (Baron et al. 2008; Rader et al. 1990; Volckens and Peters 2005), new models have resolved these issues.

APS is advantageous in aerodynamic size distribution measurement, but it is less affordable to some users. Optical particle counter (OPC), which has also been widely used in aerosol research, air pollution studies, and cleanroom monitoring, is an alternative aerosol sizing instrument because of its low cost, ability for real-time measurement, and portability (Kulkarni et al. 2011). Particle sizing using OPC is based on the principle of single particle elastic light scattering following the Mie theory (Heyder and Gebhart 1979). As the particle is illuminated by the incident radiation, a detector quantifies the intensity of the scattered light in an angular range, the signal of which is converted to equivalent optical diameter.

While convenient, the non-monotonic size dependence of the scattered light intensity, as well as the changing response with varying refractive index of different materials and shape factor of the particles of interest limit the sizing accuracy of an OPC (Szymanski et al. 2009). A

theoretical scattering light response by Mie theory is available, but OPCs are generally calibrated by solid, spherical, and non-absorptive polystyrene latex (PSL) particles as reference to obtain the relationship between the response and reference particle size (Liebhaber and Willeke 1993). However, particles in practical systems are usually non-spherical with various refractive indices depending on the particle materials, resulting in erroneous sizing (Sabbagh-Kupelwieser et al. 2011). The situation gets worse when the testing aerosol is absorptive. Liu et al. (1974a) measured coal dust samples with absorptive property (m = 1.54-0.5i) by an OPC and microscopic technique in parallel and found that particle size determined by the OPC is significantly smaller than the geometric size by the microscopic technique. This is because coal dust absorbs part of the light to yield a weaker light scattering response, resulting in an underestimate of the particle size.

A monotonic increase of the light intensity with an increasing particle size yields an ideal measurement. In reality, multi-valued responses may occur that make OPC’s particle sizing uncertain (Szymanski et al. 2009). A wide-angle scattering geometry can alleviate the situation because this design allows a more monotonic response curve, although it is at the expense of wider particle sizing channels (Szymanski et al. 2009). Note the above-mentioned situation is for non-absorptive particles. Particles with absorptive properties have a response curve that is monotonically smoother.

In spite of the above-mentioned limitation of OPCs, many studies make efforts to link optical diameter to aerodynamic diameter (Binnig et al. 2007; Friehmelt and Heidenreich 1999; Hinds and Kraske 1986; Marple and Rubow 1976). This is because aerodynamic diameter is more relevant for studies focusing on inhalation and health effects of particulate matter. Thus, OPC has been calibrated aerodynamically through theoretical and experimental approaches.
Hinds and Kraske (1986) performed a theoretical calibration by comparing the instrument-output particle size with the true size calculated according to the Mie theory. Nevertheless, this method is limited to spheres. Such a calibration for irregular shaped particles requires enormous computational effort and it is impossible for particles with an unknown refractive index. Marple and Rubow (1976) designed an impactor for calibrating OPC aerodynamically. This experimental method gives an accurate conversion from optical diameter to aerodynamic diameter, but the specific impactor is required for the calibration. Binnig et al. (2007) used a commercial PM$_{2.5}$ cyclone to calibrate PM$_{2.5}$ measured by an OPC, but calibration was done only for particles around 2.5 μm. Friehmelt and Heidenreich (1999) calibrated an OPC with an APS directly using monodisperse PSL and glycerine particles from 0.5 to 5 μm. The results of light scattering pulse height versus the volume equivalent diameter are useful for that specific OPC, but this pulse height vs diameter is not intuitive to users; what would benefit users is the relationship between optical and aerodynamic diameters that allows direct reference.

The objective of this chapter was to establish the relationship between the diameters measured by OPC and APS for liquid and solid particles. The relationship between the optical diameter and volume equivalent diameter was also investigated. Finally, a commercial parallel impactor following the respirable convention aerodynamically was applied to verify the calibration curve.

**Methods**

**Experimental Setup**

Figure 2-1 illustrates a schematic diagram of the experimental setup. Aerosol was introduced into a cylindrical test chamber made of stainless steel from the top with filtered air supplied by a compressed air cylinder. The chamber dimension was 41 cm in diameter and 71 cm in height. The corresponding air velocity through the chamber was approximately 3.8 mm/s
that satisfied calm air conditions (Vincent 2007). A honeycomb airflow straightener was installed close to the top of the chamber, and tests showed size distributions across the cross-section were nearly identical with the coefficient of variation in particle number concentration being < 3%. An OPC and an APS in parallel collected test aerosols through tubes from the chamber.

Mini Laser Aerosol Spectrometer (Mini-Las) 11-R (Grimm Technologies, Inc., Douglasville, GA, USA) is an OPC with time resolution of 6 seconds and size range from 0.25 to 32 μm in 31 channels. Running at 1.2 liter per minute (Lpm), Mini-Las 11-R uses light sources with a wavelength of 660 nm and measures the scattering light at 90°. Note that 11-R offers the size distribution in terms of optical diameter which is defined as the diameter of a particle having the same response in an instrument that optically detects PSL particles by their interaction with light (Kulkarni et al. 2011). On the other hand, TSI APS model 3321 (TSI, Inc., Shoreview MN, USA) provides size distributions from 0.5 to 20 μm in 52 channels in terms of aerodynamic diameter which is defined as the diameter of a spherical particle with a unit density that has the same settling velocity as the target particle (Hinds 1999).

Our new 11-R was calibrated by its manufacturer. The manufacturer reported that a reference unit was firstly calibrated by NIST traceable monodisperse PSL particles. Since the reference unit and the 11-R were manufactured identically, the scattering response should be identical. Then, the 11-R was calibrated by comparing with the reference unit using polydisperse dolomite particles in a Grimm Calibration Tower in a wide particle size range. The tolerance range was ± 3 % for particle number concentration ≥ 500 counts per liter. The sample flow range was also calibrated with a tolerance of 1.2 Lpm ± 5 %. The APS was also calibrated by its manufacturer. The sheath air flow rate was set to 4 ± 0.05 Lpm and 1 ± 0.05 Lpm for sampling
flow rate. The manufacture calibration was performed by relating the time-of-flight monodisperse PSL particles with 11 various known sizes (Peters et al. 2006).

**Procedures**

The test aerosol was generated using a Vibrating Orifice Aerosol Generator (VOAG, Model 3450, TSI, Inc., Shoreview MN, USA) with a liquid solution wherein the desired aerosol material was dissolved. The geometric particle size \(D_p, \text{ cm}\) can be estimated from the equation (Berglund and Liu 1973) by

\[
D_p = \left( \frac{6QC}{\pi f} \right)^{1/3}
\]

where \(Q, \text{ cm}^3/\text{s}\) is the liquid flow rate, \(C\) is the volumetric concentration of the solution, and \(f, \text{ Hz}\) is the frequency of the vibrating orifice.

The particles were electronically neutralized through a Kr-85 radiation source (TSI Model 3054) and the neutralized particles entered the chamber from the top. The operation setting included a dilution air flow rate of 30 Lpm, a disperse air flow rate of 1.5 Lpm, VOAG operating frequency of 40 kHz, and a syringe pump speed of \(8.2 \times 10^{-4} \text{ cm/s}\). NaCl and oleic acid were chosen as the testing materials for solid and liquid aerosol, respectively. Soluble NaCl and oleic acid are ideal for aerosol generation using VOAG. Oleic acid has less health concerns than traditional di(2-ethylhexyl)phthalate (DOP) (Hinds et al., 1983) and NaCl represents the very common sea salt aerosol in the ambient atmosphere. Note that crystallized NaCl was formed in this experiment because our experimental RH (12~37%) is much lower than the deliquescence RH of NaCl (75%). Material parameters that would affect the results include refractive index \((m_{\text{NaCl}} = 1.54, m_{\text{oleic acid}} = 1.46)\), particle density \((\rho_{\text{NaCl}} = 2.17 \text{ g/cm}^3, \rho_{\text{oleic acid}} = 0.895 \text{ g/cm}^3)\), and shape factor \((\chi_{\text{NaCl}} = 1.08, \chi_{\text{oleic acid}} = 1)\). Note that the aerosol number concentration in all tests
were maintained < 1000 counts/cm$^3$ to avoid particle coincidence error for the OPC and APS (Peters et al. 2006). The system was purged with filtered air for cleaning, and the sampling started 20 minutes after the system had achieved a steady-state condition. The OPC was set to sample every 6 seconds, and the results were averaged every 30 seconds corresponding to the 30-second measurement of the APS. For each particle size bin, each material was tested three times and three readings were recorded for each test.

To verify the effectiveness of the calibration regression equation, a commercial respirable personal parallel impactor (RPPI, SKC Inc, Eighty Four, PA) was applied as a reference because RPPI has been evaluated for its penetration curve as a function of aerodynamic diameter (Trakumas and Salter 2009). The penetration $P(D_{ae})$ as a function of aerodynamic diameter is defined as:

$$P(D_{ae}) = \frac{C_{down}}{C_{up}}$$

(2-2)

where $C_{down}$ is the downstream concentration of the RPPI, and $C_{up}$ is the upstream concentration of the RPPI. In addition to the RPPI mounted in the chamber, the experimental setup and test aerosol were identical to the above-mentioned comparison of Mini-Las 11-R to APS as illustrated in Figure 2-1, and the upstream and downstream concentrations were recorded accordingly. RPPI was designed to follow the respirable convention, to which we compared our experimental data. Note that the commercial sampler is configured with a base plate (filter holder) after the impactor for the time-integrated measurement of respirable particulate matter. When the commercial sampler was applied for real-time sampling, particles deposited in the interior wall of the base plate due to the impaction were so significant that the penetration was underestimated. This situation occurs when the ratio of the jet-to-plate distance ($S$) to the nozzle
width (W) is less than 5 (Hinds 1999). To avoid such an impaction, the S/W ratio was extended to 50 (S = 12.7 cm) in our test and the results showed no observable deposit.

**Data Analysis**

The aerosol size distribution is characterized by geometric mean diameter ($D_g$) and geometric standard deviation ($\sigma_g$) as:

\[
D^N_g = \prod_{i=1}^{m} D^0_i
\]

\[
\log \sigma_g = \sqrt{\frac{\sum n_i (\log D_i - \log D_g)^2}{N - 1}}
\]

where $D_i$ is midpoint particle size of $i^{th}$ channel in either optical or aerodynamic diameter, $m$ is the total size channel, $n_i$ is number of particles in size channel $i$, and $N$ is the total number of particles.

OPC exhibited multi-mode size distribution when monodisperse particles were generated in our testing system via VOAG although APS did not. For example, when oleic acid particles expected at 9 μm were generated, a major mode close to 9 μm was observed while a minor mode between 2-4 μm also occurred unexpectedly (Figure 2-2). The minor mode distribution might be due to the peripheral detection (Umhauer 1983). The measuring volume, where particles are illuminated by light sources and scattering light, is intended to be minimized to prevent coincidence counting error at high particle concentration. However, particles are more likely to move through the borders of the measuring volume when a tiny measuring volume is applied. These particles are either not completely illuminated by the light source or their scattering light is not completely collected by the detector. The results of either case are that the size of a fraction of particles is underestimated. Two peaks below 1 μm were also observed that were not
expected. Since the major mode can be estimated from VOAG preparation and confirmed by APS, the border error can be handled by using only the major mode distribution in our analysis. Following the above-mentioned criterion, the GSD became ≤ 1.2 and the difference of $D_g < 0.1 \mu m$ among replication, indicating good precision of our experimental results. $D_g$ of each experiment in either OPC or APS was recorded for further comparison.

To convert the number-based distribution measured by OPC to mass-based size distribution, optical diameter has been assumed to be equal to volume equivalent diameter (Peters et al. 2006), which can also be converted from APS measurement by

$$D_{ve,i} = \frac{D_{ae,i}}{\sqrt{\frac{\rho_p}{\rho_0} \frac{C_{ve,i}}{C_{ae,i}}} \chi}$$  \hspace{1cm} (2-5)

where $D_{ae,i}$ is the aerodynamic particle size of the $i^{th}$ channel, $D_{ve,i}$ is the volume equivalent diameter of the $i^{th}$ channel, $\rho_p$ is the particle density, $\rho_0$ is unit density (1 g cm$^{-3}$), $C_{ae,i}$ and $C_{ve,i}$ are the Cunningham correction factor in terms of aerodynamic and volume equivalent diameter, and $\chi$ is the shape factor. The volume equivalent diameter derived from APS Model 3321 was then compared to the optical diameter from Mini-Las 11-R.

Size shifting for liquid aerosol is a sizing issue for APS (Baron et al. 2008). For example, liquid samples can accumulate in the APS nozzle to narrow the nozzle size. Furthermore, droplet may distort due to acceleration. These can result in a higher particle velocity at the sensor so that the APS detector mistakenly records a faster (smaller) particle. An experimental correction is given (Baron et al. 2008):

$$\Delta = - \frac{(2.723 \times 10^{-4}) D_{ae}^2}{\sigma^{0.3864} \rho^{0.6486}}$$  \hspace{1cm} (2-6)
where $\Delta$ is the size shift in $\mu$m, $\eta$ (Pa-s) is the liquid viscosity, and $\sigma$ (N/m) is the liquid surface tension. In this study, the surface tension and viscosity of the oleic acid are 0.032 N/m and 0.0256 Pa-s, respectively.

**Results and Discussion**

**Sizing and Calibration of Liquid and Spherical Particle**

For oleic acid particles, as shown in Figure 2-3a, the optical diameter is smaller than the volume equivalent diameter due to the influence of the refractive index. The refractive index of test aerosol ($m_{\text{oleic acid}} = 1.46$) is smaller than the reference particle ($m_{\text{PSL}} = 1.60$). The test particles with the same size and spherical shape but smaller refractive index generate lower scattering intensity corresponding to an underestimated particle size. The underestimation due to the refractive effect is in agreement with other work (Hering and McMurry 1991; Liu et al. 1974b). The difference is less than 1 $\mu$m when the optical diameter is $< 4 \mu$m, but the difference is $> 1 \mu$m for optical particle size $> 4 \mu$m. Some data points were close to the 1:1 line while others deviated from it. This may be attributed by the localized undulation of light scattering intensity (Hinds and Kraske 1986). Note that such localized undulation effects are within 1 $\mu$m, and overall the oleic acid still generates lower intensity from 1 to 20 $\mu$m than PSL. Thus, optical diameter is not equivalent to volume equivalent diameter as previously assumed (Peters et al. 2006). The consequence of the assumption in which optical diameter equals to the volume equivalent diameter is shown in Figure 2-3b. The aerodynamic diameter derived from OPC is falsely underestimated by $< 1 \mu$m for $D_{\text{ae, OPC}} < 4 \mu$m and by $>1 \mu$m for $D_{\text{ae, OPC}} > 4 \mu$m.

To directly relate an optical diameter measured by Mini-Las 11-R to an aerodynamic diameter using oleic acid, the data were fitted with an empirical function by least squares method using Minitab 16 Statistical Software® (Minitab Inc., PA, USA) in Figure 2-3c. A quadratic equation was selected because a linear equation did not fit the data well and the diameter
exponent of 2 was a simple integer. The size shifting for oleic acid is > 1µm when the measured
diameter is > 10 µm, and the shifting was corrected through Equation 2-6. Thus, separate
regression was calculated before and after 10 µm.

For oleic acid aerosol, the fitting equations from 1 to 18 µm in optical diameter (for D_{op} <
10 µm, n = 19, R^2 = 0.99, and standard error of the regression = 0.29; for D_{op} ≥ 10 µm, n = 12,
R^2 = 0.92, and standard error of the regression = 0.61) are

\[
D_{ae,APS} = -0.03457D_{op}^2 + 1.433D_{op} - 0.1157, \text{ for } D_{op} < 10 \text{ µm} \tag{2-7}
\]

\[
D_{ae,APS} = -0.1201D_{op}^2 + 4.082D_{op} - 18.33, \text{ for } D_{op} ≥ 10 \text{ µm} \tag{2-8}
\]

The residual of the regression, defined by subtracting the observed data from the
prediction, is a way to understand residual dispersion. As shown in Figure 2-3d, points in the
residual plot disperse randomly and increase as the particle size increases. The residuals are
within ± 0.5 µm for D_{op} < 10 µm while they are within ± 1 µm for D_{op} > 10 µm. Note that
Equation 2-6 incorporates Equation 2-5 of experimental correction for size shifting for liquid
aerosol. The uncertainty of Equation 2-5 propagates with increasing particle size, and the
propagation results in the increasing residual manifested in Figure 2-3.

**Sizing and Calibration of Solid and Irregular-shaped Particle**

For NaCl particles, as shown in Figure 2-4a, the optical diameter is significantly larger
than the volume equivalent diameter, and the difference increases with diameter. For example, an
optical diameter of 1.89 µm was reported as a volume equivalent diameter of 1.7 µm via APS,
while an optical diameter of 9.9 µm corresponded to a volume equivalent diameter of 7.3 µm by
APS.
The enhanced light scattering intensity may be responsible for the overestimation by OPC. Though NaCl (m = 1.54) has a slightly smaller refractive index than the calibrated particle, PSL (m = 1.60), the scattering light intensity of NaCl is much higher because of the non-spherical shape (Berglund and Liu 1973). Friehmelt and Heidenreich (1999) calibrated a white-light OPC with a TSI APS through both theoretical calculation and experiments. They found the theoretically calculated calibration matched the experimental results for spherical liquid and solid particles (glycerine droplet and PSL). However, the theoretical and experimental calibration for quartz particles (m = 1.56) told a different story. The experimental calibration for quartz particles matched the theoretical one when the equivalent volume diameter was less than 0.7 μm, above which the experimental calibration showed appreciably higher scattering light intensity than the theoretical value. This demonstrated the crystallography plays an important role in addition to refractive index and particle size for the light scattering of irregular particles.

Quinten et al. (2001) demonstrated the enhancement of the light scattering for irregular crystallography by comparing light scattering intensity from aggregates of spherical particles to their equivalent volume particle. They mathematically modeled light scattering intensity from nonspherical particles by means of aggregates of closely packed spherical particles including dimer, trimer, and quadruplet, and then they validated the results experimentally. For the dimer setting, two particles can be arranged vertically or horizontally. If the dimer is perpendicular to the propagation direction of the incident light, the light arrives simultaneously at both particles. On the other hand, when the direction of the incident light is parallel to the dimer, the incident wave is phase shifted upon arrival at the second particles. For particles smaller than 0.126 μm, the phase shift is as small as the retarded excitation of the second particle. Thus, the scattering is not influenced remarkably, and consequently the scattering intensity curve of the two dimers are
similar. However, the scattering intensity curve is higher than that of the volume equivalent particle for particle size larger than 1 μm. For trimers or quadruplets, though the light intensity may slightly fluctuate due to the arrangement for particle size < 1 μm, the model shows larger scattering light intensity for particle size > 1 μm than that of particles with equivalent volume, which is in agreement with their experimental results.

If the optical diameter is assumed to be volume equivalent diameter, the corresponding aerodynamic diameter would be significantly overestimated for NaCl particles > 4 μm (Figure 2-4b). The deviation increases with the particle size. For example, a measured 9.92 μm optical diameter was calculated as 14 μm aerodynamic diameter which is significantly overestimated by its true aerodynamic diameter of 10.4 μm measured by the APS. This false assumption may result in a huge overestimation of mass concentration because the mass is proportional to the cubic volumetric diameter. For example, Peters et al. (2006) with the same assumption reported that Arizona test dust mass concentration above 2 μm estimated by PAS 1.109 (Grimm Technologies, Inc., Douglasville USA; a previous model of Mini-Las 11-R) was substantially greater than the estimation by APS. The authors were not able to explain the observation. The finding in our study could be applied to explain the unsolved question since the optic design of the two OPCs are similar. The morphology of Arizona test dust which is more irregular ($\chi_{\text{Arizona test dust}} = 1.5$) than NaCl possibly generates more scattering light compared to the reference PSL particles with the same volume equivalent diameter, resulting in a significant overestimation of optical diameter.

To convert the optical diameter of NaCl particles measured by Mini-Las 11-R to an aerodynamic diameter, a quadratic equation was applied to fit the data by least squares method as
shown in Figure 2-4c. The fitting equation (n = 41, R² = 0.998, and standard error of the regression = 0.21) from 1 to 16 µm in optical diameter is:

\[ D_{ae,APS} = -0.0045D_{op}^2 + 1.0603D_{op} + 0.4513 \]  

(2-9)

The residual plot shows a good random scatter and the residuals are within ± 0.4 µm for a wide range of optical diameter. Note that the above equations are robust for Mini-Las 11-R using NaCl or oleic acid. For other particles or different instrument, the calibration and data analysis methods in the study can be applied to link the optical diameter to aerodynamic diameter.

**Verification through a Commercial Respirable Sampler**

Figure 2-5 illustrates a good fitting of the experimental data to the respirable convention by the APS-based approach, proving the effectiveness of the above-mentioned experimental setup and the procedure. The penetration curve using the OPC-based method is also shown in Figure 2-5. The experimental data generally fit the respirable convention well within the 95% confidence interval for NaCl and oleic acid aerosols, verifying the effectiveness of the calibration. In addition to the calibration uncertainty, the other reason why the OPC-based method does not exactly follow the respirable curve as APS does is the size resolution (52 particle size bins from 0.5 to 20 µm for APS versus 31 bins from 0.25 to 32 µm for OPC).

**Summary**

The comparison of the diameters measured by Las-Mini 11-R and APS using monodisperse solid NaCl and liquid oleic acid particles illustrates that the optical diameter measured by OPC is not equivalent to volume equivalent diameter derived from APS measurement. The difference is due to the light scattering being different from that by PSL used in standard calibration. For oleic acid particles, the optical diameter is less than the volume
equivalent diameter because refractive index of oleic acid is smaller than the reference PSL particle. On the other hand, for NaCl, the optical diameter is larger than the volume equivalent diameter due to the irregular morphology. The magnitude of erroneous sizing is more prominent especially for larger particles with irregular morphology. Since particles in most applications do not have the same optical characteristics as reference PSL particles, the assumed equivalence of optical diameter to volume equivalent diameter is not true for most cases. Regression equations derived from the calibration of optical diameter to aerodynamic diameter were verified with a validated respirable sampler, proving the effectiveness of the calibration. More experiments including different materials such as H₂SO₄ or water droplet are suggested if aerodynamic-based measurement of heterogeneous materials with non-spherical shape such as ambient aerosols using OPCs is of interest.
Figure 2-1. Schematic diagram of the experimental setup.
Figure 2-2. The selected size distributions using oleic acid particles. Note $d_p$ refers to $d_{op}$ for OPC and $d_{ae}$ for APS, respectively.
Figure 2-3. Comparison of optical diameter, volume equivalent diameter, and aerodynamic diameter using oleic acid particles: (a) optical diameter vs volume equivalent diameter (b) deviation of aerodynamic diameter assuming optical diameter is equal to volume equivalent diameter, (c) regression between optical diameter and aerodynamic diameter, and (d) a residual plot of the regression.
Figure 2-4. Comparison of optical diameter, volume equivalent diameter, and aerodynamic diameter using NaCl particles: (a) optical diameter vs volume equivalent diameter, (b) deviation of aerodynamic diameter assuming optical diameter is equal to volume equivalent diameter, (c) regression between optical diameter and aerodynamic diameter, and (d) a residual plot of the regression.
Figure 2-5. The RPPI penetration curve with NaCl and Oleic acid particles using an OPC and an APS.
CHAPTER 3
FEASIBILITY TEST OF CELLULOSE FILTER FOR COLLECTION OF SULFURIC ACID MISTS

**Background**

In the steel, fertilizer and petroleum industries, about 200 million tons of H$_2$SO$_4$ are used each year worldwide (King et al. 2013). H$_2$SO$_4$ mists incidentally released into the air during the manufacturing processes irritate skin and eyes and damage the respiratory system. Accordingly, the National Toxicology Program has identified strong inorganic acid mists containing H$_2$SO$_4$ as “human carcinogens” (USDHHS 2005). To evaluate workers’ exposure to H$_2$SO$_4$ mists, NIOSH Method 7908 specifies 37-mm diameter quartz fiber filter or 0.45 μm pore size polytetrafluoroethylene (PTFE) filter to sample sulfuric acid mists (Breuer and Ashley 2014). This method overcomes the chemical interference issue of filter materials in the previous and abandoned NIOSH Method 7903 (Hsu et al. 2007b).

PTFE filter, which is chemically inert with low chemical interference, is a good candidate for accurately sampling sulfuric acid. NIOSH Method 7908 specifies the use of PTFE filters for the collection of H$_2$SO$_4$ mists (Breuer and Ashley 2014). However, for large-scale or long-term sampling programs, the expensive PTFE filters can add up to a significant cost. The price of PTFE is 5 times that of mixed cellulose ester membrane (MCE) filters and 20 times that of cellulose filters. As a result, from the perspective of sampler developers, PTFE would be the last material choice unless no alternative is available. Alternative filter materials such as cellulose ester membrane filter might sample H$_2$SO$_4$ mists as indicated in NIOSH Method 6004. However, Murdoch et al. (1995) observed decomposition of MCE filters under high concentration (0.3 - 7 mg/m$^3$) of acidic mists. Such an observation suggests durability should be considered for new material selection.
Cellulose filters were selected as an alternative in this study because of their affordable cost and good tensile strength. Mader et al. (1950) collected H₂SO₄ mists on Whatman grade 4 cellulose filters and obtained 91% - 97% recovery by pH titration method. However, H₂SO₄ may esterify cellulose or deteriorate the filters by attacking the bond in the cellulose (Wertz et al. 2010). In this study, hardened cellulose filters (e.g. Whatman grade 540, 541, and 542) were proposed as a possible solution to this problem; Alwine et al. (1979) illustrated their good mechanical strength and resistance to acidic 1-[(m-nitrobenzyloxy)methyl]pyridinium chloride, and Moore (1977) impregnated them with phosphoric acid for ambient ammonia gas collection. Hence, the first objective of this study was to assess the collection efficiency and pressure drop of different grades of hardened cellulose filters. Secondly, their integrity and chemical recovery were tested with 1% H₂SO₄ solution to evaluate the durability for the purpose of storage.

Methods

Experimental Setup for Collection Efficiency and Pressure Drop Test

Sulfuric acid aerosol was used to evaluate the performance of hardened cellulose filters. Pure sulfuric acid (H₂SO₄, MW=98.079) was not applied as nebulization solution because it was so corrosive that it might damage the nebulization system. Additionally, the National Toxicology Program has identified mists containing sulfuric acid, rather than pure sulfuric acid, as human carcinogens (USDHHS 2005). Therefore, a 1% w/w sulfuric acid solution, which was diluted from 98% sulfuric acid (ACS grade, Fisher Scientific) with DI water was adopted for nebulization in this study.

As shown in Figure 3-1, a Collison nebulizer was used to inject polydisperse liquid sulfuric acid mists into a chamber (41 cm in diameter and 71 cm in length) maintained at 30% RH (monitored by an Omega HX94C RH transmitter) and 22 °C (measured by an Omega thermometer). Three sets of cassettes were connected to the air chamber, and the coefficient of
variation among the cassettes was < 6% proving good mixing. All 37 mm round hardened cellulose discs were prepared from larger cellulose discs of Whatman grade 540, 541, and 542 using a laser cutter (Zing 25W, Epilog Lasers). Each upstream cassette contained a hardened cellulose filter that continuously collected the sulfuric acid aerosol, while the downstream hardened cellulose filter was changed during a pre-set time. The first set of experiments of 30 minutes were conducted to determine the type of filters among Whatman grade 540, 541, and 542 filters that would be suitable for the following 8-hour experiment. Also, the pressure drop of the upstream filters pumped by a Universal PCXR8 personal pump (SKC Inc. Eighty Four, PA) was measured with a manometer (Magnehelic, Dwyer Inst., Michigan City, IN). After sampling, the hardened cellulose filters were soaked in DI water for 24 hours to extract sulfuric acid. The sulfuric acid mass collected on the filters was determined by an Ion Chromatography System (ICS-1500, Thermo Fisher Scientific Inc., Waltham, MA) equipped with an AS9-HC column.

Note a real-time particle counter such as an optical particle counter was not applied to determine the collection efficiency because 1) acidic mists might irreversibly damage the instrument, and 2) an optical particle counter might give questionable counts for particles smaller than 1 µm (Chien et al. 2016). After the analysis, all aerosol mists deposited on the upstream filter ($M_{upstream\ filter}$) and the downstream filter ($M_{downstream\ filter}$) were calculated to determining the collection efficiency ($C$) defined by

$$C = 1 - \frac{M_{downstream\ filter}}{M_{upstream\ filter} + M_{downstream\ filter}}$$  \hspace{1cm} (3-1)

**Experimental Setup for Durability Test**

The filter integrity and the recovery of $\text{H}_2\text{SO}_4$ solution were conducted using 50 µg, 250 µg, 500 µg, and 5 mg $\text{H}_2\text{SO}_4$ in a 0.5% $\text{H}_2\text{SO}_4$ solution, which was pipetted onto Whatman grade
542 filters. These filters were manually folded and examined for physical damages by naked eyes every day. Recovery test was conducted to simulate the mists wetting on the cellulose filters. After dropping a known amount of H\(_2\)SO\(_4\) solution on the filter, the filter was analyzed by the Ion Chromatography System after 7 days to obtain the recovery rate.

**Quality Assurance and Quality Control**

**Collection Efficiency Test**

The fresh mist aerosolized from the Collison nebulizer with DI water was measured by an APS for its size distribution. The Mass Median Aerodynamic Diameter (MMAD) and Geometric Standard Deviation (GSD) were 6.4 \(\mu\)m and 1.6, respectively. Because RH in the chamber was lower than that in the Collison nebulizer, the droplet from the Collision nebulizer evaporated to reach equilibrium since the evaporation time for aerosol particles at 6.4 \(\mu\)m at 30% RH and 22 oC is only 0.02 second (Hinds, 1999). The time to reach equilibrium is shorter than the time for aerosol transport from the nebulizer to the sampler. The size distribution of H\(_2\)SO\(_4\) mists at equilibrium was quantified by a University of Washington seven-stage Source Test Cascade Impactor Mark III (Pilat et al. 1970) as shown in Figure 3-2. Note that APS was not applied for sulfuric acid mists due to the high risk of corrosion. The MMAD and GSD at equilibrium were 1.8 \(\mu\)m and 1.5, respectively. Liu (1978) theoretically determined RH-dependent aerosol size for sulfuric acid mists; particle size was shown to decrease by a factor of 4 from 100% RH to 30% RH. In this study, MMAD decreased by a factor of 3.6, illustrating that the experimental data agreed with the theory. Additionally, Liu (1978) reported theoretical concentration of sulfuric acid aerosol at equilibrium is 50% at 30% RH and we calculated the concentration as 45% based on the size change of 1% aerosol from 6.4 \(\mu\)m to 1.8 \(\mu\)m. Concentrated sulfuric acid solution (>70%) would hydrate the collection media, but it is not the case in this study because concentration is still lower than the threshold concentrated (70%). Tubing and the cassettes were
also tested for their chemical resistance against H$_2$SO$_4$ mists in this study and almost 100% recovery was obtained, indicating negligible chemical interference from tubing or cassettes.

A closed-faced three-piece cassette is convenient for sampling because the assembly of the pieces can be easily achieved by hands without tools. However, cassette bypass leakage has been reported if press pressure is not properly applied by hands (Baron et al. 2002). A preliminary confirmation of proper compression was conducted by observing a good sealing area at the edge of the filter. Additionally, the filter holder performance was investigated by comparing the collection efficiency of Whatman grade 41 filters held by the plastic cassette and a universal filter holder (Model XX5004700, Millipore), which has not been reported for leakage issue. 0.3 µm monodisperse polystyrene latex (PSL) (3000 Series, Nanosphere Size Standard, Thermo Scientific Inc., Waltham, MA) aerosol was nebulized by a Collison nebulizer using PSL suspension with diluted 0.02 % concentration. The aerosol flow at 2.2 Lpm went through a dilution dryer where 1.5 Lpm dilution air was introduced to yield dry PSL particles. A scanning mobility particle sizer (SMPS) (TSI, Model 3080, Shoreview, MN, USA) measured the upstream and downstream concentrations of Whatman grade 41 filters with the plastic cassette and the universal filter holder, respectively. Figure 3-3 presents the collection efficiency of the two filter holders with different face velocities. As shown, there was no significant difference between the two holders. Also, our collection efficiency curve is consistent with reported curves (Rimberg 1969; Stafford and Ettinger 1971), proving the reliability of our experiment setup.

**Pressure Drop Test**

The pressure drop test system was verified by measuring the pressure drop of a blank Whatman grade 42 filter. By using the same filter, Storr and Baker (1987) reported 20.3 inches of water at the face velocity of 5 cm/s (i.e., flow rate of 1.6 Lpm for a 37 mm filter), while 17
inches of water was measured in this study. The acceptable difference may due to experimental errors.

**Results and Discussion**

**Collection Efficiency and Pressure Drop of the Cellulose Filters**

Table 3-1 shows the collection efficiency of Whatman grade 41, 540, 541, and 542 filters with 30-min sampling. As shown, the collection efficiency was low ($\leq 80\%$) for Whatman grade 41, 540, and 541 filters. The low collection efficiency of Whatman grade 41 or 541 filter was due to their larger filter pore size, which could be represented by high particle retention rating at 98% efficiency (i.e., high void size) as shown in Table 3-1. Because Whatman grade 541 filter has the same particle retention rating at 98% efficiency but thinner thickness than Whatman grade 41, lower collection efficiency was expected. The results are similar to other reported values: Lindeken et al. (1963) reported about 80% collection efficiency of Whatman grade 41 for PSL particles ranging from 88 nm to 557 nm at 6 cm/s face velocity; John and Reischl (1978) reported 64% - 83% collection efficiency for ambient ultrafine particles.

The collection efficiency of 0.3 µm aerosol was less than or equal to 80% for the low face velocity $< 10$ cm/s, while the collection efficiency improved when the face velocity $> 10$ cm/s (Figure 3-3). For a personal sampler, the flow rate is usually low (2 Lpm for example); in other words, the face velocity of a 37-mm filter is merely 3.1 cm/s, which falls in the zone of “low collection efficiency”. Whatman grade 41 has been reported to be unfit for air sampling (Watts et al. 1987; Lowenthal and Rahn 1987). On the same basis, Whatman grade 541 filter may be not suitable for personal sampling, either.

Table 3-1 also displays the pressure drop of the hardened cellulose filters without particle loading. The hardened cellulose filters might have slightly lower pressure drop because of their smaller thickness (Whatman grade 541 vs Whatman grade 41). Among the three grades of
hardened cellulose filters, the pressure drops of Whatman grade 540 and 541 filters were similar. However, the low pressure drop was at the expense of low collection efficiency. Whatman grade 542 filters did possess high collection efficiency, though it had a higher pressure drop of 15 inches of water at 2 Lpm. In comparison, the pressure drop of a PTFE filter with 0.45 µm pore size (Zefon International, FPTPT4537) was 5.5 inches of water. The pressure drop over eight hours is shown in Figure 3-4. Although the pressure drop of Whatman grade 542 filter is higher than a PTFE filter, it is still lower than the backpressure limitation of a general personal pump (ca. 30 – 40 inches of water), i.e., a personal pump can handle the air resistance of Whatman grade 542 filter.

Figure 3-4 shows the collection efficiency over eight hours for Whatman grade 542 filters. Only this grade filter was investigated for eight-hour collection efficiency because other grade filters showed low collection efficiency as illustrated in Table 3-1. As shown in Figure 3-4, the collection efficiency varied around 95% for eight hours, but there was no discernible decrease in collection efficiency, indicating the filters did not break and maintained their performance.

The filter collection efficiency for solid aerosol usually increases over time due to the formation of filter cakes, but it is not the case for liquid aerosol (Hsiao and Chen 2015; Contal et al. 2004). After the liquid aerosol is accumulated in the filter media, part of liquid aerosol may transport to the downstream zone, and the possible fate of the accumulated liquid includes evaporation, drainage, and re-entrainment (Raynor and Leith 2000). Evaporation is possible for volatile liquid aerosol, but the possibility of H₂SO₄(g) is low because the H₂SO₄ partial pressure over 10% (w/w) aqueous H₂SO₄ acid at 20 °C is low (0.58×10⁻¹⁹ atm) (Green 2007). Drainage, such as gravity flow, was not observed. It might be because the droplet loading was not high
enough to redistribute the liquid which was deeply collected in the filter. Re-entrainment, characterized by secondary aerosol observed downstream of the filter, occurs as liquid droplets accumulated on the fibers coalesce into larger droplets, which was then transported away by air flow (Charvet and Thomas 2017). Re-entrainment could be verified by a real-time particle size analyzer to quantify the size distribution change between the upstream and the downstream. It was not performed in this study because of the high risk of corrosion to the instrument from the H₂SO₄ mists. Re-entrained droplets, if present, and the already-penetrated mists may contribute to the overall though small (ca. 5%) penetration.

Prior studies have reported a decrease in the collection efficiency and pressure drop of fibrous filter for liquid aerosol (Hsiao and Chen 2015; Contal et al. 2004). The performance evolution over time could be categorized into four stages: 1) droplets deposit on the filter surface, 2) coalescence and decreased collection area, 3) formation of liquid bridge and films, and 4) stationary regime (Contal et al. 2004). Because the collection efficiency and pressure drop for Whatman grade 542 filter neither increased nor decreased over time in this study, it was inferred that the packing density maintained the same. Also, the contact angle of Whatman paper for water is 22 degree and decreases over time (Ly et al. 2010). These conditions combined together suggest that liquid may be absorbed in cellulose fibers, and the eight-hour sampling was still at the first stage, wherein the mists collected were still localized around the fibers. The concentration (PM₂·₅) of H₂SO₄ in an occupational setting was around 181 µg/m³ (Hsu et al. 2007a), which is much lower than the average concentration (ca. 5000 µg/m³) of this eight-hour test. Therefore, the filter performance under normal occupational setting would not evolve beyond the first stage.
Recovery of H₂SO₄ Mists on a Cellulose Filter and its Damage Evaluation

The Whatman grade 542 filters loading for the integrity tests are shown in Figure 3-5 over seven days. These filters wetted by the H₂SO₄ solution of 76 µg, 278 µg, 856 µg, and 7,399 µg of SO₄²⁻ did not exhibit physical damages in our observation. The filter treated by 7,399 µg of SO₄²⁻ did not break until the 5th day for Whatman grade 542 filters. The equilibrium concentration of H₂SO₄ solution depends on RH. At 50% RH and 24 °C, water in the 50 µL droplet on the filter would evaporate to reach equilibrium. By steady-state diffusion of water through stagnant air with the liquid-vapor interface, the evaporation flux was calculated as 0.0023 kg-mol m⁻² hr⁻¹ and then the evaporate time was 1.12 hr in this study (Bird et al., 2002). In other words, the time to reach equilibrium is much shorter than the duration of integrity test. Since the concentration remained the same for different tests, the damage to the filter should have resulted from the total amount of sulfuric acid rather than the concentration for dilute sulfuric acid solution.

Figure 3-6 shows the good H₂SO₄ recovery of Whatman grade 542 filters after seven days with R-square of 1. The slope of 1.05 indicated nearly 100% recovery rate, and 5% more than 1 was likely due to experimental errors during solution extraction and analysis and error was dominated by the highest two values. Note The filters treated by 5 mg H₂SO₄, although they broke, still recovered H₂SO₄ by nearly 100 %. While H₂SO₄ esterification of the cellulose filters cannot be determined by the present study, the high recovery rate indicated the H₂SO₄ did not transform into other chemicals, and the concern for esterification can be relaxed. The remaining concern is whether the filters can resist for more than 5 mg H₂SO₄ during the sampling. In chemical fertilizer plants, the geometric mean concentration (PM₂₃) of H₂SO₄ was 181 µg/m³ (Hsu et al. 2007a). Accordingly, H₂SO₄ collected on a filter for eight hours by 2 Lpm is estimated to be 174 µg. Such a typical field sampling amount is much lower than the threshold.
limit of 5 mg. Therefore, it can be concluded that the hardened cellulose filters are capable for practical field use from the perspective of H$_2$SO$_4$ recovery. In case of high concentration events, after sampling, the cellulose filters could be immediately removed from the cassette and placed in a chemical resistant vessel with DI water as extraction solution.

**Summary**

The hardened cellulose filters of Whatman grade 540, 541, and 542 filters were investigated for their feasibility to sample H$_2$SO$_4$ mists. In 30-minute testing, low collection efficiency was found for Whatman grade 541 and 542 filters, while 95% collection efficiency was observed for Whatman grade 542 filter. This is because the pore size of Whatman grade 542 filter is significantly smaller than Whatman grade 541 and 540 filters. The eight-hour collection efficiency test showed Whatman grade 542 filter can maintain almost 95% collection efficiency. Re-entrained droplets and already-penetrated mists may contribute to the overall but small penetration. Unlike the filter collection mechanism for solid aerosol, the collection efficiency and pressure drop for liquid aerosol neither increased nor decreased over time. This might be because the mists collected during the 8 hrs were absorbed in the filter, and there was insufficient amount of the mists to coalesce that would change the filter collection efficiency. The high collection efficiency for Whatman grade 542 filter was at the expense of a high pressure drop. Although the pressure drop of the Whatman grade 542 filter could be as high as 15 inches of water, the pressure drop is still lower than the limit of personal pump backpressure. In summary, Whatman grade 542 filter is suitable for measuring H$_2$SO$_4$ mists in the occupational setting.

The integrity test showed the integrity of hardened cellulose filters could last for more than seven days for H$_2$SO$_4$ mass accumulated less than 500 µg. Filters did not break until the 5$^{th}$ day for 5 mg H$_2$SO$_4$, which was at least one order of magnitude higher than the eight-hour H$_2$SO$_4$ amount under the typical concentration in chemical fertilizer plants. In other words,
hardened cellulose filters could keep integrity for regular sampling in an occupational environment. The success of the collection efficiency and durability test provides future users an affordable and reliable alternative to collect sulfuric acid mists.
Table 3-1. Summary of performance characterization of Whatman Grade 41, 540, 541, and 542 filters

<table>
<thead>
<tr>
<th>Filter (Whatman #)</th>
<th>Particle retention rating at 98% efficiency (liquid as medium)(µm)</th>
<th>Thickness (µm)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Pressure drop (inch H₂O) at velocity = 53 cm/s&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Collection efficiency of 0.3 µm DOP at velocity = 53 cm/s&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Pressure drop (inch H₂O) at face velocity = 3.1 cm/s</th>
<th>Collection efficiency (%) of H₂SO₄ mists at velocity = 3.1 cm/s within 30 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>20-25</td>
<td>215</td>
<td>19</td>
<td>84</td>
<td>1.3</td>
<td>80</td>
</tr>
<tr>
<td>540</td>
<td>8</td>
<td>160</td>
<td>NA</td>
<td>NA</td>
<td>0.9</td>
<td>63</td>
</tr>
<tr>
<td>541</td>
<td>20-25</td>
<td>155</td>
<td>16</td>
<td>60</td>
<td>1</td>
<td>65</td>
</tr>
<tr>
<td>542</td>
<td>2.7</td>
<td>150</td>
<td>NA</td>
<td>NA</td>
<td>1.5</td>
<td>95</td>
</tr>
</tbody>
</table>

a. Whatman Catalogue

Figure 3-1. Experimental setup for the collection efficiency and pressure drop of the hardened cellulose filter.
Figure 3-2. $\text{H}_2\text{SO}_4$ mist size distribution generated by a Collison nebulizer.
Figure 3-3. Aerosol collection efficiency of Whatman Grade 41 filter as a function of sampling face velocity for 0.3 µm PSL particles.
Figure 3-4. $\text{H}_2\text{SO}_4$ collection efficiency and pressure drop on Whatman grade 542 as a function of time.
Figure 3-5. Integrity of Whatman grade 542 filters loaded with different amounts of $\text{H}_2\text{SO}_4$ (in $\mu$g) on days 1-7.
Figure 3-6. Recovery of H$_2$SO$_4$ on Whatman Grade 542 filters.
CHAPTER 4
DEVELOPMENT OF A THORACIC PERSONAL SAMPLER SYSTEM FOR CO-SAMPLING OF SULFURIC ACID MIST AND SULFUR DIOXIDE GAS

Background

About 200 million tons of H\textsubscript{2}SO\textsubscript{4} are used each year in the world, mostly by the steel, fertilizer, and petroleum industries (King et al. 2013). The production of H\textsubscript{2}SO\textsubscript{4} requires oxidation and hydration of SO\textsubscript{2}. The H\textsubscript{2}SO\textsubscript{4} mists and SO\textsubscript{2} incidentally released in the air during the processes can potentially irritate workers’ skin and eyes and damage their respiratory systems. Strong inorganic acid mists containing sulfuric acid are known to be carcinogenic to humans according to the National Toxicology Program. The health effects of H\textsubscript{2}SO\textsubscript{4} mist in the human respiratory tract is size dependent. Thoracic fraction (the mass fraction of inhaled particles penetrating beyond the larynx) is important for the human health risk assessment of H\textsubscript{2}SO\textsubscript{4} mist. Thus, the exposure limit for H\textsubscript{2}SO\textsubscript{4} in the U.S., Canada, Brazil, and the European Union (EU) have been standardized as thoracic mass (McGinnity and Nicol 2014).

The National Institute for Occupational Safety and Health (NIOSH) Method 7908, the standard method for occupational sulfuric mist sampling in the U.S., evolved from NIOSH Method 7903. NIOSH Method 7903 was widely applied to sample inorganic acids including hydrofluoric, hydrobromic, hydrochloric, nitric, sulfuric (H\textsubscript{2}SO\textsubscript{4}), and phosphoric (H\textsubscript{3}PO\textsubscript{4}) acids. The sampler is constructed of a glassfiber filter to collect aerosols followed by two sections of silica-gel to adsorb the surviving acidic gases. This method has the following drawbacks: poor aspiration sampling efficiency for large aerosols; acidic gas (e.g., SO\textsubscript{2}) reaction with the glass fiber filter plug; and residual sulfate in silica gel (Hsu et al. 2007b). The new NIOSH Method

7908 focuses on \( \text{H}_2\text{SO}_4 \) and \( \text{H}_3\text{PO}_4 \), and its sampler uses one 37-mm diameter quartz fiber or PTFE filter to collect \( \text{H}_2\text{SO}_4 \) and \( \text{H}_3\text{PO}_4 \) in workplaces (Breuer and Ashley 2014). \( \text{SO}_2 \) interference due to the reaction with aerosol sampling media should be negligible because glass fiber plugs are replaced by inert quartz or PTFE filters. However, the health-related thoracic mass for \( \text{H}_2\text{SO}_4 \) mist is still undetermined.

In addition to \( \text{H}_2\text{SO}_4 \) mists, \( \text{SO}_2 \) commonly co-exists in workplaces. \( \text{SO}_2 \) gas can be sampled by NIOSH Method 6004 using a treated 37-mm cellulose filter with a flow rate between 0.5 to 1.5 Lpm (NIOSH 1994). Such a flow rate may be too low to incorporate with existing aerosol samplers such as a size-selective impactor, which requires sufficient inertial force. Moreover, severe breakthrough occurs at low relative humidity (RH < 30%) (Huygen 1963). A multi-pollutant sampler for simultaneous measurements of aerosol and gaseous pollutants has been developed by combining an inertial impactor and honeycomb denuders (Koutrakis et al. 1993). Although this sampler measures vapor-aerosol mixtures well, its bulky design and fragile glass of the honeycomb denuder restrict its portability. Besides, such a device focuses on environmental particulate matter such as \( \text{PM}_{10} \) or \( \text{PM}_{2.5} \), which is inappropriate for interpreting the health effects of \( \text{H}_2\text{SO}_4 \) mist.

Here, we have designed a new personal sampler system (tFIPR, thoracic-Florida Industrial and Phosphate Research) for simultaneous sampling of \( \text{H}_2\text{SO}_4 \) thoracic mass and \( \text{SO}_2 \) gas by a parallel impactor and accordion-shaped porous membrane denuders (aPMDs), respectively. In addition, functionality, affordability, portability, and ergonomic design were incorporated in our sampler. Monodisperse liquid particles of various particle sizes were used to evaluate the impactor’s performance in a calm air chamber. The aPMDs were tested to evaluate
their collection efficiency and capacity for SO₂ gas. The entire sampling system was then tested in the air chamber to simultaneously sample H₂SO₄ mist and SO₂ gas.

**Sampler Design**

Figure 4-1 shows the tFIPR sampler, which was modularized into the following components: (1) an impactor compartment that includes a four-channel open-faced parallel impactor, a substrate, an impaction plate, and an after-filter to collect thoracic H₂SO₄ mist; and (2) a denuder compartment that houses four aPMDs to collect SO₂ gas. Because H₂SO₄ and SO₂ are highly corrosive, acid-resistant polytetrafluoroethylene (PTFE) (McMaster-Carr, Atlanta, GA) was chosen for the prototype parallel impactors. The flat design is easily adaptable to a lightweight and portable device that an individual can carry. The sampler is 15 cm tall with a rectangular cross-section of 10 cm × 2.6 cm. This height can be much shorter after the configuration of aPMDs are optimized. The rectangular tFIPR layout is an ergonomic design that allows a user to lay the sampler flat in a pocket. The sampler was designed to face upward to hold collected H₂SO₄ droplets on the substrate. During sampling, an external clamping frame (not shown in Figure 4-1) was required along with gaskets to ensure a leak-free seal.

**Parallel Impactor and After-filter**

To sample thoracic H₂SO₄ mist, the parallel impactor concept was applied because it can better achieve a penetration curve that approximates any defined convention by adjusting its configuration (Marple 1978). The impactor was designed with four nozzles of equal flows in a rectangular cross-section, and the cut-off size of each nozzle corresponded to 12.5% (the middle of 0 – 25%), 37.5%, 62.5%, and 87.5% penetration efficiency of the thoracic convention, the combination of which approximates the thoracic convention as shown in Figure 4-2.

The inlet nozzle width, \( W_{\text{in}} \), was determined according to the following equation (Marple and Willeke 1976):
\[ W_{in} = \left( \frac{4 \rho_p Q C_C d_{50}^2}{9 \pi n \mu Stk_{50}} \right)^{1/3} \]  

(4-1)

where \( \rho_p \) is particle density, \( Q \) is flow rate, \( C_C \) is the size-dependent Cunningham slip correction factor, \( n \) is the number of the nozzles, \( \mu \) is air viscosity, and \( Stk_{50} \) is the Stokes number corresponding to a 50% impactor efficiency. Note that \( Stk_{50} \) depends on the substrate material. Because a porous substrate with oil coating effectively reduces particle bouncing, it has been widely adopted in impactor design. Kavouras and Koutrakis (2001) indicated \( Stk_{50}^{0.5} \) decreases to 0.24 from 0.49 if a porous polyurethane foam substrate is used for a conventional impactor. \( Stk_{50}^{0.5} \) was set as 0.38 for another plastic porous substrate coated with oil (Trakumas and Salter 2009). This study used a cellulose filter (Whatman Grade 541) because of its low cost and porous surface that will readily absorb liquid aerosol rather than bouncing. To obtain the appropriate \( Stk_{50}^{0.5} \) for a cellulose substrate, preliminary tests were carried out to measure the collection efficiency vs \( Stk^{0.5} \) of a plastic porous substrate and a cellulose filter in a respirable personal parallel impactor (RPPI, SKC Inc., Eighty Four, PA). The results shown in Figure 4-3 illustrate the cellulose filters had a slightly higher efficiency than the commercial plastic porous substrate (Impaction Substrates, SKC Inc., Eighty Four, PA). Thus, \( Stk_{50}^{0.5} \) was set as 0.39 in this study.

After the first nozzle width was designed, the following three nozzle sizes were determined according to the association assuming \( Q_1 = Q_2 = Q_3 = Q_4 \) (Trakumas and Salter 2009):

\[
Q_1^2 \left( \frac{1}{W_{1,in}^4} + \frac{1}{W_{1,out}^4} \right) = Q_2^2 \left( \frac{1}{W_{2,in}^4} + \frac{1}{W_{2,out}^4} \right) = Q_3^2 \left( \frac{1}{W_{3,in}^4} + \frac{1}{W_{3,out}^4} \right) = Q_4^2 \left( \frac{1}{W_{4,in}^4} + \frac{1}{W_{4,out}^4} \right) 
\]  

(4-2)
Table 4-1 gives the configurations of our sampler. Note other design criteria such as the jet-to-plate distance and taper angle were designed according to literature (Marple and Willeke 1976).

Outlet nozzles were followed by an after-filter (9.7 cm × 2.5 cm) which serves as the collection substrate for the thoracic H₂SO₄ mass. After sampling, the H₂SO₄ mass was quantified as sulfate by ion chromatograph (IC, ICS 1500, Dionex). Hardened cellulose filter (Whatman Grade 540) was selected in this study because of the lower cost and lower pressure drop. Mader et al. (1950) qualified H₂SO₄ aerosol collected with a cellulose filter (Whatman Grade 4). However, H₂SO₄ recovery on cellulose filters using IC has not yet been reported. Sulfuric acid may esterify cellulose (Wertz et al. 2010) and the cellulose sulfate may not be extracted completely by the conventional extraction process with DI water as a result. In addition, H₂SO₄ deteriorates the filters by attacking the bond in the cellulose (Murdoch et al. 1995). To investigate the recovery, laboratory experiments were conducted by dropping 50 µl H₂SO₄ solution with the concentration at 0.1%, 0.5%, 1% and 10% on 37 mm hardened cellulose filters (Whatman Grade 540) and glass plates by weight. To examine the deterioration, the collection efficiency of 37 mm filter exposed to 1 wt% H₂SO₄ mist atomized by a Collison nebulizer was monitored for eight hours.

**Accordion-shaped PMDs (aPMDs)**

Denuders selectively collect SO₂ gas by its reaction with sodium carbonate (Na₂CO₃) coated on the surface. aPMDs, rather than the conventional denuder, were deployed for sampling SO₂ gas because of their high surface area, light weight, low cost, and easy fabrication. The collection efficiency for a conventional round denuder under steady state can be numerically derived (Gormley and Kennedy 1948), while the collection efficiency of an annular denuder was
formulated by experimental regression (Possanzini et al. 1983). However, for aPMDs, the SO₂
gas diffused in an acute triangular duct, and no theories or experiments have characterized the
collection efficiency for such a geometry. To minimize size, the height of aPMD was set as 5 cm,
and the channel number was experimentally determined for the given flow rate in this study to
ensure sufficient capacity.

**Experimental Setup**

Experiments were conducted to examine (1) the parallel impactor’s performance against
the thoracic convention; (2) the SO₂ collection efficiency of aPMD’s; and (3) the overall
performance of the new sampler system for co-existing SO₂ and H₂SO₄.

**Parallel Impactor**

Monodisperse liquid oleic acid aerosol tagged with uranine (Tsai et al. 2008) was used to
verify the parallel impactor’s conformity with the thoracic convention. Oleic acid (OA,
C₁₈H₃₄O₂, MW=282.47) has high viscosity and therefore was prepared gravimetrically rather
than volumetrically. Due to the high sensitivity of its fluorescent response, uranine (sodium
fluorescein, C₂₀H₁₀O₅Na₂, MW=376.3) was used to prepare the 0.1 g/L ethanol stock solution for
the subsequent calibration standard from 100 to 2500 µg/L.

The VOAG was used to inject monodisperse liquid oleic acid particles tagged with
uranine between 1-20 µm into a calm air chamber (41 cm in diameter and 71 cm in height). To
minimize the loss of large particles, the VOAG was inverted and installed at the top of the
chamber (Iida et al. 2014) as shown in Figure 4-4(a). The uniform concentration distribution in
the chamber was checked for quality assurance by using four reference open-faced samplers (37-
mm styrene Filter Cassettes, SKC) located upward and evenly in a cross-section in the chamber
to sample the test aerosol (16 µm). After sampling, the cellulose filters were soaked in 0.005 N
NaOH and ultra-sonicated for 30 minutes, allowing the fluorescence material to dissolve in the
solution (Tsai et al. 2008). The uranine mass collected on the filter was determined by a fluorometer (Model 112, Tuner Assoc., Palo Alto, CA). The results showed that the sampled particle concentrations of the four samplers differed within 10% (n = 3), confirming the uniformity across the test zone of the chamber.

The experimental setup for the verification is shown in Figure 4-4 (a). The tFIPR and a Thoracic Parallel Particle Impactors (TPPI, SKC Inc., USA) sampled the oleic acid aerosol with a pump in parallel with a reference open-faced 37 mm cassette sampler. The TPPI was firstly applied to reproduce experimental results to confirm the testing system. An optical particle counter (Mini Laser Aerosol Spectrometer 11-R, Grimm Technologies Inc., Douglasville, Ga, USA) monitored and confirmed that the generated particles were monodisperse but did not report the size because OPC measured optical diameter rather than aerodynamic diameter (Chien et al. 2016). The aerodynamic particle size was determined by a VOAG-based method. At the end of the sampling, all particles deposited on the substrate, the wall, and the after-filter of the sampler were included in determining the penetration (P) defined by

$$p = \frac{M_{\text{after-filter}}}{M_{\text{reference}}} = \frac{M_{\text{after-filter}}}{M_{\text{total}}} \times \frac{M_{\text{total}}}{M_{\text{reference}}}$$ (4-3)

where \(M_{\text{total}}\) includes the particle mass on the substrate, after-filter (\(M_{\text{after-filter}}\)), and the wall in the sampler, respectively. \(M_{\text{reference}}\) is the particle mass collected on the reference cassette sampler. The ratio of \(M_{\text{total}}\) to \(M_{\text{reference}}\) is the sampler’s aspiration efficiency. The extraction and mass determination of the substrate and the after-filter were similar to the process in the uniformity test. To determine the loss, wet cotton swabs were applied to recover deposited particles on the inner wall of the sampler (Tsai et al. 2008).
aPMDs

The aPMDs were fabricated from a cellulose sheet (Whatman Grade 541) using a laser cutter (Zing 25W, Epilog Lasers). The aPMDs were immersed in a solution with 10% (m/v) Na$_2$CO$_3$ + 10% (v/v) glycerol in DI water under an ultrasonic bath for 30 minutes (Shou et al. 2012). After drying in an oven at 60 °C for three hours, the coated filters were then loaded into the tFIPR sampler. Note 10% glycerol is higher than the conventional coating, which is 1%. However, using peroxide in the extraction process, the glycerol was oxidized to light acids such as acetate and formate, which eluted closely to the fluoride peak in the ion chromatogram and had little impact on the sulfate analysis (Balya 1991).

To test the collection efficiency, 9.8 ppm SO$_2$ (Airgas) was fed into aPMDs followed by an impinger with 15 mL, 9 mM Na$_2$CO$_3$ solution to collect the remaining SO$_2$ as shown in Figure 4-4(b). After the sampling, the aPMDs were extracted by 9 mM Na$_2$CO$_3$ solution. The extraction and impinger solution were oxidized into sulfate by 30 µL 30% H$_2$O$_2$ and the sulfate concentration was determined by IC. The collection efficiency ($\eta$) was determined by

\[ \eta = 1 - \frac{m_{\text{impinger}}}{m_{\text{substrate}} + m_{\text{afterfilter}} + m_{\text{aPMDs}} + m_{\text{impinger}}} \] (4-4)

where $m_{\text{substrate}}$, $m_{\text{after-filter}}$, $m_{\text{aPMDs}}$ and $m_{\text{impinger}}$ are the sulfate mass converted from SO$_2$ collected on the substrate, the after-filter, the aPMDs, and the impinger, respectively.

tFIPR Sampler System

Figure 4-4(c) illustrates the experimental setup for evaluating the performance of the tFIPR sampler system. Aerosol was generated with a Collison nebulizer (BGI, Inc., Waltham, MA), located at the center of the chamber, with high-pressure air to create mists containing H$_2$SO$_4$ from 1% H$_2$SO$_4$ solution (Schmid et al. 2002). The Collison nebulizer was selected because it is one of the few aerosol generators that can tolerate highly corrosive H$_2$SO$_4$ solution.
To simulate the environment in phosphate industry facilities, RH was controlled at 60%.
Furthermore, the H$_2$SO$_4$ mist and SO$_2$ gas concentration was controlled around 8 mg/m$^3$ and 7 ppm, respectively, corresponding to 247 and 537 µg sulfate for 1 LPM and 30-minute sampling.
For this study, three samplers were compared including the tFPIR sampler system, NIOSH Methods 7908 and 6004. For NIOSH Method 7908, 37 mm Teflon filters (Zefon International, Ocala, FL) in a polypropylene cassette sampler (Zefon International, Ocala, FL) were used to collect H$_2$SO$_4$ mists and an additional impinger was placed after the cassette sampler for any remaining SO$_2$ gas. For NIOSH Method 6004, the sampler consisted of a 37 mm Mixed Cellulose Ester (MCE) pre-filter to remove aerosol and a following 37 mm Na$_2$CO$_3$ impregnated cellulose filter for SO$_2$ gas collection. The H$_2$SO$_4$ sources and the samplers were 50 cm apart.
The total feed flow rate was 12.6 Lpm, while the total sampling flow rate was 5 Lpm and the remaining 7.6 Lpm was bypassed. The flow velocity in the chamber was 0.16 cm/s. Although our preliminary test showed homogeneous distribution of the concentration in the chamber, samplers were rotated to avoid experimental errors. After sampling, the extraction and analytical methods used were the same as mentioned in the previous section.

Results and Discussion

Recovery of H$_2$SO$_4$ Mists on a Cellulose Filter and its Damage Evaluation

A paired-t test (n = 5) for H$_2$SO$_4$ recovery on the surface of cellulose filter and glass plate showed 95% Confidence Interval (CI) for mean difference was between -0.78 and 1.18, illustrating no statistically significant difference between the cellulose filter and the glass plate.
Although the effect of esterification is still unknown, the good recovery indicated the hardened cellulose filter (Whatman grade 540) is suitable for sampling H$_2$SO$_4$. As discussed in Chapter 3, penetration might be observed using Whatman grade 540. Double filters or Whatman grade 542 filters can be applied to greatly improve the collection efficiency. The deterioration was
negligible enough that the hardened cellulose filters functioned for 8-hour sampling without issues. Note the filters collecting H$_2$SO$_4$ mist from 1% wt or less H$_2$SO$_4$ solution were not damaged for seven days, while the damage was observed on the 4th day when 10% wt H$_2$SO$_4$ mist was sampled. Therefore, it is recommended that cellulose filters be immediately stored in an acid-resistant container with DI water for extraction after sampling. Otherwise, filters may break in the sampler, causing an underestimation of the thoracic H$_2$SO$_4$ mass.

**Size-selective Performance of Parallel Impactor**

Figure 4-5 shows that the aspiration efficiency of tFIPR and TPPI is close to unity, leading to unbiased measurements as compared to the measurement using NIOSH Method 7903. The measured particle collection efficiency of the individual impactor (i.e., impactors a, b, c, and d) of the tFIPR sampler and its fitting curves are displayed in Figure 4-6. The designed 50% cutoff size (d$_{50}$) versus the measured d$_{50}$ of impactor a, b, c, and d for the parallel impactor were 17.5 µm vs 16.4 µm, 11.9 µm vs 12.2 µm, 8.9 µm vs 10.0 µm, and 4.8 µm vs 6.5 µm, respectively. The slight difference between the measured and designed d$_{50}$ could be attributed to experimental error. The sharpness of the a, b, c, and d curves is defined as (d$_{84}$/d$_{16}$)$^{0.5}$. The sharpness was 1.32, 1.33, 1.25, and 1.24, respectively, which is relatively larger than the standard impactor with a steep slope around 1.00 to 1.11 (Marple et al. 1987). The larger slope might be attributed to the nature of the substrate surface. The use of a cellulose membrane as impaction substrate modified the collection characteristics (Rao and Whitby 1978). Compared to a rigid impaction surface, the porous and rough surface of a cellulose membrane makes the penetration curve less steep (Marjamäki and Keskinen 2004). Figure 4-3 illustrates the gradual slope, and the Stk$_{50}^{0.5}$ of 0.39 was smaller than 0.49 of a stiff surface. Additionally, to design d$_{50}$ at 17.5 µm and 11.9 µm, the low-inertial-force impactor was built with a low flow velocity and a low Reynolds number (< 200), resulting in the observed gentle slope of the impactors a and b.
When the Reynolds number is low, the viscous force is large and a parabolic velocity profile will form. In other words, the velocity near the centerline being larger than the mean velocity results in a stronger inertial force to enhance the collection of particles $d_{50}$, while the near-wall velocity with relatively lower inertial force leads to partial particles $d_{50}$ to escape from the impaction plate (Kulkarni et al. 2011).

Although the individual impactor has a less steep penetration curve, the gradual slope of the integrated sampler optimized the overall penetration close to the ISO/CEN/ACGIH thoracic convention as presented in Figure 4-7. A logistic dose response model was applied to fit the measured data. The $d_{50}$ for tFIPR sampler was 10.16 µm, which was close to the $d_{50}$ of 10 µm for the thoracic convention. The modeled penetration as a function of $d_{ac}$ from 1 to 20 µm ($n = 20$, step = 1 µm) was compared to the thoracic convention by a paired t-test. It showed 95% CI as the mean difference was between 0.019 and 0.033, indicating the tFIPR sampler’s overall penetration is slightly higher than the thoracic convention. TPPI’s performance modeled and analyzed with the same approach was similar to the tFIPR sampler. $d_{50}$ of the TPPI was 10.49 µm which is just slightly larger than the tFIPR sampler. 95% CI for mean difference was between 0.021 and 0.036, indicating a slightly higher overall penetration than the thoracic convention, as reported by Trakumas and Salter (Trakumas and Salter 2009).

Particle loss to the walls in the parallel impactor in the tFIPR sampler and the TPPI ranged up to 8%, as shown in Figure 4-7. In both cases, the loss did not change with particle size. Such wall loss was relatively small since the size of the test aerosol ranged up to 16 µm. For reference, a PM$_{2.5}$ personal sampler was reported to have from 5 to 12 % wall loss for particle size ranging from 1 to 10 µm (Sioutas et al. 1999).
To define ‘acceptable performance’, a bias map of the tFIPR sampler was constructed for various particle size distributions with Mass Median Aerodynamic Diameter (MMAD) between 1 – 25 µm and Geometric Standard Deviation (GSD) between 1.75 – 4 to predict the sampler’s performance in workplaces (Lidén and Kenny 1992) as shown in Figure 4-8. Bias is the percentage difference between the actual sampled mass concentration and the concentration that would be measured by an “ideal” sampler exactly following the thoracic convention. Because the tFIPR sampler’s penetration was higher than the thoracic convention, bias in Figure 4-8 was positive. The bias increased with particle size, and the largest bias (>10%) occurred when the size distribution had very large MMAD (> 18 µm) and small GSD (~1.75). The results implied that the tFIPR sampler might oversample mass concentration in a workplace dominated by large and quasi-monodisperse aerosols. However, the chance to sample aerosol with such a distribution is low. For example, at phosphate fertilizer manufacturing facilities, the size distribution of the H$_2$SO$_4$ aerosol peaked at 10 µm with a wide GSD (Hsu et al. 2007a). Thus, the tFIPR sampler should be suitable for H$_2$SO$_4$ mist sampling in such workplaces. In addition, the overall bias within 10% is 94% in Figure 4-8 (non-shadowed area), which meets the EN 13205 standard that ≥ 85% of all the calculated sampler biases should be within ± 10% for size distribution with MMAD between 1 – 25 µm and GSD between 1.75 – 4.

**Performance of a PMDs**

First, the mass balance (i.e. the ratio of input sulfate to the output sulfate) was calculated to validate the data’s reliability. The average recovery in the system was 88% (n = 3). The 12% loss might be due to SO$_2$ absorption in tubing (Byers and Davis 1970) and the loss was excluded in our collection efficiency calculation. In other words, the real input concentration of aPMDs was 8.6 ppm (instead of 9.8 ppm). The performance of the aPMDs was then characterized by its capacity and collection efficiency. Because $m_{\text{substrate}}$ and $m_{\text{after-filter}}$ were negligible, $\eta$ was mainly
dominated by \( m_{\text{aPMDs}} \) and \( m_{\text{impinger}} \). Our preliminary results showed > 5% breakthrough at the 8th hour for a 10-channel denuder for 10 ppm SO\(_2\), but the breakthrough was < 2% over eight hour sampling when a 20-channel denuder was tested. Increasing the channel number decreases the flow rate in a channel and enhances SO\(_2\) diffusion (Shou et al. 2012). To ensure high collection efficiency over eight hours, the 20-channel denuder was chosen for subsequent tests. As shown in Figure 4-9, the 20-channel aPMDs had a mean collection efficiency of 99% over four hours with a capacity of 10760 ± 994 µg (n = 3). Note the dimension of a bulk PMD is 1.58 cm in diameter and 5 cm in height. Additionally, each denuder collected similar amounts of SO\(_2\) (relative standard deviation, RSD = 7%), showing an even flow rate distributed among the four denuder channels.

Given the 88% recovery, collection efficiency, and the known concentration of SO\(_2\), the four-hour capacity was about 11 mg with a surface area of 524 cm\(^2\). Because the denuder capacity is proportional to its surface area, aPMDs have similar capacity as compared to a commercial honeycomb denuder (ChemComb Model 3500 Cartridge, Thermo Fisher Scientific, Inc., Waltham MA, USA) with 508 cm\(^2\) surface (Koutrakis et al. 1993) and the popular six-channel annular denuder (528 cm\(^2\)) (URG-2000-30x242-3CSS). However, the bulk volume of the aPMDs is 39 cm\(^3\), which is about 60% of the honeycomb and only 27% of the annular denuder; the aPMD’s weight is merely 4 g compared to 106 g of the honeycomb denuder and 450 g of the annular denuder. Additionally, this shatter-proof and low-cost aPMD is disposable after analysis without the need to clean for reuse, which facilitates the characterization process.

The separation mechanism in this study is similar to the “filter pack method” (Perrino and Gherardi 1999), that is, a pre-filter for particle collection followed by an impregnated filter to collect acidic gas. However, this filter pack method has been criticized because (1) acidic gas
may react with the pre-filter, and (2) partition equilibrium of volatile species may evaporate a portion of particles to gases which are then collected on the impregnated filter (Perrino and Gherardi 1999). Our entire sampler system was tested for SO\textsubscript{2} collection, and the results show only < 0.1% SO\textsubscript{2} was collected on the after-filter, indicating little reaction of SO\textsubscript{2} gas with our after-filter. The partition equilibrium problem was remedied by the annular and honeycomb denuders, which permitted gas collection on the denuder with subsequent particle collection on a downstream filter. These denuders showed <5% particle loss for small particles (< 3 µm) (Possanzini et al. 1983; Sioutas et al. 1994). Note only small particles were tested for particle loss because installation of an impactor or a cyclone upstream allows only small particles (e.g. PM\textsubscript{2.5}) to enter the denuders. However, the particle size of interest in this study was from 1 to 20 µm. Our experimental results showed the oleic acid particle loss on aPMDs increased with particle size and 40% loss was observed for particles size of 8.35 µm when no after-filter was installed. This implies large H\textsubscript{2}SO\textsubscript{4} mists may deposit on the aPMDs during field work resulting in an underestimation of H\textsubscript{2}SO\textsubscript{4} concentration and overestimation of SO\textsubscript{2} concentration. The equilibrium partition is important for particles with high vapor pressure (e.g., ammonium nitrate) but has little impact on the H\textsubscript{2}SO\textsubscript{4} mists. The H\textsubscript{2}SO\textsubscript{4} partial pressure over 10% (w/w) aqueous H\textsubscript{2}SO\textsubscript{4} acid at 20 °C is so low (0.58×10\textsuperscript{-19} atm (Green 2007)) that the evaporation of H\textsubscript{2}SO\textsubscript{4}(g) is not possible. Thus, the “after-filter” was placed before the aPMDs.

**tFIPR Sampler System Performance for Simultaneously Sampling H\textsubscript{2}SO\textsubscript{4} Mist and SO\textsubscript{2} Gas**

The tFIPR sampler system performance was compared to NIOSH Method 7908 and 6004 for sampling H\textsubscript{2}SO\textsubscript{4} mist and SO\textsubscript{2} gas in the chamber. H\textsubscript{2}SO\textsubscript{4} NIOSH Method 7908 is designed for total H\textsubscript{2}SO\textsubscript{4}; hence, the total H\textsubscript{2}SO\textsubscript{4} measured by NIOSH Method 7908 was compared to the sum of H\textsubscript{2}SO\textsubscript{4} mass in tFIPR sampler system. It should be noted that the Collison nebulizer
generated H₂SO₄ mist with MMAD of 1.6 – 1.8 µm and GSD of 2.9, and the after-filter and an additional final filter can conserve 90% mists. For the tFIPR sampler system, an additional final filter was placed after the aPMD to collect penetrated H₂SO₄ mist to conserve total H₂SO₄.

For SO₂ gas (the tFIPR denuder / NIOSH Method 6004, Figure 4-10), the analysis showed 95% CI (n = 12) was from 0.9178 to 1.0301, indicating no significant difference between the two methods. Additionally, when the two samplers measured solely SO₂ side by side, the ratio of the two methods did not differ significantly (95% CI was from 0.6811 to 1.1787). The coupled experiments implied H₂SO₄ mist did not interfere with SO₂ collection on aPMDs. The coefficient of variation of the total SO₄²⁻ mass conservation among the three samplers was only 7%, ensuring homogenous concentration distribution. The distribution of H₂SO₄ on the substrate, after-filter, and final filter was 1% ± 1%, 91% ± 3%, and 8% ± 1%, respectively. Because NIOSH Method 7908 measures total H₂SO₄, the H₂SO₄ concentration on the substrate, after-filter, and the final filter was summed for comparison. Figure 4-10 shows the ratio of H₂SO₄ concentration measured by the tFIPR sampler and NIOSH Method 7908 had 95% CI (n = 12) between 0.9408 and 1.0677, indicating these two methods had no significant difference. These results prove that the tFIPR sampler system can sample H₂SO₄ mist and SO₂ gas without significant interference.

**Summary**

The tFIPR sampler system, which can sample thoracic mass of H₂SO₄ mist by its parallel impactor and SO₂ gas by its denuder simultaneously, has been developed and evaluated in a laboratory chamber. To avoid corrosion, the tFIPR sampler system is made of acid resistant PTFE. The novel flat design is easily adaptable to a lightweight and portable device that an individual can carry.
The size-selective performance of the parallel impactor was evaluated with oleic acid aerosol tagged with uranine. Because of the porous substrate and low Reynolds number, the penetration curve of each individual impactor was not as sharp as the conventional impactor. However, the combined penetration curve of the parallel impactor matched the ISO/CEN/ACGIH thoracic convention well. For aerosol size distribution ranging with MMAD between 1 – 25 µm and GSD between 1.75 – 4, the tFIPR parallel impactor showed sampling bias < 10% except for extreme conditions wherein aerosol size distribution MMAD was within 20 – 25 and GSD was < 2. The aPMD’s performance was evaluated against 8.6 ppm SO₂. The aPMD was demonstrated to have 99% collection efficiency over four hours with a capacity over 10.7 mg. With a similar surface area to commercially available Honeycomb and Annular Denuders, the aPMDs bulk volume is 60% of the honeycomb denuder and 27% of the annual denuder, and its weight of 4 g is just a fraction of the 106 g of the honeycomb denuder and 450 g of the annular denuder. When the H₂SO₄ mists and SO₂ gas coexist, sampling the mixture can be simplified into the tFIPR sampler system without chemical interference. Instead of total H₂SO₄ concentration, a health-related thoracic concentration can be reported by this system.
### Table 4-1. Configuration of the tFIPR parallel impactor

<table>
<thead>
<tr>
<th>Impactor</th>
<th>Cut-off size, $d_{50}$, $\mu$m</th>
<th>Diameter of inlet nozzle, $W_{in}$, mm</th>
<th>Air Velocity in inlet nozzle, m/s</th>
<th>Reynolds number, Re</th>
<th>Diameter of outlet nozzle, $W_{out}$, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>17.5</td>
<td>5.10</td>
<td>0.41</td>
<td>138</td>
<td>2.17</td>
</tr>
<tr>
<td>b</td>
<td>11.9</td>
<td>3.95</td>
<td>0.68</td>
<td>178</td>
<td>2.20</td>
</tr>
<tr>
<td>c</td>
<td>8.9</td>
<td>3.26</td>
<td>1.00</td>
<td>216</td>
<td>2.27</td>
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<tr>
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<td>4.8</td>
<td>2.17</td>
<td>2.26</td>
<td>324</td>
<td>5.10</td>
</tr>
</tbody>
</table>
Figure 4-1. tFIPR thoracic sampler prototype.
Figure 4-2. Illustration of a four-nozzle thoracic parallel impactor.
Figure 4-3. Collection efficiency vs Stk^{0.5} using SKC porous filter and cellulose filter (Whatman Grade 541).
Figure 4-4. Schematic diagram of the experimental setup for the performance test for (a) parallel impactor, (b) accordion-shaped PMD, (c) the tFIPR sampler system.
Figure 4-5. Aspiration efficiency of the TPPI and tFIPR sampler.
Figure 4-6. Particle penetration through individual impactors of tFIPR sampler.
Figure 4-7. Penetration and wall loss of samplers against the thoracic convention.
Figure 4-8. Bias (%) map for the tFIPR sampler.
Figure 4-9. SO$_2$ collection efficiency on aPMD as a function of time.
Figure 4-10. Comparison of tFIPR to standard method for sampling $H_2SO_4$ and $SO_2$. 
CHAPTER 5
CONCLUSIONS

To design and evaluate a novel personal sampler system to collect the mixture of thoracic H$_2$SO$_4$ aerosol and SO$_2$ gas, three studies were conducted. Because accurate sizing of the thoracic H$_2$SO$_4$ mists is critical, aerodynamic particle sizing using an OPC was calibrated. To reduce the cost without the expense of performance, the feasibility of different types of cellulose filters for sampling sulfuric acid mist was investigated. The performance of the tFIPR sampler system was designed and experimentally evaluated in a laboratory chamber. Three conclusions can be drawn from this dissertation research.

**Conclusion 1**

The OPC measures the optical diameter of a target aerosol particle, and an experimental calibration is required to obtain its aerodynamic diameter, which is necessary for particle sizing in the personal sampler experiment. While prior studies assumed optical diameter to be equal to volume equivalent diameter, experimental results in this study showed the assumption to be valid only if the aerosol has the same optical properties as standard polystyrene (PSL) particles. For oleic acid aerosol, the optical diameter was illustrated to be less than the derived volume equivalent diameter because its refractive index (m = 1.46) is less than that of PSL (m = 1.60). While the refractive index of sodium chloride (m = 1.54) is close to that of PSL, a much larger optical diameter of sodium chloride than its volume equivalent diameter was observed due to its irregular crystallography. Regression equations that can convert optical diameter directly to aerodynamic diameter with a residual bias less than 1 µm were then obtained for both materials by calibrating the OPC response with the aerodynamic diameter measured by the APS.
Conclusion 2

The feasibility of hardened cellulose filters such as Whatman grade 540, 541, and 542 filters were investigated for sampling sulfuric acid mists. 30-minute collection efficiency tests showed low collection efficiency for Whatman grade 540 and 541 filters while Whatman grade 542 filter exhibited high collection efficiency because of its smaller pore size. Eight-hour collection efficiency test for the concentration of ca. 5000 µg/m$^3$ showed Whatman grade 542 filter retained 95% collection efficiency. The collection efficiency over eight hours neither increased nor decreased, indicating the mists were absorbed into fibers and the filter configuration did not change. The high collection efficiency was at the expense of a high pressure drop; however, the pressure drop was still under the backpressure limit for most personal pumps. The integrity test showed, under the typical concentration in the occupational environment, the hardened cellulose filters can maintain integrity for more than seven days. Therefore, instead of polytetrafluoroethylene filters recommended by NIOSH Method 7908, this study showed Whatman grade 542 filter is an affordable and suitable alternative for measuring sulfuric acid mists.

Conclusion 3

A novel personal sampler, tFIPR thoracic sampler system, was designed to measure inorganic acid mists and gases for determining human exposure levels to these acids in workplaces. This sampler system consists of (1) a parallel impactor for classifying aerosol by size following the ISO/CEN/ACGIH defined human thoracic fraction, (2) a cellulose filter to collect the residual acid mist but allowing penetration of sulfur dioxide gas, and (3) an accordion-shaped porous membrane denuder (aPMD) for adsorbing the penetrating sulfur dioxide gas. Acid-resistant PTFE was chosen as the housing material to minimize sampling interference.
The laboratory testing results showed that the penetration curve of the impactor run at 2 LPM flow rate agreed well with the defined thoracic fraction. Almost all sampling biases were within 10% for particle size distributions with MMAD between 1 – 25 µm and GSD between 1.75 – 4, which meets the criteria of the EN 13205 standard. The aPMDs maintained a gas collection efficiency greater than 95% for 4 hours when sampling 8.6 ppm of sulfur dioxide gas. While the aPMD had similar performance to the commonly adopted annular or honeycomb denuders made of glass, this shatterproof aPMD is only half of the volume and 1/25th the weight of the honeycomb denuder. Testing of the entire sampler with a mixture of sulfuric acid mist and sulfur dioxide gas showed the system could sample both with negligible interference. All the test results illustrate that the new sampler, which is flat, lightweight and portable, is suitable for personal sampling and is capable of a more accurate assessment of human exposure to inorganic acid mist and SO₂ gas.
LIST OF REFERENCES


Reiner, T. and Arnold, F. (1994). Laboratory investigations of gaseous sulfuric acid formation via \( \text{SO}_3^+ + \text{H}_2\text{O}^+ \rightarrow \text{H}_2\text{SO}_4^+ + \text{M} \): Measurement of the rate constant and product identification. The Journal of Chemical Physics 101:7399-7407.


BIOGRAPHICAL SKETCH

Chih-Hsiang (Sean) was born in 1983 and raised in Taiwan. He received his Bachelor of Science and Master of Science degrees in environmental engineering at the National Cheng Kung University in Taiwan. Before joining the University of Florida, he worked in Taiwan EPA and conducted research at the National Cheng Kung University.