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WASHINGTON UNIVERSITY IN ST. LOUIS

School of Engineering and Applied Science

Department of Energy, Environmental, & Chemical Engineering

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Smoke Aerosol Characterization for Spacecraft Fire Detection Systems

by Marit E. Meyer

A dissertation presented to the Graduate School of Arts & Sciences of Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

> August 2015 St. Louis, Missouri

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Marit Meyer

Washington University in St. Louis

August 2015

+ S. D. G. +

Dedicated to my husband Craig and my children Erik Martin Hans

Elisabeth

ABSTRACT OF THE DISSERTATION

Smoke Aerosol Characterization for Spacecraft Fire Detection Systems By

Marit Elisabeth Meyer

Doctor of Philosophy in Energy, Environmental & Chemical Engineering

Washington University in St. Louis, 2015

Professor Pratim Biswas, Advisor

Appropriate design of fire detection systems requires knowledge of both the expected fire signature and the background aerosol levels. Terrestrial fire detection systems have been developed based on extensive study of terrestrial fires. Unfortunately there is no corresponding data set for spacecraft fires and consequently the fire detectors in current spacecraft were developed based upon terrestrial designs. There are a number of factors that affect the smoke particle size distribution in spacecraft fires. In low gravity, buoyant flow is negligible which causes particles to concentrate at the smoke source, increasing their residence time, and increasing the transport time to smoke detectors. Microgravity fires have significantly different structure than those in 1-g which can change the formation history of the smoke particles. Finally the materials used in spacecraft are different from typical terrestrial environments where smoke properties have been evaluated. It is critically important to detect a fire in its early phase before a flame is established, given the fixed volume of air on any spacecraft. Consequently, the primary target for spacecraft fire detection is pyrolysis products rather than soot. This dissertation is a compilation of experimental investigations performed at three different NASA facilities which characterize smoke aerosols from overheating common spacecraft materials.

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The earliest effort consists of aerosol measurements in low gravity, called the Smoke Aerosol Measurement Experiment (SAME), and subsequent ground-based testing of SAME smoke in 55gallon drums with an aerosol reference instrument. The feasibility of the moment method for characterizing smoke from limited data, including the lognormal assumption, is explored. Experiments in low gravity are very rare and expensive, so detailed studies to exploit every possible aspect of the data to increase the science outcome are warranted. Another set of experiments were performed at NASA's Johnson Space Center White Sands Test Facility (WSTF), with additional fuels and an alternate smoke production method. Measurements of these smoke products include mass and number concentration, and a thermal precipitator was designed for this investigation to capture particles for microscopic analysis. Smoke particle morphology and chemical composition are analyzed for various fuels. The final data presented are from NASA's Gases and Aerosols from Smoldering Polymers (GASP) Laboratory, with selected results focusing on realistic fuel preparations and heating profiles with regards to early detection of smoke. Additional research on ambient air quality in the International Space Station (ISS) is presented which sheds light on background aerosols that may interfere with smoke detection in spacecraft.

Chapter 1: Introduction

1.1 Background

Recent statistics on home structure fires in the United States indicate that over 40% of home fires are caused by cooking equipment, and almost 20% of home fire deaths resulted from fires beginning with upholstered furniture (Ahrens, 2013). Our fire detection systems here on Earth have been developed based on extensive study of terrestrial fires (Bukowski, 1978 and 2003). However, the next generation of fire detection systems in spacecraft require knowledge of smoke properties and behavior in an entirely different environment. There is neither cooking nor upholstery in the spacecraft environment, and aside from the difference in fire fuels, the transport of smoke deviates from its familiar behavior on Earth. The absence of buoyant flow in lowgravity increases the residence time in low-gravity fires and increases the transit time from the smoke source to the detector (Brooker et al. 2007). Low-gravity flames have radically different structure from their normal-gravity counterparts. There are limited options available for crew members to respond to a spacecraft fire, which increases the importance of early detection. Additionally, the materials used in spacecraft are different from fuel consumed in typical building or forest fires which at present, have an established body of research characterizing the resulting smoke aerosols.

Smoke is a general term that encompasses aerosol materials produced by a number of processes. It includes unburned, recondensed, original polymer or pyrolysis products that can be either liquid or solid, hydrocarbon soot, condensed water vapor, char and ash particles. Soot particles dominate the smoke produced in flaming fires while unburned pyrolysis products and recondensed polymer fragments are produced by oxidative pyrolysis in the initial stages of a fire. The goal of spacecraft fire detection is to detect smoke from the early phase of overheating and not from established flames. Therefore the research in this work focuses on smoke characterization of pyrolysis products and not soot.

Smoke detectors designed for the Space Shuttle were based upon ionization fire detector technology, the most advanced technology available at the time, and used an inertial separator designed to eliminate particles larger than 1 μ m -2 μ m. The International Space Station (ISS) smoke detectors use near-IR forward scattering, rendering them most sensitive to particles larger than 1 μ m, outside of the range of sensitivity of the Shuttle detector. If a fire originated in the habitable spaces of the ISS, the absence of buoyant flow would concentrate the smoke at the source and only the large-scale turbulence of the air handling system would transport the smoke and dilution would take place slowly. The risk associated with that scenario is that the entire cabin must reach the smoke detector concentration threshold before an alarm alerts the crew. If a spacecraft fire originated in electronics behind a wall panel on the ISS (known as a rack), then smoke would concentrate in the confined volume and coagulation (aging) will take place. Therefore, every rack that contains actively cooled electronics also contains a fire detector. The U.S. segment of the ISS contains over 40 smoke detectors: two or three in the cabin space of each module, plus 4 to 14 additional detectors in racks, depending on the location.

1.2 Motivation for this work

As described by Friedman (1992) there were six overheat and failed component events in the NASA Space Shuttle fleet during its operational lifetime. Several similar incidents have occurred on the ISS, which are briefly described here. An electrical 'odor' was traced to lamp on Service Module (ISS Expedition 10, March 2005), a smoke and solvent smell reported caused by smoldering polymeric bushing (ISS Expedition 18, September 2006), the crew reported a burning odor and smoke from the water recovery system (twice), and most recently, the crew reported a burning odor and smoke coming from a failed micro-pump at the back of a pressure suit (Thelen et al. 2009, Mudgett, 2015). None of these events became a real fire but in ongoing

human space exploration missions and with the advent of space tourism, these types of incidents will continue to occur.

The design of future spacecraft smoke detectors requires an understanding of the most likely smoke that will occur in an overheating event, particularly particle sizes of both fresh and aged smoke. To that end, the Smoke Aerosol Measurement Experiment (SAME) was designed to generate pyrolysis smoke from five common spacecraft materials with the ability to concentrate and age smoke in space. The experiment was performed in 2007 and in 2010 on the International Space Station (ISS) and provided many types of data which have been processed and interpreted (Meyer et al. 2015, Mulholland et al. 2015). Results have been verified with ground-based testing with an aerosol reference instrument, which has provided additional insight into the future design of fire detection systems.

Spacecraft fire safety programs at NASA are not only concerned with smoke detection, but also with the post-fire environment. In the event that a survivable fire has taken place and been extinguished on the International Space Station (ISS), the impacted module will have been closed off and air handling systems isolated from the rest of the station. The crew will have evacuated to an unaffected area and will be expected to clean up the aftermath, hopefully recovering the module for future use. This necessitates gas and aerosol monitoring equipment in each module which can indicate remotely the condition of the air in the affected module, so the crew will know when it is prudent to enter and begin cleanup. Spacecraft materials studied in this work emit acid gases when overheated, and each toxic gas species has been evaluated by NASA toxicologists and assigned a spacecraft maximum allowable concentration (SMAC) (Mudgett et al. 2005; Sribnik et al. 1990). Furthermore, smoke concentrations must be reduced to safe levels, and designs are currently under investigation for smoke removal devices which

can operate autonomously so that the crew can enter with personal protective equipment once the visibility is passable and particle and toxic gas concentrations have dropped. Therefore it is necessary to characterize the post-fire environment, as all of these technologies must be designed to applicable conditions and tested in a relevant environment. These technologies include gas and particle monitors, respirator/filtration masks (with known lifetimes and capacities for the toxic gases & particles) and smoke removal devices. Spacecraft fire detection and post-fire cleanup testing has taken place at Johnson Space Center's White Sands Test Facility (WSTF) in Las Cruces, New Mexico and at the NASA Glenn Research Center Gases and Aerosols from Smoldering Polymers (GASP) Laboratory in Cleveland, Ohio.

To improve the reliability of future spacecraft smoke detectors, it is necessary to understand not only the aerosol signature of the most likely smoke that will occur in an overheating event, but also the background aerosols in the spacecraft cabin environment. Limited research has been done on particles in spacecraft ambient air. The only air quality sampling experiment with a real-time aerosol instrument in space was on the Space Shuttle (Liu et al. 1991). The International Space Station (ISS) is both home and workplace for astronauts, however, the concentration of airborne particles has not been assessed by real-time measurements or rigorous particle sampling techniques for analysis on Earth. Therefore an inventory has been made to estimate and quantify, to the best extent possible, the aerosol emission rates of known sources and from common activities by crew members to determine what types of aerosols may interfere with fire detection efforts. This will allow new systems to better discriminate smoke from lint and dust to avoid false alarms.

1.3 Structure of the dissertation

This dissertation outlines the work performed to characterize smoke aerosols for improving spacecraft fire safety. It is the first comprehensive document which encompasses low gravity aerosol measurements, ground-based testing with aerosol reference instruments to verify the low gravity data, microscopy of smoke particles, and an estimate of the background aerosols in spacecraft. The comprehensive fire signature database includes acid gas concentrations which are produced along with the smoke aerosols, although they are not describe here.

Chapter two presents the Smoke Aerosol Measurement Experiment (SAME), devised to investigate smoke production in low gravity. This project produced a wealth of data which were exhaustively analyzed. Ground testing with the returned SAME flight hardware provided the opportunity to measure the smokes with an aerosol reference instrument (SMPS) using 55-gallon drums (Smoke-in-drums).

Chapter three summarizes continuing investigations into smoke from common spacecraft materials. Earlier test campaigns took place at NASA's White Sands Test Facility (WSTF) and comparisons are made of smoke from different fuels and fuel preparation methods. Later testing took place in NASA Glenn Research Center's Gases and Aerosols from Smoldering Polymers (GASP) laboratory. Selected experimental results emphasizing early detection of smoke are presented.

Chapter four summarizes the design of a thermal precipitator created for the purpose of capturing smoke particles during WSTF testing.

Chapter five presents microscopy results of smoke particles collected. Results shed light on thermal decomposition of various fuels and smoke particle formation mechanisms.

Finally in chapter six, indoor aerosols on the International Space Station (ISS) have been researched and an updated aerosol inventory was created for the purpose of air quality modeling and to understand nuisance aerosols that may cause smoke detector false alarms.

Chapter seven summarizes accomplishments in this work, and future experiments planned for GASP laboratory.

Appendix A gives a comprehensive outline of aerosol charging theory and presents a numerical

charger model that includes dynamic charging based on particle trajectories, with location-

specific ion concentrations used in birth and death calculations along each particle path.

Preliminary results of the numerical model are presented and future work is recommended.

Each chapter can be read as a separate work with a complete list of references at the end of

each section, therefore, some references appear in multiple chapters.

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<u>Chapter 2: Smoke Characterization and the Moment</u> <u>Method for Spacecraft Fire Detection</u>

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Meyer, M.E., Mulholland, G. W., Bryg, V., Urban, D. L., Yuan, Z., Ruff, G. A., Cleary, T., and Yang, J. (2015). Smoke Characterization and Feasibility of the Moment Method for Spacecraft Fire Detection. *Aerosol Sci. Tech.*, 49(5):299–309.

2.1 Introduction

The Smoke Aerosol Measurement Experiment (SAME) has been conducted twice by the National Aeronautics and Space Administration and provided real-time aerosol data in a spacecraft micro-gravity environment. Flight experiment results have been recently analyzed with respect to comparable ground-based experiments. The ground tests included an electrical mobility analyzer as a reference instrument for measuring particle size distributions of the smoke produced from overheating five common spacecraft materials. Repeatable sample surface temperatures were obtained with the SAME ground-based hardware, and measurements were taken with the aerosol instruments returned from the International Space Station comprising two commercial smoke detectors, three aerosol instruments, which measure moments of the particle size distribution, and a thermal precipitator for collecting smoke particles for transmission electron microscopy (TEM). Moment averages from the particle number concentration (zeroth moment), the diameter concentration (first moment), and the mass concentration (third moment) allowed calculation of the count mean diameter and the diameter of average mass of smoke particles. Additional size distribution information, including geometric mean diameter and geometric standard deviations, can be calculated if the particle size distribution is assumed to be lognormal. Both unaged and aged smoke particle size distributions from ground experiments were analyzed to determine the validity of lognormal assumption. Comparisons are made between flight experiment particle size distribution statistics generated by moment calculations and microscopy particle size distributions (using projected area equivalent diameter) from TEM grids, which have been returned to the Earth.

Smoke Aerosol Measurement Experiment (SAME) was developed to obtain smoke particle size distribution parameters on-orbit without returning samples to Earth. This is a challenging

endeavor because existing aerosol instruments are typically large and incompatible with spacecraft experiment constraints. Space experiments cannot require extensive crew training, equipment calibration or maintenance and instruments must have low power requirements, be compact, light-weight and easily assembled and disassembled. The approach for SAME was to use three commercial off-the-shelf instruments to measure different moments of the smoke particle size distribution. Using these moments, different moment average diameters can be calculated (some of which require assumption of a log-normal distribution) and the smoke aerosol can be characterized for the benefit of future smoke detector design. The measurements were made on smoke generated by overheating materials commonly found on spacecraft with controlled sample temperatures, flow rates, and particle aging times. Materials tested include Teflon[®], Kapton[®], cotton lamp wick (cellulose, representative of paper, wood and fabric), silicone rubber and Pyrell[®], a polyurethane foam. The experiment was designed to measure fresh and aged pyrolysis smoke because the likely origin of a spacecraft fire would be electronics in an avionics enclosure or other poorly ventilated region. In such a scenario, the smoke concentration would increase in the confined space before escaping into the cabin where large-scale forced turbulence would slowly dilute the smoke. Thus, the properties of early and aged smoke should be known for optimal fire detector design. The experiment was performed in space in 2007 and in 2010 on the International Space Station (ISS).

The purpose of this study is two-fold: 1) Report the smoke characteristics of common spacecraft materials to inform future fire detector design and 2) Evaluate the feasibility and limitations of using combined moments for measuring smoke aerosol size distribution parameters in low gravity, particularly the validity of the lognormal assumption (Meyer et al.

2015). Other aspects of SAME smoke, such as pyrolysis rate, smoke plume structure, yield and particle structure are outlined in Mulholland et al. (2015).

2.2 Moment Method for Calculating Parameters of the Particle Size Distribution

The approach used by the SAME experiment is termed the 'moment method' for convenience (Cleary et al. 2003). Three moments of the smoke particle size distribution (zeroth, first, and third) were measured, and using the properties of the lognormal distribution, the geometric mean diameter and the standard deviation of the aerosol were calculated. Two assumptions are made in this study: the aerosol particles maintain a spherical (or nearly-spherical) shape and the size distribution is lognormal.

2.2.1 Moment Method Equations

A detailed description of the moment method follows. The average particle size and the width of the size distribution are estimated from various moments of the size distribution. The number distribution, n_d , is defined as

$$n_d = \frac{dN(d_p)}{d(d_p)} \tag{1}$$

where $dN(d_p)$ is the number of particles per cm³ with diameter between d_p and $d_p + d d_p$. The moments of interest in SAME are the zeroth moment, first and third moments, denoted by M_0 , M_1 and M_3 below respectively. They are defined as

$$M_{i} \equiv \int_{0}^{\infty} d_{p}^{i} n_{d} d(d_{p}), \quad i = 0, 1, 2, 3 \dots$$
(2)

The zeroth moment is equal to the total number concentration, N_{tot} , and when particles can be characterized as spherical, the first moment is equal to the total diameter length concentration, or the integrated diameter per unit volume, L_{tot} . The 3rd moment is proportional to the total volume and/or mass concentration ($M_{tot} = \pi \rho M_3/6$) which includes the particle density.

Thus, one can obtain the commonly used count mean diameter (simple average), d_{av} , and the diameter of average mass, d_m

$$d_{av} = \left(\frac{M_1}{M_0}\right) = \frac{L_{tot}}{N_{tot}} \qquad \qquad d_m = \left(\frac{M_3}{M_0}\right)^{\frac{1}{3}} = \left(\frac{6M_{tot}}{\pi\rho N_{tot}}\right)^{\frac{1}{3}}$$
(3,4)

There is no assumption about the form of the size distribution for equations (3) and (4), which are special cases of the general expression for the *p*th moment average of the *q*th moment distribution, $d_{p,q}$ which is as follows:

$$d_{p,q} = \left(\frac{\int_0^\infty n_d d_p^{p} d_p^{q} d\left(d_p\right)}{\int_0^\infty n_d d_p^{q} d\left(d_p\right)}\right)^{1/p}$$
(5)

Thus, from three measured data, N_{tot} , L_{tot} and M_{tot} we obtain the diameters d_{av} , and d_m , regardless of what form the particle size distribution exhibits.

The determination of d_{av} is independent of shape and calculating d_m requires only that the three dimensions of a particle are isometric (ie. not fractal agglomerates). There is no assumption about the form of the size distribution. However, to determine the geometric standard deviation, σ_g , of the size distribution, or other moment diameters requires that the size distribution be lognormal and that the particles be spherical. The lognormal distribution is widely used for describing aerosols including non-flaming smoke because for most smoke aerosols, the bulk of the number concentration is associated with smaller particles (Raabe 1971; Reist 1984). Many studies have assumed that pyrolysis and combustion smoke aerosols from various fuels have a lognormal size distribution (Chen et al. 1990; Li and Hopke 1993; Zai et al. 2006; Xie et al. 2007; Janhäll et al. 2010; Chakrabarty et al. 2010; Mack et al. 2010).

If $\ln d_p$, instead of d_p , is used as the independent variable in a lognormal distribution, the distribution becomes a normal distribution function. In other words, the lognormal distribution with respect to d_p is a normal distribution with respect to $\ln d_p$. The advantage of converting a lognormal distribution to a normal distribution by using $\ln d_p$ as the independent variable is that the peak location is unchanged for a fixed geometric mean diameter, d_{gn} , as the geometric standard deviation, σ_g , varies. Furthermore, the widths of the number and volume distributions are the same when $\ln d_p$ is plotted as the x-variable, that is, the geometric standard deviation is equal for both distributions. Symmetry of a distribution, when plotted with $\ln d_p$ as the independent variable is an indication that the distribution is lognormal.

The normal distribution with $\ln d_p$ as the independent variable has the following form:

$$n_1 \left(\ln d_p \right) = \frac{dN(d_p)}{d \ln d_p} = \frac{N_{tot}}{\sqrt{2\pi} \ln \sigma_{gn}} \exp \left[-\frac{\left(\ln d_p - \ln d_{gn} \right)^2}{2 \left(\ln^2 \sigma_{gn} \right)^2} \right]$$
(6)

where the subscript *n* in d_{gn} and σ_{gn} indicate that the geometric mean diameter and geometric standard deviation are based on the number size distribution and N_{tot} is the total number concentration of the aerosol (= M_0). Similarly, a geometric mean diameter of the particle volume distribution is d_{gv} , with a corresponding geometric standard deviation for the volume distribution being denoted as σ_{gv} . The geometric standard deviation, σ_{gn} is the standard deviation of the logarithms of the particle diameters. The geometric mean diameter and geometric standard deviation are defined in the same way as for a normal distribution except in the formulas, d_p is replaced with the $ln d_p$.

$$\ln d_{gn} = \frac{\sum n_i \ln d_i}{N} \qquad \qquad \ln^2 \sigma_{gn} = \frac{\sum n_i \left(\ln d_i - \ln d_{gn} \right)^2}{N - 1} \tag{7.8}$$

Formulas (1) through (5) are valid for any particle size distribution. However, if the particle size distribution is lognormal, then σ_{gn} , σ_{gv} , σ_g are all the same and the Hatch-Choate conversion equations (Hinds, 1999) can be used to calculate many different average diameters if d_{gn} , and one σ is known (Raabe 1971; Reist 1984). The general formula for the *p*th moment average of the *q*th moment distribution is

$$d_{p,q} = d_g \exp\left[(q + \frac{p}{2})\ln^2 \sigma_g\right]$$
(9)

where σ_g is the same for particle number and volume distributions and d_g is equal to the count median diameter of the distribution and is the same as the geometric mean diameter if the lognormal assumption is satisfied. For converting to the count mean diameter, d_{av} (= $d_{1,0}$) and the diameter of average mass, d_m (= $d_{3,0}$) the corresponding values of (q+p/2) are 0.5 and 1.5. Using the two diameters d_{av} and d_m we obtain from the moment instruments in the general equation (9), we get the following explicit equations to calculate the parameters of the lognormal distribution:

$$\sigma_g = \exp\sqrt{\ln(d_m/d_{av})} \qquad \qquad d_{gn} = \sqrt{d_{av}^3/d_m} \qquad (10,11)$$

Note that σ_g can be calculated when any pair of the three diameters d_{gn} , d_{av} and d_m are known. By combining the three moments M_0 , M_1 and M_3 , it is possible to compute different mean diameters of any smoke particle size distribution, and if the distribution is lognormal, the geometric mean diameter and standard deviation can be calculated as well. Validation of this approach is discussed in Cleary, Weinert and Mulholland (Cleary et al. 2003). This statistical method is currently the best option for estimating the size distribution parameters of a smoke aerosol in low gravity. If a histogram of particle sizes is available, the diameter of an average property proportional to $(d_p)^p$ can be calculated for *i* bins with the following formula:

$$d_{\bar{p}} = \left(\frac{\sum n_i d_i^{p}}{N}\right)^{1/p} \tag{12}$$

With this formula, binned data from a reference instrument can be used to verify results from moment method calculations.

Aerosol instruments are limited in their measurement ranges, and the accuracy of the measurements may vary over the range as well. If the moments of the particle size distribution are determined by instruments that are not identical in their ranges of particle size measurement, we can quantify the truncated moment value normalized by the total moment value. This relative value indicates how much of an actual signal is captured in the limited detection range of an instrument. The formula for a bounded moment measurement which assesses the uncertainty induced by an instrument omitting particles above or below a certain diameter *D* is based on the *p* moment cumulative function of a lognormal distribution with d_g and σ_g . If *D* is the particle size below which no signal can be detected, the relative cumulative *p*th moment is

$$M_{p,rel} = \frac{1}{2} \left[1 + erf(\eta_D) \right] \qquad \text{where} \qquad \eta_D = \frac{ln\left(\frac{D}{d_g}\right)}{\sqrt{2}ln\sigma_g} - \frac{1}{\sqrt{2}}pln\sigma_g \qquad (13)$$

Note that the limiting diameter D is normalized by d_g . This relative cumulative moment function, $M_{p,rel}$ gives the percentage of the pth moment instrument signal that is captured when particles smaller than a diameter, D, cannot be detected, assuming a lognormal distribution with d_g and σ_g . Conversely, when $M_{p,rel}$ is subtracted from 1, it gives the percentage of the instrument signal that is lost due to lack of instrument range beyond diameter D. This diameter, D, can be any of the moment average diameters, as the subscript p refers to the type of moment average. This formula is also useful for quantifying the effects of using an impactor with a cutoff diameter *D* which creates a truncated particle size distribution. The derivation of the formula is given in Appendix B.

2.2.2 Uncertainty Analysis of Moment Method

Errors will be intrinsic in the measured moments and the propagation of error will affect the resulting calculated values of d_g and σ_g . Instruments used in this experiment are explained in detail in subsequent sections but are introduced here for the uncertainty analysis.

The mass concentration (third moment) was measured with the DustTrak with a repeatability uncertainty, $u_{r,repeat}(M_c)$, of 3% for mass concentrations above 5 mg/m³. The DustTrak was calibrated in a series of normal gravity experiments over the same range of heater conditions as used in the low-gravity experiments with a tapered element oscillating microbalance (TEOM). The uncertainty in the average calibration constant, $u_{r,cal}(M_{3,c})$, ranges from a few percent for lamp wick, silicone, and Teflon to about 20 % for Pyrell and Kapton. The uncertainty of the mass calibration of the TEOM, $u_{r,TEOM}(M_{3,c})$, was 10%. The combined uncertainty for M_c , $u_{r,c}(M_c)$, is the quadrature sum (square root of sum of squares) of the three uncertainties:

$$u_{r,c}(M_{3,c}) = \left[u_{r,repeat}^2(M_3) + u_{r,cal}^2(M_3) + u_{r,TEOM}^2(M_3)\right]^{\frac{1}{2}}$$
(25)

By substituting by M_0 , M_1 and M_3 in equations (3) and (4) into equations (10) and (11) we have

$$d_{g} = \frac{1}{M_{0}} \sqrt{\frac{M_{1}^{3}}{M_{3}}}$$
(26)

and

$$\sigma_{g} = \exp\left(\sqrt{\ln\left(\frac{M_{0}^{2/3}M_{3}^{1/3}}{M_{1}}\right)}\right)$$
(27)

By differentiating equations (26) and (27), we get

$$\frac{dd_g}{d_g} = -\frac{dM_0}{M_0} + 1.5\frac{dM_1}{M_1} - 0.5\frac{dM_3}{M_3}$$
(28)

and

$$\frac{d\sigma_g}{\sigma_g} = \frac{1}{\ln(\sigma_g^2)} \left(\frac{2}{3} \frac{dM_0}{M_0} - \frac{dM_1}{M_1} + \frac{1}{3} \frac{dM_3}{M_3} \right)$$
(29)

Since M_0 , M_1 and M_3 are measured independently, their relative uncertainties contribute independently to the errors of d_g and σ_g . Denoting combined relative uncertainty as $u_{r,c}$ we have

$$u_{r,c}(d_g) = \left(u_r^2(M_0) + 2.25u_r^2(M_1) + 0.25u_r^2(M_{3,c})\right)^{\frac{1}{2}}$$
(30)

and

$$u_{r,c}(\sigma_g) = \frac{1}{2\ln(\sigma_g)} \left(\frac{4}{9}u_r^2(M_0) + u_r^2(M_1) + \frac{1}{9}u_r^2(M_{3,c})\right)^{1/2}$$
(31)

It is interesting that both equations (30) and (31) show the error of M_3 contributes the least to the errors of d_g and σ_g , whereas that of M_1 contributes the most.

Similarly, for d_{av} and d_m , equations (3) and (4) have the following relative uncertainties:

$$u_{r,c}(d_{av}) = \left(u_r^2(M_1) + u_r^2(M_0)\right)^{\frac{1}{2}}$$
(32)

$$u_{r,c}(d_m) = \frac{1}{3} \left(u_{r,c}^2(M_{3,c}) + u_r^2(M_0) + u_r^2(\rho) \right)^{\frac{1}{2}}$$
(33)

2.3 Instruments used in the Smoke Aerosol Measurement Experiment (SAME)

2.3.1 SAME Aerosol Instruments

SAME flight and ground test experiment measurements were made using three commercial, instruments which had been ruggedized and re-packaged for space flight. Two are industrial hygiene instruments and one is a residential smoke detector. These instruments were chosen

because of their simplicity, low power needs, and small size. Unfortunately, they all show material or size-dependent behavior.

The zeroth moment instrument is a P-TrakTM (TSI, Shoreview, MN, USA) which is a condensation particle counter that was modified for use in space because the isopropanol condensate does not flow downwards to the wick in low-gravity (Urban et al. 2005). To mitigate this issue, very small grooves were added to the walls of the condensing section of the device to improve conductance of the condensate back to the wick. These changes were tested in a separate space experiment with good results indicating the modified device could be used successfully in low gravity. A wide range of dilution was required for the different smoke aerosols generated, so a device called a Dynamic Diluter was developed to ensure the P-TrakTM would not saturate. It consists of a proportional-integral-derivative (PID) controller, a servo valve that controls the flow rate of the diluting nitrogen gas, and a laminar flow element (LFE) for the aerosol stream. The controller reads the desired dilution ratio from the software (based on the sample material to be heated) and the pressure drop over the LFE. The controller output voltage to the servo valve controls the nitrogen flow for dilution upstream of the P-Trak.TM The PID control principle ensures that the actual dilution ratio matches the desired dilution ratio commanded by the software. Aerosol flow through the LFE ranges from 1 to 120 sccm, where the balance of the 700 sccm P-Trak[™] flowrate is nitrogen.

The first moment instrument is the ionization chamber from a residential smoke detector. This device uses an alpha-particle emitter to generate ions in a region within a DC electric field. Drifting ions in the electric field result in a current, and the presence of aerosol particles reduces the current as a result of the attachment of the ions to the particles. The mobility of the charged aerosol is too small for it to be collected on the ionization chamber electrode. Required
minimum particle concentrations are on the order of 10^5 particles/cm³ and no sample dilution is required.

The SAME third moment instrument is the DustTrakTM (TSI, Shoreview, MN, USA) which is a nephelometer using a 90-degree light scattering signal with a wide acceptance angle and output calibrated to quantify the aerosol mass concentration of Arizona Test Dust (ISO 12103-1). Material-specific calibrations and corrections were needed to account for the range of particle sizes, shapes and refractive indices in the SAME experiment, and the particle density was required to compute M_3 from the mass concentration. While some studies have shown that the DustTrakTM response is not proportional to mass (Moosmüller et al. 2001, Maricq 2013), after applying calibration factors, the DustTrakTM was found to correlate well with the mass concentration. The calibration factors with uncertainty are given in Mulholland et al. (2015).

A schematic of the SAME hardware appears in Figure 2.1. Space experiments are ideally autonomous, with minimal astronaut intervention beyond the initial assembly. Hardware with programmable experiment parameters decreases crew training requirements and increases the quantity and reliability of resulting data. Software controlled all aspects of the experiment once the crew inserted the fuel sample carousel and commenced the test sequence. For the space experiments, smoke was generated by overheating a small sample of material from one carousel segment (Figure 2.2) in the smoke generation duct for approximately 60 seconds. During this interval, a rising piston drew smoke into a 6 liter aging chamber where it could be held for a predetermined aging duration, allowing the particles to coagulate. Half of the smoke was pushed by the piston into the moment instruments almost immediately for unaged smoke measurements by the moment instruments. After a period of aging, the remaining smoke was measured. Additional information on the sample heating sequence is given in Mulholland et al. 2015.

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Figure 2.1. SAME flight hardware schematic, shown with additional ground testing apparatus within the dotted line. During ground tests, some smoke is diverted from the SAME setup to fill one of two drums which hold the diluted smoke for SMPS measurements. Two drums were needed to contain and measure both unaged and aged smoke.



Figure 2.2. Sample carousel showing samples contained within the heating wire coils.

2.3.2 SAME Instrument Calibration

An in-depth empirical calibration of the moment instruments was performed on the ground before the flight experiments. Calibration of the moment instruments used in SAME was essential to properly interpret the flight data and was performed on the ground before the flight. Calibration was accomplished using two different aerosol generators: one using mono-disperse particle generation using dioctyl phthalate (DOP) according to the approach by Mulholland and Liu (1980) and the other using polystyrene spheres. The aerosol from the generator was sampled simultaneously by the SAME instrument under test and a reference instrument. For the number count, the reference instrument was a condensation particle counter (CPC 3022A, TSI, Shoreview, MN, USA) (Fletcher et al. 2009), for the mass concentration, a tapered element oscillating microbalance (TEOM, Thermo Scientific, Franklin, MA, USA) and for the first moment an electrical aerosol detector (EAD, 3070A, TSI, Shoreview, MN, USA) was used. The results for the P-Trak[™] calibration are shown in Figure 2.3. As the number concentration increased, the effect of the particle diameter became more evident. Separate correlations were developed for each particle size and the closest correlation was used to analyze the flight data based on the initial estimates of the average particle size. The calibration of the flight units anticipated and accounted for the instruments' responses to particles as large as 1200 nm.

P-Trak[™] hardware changes to adapt the commercial off the shelf instrument for low gravity were tested in a separate space experiment with good results indicating the modifications to the device were successful. A wide range of dilution was required for the different smoke aerosols generated, so a device called a Dynamic Diluter was developed to ensure the P-Trak[™] would not saturate. It consists of a proportional-integral-derivative (PID) controller, a servo valve that controls the flow rate of the diluting nitrogen gas, and a laminar flow element (LFE) for the aerosol stream.

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Figure 2.3. P-TrakTM Calibration results with three sizes of monodisperse DOP droplets, CPC concentration plotted against P-TrakTM concentration.



Figure 2.4. Ionization Chamber Calibration results with monodisperse DOP droplets. The controller reads the desired dilution ratio from the software (based on the sample material to be heated) and the pressure drop over the LFE. The controller output voltage to the servo valve controls the nitrogen flow for dilution upstream of the P-Trak.[™] The PID control principle ensures that the actual dilution ratio matches the desired dilution ratio commanded by the

software. Aerosol flow through the LFE ranged from 1 to 120 sccm, where the balance of the 700 sccm P-Trak[™] flow rate was nitrogen.

The first moment device, the ionization chamber, showed little effect of particle size as seen in Figure 2.4. Consequently a single correlation was used for all particle sizes. The third moment device (DustTrakTM) has a response which varies with the particle refractive index. This issue was addressed by calibrating the DustTrakTM with the smoke aerosol from each material. In the results reported here, the DustTrakTM response was directly calibrated, for each smoke source, against mass concentration measurements using a tapered element oscillating microbalance (TEOM). These 1-g calibrations are assumed to be valid in low gravity.

2.3.3 SAME Thermal Precipitator

While the smoke flowed from the piston, a small aerosol stream could be sent to an autonomously operated thermal precipitator in which smoke particles are deposited on Transmission Electron Microscope (TEM) grids. The SAME software command caused a valve to open, diverting smoke into one of twelve isolated ducts containing a heated Kanthal wire above the TEM grid.



Figure 2.5. A cut-away view of one side of a Thermal Precipitator Unit with the inlet manifold exposed on the left, the hot wire leads in the center block and the outlet valves on the right. The manifold was 3D printed using stereolithography (SLA).

The thermal precipitator posed a unique engineering design challenge, in that crew members receive minimal training in the experiment procedure, often up to a year in advance of the actual flight. Hardware must be relatively simple to install, with a minimum number of larger integrated components, as small objects can escape in microgravity and are hard to retrieve. The design approach was to make interchangeable grid-containing units with a software controlled flow manifold allowing smoke particle deposition on twelve TEM grids (one grid per test point). A detail of the flow path through one half of the thermal precipitator is shown in Figure 2.5, and the fully assembled unit is shown in Figures 2.6 and 2.7. A total of six thermal precipitator units were launched for this experiment, providing a potential of 72 TEM grids for analysis. Unfortunately, approximately half of the data was lost owing to malfunctioning of the flow in the manifold. The Kanthal wire is oriented above the TEM grid and particles deposit uniformly slightly downstream of the wire, after the particle enters the region of the thermal gradient. Figure 2.7 shows the deposition boundary of the particles, and images used for size distribution analysis by microscopy were taken only beyond the deposition boundary. After the space flight experiments, six thermal precipitators were returned to earth and grids were examined in a TEM to observe particle morphology and to obtain particle size distributions by microscopy. Characterization of the particle morphology is key to determining whether the moment method is a valid for obtaining d_g and σ_g from d_{av} and d_m .



Figure 2.6. Fully assembled thermal precipitator which has a total of 12 TEM grids, 6 on each side.



Figure 2.7. TEM grid showing the deposition boundary of particles (left image), and the thermal precipitator unit with circuit card and cover removed for detail (right image).

2.4 SAME Smoke-in-Drums Ground-Based Experiment

2.4.1 Instruments

In order to assess whether the size distribution of a particular smoke is lognormal, detailed particle size distributions were measured with a reference instrument. This cannot be accomplished in low gravity, so this investigation was performed with the ground-based engineering SAME hardware which is identical to the setup on the ISS. This consists of the sample carousel, smoke generation duct, aging chamber and plenum shown in Figure 2.1. The flight aerosol instruments which had been returned to Earth were incorporated into the groundbased setup for these tests. A Scanning Mobility Particle Sizer (SMPS) Spectrometer (3936, TSI, Shoreview, MN, USA) was used as the reference instrument in the validation experiment. The SMPS requires a two minute scan through a range of voltages to acquire a high resolution particle size distribution; however, the duration of smoke supplied from the SAME aging chamber is at most 30 seconds. Therefore, the smoke was collected in an intermediate container which served two purposes. The first purpose was to sufficiently dilute the smoke from the SAME chamber in order to effectively stop coagulation (aging) of the smoke particles during the SMPS scans. The second purpose was to have a large enough quantity of dilute smoke for multiple SMPS scans. A 55-gallon drum was chosen for this purpose and the SAME smoke-indrums setup was developed to enable SMPS measurements on a portion of the smoke output from the SAME piston chamber. The smoke-in-drums configuration is shown in Figure 2.1, which shows the original SAME hardware outside the dashed outline. One DustTrak[™] was removed from the original SAME configuration and its portion of the smoke sample was diverted from the setup to one of two drums which hold the diluted smoke during multiple 2minute SMPS measurements. One drum collected fresh smoke from the heated sample material and the other drum was filled after a controlled aging period in the piston chamber. Thus both

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aged and unaged smoke could be measured with the SMPS. Unfortunately, one or more of the flight moment instruments was not functioning properly during these ground-based tests so a majority of the resulting moment data were not reliable. Therefore, the analysis of the drum test data is exclusively on SMPS results, particularly to assess whether smoke from the different test materials can be assumed to have a lognormal particle size distribution. While a comparison of the moment data with the SMPS reference data would have been preferable, lognormality is a fundamental assumption of that approach, and needs to be confirmed or refuted before spacecraft fire detection systems are further developed.

2.4.2 Drum Hardware and Experimental Process

The two 55-gallon drums were minimally modified for use in the experiment as follows: A muffin fan was bolted to the circular drum floor opposite the removable lid. All other modifications were made to the lid, including feed-through adapters for tubing and the electrical fan cord, and mounted HEPA filters through which clean air was provided for purging. A four-way crossover valve allowed the drum to be filled with smoke via a vacuum pump preceded by a flow-controlling orifice, or allowed the smoke to bypass the drum, which effectively isolated the SAME hardware from high pressure during the drum purging process. Transfer of unaged smoke into the drum began when the SAME software commanded the valve to open and lowered the piston in the aging chamber causing half of the chamber volume to be expelled (3 liters), with the remainder of the smoke retained in the chamber and allowed to age for 12 minutes. The flow rate into the drum was 1.7 lpm, matching the flow rate of a DustTrakTM instrument which the drums replaced (in the original SAME configuration there were two DustTraks). It took less than 2 minutes to transfer the smoke sample into the drum. Tubing from the SAME hardware to the drums was less than one meter in order to minimize transport losses of smoke particles. Initial

calculations from previous SAME data indicated that for all materials, the aerosol concentration in the drum would be less than 2×10^4 particles/cm³, which is below the rule-of-thumb threshold concentration of 10⁶ particles/cm³. Below this level, coagulation can be neglected since it will occur at a very slow rate (Hinds, 1999). Thus it could be assumed that very little aging took place in the drum during the SMPS measurements of unaged smoke. The drum concentration was well within the counting range of the SMPS so no additional dilution was required for the measurements. During each SMPS sample, the volume of air removed was between 0.5 % and 1.5 % of the drum volume and a correspondingly small number of particles were removed so the drum aerosol concentration was relatively constant during the measurements. Any make-up air needed during the sampling was drawn in through the HEPA filters on the drum lid. The fan in the drum was used to mix the smoke and prevent stratification which could skew the SMPS First, a 10:1 sheath-to-aerosol flow ratio was used for three consecutive measurements. measurements with high fidelity giving particle sizes up to 660 nm. Three subsequent samples were taken with a flow rate ratio of 5:1, in order to reach the largest measurable SMPS particle size of 1000 nm. Considering that aging increases particle size, the higher flow rate ratio (smaller range) gives results for only a portion of the true aged size distribution for most materials in this experiment. Therefore the larger range is important for measurements in spite of the low resolution. After six SMPS scans at two different flow rates, the drum was purged with a continuous flow of HEPA-filtered house air at approximately 309 kPa-g (45 psig), which was exhausted into a fume hood. An additional P-TrakTM was used to indicate when the drum concentration fell below 30 particles/cm³, which was considered 'clean'. One set of SMPS measurements for one smoke sample (both aged and unaged) was accomplished in approximately 30 minutes. Particle losses in the 55 gallon drums are discussed in Appendix B.

2.5 Transmission Electron Microscopy (TEM) Results

2.5.1 TEM Particle Morphology Results from Flight Tests

The TEM grids were examined with a Philips[™] CM20 Transmission Electron Microscope at 200KV and images were collected using an Olympus[™] Veleta camera. The digital camera was calibrated using a MAG*I*CAL® calibration reference which is a NIST traceable standard.



Figure 2.8 TEM images of Kapton particle morphology from ISS high temperature testing, unaged on the left, aged on the right. Sample heating temperature was 574 °C, reference length scale = $5 \mu m$.

Kapton is a low outgassing polyimide film that survives a wide temperature range and is used in electrical wire insulation and other spacecraft applications. Kapton smoke particles are the smallest of the five materials tested and are rarely agglomerated. The spherical shape and uniform density indicate growth by condensation in the saturated vapor of the pyrolysis products. Figure 2.8 shows the effect of aging, with the unaged (left) having a higher population of very small particles, and the aged particles (right) appearing only slightly larger.



Figure 2.9. Kapton ISS samples after heating to 420 °C.

The sample carousel shown in Figure 2.2 holds six samples within wire heating coils. After the experiments were performed on the ISS, these were returned to Earth for examination. It can be observed from the optical microscope images of Kapton heated samples in Figure 2.9 that the material discolors in the center of the heating coil and the film layers become brittle after heating. This is evident in the cross-section (lower right image) in which the fracture exhibits brittle failure of the layers where the sample experienced the most heat. The amber colored lighter ends of the layers are notably separate i.e., not fused. Higher temperature test specimens examined showed more discoloration and warping of the Kapton film.

Lamp wick smoke aerosols (Figure 2.10, left image) are known to be primarily spherical droplet-type particles that grow by condensation of pyrolysis gases (Mulholland et al, 1995). Occasional doublets are seen but most are unagglomerated. Two distinct large particle types are

observed: uniformly dense or lighter in the center which suggests that they arrive at the carbon film of the TEM grid as a liquid. Some TEM images display additional faint particles that covered only one or two pixels.



Figure 2.10. TEM images of unaged smoke from ISS tests: lamp wick, 265 °C (left) and Pyrell, 242 °C (center) and Teflon, 514 °C (right), reference length scale = 5 μ m.

Pyrell[®] is used for stowage foam to cushion instruments and other payloads during launch into space. Its widespread use made it a strong candidate in the survey of potential sources of smoke in spacecraft fires. Pyrell smoke particles consist of agglomerates made up of primary particles ranging from 30 nm to 100 nm (Figure 2.10, center image). Teflon[®] is present on the International Space Station in many forms, but predominantly in wire insulation. Teflon primary particles are much smaller than Pyrell and are fractal agglomerates (Figure 2.10, right image). The darker agglomerates are more electron-dense and indicate that the fainter particles may have partially evaporated in the electron beam. In addition, some particles were not completely adhered to the TEM grid and movement could be observed as the force of the electron beam influenced the loose ends of agglomerates.



Figure 2.11. Lamp wick ISS sample after heating.

Photographs of a lamp wick sample after heating are shown in Figure 2.11. The central part of the lamp wick within the heating coil undergoes charring as a result of oxidation, while the ends experienced less heat and are less discolored. The mass loss after heating this sample was approximately 3 mg.



Figure 2.12. Pyrell foam ISS sample after heating to 245 °C.

Pyrell samples did not appear significantly different after heating, however, the sample shown in Figure 2.12 had 0.5 mg mass loss after heating to 245 °C. The Teflon sample in Figure 2.13 shows evidence of the polymer expanding during heating and discoloration of the heating coil. This particular sample had 1.3 mg mass loss after heating, while others at higher temperatures had increased bubbling and swelling, and mass losses up to 10 mg.



Figure 2.13. Teflon ISS sample after heating to 515 °C.

Silicone particles were not wholly preserved on the TEM grids owing to the volatile nature of the pyrolysis products. Only very small and faint particles remained after the return flight to earth, as seen in Figure 2.14. Note that the magnification in this figure is nearly double that of the other particle images shown. Figure 2.15 shows two different silicone rubber samples after heating. Note that the heating coil is not discolored but the silicone tends to swell and become brittle. The sample on the left had 1.5 mg mass loss after heating to 349 °C and the right sample had 3.5 mg mass loss after heating to 380 °C.



Figure 2.14. TEM images of residual silicone smoke particles from SAME pyrolysis at approximately twice the magnification. Sample heating temperature was 380 °C, reference length scale = $2 \mu m$.



Figure 2.15. Silicon rubber ISS samples after heating to 349 °C (left) and 380 °C (right).

Morphology results show that only Kapton and lamp wick are spherical aerosols so they are better suited to calculating the particle diameters from TEM images. Although the TEM images of silicone do not reflect spherical morphology, it is considered a spherical smoke aerosol as it consists of liquid droplets (Mulholland, 1995). Meaningful values of d_{av} can be calculated regardless of shape, and the material-specific calibration of the DustTrak with fundamental aerosol mass measurements provides moment method values of d_m which are valid for the nonspherical materials Pyrell and Teflon (by equations (3) and (4)). No significant discernable difference was noted between the morphology of the pyrolysis particles sampled in low gravity vs. normal gravity for typical SAME flow conditions. A specific set of test points were run in low gravity with no flow through the SAME smoke generation duct, which resulted in significantly larger spherical particles. Details of these tests are outlined in Mulholland et al. (2015).

2.5.2 TEM Particle Size Distribution Results

Particle size distributions were created by image analysis of the particles captured on TEM grids as an independent verification of particle measurements and moment diameter calculations. The particle projected area equivalent diameter was computed for each particle, which is considered to be equivalent to mobility diameter in the transition regime, even for non-spherical and agglomerate particles (Rogak et al. 1993; Chakrabarty et al. 2008). The TEM volume distribution was based on the assumption of spherical particles.

The size distributions were constructed by first locating the downstream edge of the particle deposition. Sequential images were then taken by traversing the grid in a line moving from one edge of the aerosol deposition to the other. This protocol was repeated until a large number of particles were captured. Particles were measured as the projected area, even when in elongated agglomerates. The TEM particle size analysis method used ImageJ, an open source, public domain image processing progam (Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997-2012).

The limitations of silicone TEM images outlined above preclude the creation of a reliable size distribution by microscopy and the fractal nature of Teflon particles do not give size distribution statistics which are directly comparable to spherical aerosols, thus only Kapton, lamp wick and Pyrell were analyzed.

Pyrell size distributions are shown in Figure 2.16, which compares ISS TEM with SMPS ground testing. The TEM size distribution statistics of the unaged smoke are $d_g = 249$ nm and $\sigma_g = 1.84$ (1970 particles counted) and after 12 minutes of aging, d_g increases to 328 nm and σ_g increases slightly to 1.98 (1627 particles counted). The SMPS size distribution statistics are $d_g = 254$ nm and $\sigma_g = 1.88$ and after 12 minutes of aging, d_g increases to 364 nm and σ_g decreases slightly to 1.87. This comparison shows that the TEM projected area equivalent diameter is comparable to mobility diameter, even for non-spherical and agglomerate particles.



Figure 2.16. Pyrell particle size distribution from TEM image analysis of ISS high temperature testing, compared with SMPS size distribution from ground testing. Sample heating temperatures were 242 °C and 234 °C, respectively.

Representative size distributions of a typical high temperature Kapton test are shown in Figure 2.17. The unaged smoke has $d_g = 158$ nm and $\sigma_g = 1.68$ (circles) and after 12 minutes of aging, d_g increases to 210 nm and σ_g shrinks to 1.63 (squares). The size distribution is normalized by the total number of particles counted. The sample heating temperature is 574 °C.



Figure 2.17. Kapton particle size distribution from TEM image analysis of ISS high temperature testing (574 °C). The circles correspond to unaged smoke, squares to aged.

2.5.3 TEM Results from Flight tests

Results of the International Space Station (ISS) flight TEM size distribution analyses and moment method calculations appear in Table 2.1.

Sample	Temperature , °C	# parti- cles counted	$D_m \mu m$		$D_{ave}\mu m$		D _g μm		Sigma g		Hatch-Choate Diameters	
			TEM	Mom- ent	TEM	Mom- ent M1/M0	TEM D _{gn}	Mom- ent	TEM σ _{gn}	Mom- ent	Dav Hatch Choate from TEM sigma and Dg	Dm Hatch Choate from TEM sigma and Dg
Lampwick #54 (ISS) Unaged	Low Temp 264.7	511	0.403	0.253	0.304	0.11	0.255	0.072	1.84	2.493	0.307	0.445
Lampwick #55 (ISS) Aged	Low Temp 262.9	196	0.499	0.320	0.359	0.149	0.284	0.102	2.070	2.400	0.370	0.628
Kapton #94 (ISS) Aged	Low Temp 527.3	1353	0.159	0.176	0.120	0.136	0.103	0.119	1.720	1.669	0.119	0.160
Kapton #62 (ISS) Unaged	High Temp 574.3	1320	0.226	0.251	0.180	0.148	0.158	0.114	1.680	2.066	0.181	0.237
Kapton #62 (ISS) Aged	High Temp 574.3	796	0.289	0.383	0.235	0.243	0.210	0.194	1.630	1.962	0.237	0.300
Pyrell #63 (ISS) Unaged	Low Temp 225.3	3436	0.394	0.392	0.290	0.207	0.244	0.151	1.810	2.222	0.291	0.414
Pyrell #63 (ISS) Aged	Low Temp 225.3	2658	0.468	0.539	0.354	0.359	0.292	0.293	1.920	1.892	0.361	0.553
Pyrell #64 (ISS) Unaged	High Temp 242.1	1888	0.411	0.445	0.298	0.254	0.249	0.192	1.840	2.115	0.300	0.435
Pyrell #64 (ISS) Aged	High Temp 242.1	1560	0.540	0.616	0.403	0.450	0.328	0.385	1.980	1.750	0.414	0.660
Silicone #60 (ISS) Unaged	High Temp 379.9	557	0.153	0.533	0.120	0.241	0.107	0.162	1.590	2.440	0.119	0.148

Table 2.1 Flight Data Comparison of TEM and Moment Method Distribution Parameters

2.6 Results of Smoke-in-Drums Ground-based Experiments

2.6.1 SMPS Results for Spherical Smoke Aerosols

Five SAME materials were tested at two temperature levels: baseline and high temperature. Typical particle size distributions from the ground testing validation experiments of the unaged and aged smoke for the more spherical aerosols are plotted in Figures 2.18 through 2.20. Pyrell[®] and Teflon[®] are not spherical aerosols and thus are not ideal for the moment method, consequently they are not analyzed for lognormality in this section. Particle size distributions are shown in the upper left plots, Kapton (Figure 2.18a), lamp wick (Figure 2.19a), and silicon Figure (2.20a) which have open plot marker symbols for unaged smoke and solid symbols for aged smoke. The plotted lines represent a lognormal curve-fit with the MATLAB Statistics Toolbox function 'nlinfit' which performs non-linear least squares regression with the Levenberg-Marquardt algorithm (MATLAB version R2012a, The MathWorks, Inc.). Residual plots are aligned below the size distributions, showing deviations from the lognormal fits. This visual test for 'goodness-of-fit' would result in randomly scattered residual points both above and below zero, for a good lognormal fit. It is common to observe a wedge-shaped spread of residuals, as in Kapton (Figure 2.18b), where the tails of the distribution have mostly small residual values, with a wider spread of residuals around the peak diameter. In general, the spread of the residuals is more compact for Kapton and lamp wick, indicating a better lognormal fit for these materials. Note that the unaged Kapton residuals are mostly positive up to 70 nm, which indicates that the lognormal fit underestimates the data.



Figure 2.18. Smoke particle size distributions from SMPS measurements (ground tests) for a representative Kapton® baseline temperature test (510 °C) with open plot markers for unaged smoke ($d_g = 139$ nm, $\sigma_g = 1.78$) and solid symbols for aged smoke ($d_g = 209$ nm, $\sigma_g = 1.66$). The solid curves represent the non-linear least square fits. A residual plot showing the deviations from the lognormal fits is aligned below the size distribution. Plots c and d are log probability graphs unaged (above) and aged (below), based on discrete SMPS bin data. Number distributions are grey, volume distributions are black, and dashed lines are lognormal curve fits.

The lamp wick residual plot (Figure 2.19b) also shows a small but systematic deviation from the lognormal fit, which is evident by the change in sign of the unaged data residuals between 500 and 600 nm.



Figure 2.19. Smoke particle size distributions from SMPS measurements (ground tests) for a representative lamp wick high temperature test (286 °C) with open plot markers for unaged smoke ($d_g = 171 \text{ nm}$, $\sigma_g = 1.98$) and solid symbols for aged smoke ($d_g = 248 \text{ nm}$, $\sigma_g = 1.75$). The solid curves represent the non-linear least square fits. A residual plot showing the deviations from the lognormal fits is aligned below the size distribution. Plots c and d are log probability graphs unaged (above) and aged (below), based on discrete SMPS bin data. Number distributions are grey, volume distributions are black, and dashed lines are lognormal curve fits.

The silicone residual plot (Figure 2.20b) shows the least randomness, which indicates that the lognormal fit is less valid. The residuals change signs on both sides of the peak, indicating a shoulder in the small sizes (residuals go from positive to negative), the peak is offset from the fit (positive residuals around 400 nm) and the lognormal fit overestimates the SMPS data in the large sizes (negative residuals). Furthermore, the silicone residual plot has more noise and negative residuals at higher diameters, which may also be caused by losses from gravitational

settling of these larger particles in the SAME aging chamber and/or the 55-gallon drum. Several systematic deviation patterns are observed, for example, where a shoulder in the distribution exists, a corresponding set of all positive residuals show a marked departure from the lognormal curve fit. This could be attributed to an improper multiple charge correction.



Figure 2.20. Smoke particle size distributions from SMPS measurements (ground tests) for a representative silicone baseline temperature test (342 °C) with open plot markers for unaged smoke ($d_g = 257 \text{ nm}, \sigma_g = 1.84$) and solid symbols for aged smoke ($d_g = 382 \text{ nm}, \sigma_g = 1.56$). The solid curves represent the non-linear least square fits. A residual plot showing the deviations from the lognormal fits is aligned below the size distribution. Plots c and d are log probability graphs unaged (above) and aged (below), based on discrete SMPS bin data. Number distributions are grey, volume distributions are black, and dashed lines are lognormal curve fits.

It is notable that most of the extreme positive and negative values of the residuals for all materials are for unaged smoke (open symbols), which suggests that as smoke ages within the

time frame of this experiment, it becomes more lognormal. As expected, the aged (black symbol) distribution moves to the right as aging increases the geometric mean diameter and σ_g decreases as the distribution narrows by coagulation.

The SMPS setting for a 10:1 sheath-to-aerosol flow rate ratio (3.0 lpm sheath, 0.3 lpm aerosol flow) captured the complete size distribution only for unaged Kapton® smoke, whereas the other materials had larger size ranges which were only completely captured by a 5:1 flow rate ratio (1.5 lpm sheath, 0.3 lpm aerosol flow) which extended the measurement range to 1000 nm. Silicone and Teflon® high temperature distributions were not completely captured by the SMPS, even with the larger range up to 1000 nm. Some samples have an initial uptick in the small diameter tail, which is believed to be a sampling anomaly in the SMPS, possibly an artifact from the previous sample, as the scans were performed in rapid succession. This anomaly did not have a significant effect on the parameters obtained in the fitting of the SMPS data. Another possible explanation is that there could be another mode only partially captured in the lower end of the SMPS measurement range.

The log-probability plot is a graphical technique used to assess lognormality of an aerosol. Discrete data from the SMPS size bins are plotted on the probability scale in Figures 2.18 through 2.20, with parts (c) and (d) corresponding to unaged and aged smoke, respectively. Lognormal distributions will appear as a straight line, and volume and number size distributions should be parallel, indicating that σ_g is the same for both distributions but with different means. Extremes on the graphs can be neglected in the log probability plots for number distributions when they deviate from the straight line fit for 5% or less of the extremes of the probability scale (Hinds, 1999). For the SMPS data used in these log probability plots, these deviations from lognormality are the result of poor counting statistics in the large diameter tail and lack of

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measurement range (for lamp wick and silicone), which particularly affects the volume distribution plots. Thus the volume distribution plot will display a line that is slightly curved at the large sizes, which corresponds to a lack of linearity of the number distribution line beyond 95% of the distribution. Figures 2.18(c) and 2.18(d) show log-probability plots for Kapton® at baseline temperature. The plotted cumulative frequencies are quite linear for Kapton[®] and the number and volume distribution lines are nearly parallel. Lamp wick log probability plots are shown in Figures 2.19(c) and 2.19(d) (unaged and aged). The volume distributions have a smaller σ_g which is evident by the shallower slopes. This is caused by the limited SMPS measurement range, which misses a portion of the high temperature lamp wick large diameter tail, a deficiency which is emphasized in the conversion to volume concentration. Log probability plots for lamp wick demonstrate the flattening of the slope with aging, which corresponds to the narrowing of the distribution as coagulation takes place. The log probability plots for silicone, Figures 2.20(c) and 2.20(d), are not linear and thus fit a lognormal distribution poorly. The lognormal fit, Figure 2.20(a), and the residual plot, Figure 2.20(b), reflect the same result, where the lognormal curve overestimates the SMPS data for large diameters and underestimates for smaller diameters, thus the log probability plot has deviations from the straight line fits at both the smallest and largest percentages of the distributions.

Raw counts for the particle size distributions of the SMPS scans indicate the statistical reliability of the data. Of all the data taken, there are sufficient raw particle counts in the majority of bins, however, when there are less than 10 particles in a bin, the reliability is questionable (Hinds, 1999). This is a problem in the tails of the distribution, and compounded with sampling efficiency and losses of large particles in the system, the large diameter tail is particularly affected. In spite of the lower resolution of the low flow aerosol to sheath flow rate

ratio, the number of counts per channel is about twice as large for this condition which results in improved statistics. Thus, data from the lower flow rate ratio scans were used exclusively in the data analysis to reduce the uncertainty in the measurements.

Additional SMPS results for non-spherical aerosols and multiple temperature conditions are given in Appendix B.

2.7 Discussion

2.7.1 Limitations of Instrument Measurement Ranges

Calibration of SAME instruments was intended to empirically account for differences in the ranges of the instruments. In the ground validation tests, however, the truncated distribution formula (equation 13) can shed light on the limitations and uncertainty of the SMPS measurement range for the fuels tested. Particularly when the particle size distributions are converted to surface area or volume distributions, the percentage of the distribution that is lacking can be significant. Furthermore, the upper end of the SMPS size distribution measurement may not be as reliable because it can be affected by poor counting statistics and these bins are more susceptible to multiple charge correction errors. Therefore it is prudent to compare a more conservative upper SMPS limit of 700 nm along with the full recorded range to 1000 nm, to see the effect of the SMPS measurement range. Thus, if we were to consider the SMPS data to be most reliable (having the least uncertainty) in the range of 23 to 700 nm, then the truncated distribution formula for $M_{p,rel}$ can indicate what percentage of the distribution would be captured with this limitation. Figure 2.21 shows the percentage of the distributions captured by the SMPS for two example materials, Kapton and silicone. Kapton is the best candidate for SMPS validation, as the highest percentages of each type of distribution are within the SMPS measurement range. For example, considering both the conservative 700 nm limit and the 1000 nm limit, the bar graph (Figure 2.21a) indicates that 98% to 100% of the distribution has been measured. Silicone smoke is not a good candidate for SMPS validation because of the lack of measurement range, particularly when converting to surface and volume size distributions. Notably in the volume distribution in Figure 2.21b, the black bar representing a 1000 nm upper size limit is only at 40%, indicating that 60% of the distribution is missed by the instrument, but when losses are considered and a range of 700 nm is relied upon, approximately 20% of the distribution is captured (the white bar).





Thus, the truncated distribution formula for $M_{p,rel}$ can be a useful indicator of the suitability of an aerosol reference instrument and the level of uncertainty in measurements. If enough of the size distribution is known to obtain parameters for a lognormal fit from curve-fitting software, one can determine how comprehensive the size distribution measurement is and whether conversion of the distribution will produce reliable results.

2.7.2 Comparison of SMPS Data, Discretely Calculated Moment Diameters vs. Hatch-Choate Diameters based on Lognormal Fit Parameters

A useful quantitative measure of the validity of the lognormal assumption is to start with one set of data and compare diameters calculated by two different methods. The SMPS data offer the opportunity to use the grouped data discretely, and based on the lognormal fit values of d_g and σ_g , the same diameters can be calculated with the Hatch-Choate equations.

The SMPS bin data (based on a 64-channel per size decade histogram) can be used in equation (12) formulas to calculate diameters of average properties, which can then be compared with diameters calculated from equation (9) using the geometric mean diameter and σ_g from the lognormal fit of the SMPS particle size distribution. This is equivalent to calculating Ntot, Ltot and M_{tot} from SMPS binned data to obtain d_{av} , d_m , by equations (3) and (4). Thus, the continuous distribution parameters used in the conversion equations will be compared with the grouped data, and the expectation is that these diameters will be equal if the lognormal assumption is valid. Two examples of these diameter comparisons are shown in Figure 2.22, which compare the count mean diameter (also known as the number average, or d_{50} of the number distribution), surface area diameter, diameter of average mass, mass median diameter (d_{50} of the volume distribution), and the count median diameter (which is the geometric mean diameter, provided that the distribution is lognormal). As can be seen, there is good agreement in all diameters for Kapton (Figure 2.22a) but not as good agreement for silicone (Figure 2.22b). The diameters with the largest deviations are those having to do with the mass. This is not surprising, since these are heavily influenced by the large diameter particles and often the SMPS raw counts in the upper bins of the tail have fewer than 10 particles so there is the potential for discrepancies in the discrete bin calculations due to insufficient statistics.



Figure 2.22. Two examples of the comparison of diameters calculated from SMPS data (ground testing) in two ways: 1) Converted by Hatch-Choate conversion equations using SMPS dg and σg and 2) Calculated using discrete SMPS bin data. Low temperature unaged Kapton smoke (a) and low temperature unaged silicone smoke (b).

Figure 2.23 shows the results of all these bar graphs from comparison of the three spherical aerosols on one plot (including unaged and aged diameters, at all temperatures tested). The black bars of Figure 2.22 are the y-axis quantity in Figure 2.23 and the white bars are the x-axis quantity. Data falling on the 1:1 reference line meet the lognormal assumption, whereas those that differ significantly do not. While some information is lost in this scatter plot vs. the bar graphs (e.g., which data marker represents which moment diameter), the graph shows that for Kapton and lamp wick, the diameters calculated by both methods coincide and thus can be considered lognormal. It is evident that diameters above 500 nm, which are the higher moment diameters, and mostly silicone, do not coincide. Overall, the qualitative comparison of these diameters strongly suggests that the smoke particle size distributions for Kapton® and lamp wick can be considered lognormal and silicone should not.



Figure 2.23. Comparison of diameters calculated from SMPS data (ground testing) in two ways: 1) Converted by Hatch-Choate conversion equations using SMPS lognormal fit d_g and σ_g and 2) Calculated using discrete SMPS bin data. All diameters as represented in Figure 2.28 are combined here for all materials and test conditions: open markers are unaged, solid are aged; grey represents baseline temperature and black represents high temperature tests, and marker shapes are Kapton – circle, lamp wick – square, silicone – triangle.

2.7.3 Comparison Between Size Distribution Parameters from TEM and the Moment Method for Flight Data

Although meticulous calibrations were performed, a number of smoke aerosols measured in flight tests exceeded the calibration range for the ionization detector which measures the first moment. As evident in the uncertainty analysis, error in the first moment measurement has the largest influence on the resulting calculations. Kapton consists of smaller particles and was not affected by this shortcoming, so these tests provided the most reliable moment method results. Since the first moment measurement is not used in the calculation of d_m , this quantity can be compared for the other materials.



Figure 2.24. Comparison of TEM analysis and moment method diameter of average mass for smoke from ISS flight data.

Figure 2.24 shows the comparison of the flight TEM diameter of average mass with the value calculated from the moment instrument data using equation (4). Since the third moment instrument was calibrated for each smoke type with a direct-reading reference instrument, the measurements are assumed to be relatively shape-independent. For the three materials in this graph, the moment method provides a reasonably good measurement for the diameter of average mass. Thus it can be concluded that the zeroth and third moment instruments maintained their calibration sufficiently to quantify this moment average diameter from flight data.

2.8 Conclusions

The aerosols considered in SAME represent the most likely smokes that a spacecraft fire detector will have to detect. These smoke aerosols have been characterized and conclusions are summarized with the following observations:

- TEM analysis of the smoke particles from five spacecraft materials revealed distinct morphologies ranging from nearly spherical (Kapton and lamp wick) to extended agglomerates (Pyrell and Teflon).
- 2. The silicone particles were not stable enough for TEM analysis.
- Successful size distributions from the TEM were obtained for the more spherical particles (Kapton and lamp wick), as well as for Pyrell, as the projected area equivalent diameter is comparable to mobility diameter, even for non-spherical particles.
- 4. SMPS measurements were made for all 5 materials.
- Comparison of SMPS and TEM measurements showed reasonable but not complete agreement.
- 6. Comparison of the TEM and moment measurement results from the space experiments showed good agreement for the three materials whose morphology was amenable to TEM analysis (Kapton, Pyrell and lamp wick).
- 7. Statistical analysis of SMPS measurements showed that the size distributions of spherical particles Kapton and lamp wick can be characterized as lognormal.
- 8. Although a direct comparison of the TEM, SMPS and moment instruments results was not possible, the observed sizes from each system were quite consistent given the constraints of each measurement type.

The moment method used in this work for the measurement of size distribution parameters relies on two assumptions: spherical particles and a lognormal distribution. These conditions were reasonably met in two of the five materials tested (Kapton and lamp wick). However, using the output from the calibrated SAME moment instruments, one is able to partially characterize the aerosol by determining d_m and d_{av} for any particle morphology. Within the limitations of spacecraft fire detection and low gravity experiments, the moment method was considered as a candidate for smoke aerosol measurement and has been proved moderately effective.

The smokes observed for these spacecraft materials cover a broad range in particle size. Ambient aerosols in spacecraft include significantly larger particles than on Earth as gravitational settling is absent, and smoke detectors must distinguish between background aerosols and smoke in order to prevent false alarms. Therefore the typical background aerosols in manned spacecraft should be characterized and taken into account for smoke detector designs. Spacecraft fire detection systems require years of maintenance-free operation. This will be an important challenge for future longer-term space missions, as the expertise and resources necessary to calibrate and/or repair aerosol instruments in flight would not be available.

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<u>Chapter 3: NASA Fire Safety Research Facilities and</u> <u>Selected Experiment Results</u>
3.1 Introduction

Spacecraft fire safety programs at NASA are not only concerned with smoke detection, but also with the post-fire environment. In the event that a survivable fire has taken place and been extinguished on the International Space Station (ISS), the impacted module will have been closed off and air handling systems isolated from the rest of the station. The crew will have evacuated to an unaffected area and will be expected to clean up the aftermath, hopefully recovering the module for future use. This necessitates gas and aerosol monitoring equipment in each module which can indicate remotely the condition of the air in the affected module, so the crew will know when it is prudent to enter to begin cleanup. Spacecraft materials studied in this work emit acid gases when overheated, and each toxic gas species has been evaluated by NASA toxicologists and assigned a spacecraft maximum allowable concentration (SMAC) (Mudgett et al. 2005; Sribnik et al. 1990). Furthermore, smoke concentrations must be reduced to safe levels, and designs are currently under investigation for smoke removal devices which can operate autonomously so that the crew can enter with personal protective equipment once the visibility is passable and particle concentrations have dropped. Therefore it is necessary to characterize the post-fire environment, as all of these technologies must be designed to the conditions and tested in a relevant environment. These technologies include gas and particle monitors, respirator/filtration masks (with known lifetimes and capacities for the toxic gases & particles) and smoke removal devices.

Spacecraft fire detection and post-fire cleanup testing has taken place at Johnson Space Center's White Sands Test Facility (WSTF) in Las Cruces, New Mexico and at the NASA Glenn Research Center Gases and Aerosols from Smoldering Polymers (GASP) Laboratory in Cleveland, Ohio.

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Smoke characterization data from these facilities encompasses measuring aerosols and gaseous products, and measured parameters vary based on the availability of newly developed and mature gas sensors and aerosol instruments, as well as evolution of the test matrices by the investigation of new fuels and the use of various fuel preparation methods. A comparison of the capacities of the NASA fire research facilities appears in Table 3.1, including the Smoke Aerosol Measurement Experiment (SAME) hardware specifications.

The WSTF data presented here consist of aerosol mass and number concentration of the smoke from fifteen different materials or combinations of materials, at several temperatures. Data from GASP laboratory in this work is from a study on early smoke detection using a compact commercial-off-the-shelf (COTS) particle sensor.

NASA Facility	Abbreviation	Chamber Volume, liters	Heating Duration, minutes*	Temperatures, ⁰C	Fuel Masses, g
Smoke Aerosol				range from	
Measurement Experiment	SAME	6	1	225 to 575	0.1 to 0.43
Johnson Space Center				range from	
White Sands Test Facility	WSTF	623	7	340 to 640	0.5
Gases and Aerosols from					
Smoldering Polymers				ramp from	
Laboratory	GASP	326	4	200 to 640	0.2 to 2.0

Table 3.1 NASA Fire Research Facilities Comparison

* Heating durations are the typical values for the tests reported in this work.

3.2 NASA Johnson Space Center's White Sands Test Facility (WSTF) Smoke Research Facility

An instrumented chamber was developed for WSTF spacecraft fire safety testing. The

chamber, shown in Figure 3.1 has a volume of 623 liters (22 ft³) which can exhaust to a roof vent

stack, and two fans prevent stratification of smoke in the chamber. Tests were conducted in

ambient air at 12.4 psia (WSTF ambient atmospheric pressure is lower owing to the altitude

above sea level). Figure 3.2 is a schematic representation of the instrumentation used in the testing.



Figure 3.1: Photograph of smoke chamber at NASA White Sands Test Facility.

The smoke generator, also shown in Figure 3.3, consists of a quartz-lined electrical tube heater with an air supply line that introduces a low flow of air to the hot mixture. This system has been designed so that both flaming and smoldering fires can be simulated. Different smoldering conditions were explored in pursuit of a high production rates of toxic gaseous products, particularly at temperatures between 340 and 640 °C. In general, these scenarios emulate a low temperature fire that produces a maximum of volatile organic compounds with little thermal oxidation and high aerosol concentration, or a higher temperature condition that produces a significant concentration of carbon monoxide (CO). A flaming test variant of the high temperature smoldering condition was conducted by remotely igniting the volatile fuel vapors exiting the tube are after several minutes of smoke production. The furnace temperature was determined by a feedback temperature controller with a variable heating rate. Aging of the smoke in the smoke chamber cannot not be avoided, so aerosol measurements are of mixed fresh and aged smoke. This is a realistic fire scenario, particularly in low gravity, where the absence of buoyant flow will cause smoke to concentrate at the source and undergo aging, while fresh smoke is continually emitted in the same vicinity.



Figure 3.2: Schematic of aerosol instruments sampling from the chamber, including laminar flow elements (LFE) for dilution of aerosol instruments. Gas sensors were placed directly in the smoke chamber.



Figure 3.3: Smoke generator inside the WSTF smoke chamber

3.3 WSTF Sample Materials and Conditions

Materials that are common in spacecraft, particularly in electronics, are logical fuels to overheat in order to characterize the resulting smoke and gases. Tables 3.2 and 3.3 show the test matrices including fuel materials used in the two test campaigns conducted at WSTF. The Standard Mix fuel is a mixture of twelve granulated constituents represented in specific mass fractions down to the hundredth of a gram. Exact proportions and materials are outlined in (Hornung 2011), and for these tests, the mixture was created in small batches ranging from 5g to 20 g total weight. This combination of materials was originally created as a fuel for a reference fire model proportionally representative of materials used in spacecraft avionics, but on a much larger scale, at 530 g (Jagow et al. 1977). The Standard Mix fuel was predominantly used in the first test campaign and in previous WSTF testing (Ruff et al. 2011). Materials used for the first test campaign are shown in Table 3.1. The PFPI wire insulation is partially fluorinated polyimide manufactured by TRW. For the second test campaign, the current spacecraft wire Mil Spec M22759 was used, which is produced by a PTFE and polyimide tape wrapping process to produce layers over the conductor which are then thermally fused. The insulation was stripped from 12 gauge M22759/86 wire (manufactured by Nexans) in short random lengths, and used without further granulation. Nomex cloth is a heat and flame-resistant textile woven from continuous meta-aramid polymer fibers (DuPont Chemical Company). In spacecraft applications, Nomex cloth is used for acoustic insulation, cargo bags, thermal blankets and pressure suits. The Nomex cloth used in these tests was snipped into 3 to 5 mm shredded pieces. Teflon is the DuPont Company trade name of polytetrafluoroethylene (PTFE, (C2F4)n), a crystalline fluoropolymer commonly used in spacecraft for wire insulation, water storage bladders, sampling bags, suits, and cargo liners. For the first test campaign, Teflon (PTFE)

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granules were made with a rotary grater and in the second test campaign, the granulated PTFE was compared with 100 μ m PTFE powder (Sigma Aldrich). Spacecraft applications of Kapton include thin-film heaters, wire insulation, space suits, tape and multi-layer insulation (MLI).



Figure 3.4: PTFE preparation, 100 µm powder (Sigma Aldrich) vs. granulated (from grinder)



Figure 3.5: Kapton film fuel preparation, left: thin strips were cut into approximately 2 mm squares; right: granulation of film is difficult and required some hand sorting to eliminate larger pieces.

Kapton film shredded with the rotary grater but required hand sorting to eliminate larger pieces and for the second test campaign, thin strips of Kapton film were cut into approximately 2 mm squares for comparison. Figures 3.4 and 3.5 show the different preparations for Teflon and Kapton, respectively. The mixtures of Kapton and Teflon in the first test campaign combined only the granulated preparations.

Printed circuit board (PCB) fuel was from a downgraded flight spare fully populated with certified conformal coating, an example of 'typical' modern electronics and was granulated with a rotary grinder. Metal portions of the circuit card assembly were avoided during the grinding process and in weighing out the 0.5 gram samples. Figure 3.6 shows the original PCB subjected to grinding (left) and the fuel pellet of the pressed circuit board granules. Prepared fuels were held by a mica sheet which was rolled up and placed in the smoke generator, and also provided containment for the ashes as they were removed for weighing. There is potential that some trace minerals from the mica sheet to interacted with the smoke particles, as is postulated in the microscopy section of this work (Chapter 5), as the elements Al and Si were sometimes present in smoke particles but not in the fuel chemical composition. Differences in the temperatures, materials, number of replicates and total number of runs in Tables 3.2 and 3.3 represent the evolution of the WSTF testing efforts and emphases, with the first campaign exploring more temperature dependence and the Standard Mix, all with pellets; and the second test campaign investigating Teflon/Kapton and other mixtures as well as surface area dependence of some fuels.

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Figure 3.6: Circuit board that was ground for fuel (left), pelletized ground circuit board before heating in the first test campaign (right).

Material (0.5 g)	Furnace Temp/C	Ignite	Replicates	# Tests	Notes
Standard Mix	340,440,540,640	Yes	1-2	7	Granulated
Granulated Circuit Board	340,440,540	Yes	2-3	5	Populated, conformal coated
PFPI wire insulation	540,640	No	3-4	7	20AWG stripped
100% PTFE	540,640	No	2-3	5	Granulated
100% Kapton	540,640	No	2-3	5	Granulated
50:50 PTFE/Kapton mix	540,640	No	1-2	3	Mixtures of above
25:75 PTFE/Kapton mix	540,640	No	2	4	
75:25 PTFE/Kapton mix	540,640	No	1-2	3	
10:90 PTFE/Kapton mix	640	No	2	2	
90:10 PTFE/Kapton mix	640	No	2	2	

Table 3.2: First WSTF Test Campaign Summary

Total Runs: 43

Material (0.5g)	Furnace Temp/C	Replicates	# Tests	Notes
Nomex	640	7	7	HT9040, natural, untreated
Nexans Wire Insulation	640	б	б	M22759/86 12AWG stripped
100% PTFE	640	8	8	4 Granulated & 4 powdered PTFE
100% Kapton	640	5	5	3 Snips and 2 Granulated
PTFE/Kapton mixes	640	3-4	18	10/90; 90/10; 25/75; 75/25;50/50
Circuit Board (PCB)	340,440,540,640	2	8	Granulated
PVC	640	1	1	Granulated; for HC1 production
PCB+PVC	640	3	3	0.5g PCB with 0.05g PVC
PCB+PVC	640	2	2	0.5g PCB + 0.1g PVC
PTFE+PVC	640	1	1	0.4g PTFE + 0.1g PVC

 Table 3.3: Second WSTF Test Campaign Summary

Total Runs: 62

3.4 WSTF Test Procedure and Instruments

The sample tube heater near the center of the chamber is controlled by a LabView interface which determines the temperature ramp duration and magnitude. The test procedure used in all the tests is outlined in Table 3.4. A fan near the rear corner is turned on for approximately 30 seconds after the heater is turned off to provide a uniform concentration inside the test chamber. After mixing, the combustion products are allowed to decay for 5-10 minutes after which the chamber is purged with a vent fan. The front ports are opened to allow fresh lab air to be pulled into the chamber during venting. The time to complete a test, from the chamber sealing until the final venting is approximately 20-30 minutes.

Objectives of the testing campaigns were to characterize both the smoke particles and gaseous emissions from pyrolysis. Both commercial and advanced prototype gas sensors measured carbon monoxide and acid gas species evolving from pyrolysis of polymeric materials. The acid gases hydrogen cyanide (HCN), hydrogen chloride (HCl) and hydrogen fluoride (HF) are produced from the heating of polymeric materials containing nitrogen, chlorine, and fluorine,

respectively. Only aerosol data are reported here, however, gas data can be referenced in (Meyer

et al. 2013).

Step	Description
1	Load fuel, close chamber, turn off purge vent
2	Ramp furnace temperature up to target temperature
3	Turn furnace blower on when at target temperature (at t=3 min)
4	Hold furnace temperature for ~ 4min
5	Turn off furnace at t=7 min & stir chamber via muffin fan for 30 sec
6	5 to 10 min dwell/natural decay (occasionally longer)
7	Purge duct fan on to vent chamber through front glove ports
8	Remove and weigh ash

 Table 3.4: Standardized Test Procedure Timing (used for each run)

3.4.1 Aerosol Thermal Precipitator

A thermal precipitator was designed at NASA Glenn Research Center to collect smoke aerosol particles for microscopic analysis. The design takes advantage of the thermophoretic force on a particle in the presence of a large temperature gradient created by opposing thermoelectric coolers and Kapton heaters. The particles are driven to the cold side of the gradient, which in this device is set of SEM stubs prepared with a section of carbon tape and TEM grids to facilitate a variety of analyses. Information on particle morphology, size, chemical composition and agglomerate structure obtained from these tests supplements aerosol concentration data collected. A detailed description of the thermal precipitator design is given in chapter four of this work and microscopy results showing particles collected are given in chapter five of this work.

3.4.2 Tapered Element Oscillating Microbalance (TEOM) Personal Dust Monitor (PDM)

The Tapered Element Oscillating Microbalance (TEOM, Thermo Scientific, Franklin, MA, USA) is a direct-reading gravimetric aerosol instrument currently available from Thermo Fisher

Scientific, Inc., Waltham, MA) that measures aerosol mass deposited on a filter. The filter is mounted on a hollow tapered glass stalk through which air is drawn and which vibrates at a frequency proportional to the mass on the filter. The system electronics monitor the frequency changes, and changes in mass on the order of micrograms are computed and recorded every 5 seconds. Aerosol mass concentration can be derived from the change in mass on the filter and the known volumetric flow rate of air through the filter. The PDM is a wearable respirable dust sampling version of the TEOM for use in mining and other hazardous occupations.

3.4.3 DustTrak II and DustTrak DRX Monitor

Aerosol photometers measure the combined laser light scattered from many particles at once which can be correlated to mass concentration. Early testing at WSTF used the DustTrak II (Model 8520, TSI Inc., Shoreview, MN) and subsequent tests were performed using the DustTrak TM DRX (Model 8533, TSI Inc., Shoreview, MN) which combines ensemble scattering with single particle detection to provide real-time size-segregated mass fraction concentrations up to 150 mg/m³. In NASA smoke characterization testing, aerosols below 1 μ m in diameter are the predominant sizes however it is of interest in fire characterization to determine which fuels generate particles above this threshold. Optical aerosol instruments give a material-dependent response, with particle refractive index dictating the amount of light scattered. The DustTrak instruments are factory calibrated with Arizona Road Dust for the wider market of occupational hygiene applications. A custom calibration of the DustTrak II was performed with a Smoke Detector Sensitivity Analyzer, Gemini model 501-A (Gemini Scientific Corporation, Sunnyvale, California), an aerosol generator which produces particle sizes representative of smoke from fires. This instrument nebulizes Rudol[®] white mineral oil at varying flow rates, and has a calibration curve correlating the generator flow setting to smoke aerosol mass concentration.

The particle size distribution of the generated oil aerosol (at the instrument's concentration level 90) used in the DustTrak calibration (shown in Figure 3.7) has a geometric mean diameter of 148 nm and a geometric standard deviation of 1.8.



Figure 3.7: Rudol® white mineral oil aerosol size distribution generated with Smoke Detector Sensitivity Analyzer Gemini 501-A, measured with a TSI Scanning Mobility Particle Sizer Spectrometer (SMPS).

3.4.4 P-Trak 8525

The P-TrakTM (Model 8525, TSI Inc., Shoreview, MN) is a condensation particle counter that measures aerosol number concentration. This device operates by passing the aerosol-laden particle stream through a region saturated with isopropanol vapor and then into a cooler region where the vapor condenses onto the particles increasing their diameter such that they can be readily counted by a light scattering device. This instrument is designed for the occupational hygiene market and operates over a range of 0 to 10^5 particles/cm³ and 20 nm to 1 µm diameter. Dilution is required, since the smoke concentration is higher than the upper range limit.

3.5 WSTF Results and Discussion

3.5.1 Fuel Preparation Effects

Testing in the first test campaign involved mostly pelletized fuel. The textures of the constituent materials in the Standard Mix fuel varied and the pellet provided a consistent starting configuration (Hornung, 2011). A hydraulic pellet press was used to form 0.5 g granulated fuel into a ½" compact shape by applying 10,000 psi pressure for one minute (see Figure 3.5). However, some materials retained the pellet shape throughout heating in the smoke generator, whereas others collapsed into granules, providing more available surface area during thermal decomposition. When the pellet remains intact, the thermal decomposition mechanism is altered by the presence of a char front that progresses into the pellet during heating. Combustion products generated at the char front must traverse the surrounding ash in order to be liberated. This process was never rigorously investigated, however, in order to remove this variability between fuel materials, the second test campaign did not use the fuel pellet configuration. Thus all the fuels were granules or small pieces which had larger surface area available for thermal decomposition.

It was observed that the aerosol mass concentration was approximately equal for a 100% PTFE pellet in the February/March testing and the loose ground PTFE test in September. This can be attributed to the nature of ground PTFE, which does not hold its pellet shape very well in spite of 10,000 psi of the pellet press. September testing showed that the commercial 100 μ m PTFE powder made 1/3 more aerosol mass concentration than the ground PTFE. The ground PTFE had granules that were much larger than 100 μ m, as can be seen in the unburned fuel samples in Figure 3.4. However, the most significant effect of fuel preparation on aerosol output was with Kapton, where it was seen that the granulated Kapton film produced five times more aerosol mass concentration than the Kapton film squares. This can be attributed to the increased

surface area in granulated Kapton. The type of wire insulation used in the two test campaigns differed, and the average aerosol mass concentration in February/March was 0.013 g/m^3 , the September test version of insulation averaged 0.050 g/m^3 .

3.5.2 Smoke Aerosol Concentration and Sample Mass Loss

The residue from burned samples (hereafter referred to as 'ash mass') was weighed and recorded with a Mettler Toledo ATG104 with sensitivity of 0.1 mg. A complete mass balance of the pyrolysis process was not attempted, however, the general trends in mass loss can give insight into the fire signature of various materials. The aerosol mass concentration in the smoke chamber was nearly constant throughout the heating cycle after the initial temperature ramp. Thus, an approximate total aerosol mass (total suspended particulate) could be calculated from the mass concentration measured and the known volume of the smoke chamber.

Ash mass was significantly affected by pelletization for Kapton in the February/March testing. Loose samples burned in September had an average ash mass that was 15 to 30 times larger than the pelletized Kapton. Figure 3.8 shows the smoke aerosol signatures for various tests at 640° C. Unburned fuel mass is 0.5 g (the left axis limit), the ash and estimated total aerosol masses are represented by bars, and aerosol number concentration represented by circles (corresponding to the right axis). Printed circuit board (PCB) ash mass was larger than most other materials since the substrate FR-4 tends to form char under pyrolysis conditions. The combined ash mass and estimated aerosol mass account for approximately 75% of the initial sample weight, which is unusual compared to most materials tested. Nomex samples had nearly equal ash mass and estimated aerosol mass. Teflon samples had the smallest ash mass remaining after testing, with the average remaining mass only 16% of the original mass.

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Figure 3.8: Smoke aerosol signatures for various tests at 640° C. Unburned fuel mass is 0.5 g (the left axis limit), the ash and estimated aerosol masses are represented by bars, and aerosol number concentration represented by circles corresponding to the right axis.

Figure 3.8 shows the effect of fuel preparation as well, with the Teflon (PTFE) powder producing more than one third more aerosol mass concentration than the ground Teflon, which had less surface area. The most significant effect of fuel preparation on smoke aerosol output was Kapton, with the granulated Kapton producing five times more aerosol mass than the Kapton squares. Acid gases followed the same trend, with higher concentrations measured from fuels having larger surface area. Both aerosol mass and number concentrations from PVC were very high, and it can be seen that the addition of only 10% PVC to Teflon powder changes the smoke dramatically compared to pure Teflon powder, increasing the smoke mass concentration significantly.



Figure 3.9: Smoke aerosol signature for Teflon/Kapton mixture tests. Unburned fuel mass is 0.5 g (the left axis limit), the ash and estimated aerosol masses are represented by bars, and aerosol number concentration represented by circles corresponding to the right axis.

The Teflon aerosol had a higher aerosol number concentration than most materials, but is made up of much smaller particles which filled the TEOM filter, necessitating higher dilution ratios and frequent filter changes. Figure 3.9 shows the aerosol signature of the Teflon/Kapton tests, where unburned fuel mass is 0.5 g (the left axis limit), the ash and estimated total aerosol masses are represented by bars, and aerosol number concentration represented by circles (corresponding to the right axis). It can be seen that he total aerosol mass increases as the percentage of Teflon in the Teflon/Kapton mixture increases, and the sample ash mass decreases as the percentage of Teflon increases. Kapton and Teflon mixes were of great interest in gas measurements for HF production, particularly in comparison to the wire insulation fuels which combine both materials in unknown percentages.



Figure 3.10: Smoke aerosol signature for granulated circuit card tests as a function of temperature. Unburned fuel mass is 0.5 g (the left axis limit), the ash and estimated aerosol masses are represented by bars, and aerosol number concentration represented by circles corresponding to the right axis.

For circuit card fuel (Figure 3.10), aerosol mass increases slightly with increasing temperature, and there is a corresponding decrease in sample ash mass with increasing temperature. This relationship between sample mass loss and aerosol mass has been demonstrated in other NASA experiments (Mulholland et al. 2015), however smoke particle sizes vary significantly from one material to the next, so spacecraft fire detectors must have the ability to measure multiple moments of the aerosol size distribution in order to work effectively.

3.6 Gases and Aerosols from Smoldering Polymers (GASP) Smoke Research Facility

Gases and Aerosols from Smoldering Polymers (GASP) Laboratory was established at NASA

Glenn Research Center in order to perform experiments related to spacecraft fire safety and post-

fire cleanup environments. Ongoing testing in GASP is based on similar fuels used at WSTF, however, the focus is increasingly on early detection of smoke vs. the smoke characterization in the SAME ground tests (smoke in drums) and in WSTF testing. Another shift in testing practices is to use more solid (intact) materials rather than granulated fuels, owing to the surface-area dependence noted in the previous section. This creates a more realistic source of smoke, however the fuel sizes are limited by the size of the tube furnace in GASP. Another significant difference in GASP testing vs. the other facilities is the much larger fuel masses, which are necessary to generate measurable quantities of acid gases relevant to post-fire cleanup environments.

Figure 3.11 shows the configuration of the furnace, smoke chamber and measurement instruments. Safety considerations dictated that all aerosol and gas instruments, as well as all mechanical connections of tubing that would contain smoke or acid gases, must be enclosed and vented continually to avoid toxic gas exposure to operators. The materials and seals used in the facility have all been selected to minimize corrosion. One polycarbonate enclosure covers the smoke chamber and a separate larger cover is over an optical table which holds the furnace and other equipment. Access doors in the large enclosure allow samples to be loaded in the furnace and instrument adjustments between runs. A vented gas cabinet houses bottles of gas standards used for calibrations of state-of-the-art sensors which are under development for monitoring spacecraft fire and post-fire cleanup environments. A single piece of stainless steel 0.25-in. tubing, approximately 20 feet long delivers gases or filtered house air by way of calibrated flow controllers to the large enclosure in Figure 3.11. The flow of the calibration gas and dilution air is regulated by thermal-based mass flow controllers from MKS Instruments. The system is set up to allow purging of the gas lines and the rest of the system between tests for pure calibration

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gas delivery after changing bottles. Multiple mass flow controllers allow for dilution from 1-100% of the full bottle concentration to test the high and low limits of sensing devices. The smoke chamber can be vented by a purge hatch (without opening the enclosure) which directs the smoke out through the vent as HEPA-filtered house air is flushed through the smoke chamber. Thus virtually particle-free air is obtained as the baseline for smoke tests (typically less than 20 particles/cm³). Another HEPA capsule is open at all times to allow gas to escape to prevent any potential over-pressurization of the smoke chamber. A Lindberg/Blue M tube furnace (HTF55322A) is used to heat samples and generate the oxidative pyrolysis products of interest for spacecraft fire safety (as opposed to flaming combustion products). This furnace has been thermally characterized to determine the optimal heating zone for fuel samples, and this temperature is logged throughout the duration of each test with a thermocouple mounted at the fuel sample location. During heating, filtered air flows through the furnace at 4.4 lpm to push the thermal decomposition products into the 326 liter smoke chamber. This flow rate was chosen to match the velocity in the SAME smoke duct in order to create similar pyrolysis conditions for comparison purposes, and which typically matches the flow rates of all the aerosol instruments sampling air from the chamber, so the net removal rate is close to zero. The smoke chamber includes pass-throughs for the furnace tube (smoke/gas source) and tubing directed to aerosol dilution equipment and instruments, as well as data and power cables for instruments inside the smoke chamber. A small muffin fan placed in the corner of the smoke chamber prevents stratification of smoke and gases. Humidity can be added to the air flow through the tube furnace into smoke chamber by an inline water bubbler.



Figure 3.11: GASP Facility diagram showing the furnace and instruments in large enclosure on the right and smoke chamber in a second smaller enclosure on the left.

3.7 GASP Sample Materials and Conditions

Selected data presented in this work are from recent GASP tests which explored some spacecraft materials common with both WSTF and SAME data. These fuels were not granulated, but rather placed in the alumina boat as pieces. The exceptions are snipped Kapton (which was compared to bulk Kapton, rolled up and held in place with a paperclip), and Nomex which was snipped as before. Pyrell foam and Lamp wick were cut into pieces roughly the size of the boat, the Teflon fuel was a piece chipped off a solid rod of material, and the PCB was a bare copper clad circuit board (no components). Separate from the PCB, electronic components were chosen to represent typical electronics (including thin film resistors, a tantalum capacitor, an inductor, and a resin-encapsulated LED with the leads removed). Other fuels include PVC insulated wire and mixtures of wire and bulk Kapton. Tobacco was included in the fuels tested as the Sharp sensor is purported to be sensitive to cigarette smoke (Sharp, 2006). This method of heating tobacco is admittedly entirely different than environmental tobacco smoke, but it also presented an additional biomass source (in addition to cotton lamp wick), for comparison purposes. Pictures of selected fuels before and after heating are shown in Figures 3.12 and 3.13.



Figure 3.12: Several fuel samples before and after heating to 640 °C in the tube furnace, a) Kapton snips, b) components (thin film resistors, a tantalum capacitor, an inductor, and a resinencapsulated LED with the leads removed), c) Teflon piece, d) Kapton bulk was film held in place with a paper clip during heating.



Figure 3.13: Several fuel samples before and after heating to 640 °C in the tube furnace, a) Kapton and wire, b) Lamp wick, c) Nomex snips, d) Pyrell foam.

3.8 GASP Test Procedure and Instruments

The heating procedure that has been adopted for most GASP testing is designated the 'fast ramp.' Fuel samples are placed into a 9 cm alumina boat (at room temperature) which is weighed before and after heating. Starting with a furnace temperature of 200 °C and 4.4 lpm airflow through the tube furnace, the sample boat is inserted into the middle of the furnace tube. The furnace controller is set to 640 °C for rapid heating to the set point at a rate of approximately 136 °C/min which typically takes 360 to 390 seconds.

Aging of the smoke in the smoke chamber cannot not be avoided, so GASP aerosol measurements are of mixed fresh and aged smoke. This is a realistic fire scenario, particularly on the ISS, where the absence of buoyant flow will cause smoke to concentrate at the source and undergo aging, while fresh smoke is continually emitted. In some tests, the effect of humidity on the gaseous products was explored and consequently there were some runs with the inline bubbler providing humidity to the air flow through the furnace. It is documented, and past GASP tests have shown that moisture promotes the production of some acid gases (Babushok et al. 2015, Meyer et al. 2013).

3.8.1 DustTrak DRX Monitor

Aerosol photometers measure mass concentration by sensing the combined laser light scattered from many particles at once. The DustTrakTM DRX Monitor (Model 8533, TSI Inc., Shoreview, MN) combines ensemble scattering with single particle detection to provide real-time size-segregated mass fraction concentrations up to 150 mg/m³. In GASP testing, smoke aerosols are predominantly below 1 μ m in diameter; however, it is of interest in fire characterization to determine which fuels generate particles above this threshold. The DRX can detect particles between 100 nm and 15 μ m and, thus is not sensitive to ultrafine particles. Although photometers can be used at high mass concentration, smoke aerosols in these tests required significant

dilution with HEPA filtered air. The DRX was calibrated with lamp wick smoke to better correlate its output to aerosol mass concentrations of typical GASP fuels.

3.8.2 Water Condensation Particle Counter

The Water Condensation Particle Counter (WCPC, Model 3787, TSI Inc., Shoreview, MN) measures aerosol number concentration. This device operates by initially cooling the aerosol sample and then passing the sample stream through a region of supersaturated water vapor where the particles grow as water condenses on them. The particle-containing droplets pass through a laser and scatter the light, creating a pulse, which is detected and counted. This device has an extended single particle counting range with continuous, live-time coincidence correction allowing measurement from 0 to 250,000 particles/cm³ at sizes from 5 nm to 3 µm in diameter. Substantial dilution with HEPA filtered air is required, since the smoke concentration is higher than the upper counting limit. The response time of this instrument to a step change in aerosol concentration is on the order of 0.75 second. Placement of the WCPC and DRX outside the smoke chamber and dilution equipment adds to the path length the aerosol must travel before being sampled. The delay in the instrument response attributed to tubing length between the smoke chamber and the instrument inlet is 0.02 seconds and 0.06 seconds for the DRX and the WCPC, respectively.

3.8.3 Sharp Dust Sensor

A Compact Optical Dust Sensor (model GP2Y1010AU0F, Sharp Corporation) was tested for the purpose of comparing time to detection of smoke from common spacecraft materials. This commercial-off-the-shelf (COTS) device uses an infrared emitting diode and a phototransistor to determine the presence of aerosols passing through a hole in the center of the 4.6 x 3 cm device, which is less than 2 cm thick, weighing approximately 16 g. The output voltage can be

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calibrated to aerosol mass concentration (mg/m^3) with a sensitivity to 0.1 mg/m³. The Sharp sensor is shown in Figure 3.14.



Figure 3.14: The Sharp Compact Optical Dust Sensor which weighs 16 grams.

The calibration used for the GASP data is from Yang et al. 2015, which reported that the sensor output is strongly material dependent, and provided a correlation to mass concentration of incense smoke. For the purpose of this preliminary study, this calibration is assumed to be adequate, however, if the device is selected for further studies, it will be calibrated to one or more representative smoke aerosols outlined in this work. Three of the sensors were placed inside the smoke chamber, attached to the wall cantilever-style with double-sided tape. This configuration oriented the central smoke path through the sensor in the vertical direction. Figure 3.15 shows the three sensors mounted on the interior wall of the smoke chamber. The electronics accompanying the sensors were placed in the ante-chamber of the glove box to protect them from exposure to the smoke and acid gases. There was no forced convection provided for smoke through the device other than what was produced by the mixing fan in the smoke chamber. The Sharp sensor has a much lower measurement threshold than other aerosol instruments, however, the main interest for this study is the early response of a third moment device to the presence of smoke.



Figure 3.15: Positions of the three Sharp sensors mounted on the interior wall of the GASP smoke chamber.

While the GASP laboratory has an SMPS to measure particle size distributions, it is not suitable for tests performed with the fast ramp furnace profile, as smoke concentration is typically too high, and 2 min scan is too long for the dynamic conditions of aging smoke in the chamber. The 55-gallon drums used in the SAME ground-based experiments are necessary for smoke particle size distribution measurements, in order to dilute sufficiently to stop coagulation associated with aging so the size distribution can be measured with longer duration scans.

3.9 GASP Results and Discussion

3.9.1 Smoke Yield

Only aerosol results are reported here from this series of tests however, results on the gaseous pyrolysis products can be referenced in (Briggs et al. 2015). The total mass of the aerosol is computed as the product of the volume of the smoke chamber (326 liters), and the mass concentration of the smoke as measured by the DRX with suitable calibration factors. By dividing the total mass of the aerosol by the mass loss of the sample, the smoke yield is determined (Mulholland et al. 2015). This is a method of comparing smoke fuels that may not have had the same mass before heating. Unlike the WSTF testing, which maintained a consistent fuel mass of 0.5 g for all tests, the GASP tests were performed with variable fuel masses. Larger fuel masses were used for the purpose of generating high levels of acid gases relevant to the post-fire environment, but in some instances smaller masses were used for fuels that were known to generate a significant amount of sticky smoke aerosols which coat surfaces and could damage the gas sensors placed in the smoke chamber. Figure 3.16 shows the smoke yield of selected fuels that were tested, averaged from the three sensors. While different initial fuel masses can be compared by smoke yield, only those fuels subjected to the same heating profile can logically be compared, and therefore some tests are not shown in Figure 3.16 as they deviated from the fast ramp furnace timeline by several minutes of additional dwell time at 640 °C.



Figure 3.16: Smoke yield of materials heated by the fast ramp furnace profile.

3.9.2 Early Smoke Detection

Early smoke detection results of the Sharp sensor varied significantly by material. No data averaging scheme was used, so the output signal was nearly instantaneous, with data recorded ten times per second. Figure 3.17 shows the response times of the Sharp sensor to the different types of smoke from fuels shown in Figures 3.12 and 3.13. All materials saturated the sensor with the exception of PTFE & Bulk Kapton. Teflon particles in unaged smoke are so small that they do not scatter light efficiently and therefore were not expected to generate a significant mass concentration response, however, the delay of 400 seconds before detection of the onset of significant smoke shows that this device (or any third moment device) is not reliable in smoke detection by itself. It was noted that Teflon was the only material for which smoke was never visible in the chamber. The bulk Kapton did not produce as much aerosol because of much smaller exposed surface area compared to the snipped pieces. Kapton is known to have smaller

particles (as seen in the particle size distributions from the SAME smoke-in-drums experiments), but also its heat-resistance and insulating properties are demonstrated here, as the outer layer of the rolled piece protected the inner layers of Kapton from thermal degradation for the first 250 seconds. Kapton is known to remain stable up to 400 °C, so the fast ramp will not produce a significant amount of smoke unless there is much more available surface area, such as the Kapton snips. This demonstrates that choosing realistic material configurations such as bulk materials rather than unrealistically processed fuels is an important factor in smoke characterization experiments.





While the heating durations are different between WSTF and GASP, it is worth noting the similarities in smoke yield for like materials. The smoke yield for WSTF PCB populated with components (for all temperatures) ranged from 25% to 35%, and the average of GASP bare PCB and components smoke yield is 30%. WSTF Nomex smoke yield ranged from 6% to 10.2%,

with average 9.0% which compares well with GASP Nomex smoke yield of 7.6%. Kapton snips for GASP testing had a yield of 2.6%, compared to WSTF which was less than 1%. Comparison with SAME smoke yield is not comparable to GASP and WSTF because of vastly different heating temperatures and durations.

Current ISS smoke detectors have an alarm threshold of 2 mg/m³ mass concentration of smoke (Urban et al. 2008). The times for the materials to reach this detection threshold by the Sharp sensor is plotted in Figure 3.18 and range from 59 to 376 seconds (1 to 6.3 minutes).



Figure 3.18: Time for the various materials to reach the ISS smoke detector alarm threshold of 2 mg/m^3 mass concentration.

Teflon is omitted because the maximum mass concentration never reached that threshold (the maximum recorded was less than 1 mg/m³). Nomex and Pyrell foam are notoriously 'dirty' smokes in terms of deposition on the smoke chamber walls and on the surfaces of gas sensors

which are typically inside the smoke chambers during WSTF and GASP laboratory tests, so it is expected that they would reach the threshold sooner than other materials. Most of the fuels (lamp wick, tobacco, Kapton snips, wires mixed with bulk Kapton, PVC and PCB pieces) reached the alarm threshold between 125 and 175 seconds, while the components and the bulk Kapton nearly doubled these detection times.

The early response of the WCPC to smoke from the fuels is shown in Figure 3.19, and the response can be considered instantaneous on the time scale of this plot. There are two trends in the number concentrations, either a constant slope increase for steady increase in smoke production, as for the components, Kapton snips and Teflon, and exponential growth demonstrated by the other materials. Pyrell exhibits both trends, seeming to match the smoke production rates of Teflon and Kapton snips exactly, but then veering upward with exponential growth occurring at about 125 seconds. Note that the components exhibit a step increase in smoke particle concentration at about 75 seconds. This has been observed in heating combinations of components and wires as well, as the constituents thermally decompose at different temperatures and different rates.

Figure 3.19 demonstrates three groups of materials reaching high number concentrations exponentially. Tobacco is the earliest concentration spike, and this is caused by the furnace starting temperature in the fast ramp of 200 °C. The paper of the cigarette began to make smoke at once when it was placed in the tube before the furnace ramp was initiated, so smoke concentrations were high at the outset of recording data (time zero of the other materials). The second group of materials to peak in concentration are lamp wick, Nomex and Pyrell, whereas the third group consists of PVC wire, bulk Kapton and the Wire and bulk Kapton humidified mixture.

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Unlike mass concentration, there is no equivalent smoke detector threshold or rule-of-thumb value for number concentration that would be considered an appropriate early response to smoke. Figure 3.20 sheds light on the time required the smoke number concentrations of the various materials to reach 10,000 particles/cm³, 5000 particles/cm³, and 3000 particles/cm³ (red dashed lines). These are the same graphs as Figure 3.19 with the x-axis limit reduced. As noted earlier, the tobacco concentration did not start at zero, owing to the initial furnace temperature (200 °C) instantaneously pyrolyzing the cigarette paper before the furnace ramp was initiated and the instruments turned on (typically a 20 second delay which is negligible for the other fuel materials).



Figure 3.20: Refined response time to measure smoke aerosol number concentration with the WCPC for the various materials (same data graphed in Figure 19 with smaller x-axis limits). Red dashed lines are thresholds for the smoke number concentration to reach 10,000 particles/cm³, 5000 particles/cm³, and 3000 particles/cm³.

The materials can be listed in order of WCPC early detection for these three concentration

thresholds, as shown in Table 3.5.

10,000 #/cm ³	5000 #/cm ³ 3000 #/cm ³		Compare with Sharp
Pyrell	Components	Components	Nomex
Components	Pyrell	Pyrell	Pyrell
Tobacco	Kapton snips	Tobacco	Lamp wick
Kapton snips	Wire & bulk Kapton	Kapton snips	Tobacco
Nomex	Tobacco	Wire & bulk Kapton	Kapton snips
PCB	Nomex	Nomex	Wire & bulk Kapton
Lamp wick	Lamp wick	Lamp wick	PVC wire
PVC wire	PCB	PCB	PCB
Bulk Kapton	PVC wire	PVC wire	Components
Teflon	Bulk Kapton	Bulk Kapton	Bulk Kapton
Wire & bulk Kapton	Teflon	Teflon	Teflon (∞) *

 Table 3.5: WCPC Early Detection Comparison for Number Concentration Threshold

*Teflon never reached the 2 mg/m^3 threshold with the Sharp sensor.

Table 3.5 compares the order of the materials to reach the three number concentration thresholds with the time for the Sharp sensor to reach 2 mg/m^3 (Figure 3.18). The materials do not vary

significantly between the three WCPC concentration thresholds with the exception of the wire and bulk Kapton mixtures, which is the last to reach 10,000 particles/cm³, but reaches the lower concentrations significantly earlier. Every other material has a similar rank for the three concentrations (within three places). Surprisingly, Teflon is not detected earlier by the WCPC, which may be partly explained by the loss of the smallest particles by diffusion in the tubing from the smoke chamber to the instrument. Comparing the number concentration response with the Sharp sensor correlated to mass concentration shows that Pyrell is the earliest smoke to detect for both zeroth and third moment devices. Components have the largest discrepancy between WCPC and Sharp response, which are on opposite extremes of the timeline. This indicates that the smoke particles from components were extremely small. Nomex and lamp wick also have a larger spread between the WCPC and the Sharp response, with earlier detection by the Sharp, which indicates that they are much larger smoke particles.

3.10 Conclusions

Testing at both WSTF and GASP laboratory has led to the creation of a NASA database of smoke from spacecraft materials for both aerosols and gases. The initial fuels were prepared with the intent to generate significant amounts of acid gases, however, recent testing has focused on more realistic material configurations (bulk pieces), as would be encountered in a real fire.

In WSTF testing, ground circuit card was found to have increasing aerosol mass and number concentration with increasing temperature and at 640 °C, it produced the highest aerosol number concentration of any material tested (based on the 0.5 g sample sizes). Kapton and Teflon mixtures were explored to understand acid gas emissions from commercial Kapton/Teflon wire insulation, and aerosol emission results show that both ash mass decreases and aerosol mass increases with increasing fraction of Teflon, and number concentrations are higher for both pure

materials (non-mixtures). Kapton aerosol emissions were much higher for granulated samples versus larger pieces. Nomex produced prolific quantities of combustion products (gas and aerosol) which affected gas sensor performance.

In GASP testing, results reported in this work focused on early detection of smoke from materials common to both SAME and WSTF testing. A Sharp Compact Optical Dust Sensor was included in the testing as an example of a small, low power device that might serve as a third moment device in a suite of fire detection instruments after suitable calibrations with smoke from spacecraft materials. For the current tests, a calibration to incense smoke (Yang et al. 2015) was applied. Smoke yield comparison of the materials tested ranked Kapton snips and lamp wick lowest, whereas bare circuit board (PCB), PVC wire and components had the highest yields. This is consistent with smoke yields for the populated circuit board data from WSTF. The early response of the Sharp sensor to the various smokes was investigated and times to reach the current ISS smoke detector threshold of 2 mg/m³ ranged from 1 to 6.3 minutes. Nomex smoke would be the earliest to alarm and the electronic components and bulk Kapton would be the last to alarm, with most of the other materials requiring between 120 and 175 seconds to alarm. Comparing the response time of the Sharp sensor to the WCPC, it was noted that smoke from electronics components is the earliest to reach significant number concentrations, whereas there is a much later response with a third moment device. In the absence of particle size measurements, conclusions can still be drawn concerning relative size of smoke particles with this information. Data indicates that the smoke particles from components are extremely small relative to the other fuels. The converse conclusion can be drawn for Nomex smoke, as the third moment device responds quickly and the zeroth moment device (WCPC, number concentration) responds more slowly, indicating larger smoke particles. Teflon smoke was the most difficult to

detect overall, as it never reached the ISS smoke detector alarm threshold, and had a delayed

increase in number concentration recorded by the WCPC, in spite of the fact that the entire 0.5 g

piece was consumed (zero ash mass remained). Understanding Teflon smoke and improving

detection of overheating Teflon is an ongoing pursuit for spacecraft fire safety research.

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<u>Chapter 4: Design of a Thermal Precipitator for the</u> <u>Characterization of Smoke Particles from Common</u> <u>Spacecraft Materials</u>

Aspects of this chapter have been previously published in the following reference:

Meyer, M.E.: Design of a Thermal Precipitator for the Characterization of Smoke Particles from Common Spacecraft Materials. NASA/TM—2015-218746, 2015. http://ntrs.nasa.gov/

4.1 Introduction

Characterization of the smoke from pyrolysis of common spacecraft materials provides insight for the design of future smoke detectors and post-fire clean-up equipment on the International Space Station. Real-time measurements of smoke particles in terms of number and mass concentration are useful, however, a wealth of additional information can be obtained by microscopy techniques. Magnified images show morphology, degree of particle agglomeration and also provide insight into particle formation mechanisms. Further techniques such as energy dispersive X-ray spectroscopy (EDS) give elemental composition of individual particles. An appropriate sampling method must be used to obtain quality microscopy results, and thermophoretic sampling directly on microscopy substrates is preferred to minimize handling and potential contamination. The alternative, collection by electrostatic precipitation, is most appropriate for nanoparticles (Maynard et al. 1995) using a smaller collection substrate, such as a 3 mm TEM grid. Therefore, electrostatic deposition was not considered as a collection method because of the large microscopy collection substrate necessary to capture a larger size range of particles. Thus, an appropriate thermal precipitator (TP) was created to augment existing spacecraft smoke data.

The thermal precipitator design was targeted towards smoke particles from typical oxidative pyrolysis tests at NASA's White Sands Test Facility (WSTF) conducted to challenge and verify performance of post-fire cleanup equipment under development for spacecraft (Meyer et al. 2013). These tests were characterized by aerosol mass and number concentrations ranging from 40 to 70 mg/m³ and 1 x 10⁵ to 1 x 10⁶ particles/cm³ and particle diameters ranging from 100 to 1000 nm. The goal of characterizing the smoke particles by microscopy was twofold: to verify that a repeatable fire challenge was produced in the facility and to determine the particle

morphology and elemental composition resulting from various fuels and temperatures. The intention was not to perform a size distribution analysis, so numerical modeling was restricted to the 100 to 1000 nm particle size range. Sizes outside of this size range were captured, as seen in the microscopy results, however, there was no attempt to calculate deposition efficiency of the device beyond the design range. There was also no requirement to make the TP compact, low power or portable, in the first iteration effort.

4.2 Existing Thermal Precipitator Designs

At the time of the early TP design phase, there was no thermal precipitator commercially available, and it was determined that an original device should be created and tailored to WSTF smoke testing. A number of references were consulted in order to gain insight from successful instruments, and some design rules-of-thumb emerged based on the thermal precipitators listed in Table 4.1. Note that the devices are listed in order of increasing particle size ranges which were either documented as design goals or the range of particle sizes tested in experiments reported in the references.

Tuble 111 Design Future et										
	Thermal Gradient,		Flow Rate,	Intended Particle						
Reference	K/mm	Gap, mm	cc/min	Size Range, nm	Collection Substrate					
Wen & Wexler 2007	500	0.1	1500	less than 10	TEM grid					
Maynard 1995	1000	0.15	1010	less than 100	TEM grid					
Lorenzo et al. 2007	400	0.3	2000	15 to 300	TEM grid					
Azong-Wara et al. 2009	15	1.25	2	up to 300	20 mm x 6 mm plate					
Tsai & Lu 1995	83.7 and 50.3	0.38	400	40 to 500	3 cm x 7.1 cm plate					
Current TP design	56	1.25	110	100 to 1000	SEM stub with TEM grid					

Table 4.1: Design Parameters of Other Thermal Precipitators in the Literature

The basic design trade is between the magnitude of the thermal gradient and the flow rate-which determines residence time and thus deposition efficiency of the desired size ranges. Notional geometry of the phenomenon of thermophoretic deposition is shown in Figure 4.1, which shows particles traveling axially through a thermal gradient directed perpendicularly to the flow path between two parallel flat surfaces. In a thermal precipitator, the thermophoretic force acting on the particle must drive it to the cold collection substrate before it reaches the end of the thermal gradient region in the device. An added complication for the smallest particles is the effect of diffusion, which causes particle losses that increase with residence time in the TP, and simultaneously, residence time is also increased by slip. This is evident from the first three devices listed in the table, which have extremely high flow rates for short residence times, coupled with very small gaps and the largest thermal gradients, for maximum thermophoretic force leading to deposition of smaller particles.



Figure 4.21: Schematic of thermophoretic particle deposition by a thermal gradient between two parallel flat surfaces separated by a gap.

Several designs in Table 4.1 use a transmission electron microscope (TEM) grid as the collection substrate to facilitate microscopic analysis. A larger collection substrate allows more latitude in the design parameters for thermal gradients and flow rates required for high collection efficiencies. The TP designs of Azong-Wara and Tsai and Lu use larger collection substrates (4 and 74 times larger area than a TEM grid, respectively) and thus can tolerate lower flow rates and a smaller thermal gradient and still achieve a sufficient residence time for high deposition rates. Collecting particles directly on a microscopy substrate is preferable, so the goal of this TP design was to use a scanning electron microscopy (SEM) specimen holder, called a stub, integrated into the cold surface.

The TP design for smoke particles has a much larger desired size range than the other devices in Table 4.1. Since the aerosol physics influencing thermal precipitator design is determined based on the Knudsen number, the dynamics of larger particles in a thermal precipitator can be modeled using the following formulas. When the particle size is larger than the mean free path of the surrounding air ($d_p > \lambda$, or Kn is small), then the thermophoretic force on a particle, F_{th} , is given by (Hinds, 1999)

$$F_{th} = \frac{-9\pi d_p \mu^2 H \nabla T}{2\rho_g T_p} \tag{1}$$

where μ is the viscosity of air, ρ_g is the density of the surrounding gas (air), T_p is the particle absolute temperature (the temperature of the aerosol, typically considered to be ambient temperature) and ∇T is the thermal gradient in the gas. The coefficient H accounts for a temperature gradient within the particle and thus depends on particle diameter and is given by

$$H \simeq \left(\frac{1}{1 + \frac{6\lambda}{d_p}}\right) \left(\frac{\frac{k_a}{k_p} + 4.4^{\lambda}}{1 + 2^{k_a}/k_p + 8.8^{\lambda}/d_p}\right)$$
(2)

where k_a is the thermal conductivity of the air and k_p is the thermal conductivity of the particle. The thermophoretic velocity for particle diameters larger than the mean free path of air is given by (Hinds, 1999)

$$V_{th} = \frac{-3\mu C_c H \nabla T}{2\rho_g T_p} \tag{3}$$

where the Cunningham slip correction factor, C_c is included. Ambient pressure is an influencing variable by way of the gas density in the force and velocity equations. Thus, the thermophoretic force was enhanced by approximately 20% at WSTF, considering the effect of lower pressure,

which is 85150 Pa (0.84 atm) owing to the altitude in Las Cruces, New Mexico. To estimate the thermal conductivity of pyrolysis smoke particles, they were assumed to consist of re-condensed polymer vapors on small primary particles. An average of nine representative WSTF fuel polymer materials ranging from 0.12 W/m-K to 0.3 W/m-K was used to obtain the value $k_p = 0.19$ W/m-K used in calculations and modeling. At larger sizes, the effect of the particle material is more pronounced. Figure 4.2 shows calculations of the thermophoretic force (equation 1) versus particle size, and it is evident that the thermal conductivity of salt particles, which has approximately 25 times the thermal conductivity of air, results in a smaller force on particle sizes larger than 500 nm, when compared to the polymer smoke. Particle temperature is assumed to be equilibrated with the typical WSTF smoke chamber temperature of 40 degrees C (313 K).



Figure 4.22: Thermophoretic force on particles, calculated for NaCl and polymer smoke particles. The thermal conductivity of the smoke particles is estimated by taking an average of polymer densities from typical spacecraft materials of interest, based on the assumption that smoke particles consist mainly of re-condensed polymer vapor (products of pyrolysis).

4.3 Finite Element Modeling to Narrow Design Space

A design space consists of all possible configuration options to achieve an engineering outcome, which is narrowed or optimized based on constraints of the laws of physics and available hardware to generate conditions required to achieve the outcome. Finite element modeling is a rapid and cost-effective method of exploring design spaces, so that interconnected design parameters can be optimized virtually, and fully functioning hardware can be built on the first iteration. This approach was used in the TP design, with the COMSOL Multiphysics software package, version 4.2. This product is a finite element analysis (FEA) solver which provides the ability to couple various physical phenomena described by the term 'multiphysics.'

First, an Eulerian numerical model was created to represent laminar fluid dynamics and the heat transfer in the fluid of the device. Subsequently, the COMSOL Multiphysics Particle Tracing Module was used to apply user-defined forces on particles for Lagrangian simulations based on previous Eulerian solutions. Thus, the iterative design approach was to solve the Eulerian model, then calculate thermophoretic force as a function of particle size, parametrically modify the particle forces in the model (including slip-corrected Stokes drag) and simulate monodisperse particle deposition in the TP geometry through multiple simulations over the particle size range of interest. After a number of modeling iterations, the design space was suitably narrowed and one of many possible optimized solutions was chosen for the final TP configuration.

The COMSOL fluid flow interfaces uses the Navier-Stokes equations, for incompressible flow consisting of conservation of mass

$$\nabla \cdot \boldsymbol{u} = 0 \tag{4}$$

(where u is the three-dimensional fluid velocity vector) and conservation of momentum

$$\rho_f \frac{\partial \boldsymbol{u}}{\partial t} + \rho_f (\boldsymbol{u} \cdot \nabla) \boldsymbol{u} = \mu \nabla^2 \boldsymbol{u} - \nabla p$$
(5)

where *p* is pressure.

The COMSOL heat transfer in fluids model uses the simplified heat equation

$$\rho_g C_p \frac{\partial T}{\partial t} + \rho_g C_p \cdot \nabla T = \nabla \cdot (k_a \nabla T)$$
(6)

where C_p is the fluid heat capacity at constant pressure and T is the absolute temperature of the air.

The particle tracing module uses Newton's second law to define the motion of a particle, which includes the two important user-defined forces for the TP

$$m\frac{d^2x}{dt^2} = F_{th} + F_d \tag{7}$$

where the thermophoretic force is in the direction of the thermal gradient, given by equation (1). F_d is the Stokes drag given by

$$\boldsymbol{F_d} = \frac{3\pi\mu d_p (\boldsymbol{u} - \boldsymbol{u_p})}{C_c} \tag{8}$$

where u_p is the three-dimensional particle velocity vector, defined as the fluid velocity in the initial conditions (at time = 0 of the particle trajectory). No additional body forces (such as gravity) were imposed on the particles.

The TP geometry had no requirements, other than starting and ending with connectors for ¹/₄" tubing diameter. This was approximated by a square in the model, as it had no bearing on the computational fluid dynamics at the scale of interest for this project. Achieving laminar flow

through a very narrow gap was the goal that dictated the shape of the TP, and the solution was to use a cubic spline function in the COMSOL geometry tools to gradually widen the body as the height was reduced to a uniform gap on the order of a millimeter. Typical WSTF test duration of approximately 20 minutes was a design requirement for sufficient sampling, so other variables such as flow rate, temperature boundary conditions, gap height and overall geometry could be manipulated to achieve the desired particle residence time in the gradient to provide adequate deposition concentration on the SEM stubs in that length of time.



Figure 4.23: COMSOL Eulerian flow field simulation results: velocity slice plot showing that a uniform parabolic flow profile is achieved in the TP geometry which starts with ¹/₄" tubing diameter (approximated by a square in the model) and gradually reduces to a uniform 1.25 mm gap using a cubic spline function to expand the width of the body. SEM stubs are the downstream circles.

Figure 4.3 shows the flow field inside the long and narrow TP body indicating that the velocity

is reduced from a fully developed parabolic flow inlet condition to a uniform parabolic profile in

the gap (color bar has units of m/s). The initial estimate of a suitable gap height was based on spreadsheet calculations of the thermophoretic velocity for particles from 100 nm to 1000 nm and the time required for a particle to travel the entire gap at that speed. This provided insight on the range of residence times required for deposition of different particle sizes and narrowed the choice of gap heights. The Reynolds number ($Re = \frac{\rho u D_h}{\mu}$) was calculated to determine whether the internal TP flow is in the laminar regime. The hydraulic diameter, D_h , is twice the height of the TP body, as the fluid can be considered to be flowing between two plane parallel surfaces where the gap height is much less than the width. For all design iterations, Re was well below the critical value of 2300 for the full range of each design parameter considered, typically below 50.

Simple temperature boundary conditions were applied to simulate various cold and hot plate areas in the TP model, creating a gradient on the order of 50 to 100 °C/m, an initial estimate based on the design of Tsai and Lu (Table 1). Although a more detailed thermal model can easily be made in COMSOL, there was no benefit for the TP geometry design iterations. Subsequent thermal design was perfected through experiments and thermocouple measurements, as contact conductances between parts of the final assembly were unknown. The temperature gradient is the only Eulerian model input needed for the thermophoretic force which was applied in the z-direction (vertical axis in figures) using equation (1). Stokes drag (a function of the 3dimensional velocity field solved in the Eulerian simulation) was applied on particles in the xand y- and z-directions according to equation (8).

Flow field iterations were used as inputs for particle trajectory simulations corresponding to 100 nm, 500 nm and 1000 nm spherical particles subjected to Stokes drag and material-specific thermophoretic forces.

Figure 4.4 shows COMSOL Lagrangian particle trajectory simulation results with moving particles (left) and deposition pattern (right) of 1000 particles with 100 nm diameter, accounting for particle thermal conductivity in the vertical thermophoretic force and 3-dimensional Stokes drag. The deposition pattern does not reach the SEM stubs (circles), so this intermediate set of design parameters was not accepted. Subsequent to this simulation, the thermal gradient was reduced in the model so that particle deposition would be delayed and cover the circular SEM stubs further downstream.



Figure 4.24: COMSOL Lagrangian particle trajectory simulation results from one modeling iteration, showing moving particles (left) and deposition pattern (right) of 1000 particles of 100 nm diameter, accounting for particle thermal conductivity in the thermophoretic force and Stokes drag. When the residence time of particles and the temperature gradient in the thermal precipitator are properly designed, particles in the size range of interest deposit on the SEM stubs where they are saved for subsequent microscopic analysis.

Overall, COMSOL modeling narrowed the design space significantly. Simulation results showed that an elongated TP body and a correspondingly longer section of constant thermal gradient would allow for longer residence time and deposition of the size range of interest. Additionally, placing two stubs in series provided the ability to collect a larger size range of particles. Final variables in the TP design are given in the last entry of Table 4.1. The COMSOL model was considered a design tool, not an end in itself, and once the parameters were defined within the realm of available heaters, coolers and pumps, focus was placed on the physical TP design and testing to complete the project.

4.4 Mechanical and Thermal Design

The thermophoretic force on a particle subjected to a temperature gradient is directed towards the cold surface, which in this TP design is the collection substrate for microscopy, a 15 mm diameter aluminum SEM specimen mount (Hitachi M4) with threaded hole. By making two stubs in series, the collection area is increased and thus a larger range of particle sizes are deposited. A portion of each stub surface was covered with a strip of carbon two-sided sticky tape in the flow direction, in order to attach 3.01 mm TEM grids enabling multiple types of electron microscopy. The carbon tape provided an alternate surface for particle deposition in addition to the aluminum stub surface. Carbon tape backing was peeled back slightly to adhere the TEM grids and then pressed back down to maintain cleanliness of the tape surface until testing took place. The tape backing was removed prior to each sampling test after the new clean stub was installed.

Large thermal gradients in small devices can be achieved using a thermoelectric cooler, also known as a Peltier cooler or heater. A layer of semiconductor pellets between two outer plates create a heat flux between the junction of two different types of materials (N and P-type semiconductor pellets), creating a hot side and a cold side of the Peltier device, which in this thermal precipitator, was used for the cold particle collection surface. Therefore, in this work it is referred to as a thermoelectric cooler. In the TP, there are three circular thermoelectric coolers in parallel, one for each of the two SEM stubs and one on the cold plate which surrounds the stubs (upstream of the stubs). Based on numerical modeling, a 70°C thermal gradient was required to deposit particles in the desired size range, so a variable autotransformer was used to adjust the current from a voltage-limited power supply until the desired thermal gradient was achieved, with best results achieved after a warm-up period of 30 minutes or less. Opposite the

cold surface of the thermoelectric cooler was the hot side where the waste heat removed from the cold side was pumped. The efficiency of heat removal from this area is directly proportional to the cold temperatures that can be achieved on the cold side. Therefore a heat sink with a large fin assembly was designed to remove the heat, and ultimately required a muffin fan to improve the rate of removal by forced convection (see Figure 4.5). The cold plate was chosen as the upper surface to take advantage of natural convection in removing heat from the back of the thermoelectric coolers, so the thermophoretic force on particles is not assisted by gravity in this design.



Figure 4.25: (a) CAD model of the thermal precipitator SLA body without the upper cold plate lid and SEM stubs, showing the cubic spline geometry of the inlet on the left and the outlet on the right. The Kapton heater is mounted under the hot plate (turquoise section). (b)Thermal precipitator body with the cold fin/spacer/stub assembly in place, with fins in red.

Spacers were added above the SEM stubs, according to recommendations by thermoelectric cooler manufacturer, to create more distance between the intended cold surface and the hot surface attached to the fins which eject heat. Spacers are shown in grey in the CAD model image in Figure 4.6. Contact conductances between the segments were improved by using thermal grease, and insulation was added to both sides of the cold plate to reduce heat transfer in the plane of the TP body.

A Kapton heater was connected to the hot plate with thermal grease opposite of the cold aluminum plate and stubs. There was no direct control of temperature as the required thermal gradient was consistently achieved once the heat removal was improved by forced convection. Permanent type K thermocouples were installed at the hot plate and the cold plate to provide real-time information on the gradient and to indicate when the thermal precipitator had fully warmed up (reached equilibrium). Preliminary tests were performed with 1000 nm, 670 nm and 105 nm polystyrene latex (PSL) test aerosol spheres and with polydisperse NaCl aerosol and microscopy verified that good deposition was obtained for all sizes, which validated the thermal design of the precipitator. Based on Figure 4.2, the thermophoretic force on NaCl particles is expected to be weaker than that of polymer pyrolysis smoke particles, so improved collection efficiency was expected in the actual smoke testing. Additional extended durations of testing were performed with a zero filter (small HEPA filter) at the inlet of the thermal precipitator and a condensation particle counter (CPC) at the outlet in order to verify that particles were not generated from within the device itself. In this test, particle-free air entered the TP and the aerosol number concentration measured by the CPC was verified to be zero. Subsequent microscopy also showed no particles on the SEM stubs.

Figure 4.6 shows a cut-away view of the thermal precipitator CAD model. The aerosol outlet is connected to a zero filter followed by a small pump. This prevents particles from entering the pump, however, acid gases which are products of the WSTF pyrolysis tests will still enter the pump, so it must be monitored for performance and replaced when internal parts are compromised by the harsh environment.



Figure 4.26: A cut-away view of the thermal precipitator CAD model with the housing and fan.



Figure 4.27: The fin/spacer/stub assembly removed from the thermal precipitator for exchanging SEM stub (left). SEM stubs had a section of double-sided carbon tape (black strip) in the direction of the aerosol flow with two 3.01 mm grids adhered to it for TEM and HRTEM analysis (right image).

The SEM stubs were numbered 1 and 2, and there were slight differences in the temperatures

of the stubs, which may have influenced the sizes of particles deposited. A stub instrumented

with a thermocouple was used to verify the surface temperatures at both stub positions. The

downstream stub was slightly warmer as the upstream SEM stub was closer to the thermoelectric cooler for the cold plate with fewer warm adjacent surfaces. Between sampling tests, stubs were removed and replaced with clean stubs by using an allen wrench on set screws that allowed the entire fin/spacer/stub assemblies to be removed (Figure 4.7, left photo). The threaded stubs were removed and placed in a protective box (Figure 4.7, right photo), and a new stub was screwed in securely, with care to compress the o-ring that seals off a potential leak path for aerosol flow.

The highest temperature difference achieved between plates during initial testing was 79.5 °C, however, it was determined by modeling and verified with microscopy that a 70 °C difference is sufficient to successfully deposit adequate numbers of particles. This reduced the warm-up time to 30 minutes or less. During actual smoke particle sampling, the cold plate temperature ranged from -3.4 °C to 1.3 °C and the hot plate temperature ranged from 66.9 to 77.5 °C. Condensation on the SEM stubs was problem with zero and negative cold plate temperatures during preliminary experiments with PSL and NaCl, test aerosols however, this was not a problem in the WSTF smoke tests, which have negative dew point temperatures, between -9° and -18 °C. At end of each test, the thermoelectric coolers were immediately turned off by placing the power supply on standby to warm them and thus prevent condensation of room air moisture while removing and inserting stubs.

The TP body was made by stereolithography (SLA), which is an additive manufacturing technique that creates parts directly from 3D CAD data by converting liquid materials into solid cross-sections, layer by layer, using an ultraviolet laser. This technique can save significantly on cost of manufacturing unique shapes such as the cubic spline transition from the ¹/₄" round tubing connector to the wide thermal gradient section of the TP. Figure 4.5 shows the translucent SLA body (grey) which has a rectangular outer cross-section, with the internal flow path transitioning

from narrow to wide and back to narrow. The 1.25 mm gap is well within the tolerances of SLA capability, and this geometry would not have been possible to machine from metal in one piece. The potential for inexpensive re-design is a benefit of this free-form fabrication technique, as additional TP bodies can be updated and created inexpensively, however, the first iteration of the design was successful. Caution must be observed as there is a tendency of SLA parts to warp, shrink or sag over time. Therefore, before using the TP, a leak-check is performed to assure that the seals are intact.



Figure 4.28: Aluminum housing positions fan and directs air onto heatsink for heat removal. Lid opens with hinge for access to SEM stubs.

An aluminum housing was constructed to contain and protect all wires and parts. Figure 4.8

shows the outer housing with the fan and the hinged lid opened revealing the heatsinking fins.

The aerosol inlet is below the fan, and the outlet is at the opposite end of the housing.

4.5 Conclusion

The thermal precipitator was successfully built after finite element modeling iteratively determined key design parameters. Testing verified the performance of the first iteration of the device and no subsequent design modifications were necessary. The thermal precipitator was successfully operated and provided quality particle samples for microscopic analysis, which furthered the body of knowledge on smoke particulates. Morphology and chemical composition information are important aspects of smoke characterization and will be useful for future spacecraft fire detection research.

History

TP design conceived, modeled and iterated starting June 2011

Constructed November 2011

Tested December 2011 & January 2012

Successfully used February 2012

Credit & Acknowledgements

Marit Meyer: Research of previous devices, aerosol physics calculations, general design and geometry parameters, finite element modeling resulting in final design parameters, initial testing and final use in smoke experiments

Daniel Gotti (National Center for Space Exploration Research, NSCER): CAD design and modeling in ProE, thermal analysis & thermal design, packaging, hardware selection and assembly of TP, instrumentation with thermocouples, assistance with initial testing Victoria Bryg (National Center for Space Exploration Research, NSCER): Choice & preparation of microscopy substrates, microscopy (SEM and TEM)

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<u>Chapter 5: Common Spacecraft Material Smoke Particle</u> <u>Morphology and Elemental Composition</u>

5.1 Introduction

Smoke particles collected via the thermal precipitator (TP) during test campaigns at the NASA White Sands Test Facility (WSTF) were subsequently examined with a Hitachi S-5500 scanning electron microscope (SEM), Hitachi HD-2300 scanning transmission electron microscope (STEM), and a Philips Model CM20 transmission electron microscope (TEM). The microscopes are equipped with energy dispersive X-ray spectroscopy (EDS) detectors that allow for elemental information of individual particles to be collected. Four potential substrates were incorporated into the collection surface for multiple microscopy options. A strip of conductive carbon tape was placed onto the surface of the SEM stub to allow for viewing of the particles on both the aluminum stub substrate as well as a neutral carbon background. TEM grids with a) continuous carbon film as well as a b) holey carbon film were placed at the edge of the carbon tape to allow sample collection for higher magnification examination. Smoke particle morphology gives insight into the thermal decomposition mechanisms of the spacecraft materials as well as the particle formation mechanisms, both important elements of fire characterization. Elemental information on smoke particle composition gained from EDS provides additional information on individual particle characteristics. The polymeric fuel materials in this study had accompanying material data sheets, however, the specific formulations are proprietary and thus potentially many additional constituents may be present such as plasticizers or colorants, which have the potential to affect the smoke production. Thus a number of elements are often observed in the EDS spectra which do not appear in the fuel chemical formula. In addition, there are other potential sources of elements, particularly Cu, Al and Si. The presence of Cu can be attributed to the TEM grid itself and a low Al peak may be present owing to the sample holder of the microscope (therefore known as a system peak). The WSTF smoke generation process relies on

a mica liner to hold the fuel during heating, which is another potential source of Si and Al in the smoke particles.

Thermal decomposition of the common spacecraft materials shown in this work mostly follow a common pattern. Under oxidative pyrolysis, a solid matrix of polymers will degrade and give off gaseous and liquid fuels which can be combined in high temperature reactions. These pyrolysis products are molecular fragments ranging in size from polymer chains down to the size of the monomer subunit of the polymer (Mulholland et al. 2015). Lower molecular weight materials can produce volatile species by evaporation or sublimation, whereas high molecular weight species which are cross-linked must undergo thermal decomposition at higher temperatures to produce gases. Polymers release low molecular weight gases upon initial heating followed by higher molecular weight pyrolysis products (Durlak et al. 1998). Saturated vapors emitted from the fuel either homogeneously nucleate into small molecular clusters as the gas cools, becoming internally homogeneous particles, or gases can condense onto existing particles which then appear as internally heterogeneous particles with inclusions or coatings. These formation mechanisms are distinctly different from soot formation in flaming combustion, which can be generalized into a three step formation mechanism consisting of 1) precursor species formation (when the complex fuel molecules are broken down into low molecular weight radicals which participate in many reactions), 2) particle inception (in which solid particle nuclei form and undergo surface growth by absorbing available gas phase molecules and becoming 20 to 24 nm spherules which agglomerate under Brownian motion in the flame), and finally 3) further agglomeration and surface growth, until the soot particle exits the flame when it cools and can potentially adsorb organic surface coatings. (Moosmüller et al. 2009).

5.2 Overview of Heated Materials and Microscopy Results

A summary of the SEM analyses performed using a field emission SEM (Hitachi S-5500) is given in Table 5.1 which describes the fuel, heating temperature, particle coverage obtained by the TP sampling, and qualitative descriptions of the particle sizes and morphologies observed. Two different thumbnail images are also provided in the table to show representative smoke particles from each sample at 5000x and 10,000x magnification. Images of smoke particles collected on the carbon tape have a somewhat bubbled texture in the background, most likely from the non-uniform adhesive under the carbon membrane. Images of smoke particles collected on the aluminum SEM stub surfaces often have a background pattern of faint parallel lines which are striations in the aluminum surface, as the stubs were not polished before use. Additional images and analyses from SEM, TEM, high resolution TEM and high resolution STEM are shown below for smoke particles from the following fuels: printed circuit board, wire insulation, Teflon, Kapton and Nomex.

Run numbers refer to the WSTF testing and can be cross-referenced to content in Chapter 3, where material descriptions and fuel preparation methods are outlined in detail. Wire insulation tests in this chapter used PFPI insulation (partially fluorinated polyimide manufactured by TRW).

Run	Fuel	Temp/C	Particle coverage	Particle size (qualitative)	Particle Morphology	Image1 (5000X) -	10µm	Image 2 (10,000X)	5µm
Run 3 & 35 Stub 2	Wire Insulation	540°	Sparse	Larger particles up to ~2.0µm; smaller particles generally ~0.17µm.	Mostly spherical	20 14-542-512 000000 00013.5mm	22.044 ab.de 1 dea	SE 14-Rec-12 00000 WD15.3mm	9.900 x39x 3mm
Run 6 Stub 2	Wire Insulation	640°	Fairly heavy	Generally ~0.2-5μm	Some large spherical particles, square crystalline particles, and individual particles as small at ~0.05µm.	55 16-Apr-12 00000 William	22.000 al.00 " 10m	21 21-2012 2000 M21.1mm	9.944 ADK But
Run 29 Stub 2	Wire Insulation	640°	Sparse	Particles range from ~0.5 – 2.2µm. Most extremely tiny.	Most particles are spherical with those over 1.0µm appearing agglomerated; some droplet patterns visible.	58 17-Kky-12 050000 WD13.0wm	- 25. GMV #5. ok - 1. Smm	20 17-Kay-12 00000 KD13.0mm	S. GAV. 4304 Sea
Run 8 Stub 2	Circuit Board	540°	Moderate	Most <2.2μm; most ~0.2- 1.0μm.	Mostly spherical particles.	52 J#-MA32 050000 WD(a).00	1.25 GW 45 Gt 15m	12 21-Mar-12 000000 W10 (*m) 2	. 644 2001 - 244

Table 5.6: Summary of SEM analyses for WSTF Fuels

Run	Fuel	Temp/C	Particle coverage	Particle size (qualitative)	Particle Morphology	Image1 (5000X) 10µm	Image 2 (10,000X) 5µm
Run 23 Stub 2	Circuit Board	640°	Very heavy with film deposit	Many large agglomerates most <2.2µm; most particles between 0.2µm and 1.2µm.	Many particulate agglomerates; particles mostly spherical; heavy textured deposit observed.	2 28-Mar-12 00000 WD19. Rem 23. S.W. #.S.W. 1.Pm	52 28-Mar-12 000000 MD19. Avm 23. Oktiv x10k 3vm
Run 27 Stub 2	Circuit Board	340°	Film on stub surface with embedded particles	Generally range from ~0.2 – 2.2μm with many ~0.5-1.0μm	Particles generally spherical when sitting on smooth film; film appears broken in areas causing 'flakes'. Interesting salt containing droplet noted on Al.	18 18-14-12 00000 4013.2m 29.044 eš.0k 10m	55 18-Way-12 000000 WD13 Jaw 23.047 s10k Sum
Run 30 (Sept)	Circuit Board	440°	Heavy	Particles usually <2.3µm. Smallest particles ~0.1-0.2µm.	Mostly a friable coating, with a few spherical particles.	52 69-100-12 OCCOSO 10(10) 100 23. (147 15. 0) 100	52 09-100-12 000000 WD10,5mm 25.024 x10x 20m
Run 33 (Sept)	Circuit Board	640°	Heavy	Large range of particles present, <0.1 to 12.6µm.	Heavy coating with most particles similar to Run 23.	2 2 2000 Weig Son 29, 644 2, 64 104	22 (9-5kor-12 00000 Velo, tem 23, ökv sick jam

Run	Fuel	Temp/C	Particle coverage	Particle size (qualitative)	Particle Morphology	Image1 (5000X) 10µm	Image 2 (10,000X) -	5μm
Run 9 Stub 2	100% TFE	540°	Heavy	Most particles <1.0μm, some up to 2.2μm.	Larger particles are somewhat spherical and agglomerated with primary particles measuring ~0.05- 0.3µm.	20 20-May-12 000000 MD13.0mm 23.04W 45.0% 10mm	52 30-844y-12 000000 95211.0mm 33	ówysiok ius
Run 15 Stub 2	100% TFE	640°	Moderate with film deposit	Most particles on AI stub <1.5µm; droplet on carbon tape ~5.0µm.	Many spherical particles along with thin needle- like crystals; crystals more easily observed on carbon tape.	8 28-964F-12 OCCOSO WOIL.com 23.04V 91.04 Iou	8 20-Mar-12 000000 Will Jum 25	O O davi si dani
Run 42 Stub 2	100% TFE	640°	Moderate to heavy coverage with some droplet patterns visible.	Largest particles <3.3µm; generally 1- 2µm, smallest ~0.2-0.3µm.	Smallest particles deposited in droplets; larger particles generally spherical and agglomerated.	20 20-May-12 20000 WD13.1mm 25.0mV #5.0% 10mm	52 30-Huy-12 000000 HD[1,1,1,2,0,0	av site ba
Run 36 Stub 2	90%/10% TFE/Kapton	640°	Fairly heavy	Particles range from ~0.1-1.6μm with many around 0.5- 1.0μm.	Mostly spherical and 'compound' consisting of two different types of particles.	55 10-May-12 000000 0013.1mm 25.047 85.04 15mm	52 19-My-12 00000 9(1,2,m,2)	

Run	Fuel	Temp/C	Particle coverage	Particle size (qualitative)	Particle Morphology	Image1 (5000X) 10µm	Image 2 (10,000X) 5µm
Run 14 Stub 2	75%/25% TFE/Kapton	540∘	Sparse	Particles range in size from ~0.2µm- 1.6µm; most appear to be <1.1µm.	Larger particles are somewhat spherical and appear to consist of two different types of particles.	5E 11-Jul-32 050000 WD15, Jun 25 0xV x5.0k 10m	68 21-3-1-12 000009 WD13 4mm 25.04V 810K 8mm
Run 19 Stub 2	75%/25% TFE/Kapton	640∘	Film coated stub with individual embedded particles	Most ~0.2- 2.2-μm.	Spherical particles with evidence of droplet patterns on substrate; smallest particles within droplets (~0.1µm.	62 16-8ps-32 00000 9512.0mm 23.047 33.04 10mm	2 (6-4ge-12 00000 W012 (mv 2).04V x10x 3m
Run 12 Stub 2	50/50 TFE/Kapton	540°	Few particles, although beam damage indicates a coating on the stub.	Larger particles measure ~1- 6.6µm; smaller particles are ~0.1-1.0µm.	Larger spherical particles are usually agglomerates mostly of similar size, sometimes various sizes; significant beam damage evident.	20 26-Jun-12 000000 WD10. Tum 25. GAV # 3. dk 1 10m	EE 68-Jan-12 00000 WD13, fem 23, 040 x37x 5m
Run 17 & 25 Stub 2	50/50 TFE/Kapton	640°	Heavy coverage over a film.	Spherical particles generally <2.5µm; agglomerated smalls ~0.1µm.	Thick deposits along with spherical particles; some inorganic particles noted; collapsed particles seen on carbon tape.	52 28-Mar-12 2000 WEID, Two 23, day ab, da Jam	D 28 28-44xx-12 000000 W010, 4mm 25, 0.04 #30% 5mm

Run	Fuel	Temp/C	Particle coverage	Particle size (qualitative)	Particle Morphology	Image1 (5000X) 10µm	Image 2 (10,000X) 5µm
Run 13 Stub 2	25/75 TFE/Kapton	540°	Medium coverage over a film.	Most particles <2.2µm; much smaller particles >0.1µm.	Mostly spherical. Agglomerates typically composed of similarly sized particles.	55 Ge-Jun-12 050050 KD10.7mm 25.0kV s.5.0k 10mm	55 08-Jun-12 050000 WD19.7mm 25.0kV x10k 5um
Run 18 & 38 Stub 2	25/75 TFE/Kapton	640°	Sparse	Particles generally ~0.2μm- 3.5μm; most <1.1μm.	Particles appear larger and somewhat spherical, larger particles appear to consist of two different types of particles	28 31-h1-12 000000 W214 1m 23.94% 25.94 1.0m	52 31-5-1-32 050000 WD14.3mi 23.0W a105 20mi
Run 11 Stub 2	100% Kapton	540°	Extremely heavy	Particles range from ~0.1μm – 3.3μm, with most less than 0.5μm.	Most particles are spherical, some adhere to each other in strings.	25 11-Jul-12 050000 WD11. Jum 25. Div 5. Jul 10.	EE 11-Jul-12 000000 WD13, dmg 29, dxV x104 5mg
Run 16 Stub 2	100% Kapton	640°	Heavy	Most particles <1.0μm; including a significant population 0.3 μm and below.	Larger particles are agglomerates; some doublets and triplets.	82 28-Mar-12 00000 WD.0. em 23. dav n.d. k. 10m	56 28-Mar-12 000000 0519.5mm 29.04V x104 5mm

Run	Fuel	Temp/C	Particle coverage	Particle size (qualitative)	Particle Morphology	Image1 (5000X) 10µm	Image 2 (10,000X)	5μm
Run 2 (Sept)	Nomex	640°	Moderate	A few larger particles >4μm, with most spherical particles <0.5μm.	Most particles are spherical, with some crustal and some compact amorphous particles.	52 09-56-12 050000 WD10.5mm 25.dtx v5.dt 10-m	E 09-Roy-12 000000 MD10.5mm 25	.O.W BICK Funk
Run 1 Stub 2	<u>Std</u> Mix	540°	Moderate	Up to ~5.5μm, most <0.2μm through 0.5μm.	Spherical, some appearing to be collapsed; some appear as coated agglomerates of smaller particles.	2 14-#47-12 000000 WD14, fram 23. 0.4KV #3. 0.K. fram	28 24-84-52 00000 KD14.0mm 2	9. Sev sige in
Run 2 (ignited after initial pyroly- sis) Stub 2	<u>Std</u> Mix	540°	Heavy	Usually <1.0μm; most ~0.1-0.7μm.	Large loose agglomerates (from combustion [ignition of gases] after initial oxidative pyrolysis)	22 14-46-13 00000 W019 Jun 23 0000 A. 01 10m	28 24-861-22 0000 MDT 7. 76 12	5. Sec alor da
Run 4 Stub 2	<u>Std</u> Mix	540°	Moderate	Generally <2.2μm; majority ~ 0.2-1.0μm.	Mostly spherical with larger particles consisting of agglomerated primary particles (<100nm).	22 24-564-12 00000 MPG 15, Jong 25, GW 45, GK 10m	8 14-942-12 00000 WEIS. Mar A	i. šuvi niok i šeni

5.3 Smoke Particles from Printed Circuit Board Populated with Components

A spacecraft fire could originate by overheating electronics, so circuit board materials are an important candidate for smoke characterization. As circuit boards are heated to above 250 °C scission of high energy bonds takes place and small fragments are liberated along with monomers of the constituent materials. Above 500 °C, aromatic condensed ring systems (native to the original polymer or formed by reactions) will thermally decompose (Lambert, 1993).

The construction of the FR-4 begins with a woven glass fabric (E-glass, an aluminoborosilicate glass (Baker et al. 2004)) which is impregnated with epoxy resin. Circuit boards can be plated with tin, gold, nickel or copper, and the circuit board fuel in these tests was granulated and included components (integrated circuits [IC] microcircuits attached to the board with tinlead solder) which can contain many other materials: silicone encapsulent; aluminum, gold or copper wires; copper or nickel alloy leadframes, among others. Printed circuit boards and components thermally decompose at different rates, with components having higher thermal stability owing to the prominence of Si which enhances char formation (Duan and Li, 2010). The printed circuit board fuel used in the smoke tests is the composite material FR-4, which has been developed to be flame retardant (hence the abbreviation 'FR'). Halogens are added to the glass-reinforced epoxy laminate to make the boards flame resistant, or self-extinguishing, and studies on thermal recycling of circuit board waste show that bromine is present as high as 8.5 weight percent (Chien et al. 2000).

In several tests, collection of printed circuit board smoke particles on an aluminum SEM stub in the thermal precipitator often resulted in a film layer with distinct embedded particles and clusters of particles as small as 150 nm to 200 nm, as seen in Figure 5.1.



Figure 5.1. SEM images of circuit board smoke particles, left: at 640° C (Run 33), and at 340° C (Run 27).

Most particles observed on the SEM stub were somewhat spherical or compact agglomerates, however, the TEM grid analyses revealed other distinct types and features, including encapsulated and coated particles, char particles as well as crustal particles. Sheridan et al. (1994) defined the compositional category of crustal particles for atmospheric aerosols, to include O and at least two elements common in the Earth's crust: Si, Al, Ca, and Fe. It has since become a common particle characterization category, with some authors including additional crustal elements (Ramirez-Leal et al. 2014, Li et al. 2011, Furutani et al. 2011, Mogo et al. 2005, Chen et al. 1998).

Figure 5.2 shows a limited number of particles in the left image (highlighted with arrows) with diameters on the order of 200 to 400 nm, and a detail of the particle (red box) in the right image (approximately 350 nm in diameter) with its corresponding EDS spectrum below. Note that in the EDS spectra shown, some Cu can be attributed to the copper TEM grid which supports the lacey carbon, although this peak is relatively large compared to other circuit board particles and it logically is expected to appear in the circuit board smoke particles from copper layers in the

board or the clad laminate. Figure 5.2 has a prominent bromine peak, as well as Pb, which is also common in many circuit board smoke particles sampled with the thermal precipitator.



Figure 5.2. Lacey carbon TEM grid with circuit board smoke particles at 540° C (Run 31). Left image shows typical rounded multi-component particles on the order of 200 to 400 nm in diameter. Right image is a detail of one particle (red box), approximately 350 nm in diameter with its corresponding EDS spectrum below showing Br, Cu and Pb, which are typical constituents of circuit board and component materials. Cu can also be attributed to the TEM grid.

Figure 5.3 is an example of an irregular particle with inclusions (the particle is distinctly internally heterogeneous). The inclusions range from 40 to 60 nm, and some may be agglomerated to the surface, but most appear to be bound within the coating of the particle. Elements in the EDS spectrum include Cu, Br, Pb and Si. Cu can be attributed to the copper

TEM grid which supports the lacey carbon grid and the Si signal may be attributed to the mica sheet in the smoke generator.



Figure 5.3. TEM grid image and EDS spectrum of a circuit board smoke particle at 540° C (Run 31). The rounded particle has multiple inclusions and EDS shows the presence of Cu, Br, and Pb, typical constituents of circuit board and component materials. Cu can also be attributed to the TEM grid and the Si signal may be attributed to the mica sheet in the smoke generator.



Figure 5.4. High resolution STEM images show further details on inclusions within circuit board smoke particles at 540° C (Run 31). EDX spectra of these types of particles demonstrated a Pb/Br-rich particle with a Br-rich coating, with Si often present in the coating as well.

Figure 5.4 shows High resolution STEM (Hitachi HD-2300) images of inclusions in circuit board smoke particles, which demonstrate a Pb/Br-rich particle with a Br-rich coating, with Si often present in the coating as well. Note that the inclusions in the right image appear to be crystalline, with recognizable angular crystal faces.

Figure 5.5 is an image of a crustal particle along with its EDS spectrum showing a significant Si peak and a minor Al peak (both can attributed to the E-glass in the circuit board, although the Al may be a system peak). Elements detected within circuit board smoke particles (including other EDS spectra not shown) are C, O, F, Fe, Cu, Al, and Si. Gases evolved from overheating circuit board include CO, HF, HCl and off-line ion chromatography analyses also show HBr from these tests (Meyer et al. 2013).



Figure 5.5. TEM image and EDS spectrum of a circuit board smoke particle at 540° C (Run 31). The jagged crustal particle is much larger than the typical rounded particles and EDS shows a significant Si peak as well as Cu and Al, all typical constituents of electronics (circuit board and components). Cu and Al are also potentially system peaks and a portion of the Si signal may be attributed to the mica sheet in the smoke generator.

5.4 Smoke Particles from Wire Insulation

Along with circuit boards, thermal degradation of wire insulation has high potential as a source of smoke in spacecraft. Samples of partially fluorinated polyimide (PFPI) wire insulation manufactured by TRW were overheated and smoke particles collected with the thermal precipitator. PFPI polymers were invented under NASA Lewis Research Center sponsorship in the late 1970's and were targeted as superior candidates for high temperature wire insulation products (Jones, 1994). This PFPI wire insulation was shown to generate smoke in previous testing within 35 seconds at current levels from 10 to 15 amps, and smoke reportedly vented from bubbles and imperfections in the insulation (Hammoud et al. 1995). Figure 5.6 shows two

distinct PFPI smoke particle morphologies from thermal precipitator sampling, spherical and crystalline.



Figure 5.6. SEM images of wire insulation smoke particles at 640° C (Run 6). Smaller particle populations are mostly spherical (left) and some particles have square crystalline morphology (middle and right).

The majority of the wire insulation smoke particles captured are spherical, some appearing as doublets, as in the left image of Figure 5.6, and in Table 5.1. Square and angular crystalline particles are less common, as shown in the center and right images of Figure 5.6.

Some notable yet infrequent large spherical particles were observed ranging in diameter from 4.0 to 4.6μ m, as shown in Figure 5.7. These larger particles appear to have somewhat irregular surfaces which are most likely smaller particles agglomerating on the surface, as evident in the right image of Figure 5.7. The advantage of collecting SEM images is the ability to observe particle surface features and morphology with distinct details, including the 300 nm particle and other particles adhered to the sphere in the right image. Striations in the aluminum surface finish SEM stub are evident in the right image.



Figure 5.7. SEM images of wire insulation smoke particles at 640° C (Run 6). These large spheres range from 4.0 to 4.6 µm in diameter. Note the smaller particles adhered to the large particle (right).

5.5 Smoke Particles from Teflon

Teflon is the DuPont Company trade name of polytetrafluoroethylene (PTFE, $(C_2F_4)_n$), a crystalline fluoropolymer commonly used in spacecraft for wire insulation, water storage bladders, sampling bags, suits, and cargo liners. The thermal decomposition of Teflon differs from the other polymers analyzed in spacecraft fire characterization testing. Teflon polymer fragments are released during the pyrolysis of Teflon, as opposed to polymers which release low and high molecular weight gases. These fragments, ejected under the same temperatures as the heating range of these tests, grow through nucleation, condensation and coagulation (Mulholland et al. 2015).

Teflon smoke particles collected with the thermal precipitator had nearly spherical morphology of varying sizes, as seen in Table 5.1. Figures 5.8 and 5.9 show high resolution SEM images (Hitachi S-5500) of typical Teflon smoke particles which are nearly spherical. Although these particles are fairly large (typically greater than 500 nm), it is evident that many smaller particles have agglomerated to the surfaces, some as small as 50 nm in diameter.


Figure 5.8. High Resolution SEM images of Teflon smoke particles at 540° C collected onto a carbon film TEM grid. Particles range from 250 nm to 1.5 μ m in the left image, center image particles are 500 nm and 700 nm and the particle on the right is 700 nm.

Smoke particles in Figures 5.8 and 5.9 were collected on two different types of TEM grids that were attached to carbon tape on the SEM stubs, one with continuous carbon film between the copper grid matrix, and the other with lacey carbon between the copper grid openings.



Figure 5.9. High Resolution SEM images of Teflon smoke particles at 540° C collected onto a lacey carbon TEM grid; particles in the right image are 700 nm and approximately 400 nm.

An EDS spectrum and image of a Teflon smoke particle are shown in Figure 5.10. The prominent fluorine peak is expected, and indicates that the material did not completely thermally decompose during heating, substantiating that intact fragments of polymers are liberated in the smoke.

However, the elements Al and Si are not expected to appear in Teflon smoke particles. The Al is most likely a system peak, Cu can be attributed to the copper TEM grid which supports the lacey carbon, and Si is potentially from the mica liner in the WSTF smoke generator.



Figure 5.10. High Resolution SEM image of Teflon smoke particles at 540° C on a lacey carbon TEM grid and corresponding EDS spectrum with a prominent F peak. The Al is most likely a system peak, Cu can be attributed to the copper TEM grid and Si is potentially from the mica liner in the WSTF smoke generator.

Several typical Teflon smoke particles were examined at higher magnifications in a TEM (Philips Model CM20) in order to reveal some chemical information about the structure and order of the particle material. Figure 5.11 shows high resolution TEM images of a Teflon smoke particle (640° C) approximately 400 nm in diameter adhered to the lacey carbon. The irregular rounded particle on the left appears to be composed of layers and/or agglomerated smaller particles, as seen by the varying density (darkness) and has tail which is magnified in the center and right images. The particle tail is thinner than the particle itself and it is hanging over the edge of the lacey carbon support structure, which allows imaging of the microstructure. The center image shows smaller particles in the tail which have either agglomerated or become encapsulated. The far right image shows the amorphous interior structure of the tail.



Figure 5.11. High Resolution TEM images of a Teflon smoke particle at 640° C (test 15) adhered to a lacey carbon TEM grid. The irregular rounded particle on the left is approximately 400 nm in diameter with an extended tail. The center image shows a detail of the particle tail which contains smaller particles. The right image shows the amorphous interior structure of the tail.

Figure 5.12 shows a 250 nm spherical Teflon smoke particle, which appears to consist of many smaller particles bound together by amorphous material as seen in the right image of Figure 5.12, which is at higher magnification and interior particles are on the order of 20 to 30 nm. This primary particle size has been confirmed by initial particle size measurements of fresh smoke in the test chamber, however, within seconds, the extremely small particles rapidly combine into larger agglomerates in the high concentrations typically seen in the smoke chamber. Teflon particles are known to escape detection by photoelectric smoke detectors owing to their small size.

Figure 5.13 shows a portion of a much larger agglomerate with distinctly angular shaped protrusions. The center and right images are magnified portions of the angular agglomerate and the morphology shows evidence of crystallinity. This is not unexpected for Teflon, which can be up to 90% crystalline.



Figure 5.12. High Resolution TEM images of a Teflon smoke particle at 640° C (test 15) adhered to a lacey carbon TEM grid. The compact agglomerate is approximately 250 nm in diameter and contains smaller particles bound together by amorphous material.



Figure 5.13. High Resolution TEM images of a Teflon smoke particle at 640° C (test 15).

Images in Figure 5.14 are the highest magnification images which illustrate the individual carbon fringe structures or nanostructures of the agglomerate particle of Figure 5.13. The linear pattern in the interior of the particle shows the alignment of crystal fringes within an amorphous carbon coating. This substantiates that the original crystalline material fragments have persisted through the heating cycle and were subsequently coated by amorphous products condensing on the surface.



Figure 5.14. High Resolution TEM images of a Teflon smoke particle at 640° C (test 15) showing a crystalline interior with an amorphous coating



Figure 5.15. Teflon smoke particles collected with the SAME thermal precipitator on the ISS, showing vastly different morphology compared to WSTF samples (TEM, Philips Model CM20). Teflon smoke particles from the WSTF thermal precipitator pictured here (Figure 5.15) are very different from the morphology observed in the NASA Smoke Aerosol Measurement Experiment (SAME), most likely because of different heating methods and fuel preparation (Meyer et al. 2015).

5.6 Smoke Particles from Kapton

Kapton, a polyimide with chemical formula $(C_{22}H_{10}N_2O_5)_n$ performs well at both high and low temperatures and has excellent insulating properties and fire resistance. Spacecraft applications of Kapton include thin-film heaters, wire insulation, space suits, tape and multilayer insulation (MLI). Thermal decomposition of Kapton results in liquid aromatic products, and the general spherical shape of the particles observed with the TEM is consistent with the particles starting as a liquid solution with many components (Mulholland et al. 2015). Kapton smoke particles under heating conditions of these tests can form string-like agglomerate structures.



Figure 5.16. SEM images of Kapton smoke particles on the Al SEM stub: (left) at 540° C are compact and either spherical or angular, (right) at 640° C exhibit chain-like agglomerate structures, some doublets and longer chains are coated.

Figure 5.16 shows SEM images of Kapton smoke particles generated at 540° C (left image) which are either spherical or angular, ranging from 100 to 500 nm in diameter. The right image of Figure 5.16 shows particles generated at 640° C in the same size range, which exhibit chain-like agglomerate structures and are coated by condensation of pyrolysis products. These particles are on the aluminum SEM stub, and the striations in the unpolished surface are evident in the left image.



Figure 5.17. High Resolution SEM Analysis of Kapton smoke particles at 640° C on a lacey carbon TEM grid showing irregular surfaces and angular edges (upper right image, ~700 nm long, lower right image 500 nm). The coating on spherical particle chain appears to have primaries connected by liquid bridges that solidified and connected primary particles ranging from 100 to 350 nm.

Figure 5.17 shows high resolution SEM images of Kapton smoke particles on the lacey carbon TEM grid. These particles are in the same size ranges as the SEM images in Figure 5.16, although at higher magnification, some particles appear to have angular edges and uneven surfaces. In the lower left image of Figure 5.17, the string of primary spherical particles ranging from 100 to 350 nm seem to be held together by liquid bridges that solidified. Figure 5.18 shows an angular Kapton smoke particle 640° C with its EDS spectrum with peaks for O, Si and Al. In all the spectra shown, Cu is attributed to the copper TEM grid which supports the lacey carbon, Al may be a system peak and the presence of Al and Si may be attributed to the mica liner in the WSTF smoke generator.



Figure 5.18. Angular Kapton smoke particle, approximately 270 nm (640° C) with its EDS spectrum showing O, Si and Al. The Al is most likely a system peak, Cu can be attributed to the copper TEM grid and Si is potentially from the mica liner in the WSTF smoke generator.



Figure 5.19. High Resolution SEM images of Kapton smoke particles (640° C).

Figure 5.19 shows the coverage achieved with the thermal precipitator during a 640° C test. The Cu grid around the carbon film appears on either side of the left image. The middle image shows a 450 nm spherical particle with a surface similar to previous particles, but with multiple smaller particles adhered to it. The right image of Figure 5.19 shows a chain of three particles all close to 350 nm in diameter, one irregularly shaped which is attached to two more spherical particles with rough surfaces, most likely from smaller agglomerated particles. Figure 5.20 shows a 400 nm Kapton smoke particle with a similar rough surface texture.



Figure 5.20. EDS spectrum of a 400 nm Kapton smoke particle (640° C) on a carbon film TEM grid showing Cu, Si, Al. The Al is most likely a system peak, Cu can be attributed to the copper TEM grid and Si is potentially from the mica liner in the WSTF smoke generator.

Both the compact irregular Kapton smoke particle in Figure 5.18 and the more spherical particle with a textured surface in Figure 5.20 contain the same elements, although the former has a higher C peak. The Al is most likely a system peak, Cu can be attributed to the copper TEM grid and Si is potentially from the mica liner in the WSTF smoke generator. Kapton smoke particles shown here compare well to the morphology observed in the NASA Smoke Aerosol Measurement Experiment (SAME), in spite of very different heating methods and fuel preparation (Meyer et al. 2015). Figure 5.21 shows aged Kapton particles collected with the SAME thermal precipitator on the ISS, which have similar spherical morphology and connected as doublets, triplets and longer chains and some appearing to have a somewhat rough surface. Furthermore, all the diameters of single particles shown in the WSTF micrographs are within the ranges of the smoke particle size distributions measured with the Scanning Mobility Particle Sizer Spectrometer (SMPS) in the ground testing of SAME flight hardware heating Kapton and the size distribution obtained from image analysis (projected area equivalent diameter) of pyrolysis smoke particles collected on a TEM grid on board the International Space Station (ISS).



Figure 5.21. Aged Kapton smoke particles collected with the SAME thermal precipitator on the ISS, showing similar morphology to WSTF samples (TEM, Philips Model CM20).

5.7 Smoke Particles from Nomex

Nomex cloth is a heat and flame-resistant textile woven from continuous meta-aramid polymer fibers (DuPont chemical company). It is an aromatic polyamide produced by condensation reaction from two monomers, m-phenylenediamine and isophthaloyl chloride (Chanda and Roy, 2008). In spacecraft applications, Nomex cloth is used for acoustic insulation, cargo bags, thermal blankets and pressure suits.

Nomex affords a longer heat-resistance owing to carbonization during thermal decomposition (Vilar-Rodil et al. 2001). Zhang (2010) performed analysis of the thermal degradation of Nomex fibers using TGA-DTA/FT-IR (Thermogravimetric analysis – differential thermal analysis/Fourier Transform – Infrared) and reported that above 500 °C, complex depolymerization, random rupture, restructuring and other chemical reactions take place. As the Nomex is heated without combustion (oxidative pyorolysis), many organic species are liberated leaving a carbon-rich ash or char.

Nomex smoke particles were observed with four types of morphology: irregular char-like, irregular with inorganics, rounded irregular and spherical. Figure 5.22 shows the Nomex smoke particles on the aluminum SEM stub, with many spherical particles, some irregular rounded particles, and one large crustal particle in addition to several other smaller irregular crustal particles.



Figure 5.22. SEM image showing spherical Nomex smoke particles in the range from 300 to 600 nm and a large irregular particle (on the right), possibly char. Light areas indicate charging by the electron beam, however, the spherical particles are stable and did not volatilize under the beam.

Figure 5.23 shows what appear to be a char particles as the accompanying EDS spectra show very large carbon peaks. In all the spectra shown, Cu is attributed to the copper TEM grid which supports the lacey carbon. The upper spectrum shows the presence of Al which is a system peak and Si is potentially from the mica liner in the WSTF smoke generator.



Figure 5.23. The SEM images and corresponding spectra from Nomex smoke of what appear to be char particles owing to the high C peaks. Cu in both spectra are attributed to the copper TEM grid. In the upper spectrum, Al is a system peak, and Si is potentially from the mica liner in the WSTF smoke generator.

Figure 5.24 shows an irregular Nomex smoke particle with the EDS spectrum showing a large

oxygen peak along with the inorganic elements Mg, Ca and Si, which appears larger than other

system peaks.



Figure 5.24. The SEM image and corresponding spectrum of an irregular Nomex smoke particle with distinct angular inclusions, containing O as well as the elements, Si, Ca, Al and Mg. The Al may be a system peak and Cu can be attributed to the copper TEM grid.

Figure 5.25 is an irregular rounded Nomex smoke particle that is amorphous, and appears to have arrived at the TEM grid in a partially-solidified viscous liquid state. The EDS spectrum shows the particle contains C, O, N, Al, Si and Cl. The presence of Cl in the Nomex smoke particles is explained by the polymer formation process which uses a condensation reaction with isophthaloyl chloride, and furthermore, the reaction is catalyzed with LiCl, and the solution used in spinning Nomex fibers typically contains more than 3% calcium chloride (CaCl₂) by weight (Fink, 2008, Gabara et al. 2006). The Nomex used for fuel in these tests emits HCl gas in WSTF and GASP testing at levels ranging from 20 to 115 ppm, depending on the fuel mass, while HCN and HF are also emitted in lesser concentrations (Briggs et al. 2015, Meyer et al. 2013).



Figure 5.25. SEM image and corresponding EDS spectrum of a non-spherical 700 nm Nomex smoke particle with a rounded irregular shape and contains C, O, N, Al, Si and Cl. The Al may be a system peak, Cu can be attributed to the copper TEM grid and Si is potentially from the mica liner in the WSTF smoke generator.

The process of carbonization during Nomex pyrolysis can be seen as a parallel to the carbonization taking place in making charcoal and to biomass burning in general, as well as to coal pyrolysis. Tar has been generally defined in the literature as any condensable product emitted from the heating of solid fuel (Bond and Bergstrom 2006). More specifically, in coal combustion research, it is referred to as aromatic cluster fragments with lower molecular weights (Wang et al. 2013, Wang et al. 2015). In the biomass combustion/pyrolysis literature, tar is

referred to as high-molecular weight water-insoluble organic polymer species, and a liquid from biomass distillation products (Hand et al. 2005, Tóth et al. 2014, Fang et al. 2014). The definition of tar with regards to thermal decomposition of organic materials (coal, biomass and polymers) is of importance in the classification of particles as 'tar balls'. Tar balls have been observed in wildfire emissions as well as laboratory generated smoldering and combustion, in both fresh and aged smoke (Pósfai et al. 2003, Li et al. 2003, Pósfai et al. 2004, Tivanski et al. 2007, Chakrabarty et al. 2010, Turmolva et al. 2010, Adachi and Buseck, 2011, China et al. 2013, Tóth et al. 2014). Characteristic descriptions of tar balls in the above-mentioned literature vary somewhat, depending on the smoke source sampled and analyzed, but most include the following traits: carbonaceous, perfectly spherical to near-spherical, amorphous and with homogeneous composition (without inorganic inclusions, crystalline structure, graphene microstructures or internal cores). Tar balls are stable/resistant to electron beam damage under high magnification and are classified optically into two types: dark and bright, based on degree of oxidation and coating. Their absorption Ångström coefficients indicate they can be categorized as brown carbon, which is a type of organic carbon that is brownish or yellowish in appearance and has an imaginary refractive index that varies with wavelength (Moosmüller et al. 2009). Tar ball EDS spectra reportedly consist of C, N, O, (some sources include inorganic species S, Cl, K and Si as well) and have a high C/O atomic ratio. Tar balls appear externally mixed, that is, they do not agglomerate with other particle types. They are reportedly produced from smoldering combustion, nucleated from the gas phase within smoke plumes (gas to particle formation mechanism), and vary based on environmental conditions: fuel type, formation temperature and transport/aging in the atmosphere (Pósfai et al. 2003, Li et al. 2003, Pósfai et al.

2004, Tivanski et al. 2007, Chakrabarty et al. 2010, Turmolva et al. 2010, Adachi and Buseck, 2011, China et al. 2013, Tóth et al. 2014).

Tóth et al. (2014) created the first laboratory-generated tar ball particles by droplet emissions of liquid tar obtained by dry distillation of wood. After aerosolization of the liquid, the tar droplets had a residence time of about 0.3 seconds in a heated zone between 560 and 630 °C which solidified the droplets into particles with all the characteristics of tar balls. They hypothesize that tar balls may be formed by expulsion of liquid tar from biomass pores upon pyrolysis which are solidified by a short residence time in the flame zone of a fire.



Figure 5.26. High resolution SEM images of Nomex smoke particles that appear to have arrived on the TEM grid as liquid droplets of varying solidity, some with perfectly spherical tar ball morphology. Diameters of single particle images range from 300 nm to 800 nm.

The thermal decomposition of Nomex creates liquid smoke particles, so surface tension dictates the final shape. Some particles arrive at the TEM grid mostly solidified, as spheres, while some adhere to the lacey carbon grid before solidifying, as seen in Figure 5.26. The temperatures used in the generation of tar balls from liquid tar by Tóth et al. (2014) are similar to the conditions of the Nomex heating test (640 °C). Nomex smoke samples collected with the thermal precipitator had some perfectly spherical particles which have a striking resemblance to tar balls, and it can be assumed that the tar droplets had long enough residence time in the heated zone of the smoke generating tube furnace to solidify, however, there are a number of particles that were clearly liquid when they were captured on the TEM grid.



Figure 5.27. SEM image and corresponding EDS spectrum of a tar ball-like 600 nm Nomex smoke particle with peaks of C, O, N, Al, Si and Cl. The Al is a system peak and Cu can be attributed to the copper TEM grid.

Figure 5.27 shows a tar ball-like Nomex smoke particle which is attached to the lacey carbon by a small liquid bridge. The EDX spectrum shows the elements C, N, O, as reported in tar ball descriptions in the literature, but also the presence of Al. All the magnified smoke particles in Figure 5.26 have the same elements in their EDX spectra as the one shown in Figure 5.27 (C, N, O and Al), and the upper right image has Cl in its spectrum as well.



Figure 5.28. Nomex snips before heating (0.5 g fuel sample) (left), after heating, the many Nomex snips became one or two compact pieces of char/ash, as shown in the remains of five different tests (middle). TEOM filters after mass concentration measurements of Nomex smoke particles show the characteristic yellowish color of brown carbon (right).

Figure 5.28 shows the Nomex fuel before and after heating. The left image shows 0.5 g of the fluffy unburned fabric, randomly snipped into pieces 1 cm or less per side. The fuel undergoes carbonization in the furnace, reducing the small pieces of fibrous Nomex to individual clumps of char as the fibers thicken and combine when subjected to intense heat (Nomex Technical Guide, 2001), as seen in the center image of Figure 5.28. A Tapered Element Oscillating Microbalance (TEOM) was used as a reference instrument for mass concentration in these experiments. This instrument uses consumable filters which must be replaced when the instrument pressure drop becomes too high. Upon removal, most TEOM filters from other polymer fuels were barely discolored (mostly white), with the exception of PVC smoke, which was very dark brown, nearly black. Another notable exception was Nomex smoke which made the TEOM filters are shown in Figure 5.28 (right image). This is additional evidence to support the hypothesis that Nomex smoke from oxidative pyrolysis includes tar balls.

5.8 Conclusions

The thermal precipitator successfully collected an abundance of smoke particles for microscopic analysis. A comprehensive characterization has been performed for each material, although

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there are many additional sampled particles which have not been examined. From the analyses to date, the following general conclusions are made:

- Ten types of common spacecraft materials or mixed materials underwent oxidative pyrolysis at different temperatures and the resulting smoke particles were characterized according to morphology and elemental composition.
- Results are consistent with known thermal decomposition mechanisms in the literature and chemical make-up of spacecraft fuels.
- Teflon particles show evidence of native polymer shards liberated from the bulk material based on elemental mapping and high resolution TEM micrographs showing a crystalline interior with an amorphous coating.
- Under the heating conditions of these tests, Teflon particles coagulate into compact spherical agglomerates, unlike SAME Teflon smoke particles which were fractal agglomerates in both ground testing and ISS tests.
- Kapton smoke particles are consistent in size and morphology with SAME smoke from ISS experiments and ground testing.
- Crustal particles, rich in inorganic species, were observed in circuit card smoke.
- Tar ball morphology was observed for Nomex smoke particles.

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<u>Chapter 6: Indoor Aerosols in the International Space</u> <u>Station</u>

6.1 Introduction

Indoor air quality is of great importance to human health, and has been studied extensively in homes and work places. On Earth, a large proportion of the indoor aerosol sources are from cooking, smoking and cleaning (Spengler 2001). Homes and workplaces have different activities and thus different sources. Additionally, outdoor air is a major source of indoor pollutants, bringing vehicle and industrial emissions, pollen and dust into buildings. The International Space Station (ISS) is a unique indoor environment that serves as both home and workplace for astronauts, and has some aerosol sources in common with buildings on earth, but can be considered an isolated volume of air with only internally generated aerosols from occupants, their activities and ISS infrastructure. There are no outdoor sources of aerosols on the ISS, as the vacuum of space can be considered particle-free and sealing systems keep the vehicle pressurized for a habitable environment which would preclude the ingress of any particulate matter from the outside. Therefore the ISS filtration system is of utmost importance for quality of life and health. An aerosol source model was developed for the purpose of filtration and ventilation systems design, and has been successfully applied, however, since the initial efforts, the number of crewmembers on board the ISS has increased from 3 to 6 and they are engaged in new processes and activities. Therefore, it is prudent and necessary to evaluate the current state of ISS ambient air quality in terms of particle emissions and determine what new aerosol sources should be identified, even if they are not quantified. Only aerosols generated in living spaces are considered in this effort which excludes potential aerosol generation from equipment in racks and from other ISS life support subsystems. This topic should be periodically revisited as existing sources change or new aerosol sources become evident in the future.

6.2 Aerosol Transport Properties on ISS

Sizes of indoor aerosols typically span several orders of magnitude, but on ISS, the range of interest is much larger. Respirable particles are 10 µm and below (Hinds 1999), and can travel to the pulmonary portion of the lungs where gas exchange takes place in the alveoli, whereas particles from 10 to 100 µm that are inhaled typically impact in the nose or possibly the bronchi. Not all particles in this size range are inhaled, for example, only 50% of particles with aerodynamic diameter of 100 µm are inhaled (Hinds 1999). The smallest particles can be detrimental in the long-term (Oberdörster et al. 1995, Peters et al. 1997, Oberdörster et al. 2005, Brown et al. 2013), but larger particles can potentially cause eye, nose and throat irritation, as well as allergies. Particles behave differently on ISS compared to Earth with the absence of gravitational settling. Thus, extremely large particles persist in the air until they are removed by an ISS Bacterial Filter Element (BFE), which has near-HEPA performance in removing particles through flow into the air handling system (Green et al. 2014). Figure 6.1 shows the 4" x 29" face of a BFE on ISS. The filter has no anti-bacterial material properties, but was given the name because it filters the size range of bacteria aerosols, from 300 nm to 10 µm (Hinds 1999).



Figure 6.1. Bacterial Filter Element (BFE) face on ISS (with area 4" x 29"), shown in clean condition.

An important variable to consider for particle removal is the transport behavior of the particle in air. Particles are subject to aerodynamic drag which is a function of particle diameter and the ambient air pressure. In atmospheric pressure, particles greater than about 3 μ m in diameter experience the same type of resistance to motion as larger rigid bodies, since the air is considered a continuum which exerts a drag force on the surface of the body. Below this size, air surrounding the particle cannot be considered a continuous medium, and the particle experiences fewer collisions with air molecules, so drag is reduced and can be estimated based on the Cunningham correction factor. Particles with diameters less than 20 nm are considered to be in the free-molecule regime where Knudsen diffusion effects dominate. In-between these two extremes (for particle diameters from 20 nm to 3 μ m) is a transition regime. For planetary or lunar missions with lower pressure cabin environments, as well as the ISS airlock where pressure is reduced to 70.3 kPa prior to extra-vehicular activity (Anderson et al. 2015), there are fewer air molecules present resulting in reduced drag. In these conditions filtration is enhanced once the particle enters the filter, as reduced drag enhances the inertial capture of the particles on the filter media (Agui et al. 2010).

Another factor affecting particle motion is shape, as spherical particles will experience less drag than non-spherical particles. Dust is defined as a solid particle resulting from mechanical disintegration of material (Hinds 1999). Most dust particles have jagged, irregular morphology which will slow their motion in air, relative to smooth spheres. Fibers also have increased drag which is accounted for analytically by a dynamic shape factor. For example, spheres have shape factor 1.0 whereas cubes have shape factor 1.08—the drag is 8% higher for cubes (Hinds 1999). Cylinders have different dynamic shape factors based on their aspect ratio and orientation relative to the flow. Averaged over all orientations, a fiber with a 2 to 1 aspect ratio has a shape factor of 1.09, whereas a fiber with 10 to 1 has a dynamic shape factor of 1.43 (effectively increasing the drag by 43%). Fibers undergo both translational and rotational motion as well

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(Dastan et al. 2014). Generally, the filtration efficiency of fibrous aerosols is higher than that of spherical particles, with a strong dependence on aspect ratio: the longer the fiber, the greater the collection efficiency (Asgharian et al. 2002).

6.3 Original Aerosol Source Emission Rates for Filtration Design

The initial aerosol source model for filtration design was based on reports which quantified rates for human-generated particles from the literature, as well as several Space Shuttle cabin air filter analyses (Perry 1988). This inventory included particles ranging from 1 μ m to 1270 μ m, with binned size distribution information for coughs and sneezes. The remaining sources are described by a range of particle sizes, with no mean or standard deviation to describe the particle size or mass distributions. Eight types of fabric fibers were listed individually in the table, most with only one dimension given. Emission rates in the table were specified in terms of both aerosol number and mass generated per person, and quantified viable colony forming units of bacteria and fungi in these particles. The original aerosol emission rates based on Space Shuttle data is shown in Table 6.1.

This effort to update spacecraft aerosol sources and generation rates does not attempt to address microbial contamination, therefore, the microbial data from the original source is not included in Table 6.1. The purpose of this effort is to summarize known aerosols on the ISS as they relate to general air quality and filter performance, and to estimate emission rates based on the indoor air quality literature, in terms of mass and/or number concentrations, where possible.

Туре	Particle size, μm	Distribution		Generation Rate		
		By Part (%)	By Mass (%)	Particulate (#/person-minute)	Mass (mg/person-minute)	
Skin Fragments	20.0	8.44E+01	5.00E-03	1.91E+04	1.54E-05	
	< 10.0	9.38	1.39E-04	2.30E+03	4.27E-07	
Sneeze	> 22.0	1.38E-02	5.64E-09	3.12	1.74E-11	
	8.0 - 16.0	1.10E-01	1.74E-08	2.50E+01	5.34E-11	
	4.0 - 8.0	4.10E-01	8.08E-09	9.31E+01	2.49E-11	
	2.0 - 4.0	8.58E-01	2.11E-09	1.94E+02	6.49E-12	
	1.0 - 2.0	2.10E+00	6.46E-10	4.76E+02	1.99E-12	
	< 1.0	2.45	9.42E-11	5.56E+02	2.90E-13	
Cough	> 22.0	2.60F-04	1.07F-10	5.90F-02	3.28F-13	
	8.0 - 16.0	1.50E-03	2.36F-10	3.40F-01	7.27F-13	
	4.0 - 8.0	3.95E-03	7.78E-11	8.96E-01	2.39E-13	
	2.0 - 4.0	4.90E-03	1.21E-11	1.11E+00	3.71E-14	
	1.0 - 2.0	6.43E-02	1.98E-11	1.46E+01	6.09E-14	
	< 1.0	2.02E-01	7.77E-12	4.58E+01	2.39E-14	
Cotton fiber	12.9	3.38E-03	2.19E+01	7.67E-01	6.74E-02	
Wool fiber	20.5 - 23.0	3.81E-05	8.18E-01	8.64E-03	2.52E-03	
Acrylic fiber	20.3	4.55E-05	1.53E-01	1.03E-02	4.71E-04	
Polvester fiber	16.0 - 18.0	5.29E-05	2.92E-01	1.20E-02	8.98E-04	
Glass fiber	4.0 - 5.6	2.52E-04	4.86E-01	5.72E-02	1.49E-03	
Nylon fiber	16	3.08E-06	5.34E-04	6.97E-04	1.64E-06	
Nomex fiber	14	8.49E-05	7.35E-01	1.92E-02	2.26E-03	
Cashmere fiber	16.7	5.54E-06	1.35E-01	1.25E-03	4.16E-04	
Human hair	58.8 - 68.4	2.32E-05	4.89E+00	5.30E-03	1.50E-02	
Metallics	813	1.66E-04	9.70E+00	3.76E-02	2.98E-02	
Paint chips	51.0 - 1270.0	1.44E-04	3.85E+00	3.26E-02	1.18E-02	
Plastics	813	3.96E-04	1.32E+01	8.98E-02	4.05E-02	
Miscellaneous*	> 2540.0	2.77E-06	4.38E+01	6.27E-04	1.35E-01	
τοται		100.00	100.00	2 28F+04	0 31	
* Tissue food varn woven and glass tang finger nail clippings poncil load						

Table 6.1: Original Airborne Particulate Generation Load Model (based on Space Shuttle data)

Intakes for the air handling system in the U.S. portion of the ISS have a 20 x 20 pre-filter Nomex mesh with opening size 841 µm which prevents larger particles from entering the ISS filter media, as shown in Figure 6.2c (Perry 1988). In the absence of gravitational settling, these large particles can remain airborne but are easily entrained in the flow towards the filters. Regular vacuuming of the pre-filter is necessary to prevent a significant build-up of these larger dust and lint particles on the screens (Figures 6.2a and b, and 6.3). Air quality on ISS is affected by all the sources listed in the table, whereas filter performance is influenced by the particles that can pass through the $841 \mu m$ mesh openings.



Figure 6.2. a) BFE shown with a number of days of debris accumulation on Nomex screen. b) Close-up photo of accumulated debris. c) Nomex pre-filter screen detail showing fibrous debris and a hair trapped between the upper filter pleats and the screen.



Figure 6.3. Crewmember Tracy Caldwell Dyson vacuuming as part of ISS Housekeeping chores.

Approximately 25% of the total particle mass in Table 6.1 is attributed to fibers, mostly clothing (with the exception of glass and Nomex fibers). It is assumed that the particle sizes given in the table are fiber diameters, and that the geometry of particles attributed to these sources have a large aspect ratio, with the aerodynamic behavior of cylinders. Nearly 5% of the particle mass is human hair, but it is assumed that the pre-filter mesh will prevent most hairs from entering the ISS filter. The rule-of-thumb width of a human hair is about 100 μ m (give or take 50 μ m), so a very short hair could conceivably pass through the mesh if it had the proper orientation. This is consistent with a recent debris analysis performed on a HEPA vacuum bag returned from ISS, which showed that hair remained in the sieving operation that removed debris smaller than 500 μ m, but was not identified in the smaller fractions (Perry 2013). Similarly, the 'Miscellaneous' category of particles in Table 6.1 does not affect filter performance, as the size of these fragments exceed the pre-filter mesh opening size.

Cough and sneeze are important for microbial analysis but do not contribute significantly to the ambient aerosol on ISS. These particles in Table 6.1 make up 6.2% of the number count, but account for a miniscule percentage (3.4E-08%) of the total mass of particles. Cough aerosols are assumed to be liquid droplets that would evaporate quickly in the typical ISS environment (4.4 to $15.5 \,^{\circ}$ C dew point). Numerical computations modeling droplets expelled in respiratory activities show that a 20 µm droplet will evaporate in about 0.5 seconds under this range of conditions (Xie et al. 2007). Sneeze aerosols may be liquid and evaporate, or possibly have a solid core. Cough and sneeze droplets are not expected to significantly contribute to the ISS aerosol concentration and thus will be neglected in the updated table.

6.4 Updated Aerosol Sources on ISS

While the original table of particle sources is based on reported data, only larger aerosol sizes are accounted for. Particles less than 100 μ m are considered inhalable, and are further classified based on their deposition location in the upper airways, or pulmonary regions (Hinds 1999). Many governments have regulations for ambient aerosol concentrations for particles with diameters less than 10 μ m and less than 2.5 μ m (known as PM10 and PM2.5 [the latter are also known as fine particles]). These regulations do not apply to indoor environments, however, they are important in the context of human health. Age, gender and level of activity are all factors affecting penetration and deposition of inhaled particles, but research shows that smaller particles present greater risks to human health (Oberdörster et al. 1995, Peters et al. 1997, Oberdörster et al. 2005, Brown et al. 2013). Therefore the updated aerosol inventory should include known particle emissions below 10 μ m, including the ultrafine range (100 nm and below). Furthermore, particles that are close to 300 nm are considered the most penetrating particle size in filtration, so size segregated aerosol sources in this range are very relevant to filter efficiency calculations.

Table 6.2 contains the updated aerosol sources, each of which will be explained in detail. Most generation rates found in the literature were in terms of number of particles per unit time. Some sources were in terms of aerosol mass per unit time. In general, it is difficult to convert between aerosol number and mass, because the particles must be assumed spherical and also a density must be known. Often particle material densities differ significantly from the density of a parent material because of occlusions and/or complex shapes. Therefore, in Table 6.2, when both mass and number generation rates were available, they were both included in the table from the separate literature sources (they were not converted).

Aerosol Source	Particle size	Generation Rate per Person			
		Number of particles [#/(person*minute)]	Mass [mg/(person*minute)]	Reference, Comments	
Squames	0.3 - 40 μm	2.0E+5 to 2.0E+6	0.5 to 2.1	Anderson 2015,Weschler 2011, Milstone 2004, Gowadia 2001, Wydeven, 1989	
Personal Cloud	.35 μm	2583.33		ן ן	
	.5 - 1 μm	1041.67			
	1 - 2 μm	125.00			
	2 - 5 µm	66.67		You et al. 2013	
	5 - 10 μm	7.67		Combined Lint Generation Rate	
	>10 µm	2.54			
	total	3826.88			
Cotton Fiber Lint	12.9 μm	0.767	0.0674	Table 1	
Other Fiber Lint	19.5 µm	0.109	0.00806	Table 1	
Human hair	58.8 - 68.4 μm	0.0053	0.0150	Table 1 (not expected to load the filter significantly)	
Metallics	813 μm	0.0376	0.0298	Table 1	
Paint chips	51.0 - 1270.0 μm	0.0326	0.0118	Table 1 (particles > 841 µm will not enter the filter)	
Plastics	813 μm	0.0898	0.0405	Table 1	
		Generation Rate by Event or Activity			
		Number of particles [#/minute]	Mass [mg/minute]		
Vacuuming	.023 μm	3.797E+10		Afshari et al. 2005	
	.3 - 1 μm	3.00E+07			
	≤2.5 μm		0.45	Ferro et al. 2004	
	2.5 - 5 μm		0.27		
Laser Printer	median ~100 nm	2.50E+08	0.0667	CARB rpt. CEC-500-2011-046, Blue Angel Env. Standard	
Velcro	7 - 50 nm			GASP Laboratory Testing	
SOA	30 - 200 nm			Wierzbicka et al. 2009, Sarwar & Corsi 2006	

Table 6.2: Updated Aerosol Generation Rates

Also, a number of entries from Table 6.1 were retained, as there was no newer data available in the literature for these sources. Additional aerosol sources that are not quantified are listed at the bottom of Table 6.2, and these are the subject of ongoing research to either quantify them or determine whether they can be omitted.

The human body is a significant generator of indoor aerosols from both skin and clothing, and research shows that the level of activity has a direct effect on emission rates (Hussein et al. 2005, You et al. 2013). Skin flakes, also known as squames, are the result of normal shedding of the outer skin layer (ranging from 1 to 40 μ m in diameter, with average diameter of 14 μ m (Spengler et al. 2001). In an indoor environment, the rate of squame generation per person has been quantified at 200,000 to 600,000 per minute, or 30 to 90 mg per hour for humans on Earth (Gowadia et al. 2001, Milstone, 2004). These rates vary dramatically from person to person,

which makes this input a good candidate for a sensitivity study in future filtration performance modeling. Previous estimates used as baseline assumptions in NASA Life Support programs are similar to the higher end of the range in literature values. Skin cell aerosol generation rates were estimated to be 3 grams per crew member per day (Anderson et al. 2015), and a separate estimate in terms of number concentration was 1.22E+8 per person per hour, with size-segregated emission rates ranging from 0.3 µm to above 10 µm (Wydeven and Golub, 1990). Values for this emission source are given as a range in the updated table, combining the high and low end of the ranges of these literature sources referenced. Thus, the most significant change from the original aerosol source model is the squame emission rate per person, and it is of great importance since the number of crewmembers on the ISS has doubled since the original calculations for filtration performance.

The concept of a 'personal cloud' has been studied, as people emit aerosols not only from their skin but also from their clothing. Clothing on the body has the effect of capturing some squames, thus reducing emissions, however this is balanced by the emission of lint. Byrne et al. investigated the relative contribution of human body surfaces to the 'personal cloud' by selectively covering the face, hands and hair of test subjects with plastic wrapping while they carried out a repeatable activity pattern which was not specified (Byrne et al. 2002). A laser particle counter provided number concentration in bins with sizes <500 nm, 500 nm to 1 μ m, 1 μ m to 2 μ m, 2 μ m to 3 μ m, 3 μ m to 5 μ m, and 5 μ m to 10 μ m, which are substantially smaller than the sizes of clothing fibers in Table 6.1. The results of this study showed that face, hands and hair contribute a negligible portion of the concentration compared to the clothing, that is, concentrations for skin and hair particles were at most 1/6 of the measured concentration of lint in the 3 to 5 μ m range and only 1/20 of the measured concentration in the < 500 nm bin.

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Emission rates were not given in this reference, and it is assumed that no attempt was made to account for particles that were exhaled by the test subjects while in the test chamber. You et al. (2013) studied the short term personal cloud emission rates of males with different clothes and activity rates, which included both particles emitted from the clothed human body, as well as particles that may have been exhaled (You et al. 2013). The exhaled particles were shown to have a negligible contribution to the personal cloud. The clothing tested included a clean room smock, polyester jogging suit, and a cotton suit. As expected, the clean room smock had the lowest particle emissions, but the polyester typically emitted slightly more than the cotton clothing. Emission rates are measured for different size ranges up to 10 μ m, with the largest fraction of particles between 300 to 500 nm in diameter. The upper size limit for the personal cloud is based on the measurement range of the aerosol instrument used in this study. The classification of 'strong activity' consisted of brisk walking combined with periods of sitting with vigorous upper body and arm movements, and the 'slight activity' consisted of less vigorous walking and sitting with slight arm movements.. Although the activities measured by You et al. did not include running on a treadmill (which is one exercise method the astronauts engage in), this reference provides a guideline for estimating different emission rates between crewmember diurnal activities such as exercising and working versus sleeping.



Figure 6.4. Personal cloud and fiber emission rates combined to account for a larger size range of lint data. Solid symbols are from personal cloud data (You et al.) and open symbols are the original fiber emission data in Table 6.1.

For the values of this aerosol source in Table 6.2, active and still rates were averaged for the given rates per minute, as it was assumed that crewmembers would spend 12 hours active (exercise and work) and 12 hours still (sleep and quiet work) per day.

Fibers are generated not only in the personal cloud, but also from other fabrics present in spacecraft, as seen in Table 6.1. Crewmembers prefer cotton clothing, so part of the lint emission rate estimate in the new table is based on the cotton suit 'personal cloud' data, with each 24 hour period assumed to be divided equally between strong activity and still activity. However, lint particles are known to be much larger than 10 μ m, as evident in the original table. Figure 6.5 shows fibers obtained from destructive testing of a BFE. These fibers from the filter were once airborne on ISS, and the diameters are consistent with both data sources. Therefore, the personal cloud data from You et al. is used for the lower size range of the lint emissions estimate, and is augmented by the fiber emission rates in the original load of Table 6.1. Figure

6.4 shows that the approach of combining data from the two sources creates a feasible curve for fiber emissions, with the two large fiber data points from Table 6.1 data following the decreasing trend of the personal cloud data as particle sizes increase. Note the logarithmic scales for both axes, which accounts for lint in all size ranges, from 300 nm to about 20 μm. The majority of the fiber emissions in Table 6.1 were cotton, and all other fiber types were combined in a single data point in Figure 6.4 for simplicity. While Nomex and glass fibers cannot be attributed to crewmember clothing, they were separate entries in the original table, making up only 0.08% of the particle number emission rates. They are not treated separately in the new table, although this could be re-considered in future updates if data provided justification that they are significant aerosol sources.



Figure 6.5. High magnification of cotton fibers and cotton linters (very thin, short fibers) on left, more cotton fibers and a yellow synthetic fiber (right), 443X magnification. Photos courtesy of Victoria Bryg, from destructive BFE analysis.

The large proportion of lint in the load model is consistent with data from the ISS vacuum bag sieving analysis in which 51% of the total weight of debris greater than 500 µm consisted of lint (Perry 2013). Another NASA report summarized the destructive analysis of a used ISS BFE by microscopy, which observed that most of the debris was fibrous, predominantly cotton lint (Bryg, 2011). Pictures of lint fibers from the ISS filter analysis in Figure 6.5 generally confirm the fiber diameters in Table 6.1.

A third set of data is from a 2003 Boeing report outlining widespread deposition of particles on all surfaces of a smoke detector that had been returned to Earth, shown in Figure 6.6 (Turner, 2003). These particles can be assumed to be representative of the aerosols in the spacecraft cabin. Three separate samples of these deposited particles were analyzed and it was determined that hair and fibers made up 52%, 55% and 54% of the relative number distribution of all identified particles, respectively. Skin cells were consistently quantified at around 40% of the particles sampled. These analyses were based on sample sizes of 487, 526 and 642 total particles.



Figure 6.6. Smoke detector from ISS showing widespread deposition of particles from the cabin environment. Samples of these particles were analyzed and over 50% of the total numbers were hair and fibers, and 40% were skin flakes.

Vacuuming is a common source of indoor aerosols, and this is a known phenomenon on ISS since it is a common practice to turn off the smoke detectors during cleaning to avoid false alarms. Some emissions from vacuuming are from the vacuum motor brushes which emit particles below 0.3 μ m (He et al. 2004); however, the largest sources of vacuum particle emissions are from re-suspension of disturbed dust on adjacent surfaces, or re-emission of
vacuumed particles when the incoming air passes through a paper or cloth vacuum bag. The ISS vacuum does not emit the latter type of dust since the air sucked into the machine passes through HEPA filter to remove dust from the exhaust air. A realistic estimate for aerosol mass concentration emissions from vacuuming on ISS is a literature value measured in a house with wood floors partially covered by thin area rugs, which results in less emissions than carpeted areas. The particle emissions for the size range 2.5 µm and below is 0.45 mg/minute, and for the size range of 5 µm and below is 0.27 mg/minute (Ferro et al. 2004). These are entered in the updated table for two particle size ranges by subtracting the rates. An alternate source gives size-segregated data in terms of number emissions of 3.797E+10 particles/ minute for 0.02 to 0.3 μ m, and 3.0E+7 particles/ minute for 0.3 to 1.0 μ m (based on the measurement ranges of the research instruments) (Afshari et al. 2005). The given size ranges of the number emissions data are important for modeling size-dependent filter performance. These generation rates are considered conservative because the type of vacuum used for this data was not specified, but in all likelihood was not a HEPA vacuum. Squame and lint can be classified as 'dust' in this context, and these two combined make up the largest proportion of the matter that is removed by vacuuming. This is confirmed by the debris analysis on the contents of the vacuum bag returned from ISS (Perry, 2013).

A source of particles on ISS that was not in the original load model is laser printer emissions. Early studies showed a large range of particle emission rates from one printer to another (He et al. 2007, Kagi et al. 2007, He et al. 2010). There are various particle formation mechanisms, and emissions vary with cartridge age, toner coverage and temperature (which is related to number of pages printed in succession). A 2011 study by the California Air Resources Board (CARB) on office equipment showed that an emission rate in terms of particles per second of printer operation is approximately the same as the number particles emitted during the printing of one page (Maddalena et al. 2011). The emission rate of 1.E+09 particles per page is a conservative value to assume for standard conditions covering a variety of cartridge ages, and at both cold and warm starting temperatures. The table 6.2 entry reflects an estimate of 15 pages printed per minute. For a mass concentration emission rate, the German eco-label The Blue Angel award criteria requires, among other things, that particle emissions should be below 4 mg/(device-hr) (Wilke et al. 2009). Toner particles range between 2 and 10 μ m, however, particles emitted from printers have much smaller median diameters, on the order of 100 nm (Bello et al. 2013) and are thought to be formed by secondary chemistry during the printing process which produces volatile organic compounds from heated paper and toner, and ozone which is a by-product of the electrophotographic process. Currently there are two printers, one in the U.S. lab and the other in the Service Module. The amount of laser printing on ISS varies, but a realistic estimate is an average of 10 pages per day¹ which would result in 2.50E+08 particles per minute, or 0.0667 mg per minute, as recorded in Table 6.2.

Another potential source of particles emitted during exercising are mechanically generated metal wear particles from exercise equipment. The time allotted for exercising is 2.5 hours per crewmember per day on ISS, although it has been documented that the average time spent exercising is substantially less owing to 'overhead' attributed to setup time, stowage and logistical transitions (Cavanagh et al. 2010). Table 6.1 includes a particle category called 'metallic', which would encompass emissions from metallic exercise equipment, with only one particle size, 813 µm. Some estimates could be made based on experiments in which particles were generated from a metal sliding contact, in particular, from friction testing with a pin-on-

¹ Personal communication with astronaut Karen Nyberg.

disk tribometer. Particles ranging from 20 nm to 10 μ m were generated from chrome steel (100Cr6) at rates between 500 and 4000 particles per minute under different conditions (Olofsson et al. 2009). Generation rates are a function of sliding speed and contact pressure, which are highly design-dependent. The original entry of 813 μ m 'metallic' particles is nowhere near the size range of the wear particles in Olofsson et al, although the measurement capability in those tests had an upper limit of 32 μ m. There may be an opportunity to measure emissions from a prototype of ISS exercise equipment or from similar exercise devices in order to quantify this source. For the current study, the metallic category from Table 6.1 is retained as it originally appeared, with a 'per person per minute' generation rate.

An additional known source that has not been quantified is the generation of secondary aerosols from organic compounds reacting with ozone (which was discussed in the laser printer section). In most buildings, the typical indoor concentration of ozone (which often originates outdoors) ranges from 10 to 50 ppb (Gard et al. 1997). The secondary organic aerosol (SOA) emissions are highly dependent on species of reactive organic gases that are present, some which would be generated from ISS infrastructure, and other gases from cleaning products, personal care products and cosmetics brought by crewmembers which are unquantified. The cleaning product used outside the hygiene compartment consists of disinfectant wipes, which are used to wipe down panels which capture sweat, dust and lint. An upper bound of organic gas quantities can be based on published SMAC (spacecraft maximum allowable concentration) limits, although ozone is not monitored and there is no SMAC limit. From the many papers available about specific reactions that produce SOA, mean particle sizes are in the range from 30 to 200 nm (Wierzbicka et al. 2009, Sarwar et al. 2007). Recent studies conclude that sorptive processes play a role in the combination of SOA with other indoor particles, but quantification methods are as yet unreliable and the subject of ongoing research (Alves et al. 2014).

Velcro is ubiquitous on ISS, and is a known source of particles, however, it was not included in the original Table 6.1. Measurements of Velcro particle emissions were made in the fire characterization facility at Glenn Research Center (Gases and Aerosols from Smoldering Polymers [GASP] Laboratory), which has a 326 liter glovebox which can be purged to nearly zero initial concentration. Both a Scanning Mobility Particle Sizer (SMPS) Spectrometer (Model 3936, TSI, Shoreview, MN, USA) and a Water Condensation Particle Counter (WCPC, Model 3787, TSI Inc.) were used to measure particles generated from Velcro. Instrument specifications from the manufacturer list the particle measurement range for the WCPC from 5 nm to 3 µm. The maximum allowable size of a Velcro piece on ISS is 4" x 4", per JSC 27301F and Cargo Mission Contract CMC-NFS-000078-MP-SPL Rev. E. Three different samples were tested: unused flight Velcro (black), unused 'Industrial Strength' Velcro from a retail store, and one used piece from a Space Food Kit from the Glenn Research Center Education Office, which had been returned from a Space Shuttle mission (this piece was only 1" x 4"). The goal for this sample was to see if any existing debris from use in space that may be embedded in the Velcro would become resuspended, potentially creating significantly larger particles than those generated from the Velcro itself.

Particle from the Velcro were measured with the SMPS once steady-state concentrations were achieved in the glovebox while mating and demating the samples approximately 48 times per minute. The unused flight qualified Velcro samples produced very high particle concentrations, with the steady-state WCPC concentrations at 3.76E+5 particles/cm³ for the black Velcro, and 3.87E+5 particles/cm³ for the Food Kit Velcro (from 5 nm to 3 µm). The white sample

purchased at a retail store had substantially lower particle concentrations over the entire size distribution, reaching a steady-state WCPC concentration of 1.85E+4 particles/cm³. The Food Kit Velcro had been in service for an unspecified time period, which gives the potential for detecting a second mode at larger sizes, indicating the liberation of embedded debris in the Velcro pile into the air. There was a small increase in the particle population above 400 nm, however, further testing would be required to verify this behavior, preferably using Velcro with a known use history and an aerosol instrument with a larger measurement range. The unused flight qualified Velcro samples required much more force to mate and de-mate compared with the sample from the retail store.

The Velcro pile side of the fasteners are mounted on ISS walls, while the hook portions are mounted on the object to be secured. Dirt, lint and sweat are undoubtedly collecting in the fibers of the pile and are available to be re-entrained in ISS cabin air upon de-mating. Resuspension of particulate matter from carpets due to human activity has been studied and modeled, having a significant effect on indoor air quality (Rosati et al. 2008). The Velcro on ISS walls can be considered a similar source of pollutants. Therefore, high concentrations measured in initial testing indicate that particle emission rates from Velcro should be quantified and included in a future refinement of the ISS aerosol inventory.

6.5 Conclusions

ISS aerosol emission rates used in original ISS filter modeling have been updated with literature sources, and health-relevant particle sizes have been included, bringing particle sizes down to the nanometer range. Additionally, three independent sources of data indicate that just above 50% of all ambient aerosols on ISS consist of fibrous aerosols (lint). Results from recent analyses of dust samples from ISS have been combined with a literature review to provide new

predicted aerosol emission rates onboard the ISS in terms of both size-segregated mass and number concentration. Some new aerosol sources have been considered and added to the existing array of materials. Laboratory testing of Velcro particle emissions demonstrated that this ubiquitous fastener emits particles in significant quantities in the ultrafine size range. This inventory of aerosol sources is applicable to other spacecraft, and is of fundamental importance to understand nuisance aerosols that may cause smoke detector false alarms.

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Chapter 7: Dissertation Accomplishments and Future Work

7.1 Dissertation Accomplishments

This dissertation outlines the work performed to characterize smoke aerosols for improving spacecraft fire safety. The Smoke Aerosol Measurement Experiment (SAME), devised to investigate smoke production in low gravity, produced a wealth of data which were exhaustively analyzed. Ground testing with the returned SAME flight hardware provided the opportunity to measure the smokes with an aerosol reference instrument (SMPS) using 55-gallon drums (Smoke-in-drums). Continuing investigations into smoke from common spacecraft materials took place at NASA's White Sands Test Facility (WSTF) and later in NASA Glenn Research Center's Gases and Aerosols from Smoldering Polymers (GASP) laboratory. Microscopic analyses of smoke particles collected with a thermal precipitator shed light on thermal decomposition and particle formation mechanisms. Finally, indoor aerosols on the International Space Station (ISS) have been researched and an updated aerosol inventory was created for the purpose of air quality modeling and to understand nuisance aerosols that may cause smoke detector false alarms.

Highlights of the aforementioned topics are given below.

SAME Data Analysis - The Smoke Aerosol Measurement Experiment (SAME) has been conducted twice by the NASA and provided real-time aerosol data in a spacecraft micro-gravity environment. Flight experiment results have been analyzed with respect to comparable ground-based experiments. The ground tests included an electrical mobility analyzer (SMPS) as a reference instrument for measuring particle size distributions of the smoke produced from overheating five common spacecraft materials. Repeatable sample surface temperatures were obtained with the SAME ground-based hardware, and measurements were taken with the aerosol instruments returned from the International Space Station. The SAME smoke-in-drums setup

was developed in which smoke was collected in 55-gallon drums, serving two purposes 1) to sufficiently dilute the smoke in order to effectively stop coagulation (aging) of the smoke particles during the SMPS scans; 2) to have a large enough quantity of dilute smoke for multiple SMPS scans. Smoke aerosols from these materials have been extensively characterized in ground testing: particle morphology, forms and parameters of the particle size distributions, and various moment diameters. A comprehensive data reduction and statistical analysis with regards to the lognormal assumption for smoke from SAME fuels was performed. The application of the moment method for the measurement of size distribution parameters in this work relies on two assumptions: spherical particles and a lognormal distribution. These conditions were reasonably met in two of the five materials tested (Kapton and lamp wick). Results of the experiments and comprehensive investigation into the lognormality of smoke particle size distributions have been documented in an *Aerosol Science and Technology* journal paper (Meyer et al. 2015).

Fire Characterization Experiments at WSTF and GASP Laboratory: Spacecraft fire detection and post-fire cleanup testing has taken place at Johnson Space Center's White Sands Test Facility (WSTF) in Las Cruces, New Mexico and at the NASA Glenn Research Center Gases and Aerosols from Smoldering Polymers (GASP) Laboratory in Cleveland, Ohio. Smoke characterization data from these facilities encompasses measuring aerosols and gaseous products, and measured parameters vary based on the availability of newly developed and mature gas sensors and aerosol instruments, as well as evolution of the test matrices by the investigation of new fuels and the use of various fuel preparation methods. Testing at both WSTF and GASP laboratory has led to the creation of a NASA database of smoke from spacecraft materials for both aerosols and gases. Selected results reported in this work include temperature- and

preparation-dependent smoke properties for spacecraft materials of interest, or relevant mixtures of materials. Early smoke detection was explored with a compact and inexpensive commercialoff-the-shelf dust sensor for eleven materials or combinations of materials.

Design of a Thermal Precipitator for Smoke Particle Collection: A thermal precipitator was successfully built after finite element modeling iteratively determined key design parameters. Testing verified the performance of the first iteration of the device and no subsequent design modifications were necessary. The thermal precipitator was successfully operated and provided quality particle samples for microscopic analysis, which has furthered the body of knowledge on smoke aerosols of common spacecraft materials.

Microscopy of Smoke Particles: Ten types of common spacecraft materials or mixed materials underwent oxidative pyrolysis at different temperatures and the resulting smoke particles were collected via the thermal precipitator (TP) during test campaigns at the NASA White Sands Test Facility (WSTF). Smoke particles were subsequently examined and characterized by microscopy considering both morphology and elemental composition. Smoke particle morphology gives insight into the thermal decomposition mechanisms of the spacecraft materials as well as the particle formation mechanisms, both important elements of fire characterization. Elemental information on smoke particle composition gained from EDS provided additional information on individual particle characteristics.

Inventory of Aerosols on ISS: ISS aerosol emission rates used in the original ISS filter modeling has been updated with literature sources, and health-relevant particle sizes have been included, bringing particle sizes down to the nanometer range. Additionally, three independent sources of data indicate that just above 50% of all ambient aerosols on ISS consist of fibrous aerosols (lint). Results from recent analyses of dust samples from ISS have been combined with

a literature review to provide new predicted aerosol emission rates onboard the ISS in terms of both size-segregated mass and number concentration. Some new aerosol sources have been considered and added to the existing array of materials. Laboratory testing of Velcro particle emissions demonstrated that this ubiquitous fastener emits particles in significant quantities in the ultrafine size range. This inventory of aerosol sources is applicable to other spacecraft, and is of fundamental importance to understand nuisance aerosols that may cause smoke detector false alarms.

7.2 Future Work

The ultimate goal of NASA fire characterization research is the design of the next generation of smoke detectors and post-fire cleanup equipment. GASP laboratory will continue to be the center of research, testing and instrument validation toward that end.

A goal for future GASP testing is to add surface area concentration measurement capability to determine the value of this metric for environmental monitoring and/or fire detection in spacecraft. While surface area concentration is not an intuitive quantity, it can be correlated to health effects of aerosols by conversion to Lung Deposited Surface Area (LDSA). Several portable diffusion charging instruments are commercially available which measure LDSA concentration (Asbach et al. 2012). Understanding the surface area concentrations of smoke from the various fuels can give insight into a potential second moment device in a suite of moment instruments for fire detection. Furthermore, LDSA could be a valuable metric for ambient aerosol monitoring in the spacecraft cabin with regards to crew health.

The next generation technology for fire suppression on space missions is a portable water mist fire extinguisher which is under development (Rodriguez and Young, 2013). The introduction of water droplets and vapor will influence the post-fire environment significantly and future work

will entail incorporating different levels of humidity in smoke tests, not only for the purpose of promoting acid gas production, as mentioned in chapter 3 (Babushok et al. 2015), but also to determine the effects on aerosol measurements and the performance of the aerosol monitor that will ultimately be used to characterize the post-fire environment. In addition to varying levels of humidity in the GASP smoke chamber, experiments will be performed to characterize acid gas and aerosol concentrations in the smoke chamber before and after the introduction of water mist. There is potential for the water mist extinguisher to 'clean' the post-fire environment and experiments are planned to determine the affinity of the water droplets for the acid gases and particles. This will shed light on the cleanup process for the water introduced for fire suppression and the potential for corrosive damage to spacecraft infrastructure by the water (Peacock et al. 2012)

While most of the ISS is at ambient temperature and pressure for the comfort of the crew, airlocks have protocols for different conditions for the purpose of preventing decompression sickness before and after space walks or extra-vehicular activity (EVA) in pressurized space suits. The airlock pressure is reduced to 70.3 kPa (from 101 kPa) with varying oxygen levels over a period of time (Anderson et al. 2015). Understanding the implications of the altered environment on fire signatures and smoke detection is a question that will be addressed in future GASP testing.

Further testing is planned to evaluate smoke removal technologies, such as the Soft-X-Ray-Enhanced Electrostatic Precipitator (Kettleson et al. 2013) in the GASP smoke chamber. The reduction in aerosol concentrations will be measured and compared for the various spacecraft fuels. Size-dependent removal efficiency will be noted, particularly for Teflon smoke particles (which are the smallest among the materials of interest).

An aerosol sampling experiment has been proposed for the ISS and has recently been funded by the NASA Advanced Exploration Systems Program. This will validate and update the ISS aerosol inventory documented in chapter 6. Both active thermophoretic sampling and passive sampling (directly on microscopy substrates) will be performed by the astronauts in different ISS modules and samples will be returned to Earth for microscopic analyses. Resulting data will include the following data: average number concentration, mass concentration (PM10, PM2.5), size distribution, morphology, and elemental composition of airborne particles. This will provide important information for the down-selection of appropriate aerosol monitoring devices for future manned space missions, and knowledge of background aerosols will contribute to smoke detection systems that are resistant to false alarms.

7.3 References

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Appendix A: Numerical Modeling of a Unipolar Coronabased Aerosol Charger

A1 Introduction

Particle charging is an important phenomenon in the field of aerosol science and technology. It is the basis for particle sensing and measurement in the differential mobility analyzer. One limitation of this instrument is that the quality of data depends on the accurate characterization of the charge state of the aerosol, which is an input in the inversion algorithm that corrects for multiply charged particles. Knowing the resulting charge distribution of a charger is an important step in the deconvolution of data to provide the final particle size distribution in electrical mobility classifying instruments (Hogan et al. 2009). Furthermore, attaining a high particle charging efficiency for particles in the nanometer range is very challenging (Wiedensohler et al. 1994). Increasing charging efficiency and accurately characterizing the final charged state of an aerosol is an important research pursuit that can be approached through numerical modeling and simulation. Unipolar diffusion charging most often employs a corona discharge that provides an abundant source of ions that collide with particles, imparting charge on them (Hinds, 1999). A numerical model of a particle charger is a useful tool for parametrically studying charger design variables and improving charging efficiency. A review of unipolar chargers for nanoparticle charging by Intra and Tippayawong (2011) outlines the need for numerical modeling of particle charging. Specifically, they recommend numerical investigation on phenomena affecting charging performance, such as non-ideal flow fields, electric field lines or alignment of the components within the charger. Furthermore, they assert that improvements in nanoparticle charging can be realized by investigating particle residence times in the charger, including characterizing residence time distributions. For detailed modeling, the following phenomena should be included: fluid flow field, ion source, species

transport (ions, neutral particles and charged particles with different charge levels), the electric field present in the charger and the birth and death equations for particle charging. Most models are not based on detailed modeling of charger geometry, but rather generalize a constant ion concentration and particle residence time product (known as $N_{ion}t$) which is a non-physical assumption often created to fit the experimental data. Often this type of model does not correlate to experimental charge distribution measurements, which is the case for the charger under the current investigation (Qi et al. 2008). Even if the N_i were relatively constant, the residence time of a particle in the charger, t, can vary significantly, depending on the charger geometry and flow field. The unique feature of this charger modeling approach is the use of location-specific ion concentration within the charger and neutral and charged particle trajectories to determine the aerosol charge distribution with the birth and death equations. This level of fidelity takes into account details which affect the final charging efficiency, such as non-uniform ion concentration, or flow patterns resulting in a distribution of particle residence times within the charger. The charger to which this model is applied is a mini-charger used in a personal particle sizer (Qi et al. 2008), shown in Figure A1. The numerical modeling effort to characterize this charger was funded by NASA's Advanced Exploration Systems (AES) Fire Safety Project, as it was under consideration for use in future spacecraft fire detection systems. This charger, along with a miniature electrostatic classifier, was a candidate aerosol instrument for use in low gravity; however, it has been overcome by events, and is not currently planned for use by the AES program.



Figure A1: Mini-charger Design (Qi et al. 2009)

In the interest of documenting the modeling effort, this appendix gives pertinent information on the aerosol physics, charging model, equations and a complete description of the unique charging algorithm, along with preliminary results. Suggestions for future work that will improve and apply the charger model is also described.

A2 Physical Properties Considered in Detailed Charger Model

Aerosols are particles suspended in a gas, therefore both the gas and particle phases must be accurately described in theoretical detail in order to capture their behavior in a numerical model. Modeling an aerosol charger requires additional information on the ions, their properties and charging theories. This section gives an overview of the aerosol physics and electrostatic effects necessary for modeling the unipolar charging process.

A2.1 Fluid Properties

Although fluids consist of discrete molecules, they can be assumed to have continuous properties at certain length scales.

A2.1.1 Properties of Air

Kinetic theory postulates that air molecules are continually colliding with one another in a random manner, but this is not evident from the perspective of the length scale of an aerosol

charger through which air flows at a constant rate. However, when the behavior of air is considered with respect to a 25 nm particle, collisions become important. The average distance a molecule travels between successive collisions is known as the mean free path of a gas, which can be calculated from the kinetic theory of gases. The Knudsen (Kn) number is used to determine whether the aerosol particle is considered to be in a discontinuous or continuous medium. Kn is defined as the ratio of the molecular mean free path, λ , to a characteristic length. If Kn << 1, the fluid flows as a continuum, but Kn >> 1 indicates that the more complex physics of the free molecular regime models the fluid behavior. In between these extremes lies the transition regime, where neither theory can be assumed.

Viscosity is a property of a fluid that describes its resistance to deformation or flow. For a Newtonian fluid, the velocity gradient is proportional to the shear stress, with the dynamic viscosity as the constant of proportionality:

$$\tau = \mu \frac{\partial u}{\partial y} \tag{A1}$$

Another important parameter for describing fluid flow is the Reynolds number (Re), which compares the magnitude of the inertial forces to the frictional forces acting on a fluid element. The fluid Reynolds number is dependent on geometry, and is defined differently for internal flow in a cylinder vs. an annulus:

$$Re_{cyl} = \frac{\rho_f U d}{\mu} \tag{A2}$$

$$Re_{annulus} = \frac{U\rho_f d_{out} \left(1 - \frac{d_{in}}{d_{out}}\right)}{\mu}$$
(A3)

where ρ_f is the fluid density, *U* is the flow velocity, μ is the viscosity and the characteristic linear dimensions are either the cylinder diameter or a combination of the inner and outer diameters of the annular flow path. Internal air flow is considered laminar for Re < 2300.

A2.1.2 Properties of Ions in Air

The mini-charger relies on a corona discharge to generate ions that impart charges to the particle. These ions enter the charging zone where they interact with the particles, so the pertinent ion properties are needed for modeling transport and charging. The mass, m_{ion} , mean free path, λ_{ion} , mean thermal speed, \bar{c}_{ion} , diffusion coefficient, D_{ion} , and electrical mobility, Z_{ion} are interrelated, so knowing two properties, the mass and the mobility, allows the calculation of the remaining parameters.

If the mass of an ion is known, the mean thermal speed, \bar{c}_{ion} , can be calculated from the kinetic theory equation:

$$\bar{c}_{ion} = \sqrt{\frac{8kTN_A}{\pi m_{ion}}} \tag{A4}$$

In the above equation, k is Boltzmann's constant and T is the temperature in Kelvin, m_{ion} is the mass of the ion in kg/mol and N_A is Avogadro's number. This is the average of a distribution of speeds of the ions which are in constant, random motion. The diffusion coefficient can be calculated using the Stokes Einstein equation when the ion electrical mobility is known:

$$D_{ion} = \frac{kTZ_{ion}}{ne} \tag{A5}$$

Here *n* denotes the charge number of the ions, which is typically unity for ions generated by corona discharge, and *e* is the elementary charge on an electron, 1.6×10^{-19} C. The mean free

path of an ion is calculated using the ion mass and mobility with the following formula (Reischl, (1996), Fuchs & Sutugin (1971), Liu & Pui (1977), Adachi et al.(1985), Romay & Pui (1992))

$$\lambda_{ion} = \frac{16\sqrt{2}}{3\pi} \frac{D_{ion}}{\bar{c}_{ion}} \sqrt{\frac{m_{air}}{(m_{ion} + m_{air})N_A}}$$
(A6)

In the above expression, and mair is the molecular mass of the surrounding air in kg/mol.

These equations use ion mass and electrical mobility, which varies depending on the ionic species and the composition of the background gas. Corona-based aerosol chargers typically operate in air at standard temperature and pressure. Therefore the most likely ions that will be generated in ionization layer of the positive corona discharge are the singly ionized species N_2^+ and O_2^+ (Chen and Davidson, 2002). Ion charge states greater than one are much less likely due to energetics (Brown, 2004) since the ionization energy for stripping the second electron from the atom is much higher than the first. However, studies of ions from corona discharge using mass spectrometry have shown that the dominant ions are the much larger proton hydrates $H^+(H2O)_n$, with the value of n dependent on the amount of moisture in the air (Chen and Wang, 2005). Laboratory air typically has a humidity level that is consistent with human comfort. Water molecules in the air are attracted to the primary ions and a clustering process takes place quickly, on the order of 1 μ s (Kaune et al. 1983). Held and Peyrous (1999) have suggested the following mechanism for the evolution of proton hydrates from N_2^+ :

$$e^{-} + N_2 \rightarrow 2e^{-} + N_2^{+}$$
 (A7)

and the following possible reactions:

$$N_2^+ + H_2O \rightarrow N_2H^+ + OH, \tag{A8}$$

$$N_2H^+ + H_2O \rightarrow H_3O^+ + N_2 \tag{A9}$$

and

$$N_2^+ + H_2O \to H_2O^+ + N_2,$$
 (A10)

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH.$$
 (A11)

Similarly, O₂ participates:

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+,$$
 (A12)

$$H_2O^+ + O_2 \rightarrow H_2O + O_2^+$$
. (A13)

Finally, three-body reactions are suggested for the creation of proton hydrates:

$$O_2^+ + H_2O + M \to O_2^+(H_2O) + M,$$
 (A14)

$$O_2^+(H_2O) + H_2O \to H^+(H_2O) + OH + O_2,$$
 (A15)

$$O_2^+(H_2O) + H_2O \to H_3O^+(OH) + O_2,$$
 (A16)

$$H_{3}O^{+}(OH) + H_{2}O \rightarrow H^{+}(H_{2}O)_{2} + OH,$$
 (A17)

$$H^{+}(H_{2}O)_{n} + H_{2}O + M \rightarrow H^{+}(H_{2}O)_{n+1} + M$$
 (A18)

Pui et al. (1988) reports that the most probable positive ion from corona discharge is the hydrated proton $H^+(H_2O)_6$ with a mass of 109 amu and mobility of $1.4 \times 10^{-4} \text{ m}^2/\text{V-s}$.

This agrees well with a study on hydrated cluster-ion formation in corona discharge clean room neutralizers by Sakata and Okada (1994). They performed experiments with an atmospheric pressure ionization mass spectrometer (API-MS), in which ionization by corona takes place at atmospheric pressure and analysis takes place under a vacuum (Chang et al. 1991). The results of the study show that the degree of hydration, n increases with absolute humidity. At a dew point temperature of -22° C (which corresponds to 3% relative humidity at 25°C), the majority of ions from a positive corona were H⁺(H₂O), and at a dew point temperature of 20.6°C (which corresponds to 76% relative humidity at 25°C), significant quantities of all proton hydrates from

 $H^+(H_2O)$ through $H^+(H_2O)_{10}$ were present. Laboratory air is between these humidity extremes, but they qualitatively confirm Pui's conclusion, along with Keesee and Castleman (1985) who assert that the most abundant protonated water clusters are $H^+(H_2O)_4$ and $H^+(H_2O)_5$. In addition to relative humidity, another factor that determines the type of ion in aerosol charging is the age of the ion. The farther an ion must travel from the corona discharge source before entering the mass spectrometer or encountering particles in the charging zone, the higher the chances for the ion to encounter additional molecules that will cluster with it. An ion in air at atmospheric pressure makes about 10⁹ impacts per second with gas molecules (Loeb, 1939), so any impurities or water in the air can attach to the original ion, altering its mass and mobility. In the distance from the mini-charger corona needle to the perforated field cage, an ion will have approximately 1.5 x 10⁵ collisions, based on $\lambda_{ion} = 1.45 \times 10^{-8}$ m (Pui, 1988).

Reference	$\begin{array}{c} Z_i^+ \\ (m^2 {\cdot} V^{-1} {\cdot} s^{-1}) \end{array}$	m ⁺ _i (amu)
Hussin et al. (1983)	1.15.10-4	140
Vohra et al. (1969), Adachi et al. (1985), Pui et al. (1988)	$1.40 \cdot 10^{-4}$	109
Mohnen et al. (1974), Adachi et al. (1985), Adachi et al. (1986)	$1.40 \cdot 10^{-4}$	130
Wiedensohler et al. (1986)	$1.35 \cdot 10^{-4}$	148
Hoppel and Frick (1986)	$1.20 \cdot 10^{-4}$	150
Hoppel and Frick (1990), Reischl et al. (1996)	$1.33 \cdot 10^{-4}$	200
Wiedensohler and Fissan (1991)	$1.40 \cdot 10^{-4}$	140
Alonso et al. (1997), Alonso et al. (2002)	$1.15 \cdot 10^{-4}$	150
Alguacil and Alonso (2006)	$1.10 \cdot 10^{-4}$	200

Table A1: Ion Masses and Mobilities Reported by Different Authors

Positive ion masses and mobilities used by various authors in aerosol charging studies have been tabulated by Vivas et al. (2008), shown in Table A1.

All the data in the table were not necessarily measured by each author, and some values were not even measured, just assumed, and used as fitting parameters for attaining better agreement between the Fuchs charging theory and experiments. Most authors do not venture to identify the type of ion that is charging the aerosol. Gopalakrishnan (2013) has detailed ion distributions which can be incorporated into numerical charging models that allow for multiple ion species. For the current charger, a single ionic species, the hydrated proton $H^+(H2O)_6$ with mass 109 amu and mobility of 1.4 x 10⁻⁴ m²/V-s (Pui et al. 1988) was used in the model development.

The fact that there is a positive corona discharge in the aerosol chargers to be modeled precludes the existence of significant numbers of electrons in the charging zone of the charger. This is not the case for other charger designs with negative corona where free electrons and negative ions populate the drift region. Free electron charging of aerosols is often addressed by authors dealing with negative corona discharges (O'Hara, 1989, Aliat et al. 2008). The drift region is dominated by space charges of the corona polarity (Sigmond, 1978), which is positive, in the case of the mini-charger. However in the ionization region of a positive corona, close to the needle electrode where the electron avalanche takes place, free electrons exceed the positive ion population (Beynon, 1972). These electrons are accelerated toward the corona needle which has a positive applied voltage. Near the needle, where the electric field strength exceeds 30 x 10⁶ V/m, collisions between neutral gas molecules and electrons produce new pairs of positive ions and electrons. As the free electrons stream toward the needle, some may be attached to electronegative gas molecules, such as O_2 , but the negative ions formed will also be accelerated by the electric field to the needle which has a high positive applied voltage. Other free electrons may recombine with positive ions to form neutral molecules, but this effect is negligible (Chen and Davidson, 2002). Outside of the ionization region, the dominant species is positive ions. Ions are massive and slow compared to electrons, so they rarely have enough energy to create more ions by collisions. A simple calculation can be performed to compare the kinetic energy of a nitrogen or oxygen ion with the ionization energy needed to remove an electron. The mean thermal speed of an ion is given by

$$\bar{c}_{ion} = \sqrt{\frac{8kTN_a}{\pi M_i}} \tag{A19}$$

and is on the order of 650 m/s for nitrogen and oxygen ions so the kinetic energy is on the order of 3 kJ/mol. Considering that the ionization energies for oxygen and nitrogen are over 1000 kJ/mol, it is evident that ions in the drift region and the charging zone will not be able to create free electrons. Secondary ionization in the drift region takes place when photons emitted from the plasma liberate electrons from neutral gas molecules. These electrons are attracted to the corona needle, traveling into the plasma where they gain energy and cause further electron avalanches. The transit time for an electron to cross the inter-electrode gap of this charger is on the order of 0.1 μ s. The corona current in the drift region is due to positive ions which are attracted to the grounded electrode (the screen). Thus, there will be no free electrons traveling from the ionization region toward the screen covering the corona electrode. Therefore there will be no free electrons exiting the hemispherical perforated field cage into the charging region, and there is no need to address charging of aerosol particles by free electrons.

A2.1.3 Corona Discharge Ion Source

A corona discharge consists of a series of phenomena that occur in a gas at the microscopic level resulting in a shower of ions and electrons. An electrode with a large radius of curvature is grounded and adjacent to another electrode with a sharp radius of curvature (needle electrode or wire) with an applied voltage. This causes an intense electric field near the sharp electrode which exceeds the breakdown voltage of the gas, causing it to literally break up into ions and electrons.

The corona needle tip radius is like a singularity in the electric field where ionization occurs at a critical potential difference between the electrodes. The ions and electrons collide with neutral gas molecules and create more ions by impact ionization (Cross, 1987). There are two ionization processes that take place in different regions. Primary ionization occurs in the region adjacent to the sharp electrode where an exponential increase in electrons occurs by the following process. A liberated electron collides with a neutral gas molecule, creating another ion/electron pair. The two electrons quickly gain energy and collide with other molecules. Thus one electron will produce $n = e^{\alpha s}$ electrons, which is known as an avalanche of electrons (Loeb, 1965). The primary Townsend ionization coefficient, α , describes the extent of this phenomenon for different gases. Secondary ionization takes place in the drift region and is characterized by the secondary Townsend coefficient, γ , which is the efficiency of production of secondary electrons per ion pair formed in the gas (Brown, 1966). The mechanism for secondary ionization differs in negative and positive corona discharges. For positive coronas (in which the high voltage electrode is positive), photons emitted from the plasma region causes a visible bluish glow and ultraviolet radiation (Chen et al. 2002). These cause photo-ionization in the drift region, releasing electrons which quickly re-enter the ionization region where they produce further avalanches. Secondary ionization is necessary in order for the breakdown to be sustained (Loeb, 1939). This is seen in the criterion for a sustainable discharge, also known as the Townsend replenishment condition (Sigmond, 1978)

$$\int \alpha (r)dr = \ln(1 + \frac{1}{\gamma}) \tag{A20}$$

The ionization rate is a function of the electric field strength (due to the potential difference) and the gas pressure (the number of neutral gas molecules available for ionization). Therefore Townsend coefficients are found in the literature plotted vs. E/p for various gases.

A2.1.4 Neglect Corona Wind in Charger Model

The ionization layer at the surface of the high voltage electrode in a corona discharge gives rise to a shower of drifting unipolar ions which collide with neutral gas molecules, transferring momentum and resulting in an electrohydrodynamic (EHD) flow known as corona wind, ion wind, or electric wind. The overall motion of the gas is dependent on the geometry of the corona electrodes and surrounding walls. EHD flow is also possible in dielectric liquids, where the resulting fluid velocity is much higher than in gases (Vazquez et al. 2000). EHD has sometimes been called an ion drag phenomenon, which in the strict sense is a misnomer, since the Coulomb force ($F = \rho_e E$) exerted by the electric field on the space charge induces the fluid motion by momentum transfer. The initial fluid motion is in the direction of the electric field which in a one-dimensional corona (wire-cylinder configuration) is directed radially. In a two-dimensional axisymmetric point-plane electrode configuration, the wind is directed primarily from the tip of the needle (in the axial direction) to the plane. For both geometries, the confining walls give rise to vortices. Since the mini-charger has a screen as the grounded electrode, the corona wind can exit through the openings and potentially assist the transport of ions into the charging region. The importance of this effect can be estimated by non-dimensionalizing the charge transport equation and evaluating the order of magnitude of each of the terms (Nagornyi, 2000 and Feng, 1999).

$$\boldsymbol{J} = \rho_e (Z_i \boldsymbol{E} + \boldsymbol{u}) - D_i \nabla \rho_e \tag{A21}$$

The first term is the ion drift due to the electric field, the second is the convection of ions due to the corona wind and the last term is the diffusion of ions.

$$\boldsymbol{J}^* = \rho_e^{*} (\boldsymbol{E}^* + R\boldsymbol{e}_E \boldsymbol{u}^*) - \frac{1}{P\boldsymbol{e}_E} \nabla^* \rho_e^{*}$$
(A22)

The scalar characteristic scales are ρ_{eo} , j_o, v_{wind}, E_o, and the dimensionless operator becomes $\nabla^* = \nabla/d$, where d is the gap distance between electrodes. This equation is evaluated in the absence of any free stream velocity and considers only the velocity, v_{wind} from corona wind. The dimensionless numbers are electric Reynolds number Re_E and the electric Peclet number Pe_E, which are defined as

$$Re_E = \frac{Convective\ current}{Conduction\ current} = \frac{v_{wind}}{Z_i E_o} \tag{A23}$$

$$Pe_E = \frac{Rate \ of \ motion \ of \ charges \ in \ Efield}{Rate \ of \ diffusion \ drift \ of \ charges} = \frac{Z_i E_o d}{D_i}$$
(A24)

The quantities used in estimating the order of magnitude of the dimensionless numbers are given in Table A2. Estimates of the corona wind vary somewhat in the literature (Dascalescu et al. 1995) and are dependent on electrode geometry, but give similar magnitudes. The estimate in Table A2 uses the formula from Ahmedou et al. 2009:

$$v_{wind} = \sqrt{\frac{Id}{\rho_f Z_i A}} \tag{A25}$$

The magnitude of the space charge density ρ_{eo} , is calculated as the product of the charge on an electron and the ion density, N_i, which is given by (Romay et al. 1992; Adachi et al. 1985)

$$N_i = \frac{I}{eZ_i E_o A} \tag{A26}$$

where A is the area of the grounded electrode. Other estimates used in the calculations are

$$E_o = \frac{V}{d} \qquad \qquad j_o = \frac{I}{A} \tag{A27}$$

Corona Current	I, A	1.00E-06
Needle voltage	V, Volts	2000
Interelectrode gap	d <i>,</i> m	2.70E-03
Ion diffusion coeff	D _i , m^2/s	3.54E-06
Ion mobility	Z _i , m^2/V-s	1.40E-04
Density of air	ρ _f , kg/m^3	1.2
Approx electric field	E _o , V/m	7.41E+05
Approx current density	j _o , A/m^2	2.33E-02
Approx space charge	ρ _{eo} , C/m^3	2.24E-04
Corona wind estimate	v _{wind} , m/s	0.61
Surface area of grounded electrode	A, m^2	4.30E-05
Dimensionless operator	∇*, 1/m	∇/d
Electric Reynolds #	Re _E	5.90E-03
Electric Peclet #	Pe _E	7.91E+04
Inverse of Electric Peclet	1/Pe _E	1.26E-05

Table A2: Parameters for the Evaluation of Corona Wind Dimensionless Numbers

The orders of magnitude of the dimensionless numbers in the charge transport equation are

$$J^* = \rho_e^{*} (E^* + 10^{-3} u^*) - 10^{-5} \nabla^* \rho_e^{*}$$
(A28)

The magnitude of the electric Reynolds number clearly shows that the corona wind will not contribute significantly to the transport of ions from the drift region through the screen and into the charging region of the mini-charger. Thus it can be safely neglected. The drift term of the transport equation is dominant, so the strength of the local electric field will determine the velocity of the ions. The electric Peclet number is so small that ion diffusion can safely be neglected as well.

The corona wind has been studied by many, including Michael Faraday, who extended his experiments to include dielectric liquids in addition to gases (Robinson, 1961) however there was not significant interest in the phenomenon for many years as there were no engineering applications for it. Recently it has been considered useful for cooling of electronics, in food

drying, viscous drag reduction, sonic boom mitigation, boundary layer control and other applications (Macheret et al. 2004, Ahmedou et al. 2009). Numerical modeling of corona wind was first reported in the literature in 1992 (Batina, et al. 2001). Governing equations include the continuity and Navier-Stokes equations from fluid mechanics, Maxwell's equations and Ohm's law, and one additional term is needed in the Navier Stokes equations to add the influence of corona wind: the Coulombic body force acting on the air, $F = \rho_e E$. The effect of the corona wind in the mini-charger would be largest in the high electric field region, which is closest to the corona needle and would diminish with distance from the tip.

A2.2 Particle Properties

There are many particle properties that directly influence the charging process. Owing to the compact size of the charger, and considering reasonable flow rates for this geometry, the designated particle size range for this device is between 20 nm and 300 nm. An alternate instrument was intended to measure larger particles for spacecraft cabin fire detection, and thus would be removed from the aerosol sample flow with an inertial separator preceding the charger. Particles are assumed to be spherical in this model due to foundational charging theory (discussed in a later section) which is derived based on one-dimensional, rotationally symmetric geometry. Consideration of only monodisperse aerosols in the charger numerical model is typical of standard benchmark studies on charging, and is an assumption upon which the charging theory is based. While modeling polydisperse aerosols would be realistic, it would not significantly contribute to the overall goal of charger design optimization, and would increase the complexity and computational demands of the model multi-fold. The data for the charger model validation is from experiments using monodisperse aerosols, and charging performance can be sufficiently demonstrated by considering monodisperse particles of different sizes.

A2.2.1 Particle Mobility

Stokes' law is a solution of the Navier-Stokes equations describing laminar flow around a single isolated particle with the following simplifying assumptions: inertial effects are negligible compared to viscous effects in an incompressible fluid and the particle moves at a constant rate, behaving as a rigid sphere with a no-slip condition at the particle surface. The particle Reynolds number determines whether the particle motion is in the Stokes region:

$$Re_p = \frac{\rho_f(U-u_p)d_p}{\mu} \tag{A29}$$

Here, *U* is the fluid velocity and u_p is the particle velocity. If Re_p is << 1, then Stokes' law applies, and the drag on a particle depends only on the particle diameter, as in the following formula:

$$F_D = 3\mu\pi d_p \big(U - u_p \big) \tag{A30}$$

Alternately, if Re_p is >> 1, then inertial forces are much larger than viscous forces and Newton's macroscopic equation for the drag force must be used, which depends on the square of the particle diameter. Although Stokes' law assumes no slip at the particle surface, there are non-continuum effects associated with particle sizes on the order of the mean free path length of the surrounding gas. These are accounted for with the Cunningham correction factor, C_c , given by Allen and Raabe (1982, 1985):

$$C_{c} = 1 + \frac{\lambda}{d_{p}} \left[2.34 + 1.05 \exp(-0.39 \frac{d_{p}}{\lambda}) \right]$$
 (A31)

This equation can be applied to particles $10 \ \mu m$ and smaller in the molecular, transition and continuum regimes at atmospheric pressure.

A particle's trajectory is significantly influenced by how quickly it can adjust to an applied force. Consider a particle in a fluid that is suddenly subjected to a constant force field. At first it accelerates, but eventually it achieves a terminal velocity. The steady motion occurs when the Stokes drag force on the particle is finally balanced by the acting force and the resulting particle velocity is proportional to this force. The mechanical mobility, B, is the factor that relates the two:

$$B = \frac{u_p}{F_{drag}} = \frac{C_c}{3\mu\pi d_p} \tag{A32}$$

where u_p is the particle terminal velocity. Similarly, when a charged particle is subjected to the force of an electric field, its electrical mobility is

$$Z_p = neB = \frac{neC_c}{3\pi\mu d_p} \tag{A33}$$

where *e* is the elementary charge on an electron, 1.6×10^{-19} C, and *n* is the number of elementary charges on the particle. Applying Newton's second law to the particle subjected to Stokes drag leads to a velocity expression containing a decaying exponential function, so the time that it takes for the particle to reach 95% of the new terminal velocity (the asymptotic value) is three times the time constant of the system. This time constant is called the particle relaxation time, τ , which is the product of the particle mass and its mechanical mobility.

$$\tau = m_p B = \frac{d_p^2 \rho_p c_c}{18\mu} \tag{A34}$$

This is valid in the Stokes region where $\text{Re}_p \ll 1$.

A2.2.2 Particle Material

Aerosol charging depends on the particle relative permittivity, which is a measure of the ability of the particle to influence the surrounding electric field and concentrate electrostatic lines of flux. The permittivity, ε , is the amount of electrical energy that is stored in a material due to an applied voltage, and the relative permittivity, ε_{rel} , is the permittivity of a material divided by the permittivity of a vacuum (ε_{vac} = 1). A material with higher relative permittivity will have more electric flux (per unit of charge on the particle) due to polarization effects. Nonpolar materials have lower relative permittivity whereas conducting materials are infinite.

A2.3 Particle Charging Theory

The two aerosol charging mechanisms that can take place in the mini-charger are diffusion charging and field charging. When unipolar ions move randomly in a neutral gas, they make contact with particles, sticking and imparting charge to the particle. This is known as diffusion charging (Gentry and Brock, 1967). Field charging takes place when a strong electric field is present in the charger. An uncharged conducting particle will intersect multiple lines of electric flux which will serve as ion paths, which bring the ions to the particle and thus transfer charge to it. In each of these charging modes, the rate at which ions intersect particles is reduced as the particle becomes more highly charged. This is because the particle either begins to repel ions (as in diffusion charging), or because the electric field becomes weaker on a highly charged particle, causing fewer field lines to converge on the particle which in turn reduces the number of ion paths to it. The mini-charger has a relatively weak electric field in the charging zone, so the main charging mechanism is considered to be diffusion charging.

A2.3.1 Particle Charging Regimes for Fuchs Charging Theory

Unipolar charging theories are classified according to ionic Knudsen number which compares particle radius to the mean free path of ions surrounding the particle ($Kn_{ion} = 2\lambda_i/d_p$,). In this work the ionic mean free path is considered to be 15 nm at 300 K (Pui, et al.1988 and Biskos, et al. 2004).

In the continuum regime, $Kn_{ion} \ll 1$, therefore, at room temperature and atmospheric pressure this applies to larger particles surrounded by an abundance of ions which collide frequently. In this regime, charging models are based on the solution of the convective diffusion equation for bulk ion concentration. The one-dimensional, rotationally symmetric flux of ions towards a spherical particle is given by

$$J_{ion}(r) = -4\pi r^2 \left(D_{ion} \frac{dN_{ion}}{dr} - Z_{ion} N_{ion} E(r) \right)$$
(A35)

where N_{ion} is the ion concentration and E is the electric field strength at a distance *r* from the particle center. Considering a particle with radius *a*, the flux formula can be rewritten in the following form:

$$J_{ion} = \frac{4\pi D_{ion} N_{ion}}{\int_a^{\infty} \frac{1}{r^2} \exp\left(\frac{\phi(r)}{kT}\right) dr}$$
(A36)

where $\phi(r)$ is the interaction potential as a function of radial distance from the particle center. This is the electrostatic potential energy of an ion moving in the electric field of the charged particle, given by

$$\phi(r) = \int_{r}^{\infty} F dr = K_{E} e^{2} \left[\frac{n}{r} - \kappa \frac{a^{3}}{2r^{2}(r^{2} - a^{2})} \right]$$
(A37)

in which K_E is a factor necessary for the SI system of units, κ is the image force parameter which corrects for non-ideal conductors and ε and ε_0 are the permittivities of the particle material and free space, respectively:

$$K_E = \frac{1}{4\pi\varepsilon_0} \qquad \qquad \kappa = \frac{\varepsilon - 1}{\varepsilon + 1} \tag{A38}$$
This equation includes the Coulomb force between two charged bodies (first term) and the image force induced on the particle by an approaching ion (second term). The image force is the polarization force due to an induced dipole and it becomes negligible for smaller and smaller particles, so it is typically omitted from continuum charging theory for particles larger than a few hundred nanometers (Pui 1988).

In the free molecular regime where macroscopic equations do not apply, Kn_{ion} >> 1, which is the case of particles 3 nm and below at room temperature and atmospheric pressure. Ion concentration surrounding the particle cannot be considered a bulk property so the kinetic theory of gases must be used. White (1951) developed the first diffusion charging model for the free molecular regime which solves the Boltzmann equation for the ion distribution around a particle, giving:

$$J_{ion} = \pi d_p^2 \bar{c}_{ion} N_{ion} exp\left(-\frac{2K_E n e^2}{d_p kT}\right)$$
(A39)

The integrated form of this equation can be used to predict the number of charges acquired by a particle over time with limited accuracy, considering that it does not include the image force. Subsequently, other approximate solutions to the Boltmann equation were developed by Natanson (1959), Gentry and Brock (1967), Liu (1967), Brock (1970), Gentry (1972), Lushnikov and Kulmala (2005) and others which either apply more complex solutions methods or include additional ion-particle interaction forces.

In the transition regime, $0.1 < Kn_{ion} < 10$, particle and ion behavior cannot be assumed to follow the continuum hypothesis or the kinetic theory of gases. The earliest transition regime charging model is the Fuchs limiting sphere theory (Fuchs, 1963). Fuchs' landmark paper in 1963 uses the limiting sphere concept for jump conditions originally conceived for droplet evaporation by Wright (1960). It was subsequently applied to particle charging by Natanson (1959 and 1960). This limiting sphere is of radius δ and is concentric with the spherical particle. The space between the particle surface and the limiting sphere contains neutral air molecules as well as ions and serves as a boundary between the free molecular regime (inside the limiting sphere) and the continuum regime (outside the limiting sphere). Ions inside the sphere only collide with the particle. The radius δ is a function of the ionic mean free path and the particle radius, and is given by

$$\delta = \frac{a^3}{\lambda_{ion}^2} \left[\frac{\left(1 + \frac{\lambda_{ion}}{a}\right)^5}{5} - \frac{\left(1 + \frac{\lambda_{ion}^2}{a^2}\right) \left(1 + \frac{\lambda_{ion}}{a}\right)^3}{3} + \frac{2}{15} \left(1 + \frac{\lambda_{ion}^2}{a^2}\right)^{5/2} \right]$$
(A40)

Ionic flux from each regime is matched at the boundary, which leads to the following expression for the ion flux to the particle:

$$J_{ion} = \frac{\pi \alpha \bar{c}_{ion} \delta^2 N_{ion} \exp\left(-\frac{\phi(\delta)}{kT}\right)}{1 + \exp\left(-\frac{\phi(\delta)}{kT}\right) \frac{\alpha \bar{c}_{ion} \delta^2}{4D_{ion}} \int_{\infty}^{r} \frac{1}{r^2} \exp\left(\frac{\phi(r)}{kT}\right) dr}$$
(A41)

where α is the probability of an ion entering the limiting sphere to intersect the particle and impart its charge (collision probability), and N_{ion} in this formula is the ion concentration in the continuum sense, outside the limiting sphere. The image force is included in this theory, as $\phi(\mathbf{r})$ is the interaction potential as a function of radial distance from the particle center.

The collision probability, α , is reduced to a^2/δ^2 when there are no electrical forces. For the case of charged particles, α is calculated using the collision parameter *b*, the minimum apsoidal

distance. This represents the fraction of ions that enter the limiting sphere and are captured by the particle, and was proposed by Natanson (1960) to be

$$b^{2} = r^{2} \left(1 + \frac{2}{3kT} [\phi(\delta) - \phi(r)] \right)$$
(A42)

Setting the derivative of b^2 with respect to *r* equal to zero enables the calculation of the minimum apsoidal distance and the corresponding collision parameter b_{min} . If there is no minimum of b^2 between the particle surface and the limiting sphere boundary, then the collision probability, $\alpha = 1$ and all the ions entering the sphere reach the particle surface. If there is a minimum value of b^2 , the corresponding collision probability is given by $\alpha = \frac{b_{min}^2}{\delta^2}$.

A2.3.2 Combination Coefficients

The ionic flux expressions from the different regimes described previously can be used to calculate the combination coefficients, β_{n} , which predict aerosol charge distribution when particle and ion concentrations are known.

$$\beta_n = \frac{J_{ion}}{N_{ion}} \tag{A43}$$

Here the values of *n* are discrete multiples of the elementary charge (integers). Combination coefficients (also known as collision frequency functions or attachment coefficients) are used in the population balance equations to be described in a later section. In the detailed charger model, combination coefficients will be calculated with the corrected Fuchs theory according to Hoppel and Frick (1986). The correction was warranted owing to the erroneous assumption that the collision probabilities were unity when only attractive encounters were considered, as well as the use of some unrealistic ion parameters by Fuchs. The combination coefficient β_n indicates the frequency at which particles with n charges will collide with ions:

$$\beta_n = \frac{\pi \alpha \bar{c}_{ion} \delta^2 \exp\left(-\frac{\phi(\delta)}{kT}\right)}{1 + \exp\left(-\frac{\phi(\delta)}{kT}\right) \frac{\alpha \bar{c}_{ion} a \eta^2}{4D_{ion}} \int_0^{1/\eta} \exp\left(\frac{\phi(a/x)}{kT}\right) dx}$$
(A44)

where $\eta = \delta/a$ and x = a/r.

A fundamental assumption in Fuchs theory is that the particle is spherical. Particles are referred to as having only one dimension, a radius, and the limiting sphere is concentric with the spherical particle. This assumption must be carried over to the detailed charger model which uses the combination coefficients from Fuchs theory. Another assumption that is made in diffusion charging theory is that the ion that hits the particle surface will adhere, that is, the accommodation coefficient of ion-particle collisions is unity. While an accommodation coefficient other than one can be modeled, it is not necessary due to the large body of experimental work that report good agreement with Fuchs charging theory with this customary assumption (Hussin, et al. 1983; Adachi et al. 1985, Adachi et al. 1986; Reischl et al. 1986; Wiedensohler et al. 1986; Pui et al. 1988; Wiedensohler et al. 1991; Romay et al. 1992; Büscher et al. 1994; Alonso et al. 1997; Alonso et al. 2002; Biskos et al. 2005; Alguacil, 2006). This is indirect evidence that assuming an accommodation coefficient of unity is valid.

The accuracy of Fuchs' limiting sphere theory based on flux matching has been questioned, and recently (Gopalakrishnan et al. 2013a) a new method of determining combination coefficients has been developed (Gopalakrishnan 2013b). In these works the authors use the term collision kernel rather than combination coefficient. Their collision kernel derivation is based on dimensional analysis, Brownian dynamics and molecular dynamics simulations, and the resulting quantities are equally valid for continuum, free molecular and transition regime. The simulations of the unipolar charger model did not make use of the new collision kernels, however, this has no bearing on the model structure as it is only an input in the charging algorithm. Using Gopalakrishnan's collision kernels is planned for future applications of this charging model.

A2.3.3 Charging Equations

Charging is by nature a stochastic process, and has been traditionally modeled for monodisperse particles with the birth and death system of differential difference equations (Boisdon and Brock, 1970). These equations are also known as population balance equations, or source-and-sink equations, and have been used to model many phenomena including bubble size distributions in aeration processes, particle agglomeration or break-up, crystal growth in a reactor, and, as the names suggest, demographic analyses (Randolph & Larson, 1988). These charging equations are stochastic in the sense that they are based on ions and particles colliding in the course of their constant, random motion (free molecule regime behavior). The collisions can be treated statistically since the concentration of ions is assumed to be so large that they are never depleted. In particle charging, numbers of particles and their charged states are both discrete quantities, thus simplifying the solution of the equations.

In the application of the birth and death equations to aerosol charging, Boisdron & Brock (1970) specified the following assumptions: (1) Both the particle and ion concentrations are much less than the concentration of the surrounding neutral air molecules, (2) All species are assumed to be in equilibrium, (3) Brownian motion of the particles is negligible compared to the thermal motion of the ions, (4) Ion concentrations are steady-state. Additional assumptions for applying these to aerosol charger, are: steady-state incompressible plug flow through the charger (which implies all residence times are the same), and there are no sources or sinks of charged species other than the incremental addition to the populations by the birth and death terms.

The birth and death equations are coupled differential difference equations expressing the rate of change of populations of charged species:

$$\frac{dN_0}{dt} = -\beta_0 N_0 N_{ion} \tag{A45}$$

$$\frac{dN_1}{dt} = \beta_0 N_0 N_{ion} - \beta_1 N_1 N_{ion} \tag{A46}$$

$$\frac{dN_n}{dt} = \beta_{n-1}N_{n-1}N_{ion} - \beta_n N_n N_{ion} \qquad n = 2, \dots, n_{chgmax}$$
(A47)

 N_0 = number concentration of neutral particles (with zero elementary charges) N_n = number concentration of particles with n elementary charges N_{ion} = number concentration of ions in the surrounding air β_n = combination coefficient of ions with particles having *n* elementary charges n_{chgmax} = maximum number of elementary charges modeled

These equations can be considered kinetic rate equations (Vetter et al. 2013), or binary reaction kinetics (Gopalakrishnan 2013) where β [m³/sec] is a reaction rate, or collision rate coefficient/kernel for the following pseudo-reaction:

$$P_n + ion \xrightarrow{\beta} P_{n+1} \tag{A41}$$

Where P_n denotes a particle with *n* elementary charges. The neutral population can only decrease by exposure to ions, as the first equation has only a negative term. Equations for the rate of charge of charged particle populations have both birth and death terms on the right-hand side of the equations: the positive term accounts for an increase in the population and the negative term is the decay of the population of that species. For example, a collision between an ion and a particle carrying two elementary charges will decrement the population of doubly charged particles and will increment the population of triply charged particles. Thus, both of

those populations are influenced by that event, one growing by one and the other shrinking by one, while the total number of particles stays constant.

A3 Unipolar Corona Aerosol Charger Model

Macroscopic numerical particle charging models exist with many different levels of detail and for different aerosol conditions. In the atmospheric sciences, Rapp (2001) and others have modeled diffusion charging in the mesosphere. Other numerical charging models, such as Jiang et al. (2007) model charging mechanisms generally (in this case, diffusion, photoionization and thermionization) and arrive at aerosol charge level distributions, without specific geometry, physics of flow or the influence of an electric field within the charger.

In order to simulate a specific charger design, the air flow carrying the particles through the charger geometry must be modeled. Two general modeling approaches can be taken for multiphase flows: Eulerian and Lagrangian.

The Eulerian method is a continuum approach (or continuous-phase flow method) which does not model discrete particles, but instead considers them to be a separate species with properties averaged over the fluid medium. For charging models, the necessary species are ions and neutral particles. Eulerian models solve partial differential equations for the flow in a fixed computational grid. This is computationally efficient, especially for steady flow (Crowe et al. 1997). Drawbacks of this method include lack of information on the motion of the particles and nonphysical numerical diffusion, which arises from error in the interpolation of the dissipative term in regions with high gradients (Patankar, 1980). The numerical diffusion problem can be alleviated with a smaller mesh-size which makes the model more computationally expensive (Ferziger, 1998). The outputs of an Eulerian two-phase flow simulation that are useful in modeling particle charging are the steady-state ion concentration and the fluid velocity field as a function of position in the charger.

The alternative multi-phase flow modeling method is Lagrangian, with each individual fluid particle or aerosol particle modeled as a point or an entity with a resolved surface. This method is also known as trajectory modeling, since the motion of a particle can be calculated by a force balance including all the relevant influences on an individual particle. The advantage is that discrete and transient movement of a particle is possible, even to the extent that one particle can cross the wake of another particle. Rates for field or diffusion charging can be integrated to give the particle charge. If the particles are modeled with a resolved surface then surface-fluid interactions are taken into account and pressure and shear stress distributions are integrated over the particle surface area to obtain hydrodynamic forces. This level of detail is not necessary for a macroscopic model of aerosol charging. Instead, the particle can be considered a point entity which does not displace fluid or influence the flow. This entity can be assigned a mass, or varying numbers of elementary charges for the purpose of calculating forces that influence the particle trajectory.

For typical aerosol charging concentrations, the gas phase can be modeled as a continuum by the Eulerian method and a one-way coupling employed to allow fluid behavior to influence the Lagrangian particle trajectories. This sparse or dilute two-phase flow is more computationally efficient because the Eulerian and Lagrangian portions of the model are solved separately, with an initial steady-state solution for the flow field followed by separate time-dependent solutions for particle trajectories. This approach is used for the model described here, and forms the basis for the subsequent particle charging portion of the model. An aerosol charging model is inherently a multiphysics problem. That is, it must simultaneously address phenomena across

separate physical disciplines and combine them to generate realistic mathematical models. The Eulerian-Lagrangian gas and particle flow approach is the fluid mechanics portion, which is combined with an electric field in the charger (electrostatics). The ions are modeled as dilute species, and particle trajectories are influenced by Stokes drag and the surrounding electric field in the charger. These separate aspects of this multiphysics model will be described individually in subsequent sections.

There is no way to generalize this charging model to 'typical' or undefined aerosol chargers. Particle motion is dependent on charger geometry and voltage boundary conditions. This algorithm considers the possible trajectories of all the different charged species, and what influences these neutral and charged species would encounter along their three-dimensional paths from the beginning of the charging zone until they exit of the charger. The initial step is to solve the Eulerian fields in the charger which are used to create lookup tables for all subsequent simulations. One Eulerian simulation is sufficient for a given flow rate, ion species, ion source, and applied voltages on the charger. As long as these parameters are unchanged, then these lookup tables need not be changed for different particle sizes or materials. Aerosol modeling begins with a set of starting points or origins for trajectories. Particle trajectories are then run for up to 150 particles from initial positions, or start points, distributed throughout an annular slice preceding the charging zone. These trajectories are dependent on the particle diameter (for Stokes drag and Cunningham slip correction factor) and density (for particle mass in Newton's 2^{nd} law) which are inputs in the particle trajectory model. Each particle starting point is solved for every charged species in the simulation, that is, for the range from neutral particles, up to the maximum number of charges simulated (n=0 to n_{max}). If the particle size is small and, in a practical sense (based on the residence time in the charger), only a maximum of four charges can

be obtained, then trajectories are simulated for five different charge states (neutral, plus n=1 through n=4). The part of the model is the charging algorithm which solves the population balance equations resulting in the charge distribution of particles exiting the charger.

A3.1 Previous Aerosol Charger Models

A detailed unipolar diffusion charging simulation should include charger geometry, particles in the fluid flow, effects of an electric field, a source of ions and local ion concentration. Not all of these aspects are included in the models found in the literature. Basic models have been created for electrostatic precipitators with corona wires, such as Benamar et al. (2007). Goo and Lee (1996) used a Lagrangian particle tracking method to model an electrostatic precipitator with turbulent flow and corona discharge for 4 μ m particles. However, the majority of charger models use the Eulerian approach. A model of 1 millimeter particles passing through combined corona-electrostatic fields was created by Dumitran et al. (2008), but the geometry consists only of a wire and a ground plate. Alonso (2009) studied the effect of ion-aerosol mixing on charged fraction for 10 nm and 3 nm particles in a laminar flow tube without an electric field. Aliat et al. (2009) modeled a one-dimensional corona discharge coupled with two-dimensional turbulent flow in a cylinder for charging 65 nm particles. Park et al. describes a Lagrangian model for a chip-type (MEMS) charger which includes laminar flow in a channel with an electric field and computes particle trajectories, ion motion, and average particle charge for 30 nm to 120 nm particles. None of these models include detailed geometry and none model charging based on the different behavior and concentrations of many multiply charged particle species within the charger. While the previous models are useful for general predictions, they do not have sufficient detail for charger design optimization studies or for charger-specific data reduction schemes. A more recent review of numerical models simulating electrostatic precipitators

provides a good comparison of charging models that have been reported in the literature over the past thirty years and the progression of accuracy and fidelity in these models (Adamiak, 2013). The author emphasizes the need for dynamic particle charging with the Lagrangian approach which includes forces in the particle equation of motion during charging, namely air drag which depends on the flow field, the influence of the electric field once the particle is charged, and the effect of space charge.

A3.2 Charger Geometry

The geometry of the modeled charger is shown in Figure A2. Aerosol is introduced in the radial direction, expanding into an annular flow field which opens into a cylindrical charging zone that just the outlet.



Figure A2: Finite Element Geometry of Charger with the internal field cage geometry visible within the transparent charger body which has the perforated hemispherical (highlighted in blue) through which ions enter the charger.

The corona needle is housed in a field cage (the inner cylinder), which has a perforated hemisphere to allow ions to escape. There is no air flow in the field cage to drive the ions out, however, there is an ion-driving voltage applied to the outer charger body, which creates an electric field to attract the ions through the porous cage so they are freely available in the charging zone. The corona discharge ion source is not modeled in this effort, and ion concentration is applied as a boundary condition on the hemispherical cap of the field cage which is highlighted in Figure A2.

A3.3 Governing Equations

The finite element software package COMSOL Multiphysics was chosen for the detailed charger model because of its ability to easily couple many partial differential equations for multiple physical phenomena and solve them simultaneously or in sequence. It is a programming interface for multiphysics simulations which has many different problem-specific physics modules. The supplemental modules used in the charger model were the Computational Fluid Dynamics and the Particle Tracing in addition to the general multiphysics license which provides the Electrostatics interface for the electric field. COMSOL is uses the Galerkin discretization method after converting the problem to the weak form, which enables the solution of strongly nonlinear models (Zimmerman, 2008). Other software packages exist which would be equally suitable for this coupled Eulerian and Lagrangian modeling approach.

A3.3.1 Governing equations for Eulerian Portion of Numerical Model

The Eulerian portion of the model calculates fields: Fluid flow field, electric field, and ion concentration. This method solves the Navier-Stokes equations, which assume the fluid is a continuum, and no-slip boundary conditions are used. This charger was designed to be used in air at standard temperature and pressure, which has a mean free path of $\lambda = 0.066 \mu m$, while the charger dimensions are on the order of tens of millimeters. Thus, Kn $\approx 1.0e-5$ and the fluid can

be assumed to behave as a continuum. The COMSOL fluid flow interfaces uses the Navier-Stokes equations, for incompressible flow consisting of conservation of mass

$$\nabla \cdot \boldsymbol{u} = \boldsymbol{0} \tag{A1}$$

(where \mathbf{u} is the three-dimensional fluid velocity vector) and conservation of momentum

$$\rho_f \frac{\partial \boldsymbol{u}}{\partial t} + \rho_f (\boldsymbol{u} \cdot \nabla) \boldsymbol{u} = \mu \nabla^2 \boldsymbol{u} - \nabla p \qquad (A2)$$

where p is pressure and μ is the dynamic viscosity.

The flow field in the charger is considered to be steady-state with a constant volumetric flow into and out of the body, thus the time derivative terms in equations (1) and (2) can be eliminated. These equations can be simplified further by assuming that the flow is incompressible, which is justifiable when the characteristic speed of the flow is much less than the speed of sound in the fluid.

Boundary conditions for these equations in the charger model consist of inlet, outlet and noslip wall conditions. The fluid velocity is considered to be zero at the walls and the inlet boundary has a fully developed flow parabolic velocity profile. The outlet boundary of the charger model is considered to be at zero pressure with no viscous stress so the fluid flows freely out of the outlet without restriction. Streamlines of the fluid flow field in the aerosol charger are shown in Figure A3.



Figure A3. Streamlines of the fluid flow field and the electric potential in the aerosol charger.

The electrostatics portion of the charger model is governed by the following equations where the electric field, \vec{E} is defined as the negative gradient of the scalar electric potential, V

$$\boldsymbol{E} = -\nabla \boldsymbol{V} \tag{5}$$

Boundary conditions for the electrostatics portion of the model are applied voltages on the inner and outer cylinders of the model as shown in Figure A4, and the inlet and outlet boundaries have a zero charge boundary condition $\vec{n} \cdot \vec{D} = 0$, which specifies that the normal component of the electric displacement is zero. Electric potential in the aerosol charger is shown in the fringe plot of Figure A3 and electric field lines are shown in Figure A5.



Figure A4: Positive Corona Voltages in Mini-Charger

A corona discharge can be modeled numerically, however, it would be difficult to incorporate into the Eulerian COMSOL model, for several reasons. The level of mesh refinement required to model the scale of the physics of a corona discharge is not compatible with the mesh in the Eulerian model (the flow and electric fields). With proper electrode design and optimized applied voltages, a corona can be considered to be at a steady state under normal operation inside a charger. Therefore it does not add value to simulate this physics for repeated charger simulations as the ion output can be applied as a source or a constant concentration boundary condition in COMSOL and the ion transport portion of the model will disperse ions according to the equations in previous sections.



Figure A5. Electric field arrows and the electric potential (fringe plot of cutplane) in the aerosol charger

Ions created by the corona discharge are modeled as a separate species with number concentration N_i which is multiplied by the charge on an electron to get space charge density, ρ_e . Only positive ions will populate the drift region because the corona discharge is positive. Their motion is governed by

$$\boldsymbol{J}_{i} = -\boldsymbol{D}_{i} \nabla \rho_{e} + \rho_{e} \boldsymbol{Z}_{i}^{\dagger} \nabla \boldsymbol{V} + \boldsymbol{N}_{i} \boldsymbol{u}$$
(A42)

$$D_i = \frac{kTZ_i^+}{e} \tag{A43}$$

where Z_i^+ is the mobility of the ionic species with one charge and e is the charge on an electron. The first term in the above equation is the Fickian diffusion of ions, the second term is the migration of ions in the electric field, and the last term is the convection of ions by the air velocity inside the charger.



Figure A6. Ion concentration in the aerosol charger (cutplane fringe plot) and ion concentration gradient (arrows).

The solver sequence for the Eulerian model first solves for the electric field in the electrostatics application mode, followed by the fluid flow and finally the transport of dilute ions. The order of the solver sequence is chosen based on one-way couplings in the model.

A3.3.2 Governing Equations Lagrangian Portion of Numerical Model

The Eulerian fields just described (fluid flow, electric field and ion concentration) form the environment in which particle trajectories are simulated in the Lagrangian section of the numerical charger model. Note that the term 'steady state' refers to the Eulerian portions of the code only. Trajectories consist of particle position and velocity as a function of time and number of charges on the particle. These trajectories, by nature of the laminar flow in the model, can be considered the steady state solution of particle paths since they are based on the steady-state air flow and electric fields, and would be identical each time they are computed with the same inputs at the same starting locations. There is currently no random component in these calculations, as there is no turbulent flow or particle Brownian motion. Brownian diffusion of particles can be added as a future refinement.

The COMSOL particle tracing module uses Newton's second law to determine the path of a particle, and user-defined forces included Stokes drag and electrostatic force on particles in the charger

$$m\frac{d^2x}{dt^2} = F_d + F_E \tag{A44}$$

where m is the mass of the particle and x is the position of the particle.

 F_d is the Stokes drag given by

$$\boldsymbol{F_d} = \frac{3\pi\mu d_p (\boldsymbol{U} - \boldsymbol{u_p})}{c_c} \tag{A45}$$

where u_p is the three-dimensional particle velocity vector, and U is the fluid velocity vector from the Eulerian model. The inlet boundary condition of particles specifies that their initial velocities are in equilibrium with the air flow, although there is virtually no difference between this assumption and simulations with initial particle velocity equal to zero. The electrostatic force on a particle is a function of the number of elementary charges on the particle, n, and is given by

$$\boldsymbol{F}_{\boldsymbol{E}} = n\boldsymbol{e}\boldsymbol{E} \tag{A46}$$

Where E is the three-dimensional electric field from the Eulerian model and e is the elementary charge.

For this charger, the trajectory start points originate in a 2-dimensional cutplane at the edge of the perforated hemispherical field cage, because that is the location where particles will first encounter ions. Figure A7 shows the annular cutplane in the model geometry. There is virtually no ion concentration upstream of this location because the electric field is transporting ions toward the charging zone and charger exit (this is the purpose of the ion-driving voltage in the design). This saves significantly on computation time in simulating particle trajectories. There would only be one benefit of having the particles start at the inlet tube of the charger—to have the trajectory duration equal the particle residence time in the charger. Considering the computer resources and simulation times, this was not ideal for the current charger model. As it is, the trajectory time can be considered the particle residence time in the charging zone, not in the charger. This is an important distinction and precludes comparison with *N*_{iont} product type models that define residence time differently. Other charger geometries may have similar simplifications, which must be evaluated based on the location of the ion source and whether there is a driving voltage which forces ions in one direction.

Figure A8 visualizes a time point during selected particle trajectories originating at a single line of the cutplane in which some particles are lost. Those closest to the outer charger wall stuck to the edge of the exit tube and those closest to the hemispherical cap were attracted to the field cage surface and stopped.



Figure A7. Annular cutplane is highlighted in blue which is the origin of all the particle trajectories in the Lagrangian model.







Figure A9. Particle trajectories from one starting point originating at the annular cutplane (in Figure A7) plotted in MATLAB. Charger outline is notional, with ends of the cylindrical body depicted by circles, omitting the field cage and the inlet and exit tubes. The neutral trajectory is in red on the upper plot. The lower plot shows all the trajectories from n=0 to n=8 charges, where the effect of the electric field is seen as the charged particles trajectories deviate from the neutral particle path, most predominantly in the charging zone.

Figure A9 shows particle trajectories from one start point plotted in MATLAB. The plot above shows the neutral particle trajectory, and the lower plot shows all nine relevant trajectories (for n=0 to n=8). The electric field exerts a Coulombic force on the charged particles, driving them towards the outer wall of the charger. This is the mechanism whereby highly charged species can be lost to the walls. As the particles approach the exit tube, the effect of the electric field is diminished and the trajectories converge at the outlet.

The COMSOL Eulerian portions of the charger model have been described in the previous sections. Figure A10 shows a block diagram of the model couplings and the outputs from the different portions of the simulation. Blue boxes indicate sections which use COMSOL software. When the model was first approached, a two-dimensional axi-symmetric assumption was made and the trajectories were calculated with a MATLAB script. When the scope of the project changed to a three-dimensional model, COMSOL Particle Tracing module was used for the Lagrangian portion for faster computation and data handling for the lookup tables. Other software packages exist which are capable of calculating particle trajectories as well. A full three dimensional model was needed because of swirling air flow owing to the radially directed aerosol inlet tube. This charger has a side entrance which does not lend itself to the use of symmetry for either the Eulerian or Lagrangian portions, however, an alternate charger may have the aerosol enter along the axis of the charger (coaxial entrance and exit) in which case, both portions could ideally take advantage of symmetry. If relevant charger flow rates had been significantly lower, then it would have been possible to take advantage of symmetry and use 1/4 model for the Lagrangian portion to save dramatically on trajectory computation time. This decision is made by running a three dimensional model parametrically within the range of

pertinent flow rates and check the streamline plots to see if symmetry can be assumed for trajectories starting at the annular cutplane of start points.



Figure A10. Flow chart of charger model sections, represented by the following colors: COMSOL = blue, MATLAB = dark purple, Simulink = lavender, and results (output of the model) are in green.

A4 Charging Algorithm

There is one birth and death equation for each modeled charged species (particles from n=0 to n_{max}), which expresses the rate of change in the size of a particular population. Maximum charge limits on particles in this modeling effort were based on combination coefficients calculated using formulas in section A2.3, which are shown in Table A3 for selected sizes of silver and NaCl particles. Values of β decrease with increasing number of charges on the particle, and the practical limit for maximum charges to simulate was determined by a sensitivity study. When omitting charging beyond $\beta < 10^{-17}$, there was no effect on the resulting charge distribution. This is a function of particle residence times in this charger and to a lesser degree on the particle material (dielectric constant). However, for different charger geometries, higher charged states

could be feasible with longer residence times and sensitivity to maximum particle charge must be considered on a case-by-case basis.

					Diameter (nm)		
	Ag				NaCl		
n Charge	20	25	35	50	50	75	100
0	2.349412E-13	3.242884E-13	5.200007E-13	8.361435E-13	7.579285E-13	1.275982E-12	1.830574E-12
1	1.077986E-14	2.619244E-14	8.085515E-14	2.237892E-13	1.903141E-13	5.133757E-13	9.311763E-13
2	0.000000E+00	1.125385E-15	9.553185E-15	4.927014E-14	3.951430E-14	1.824412E-13	4.370163E-13
3	0.000000E+00	0.000000E+00	9.014487E-16	9.711247E-15	7.329224E-15	5.970787E-14	1.928849E-13
4	0.000000E+00	0.000000E+00	5.236338E-17	1.776925E-15	1.242514E-15	1.854117E-14	8.126928E-14
5	0.000000E+00	0.000000E+00	0.000000E+00	3.032744E-16	1.886651E-16	5.557838E-15	3.314659E-14
6	0.000000E+00	0.000000E+00	0.000000E+00	4.725775E-17	2.334619E-17	1.622497E-15	1.321151E-14
7	0.000000E+00	0.000000E+00	0.000000E+00	6.261928E-18	1.364875E-18	4.630273E-16	5.177563E-15
8	0.000000E+00	0.000000E+00	0.000000E+00	5.205486E-19	0.000000E+00	1.292458E-16	2.002869E-15
9	0.000000E+00	0.000000E+00	0.00000E+00	0.000000E+00	0.000000E+00	3.521337E-17	7.666409E-16
10	0.000000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.000000E+00	9.317199E-18	2.908018E-16

 Table A3. Selected Combination Coefficients Computed According to Fuchs' Charging Theory

Charged species and neutral particle populations at the end of the simulation all add up to the original number of particles specified in the initial conditions. For the charger model, the birth and death equations are solved as a time-marching initial value problem, producing output in the form of a histogram of populations of charged particles, discretized according to number of elementary charges. Simulink is a graphical programming interface which is a MATLAB add-on toolbox and is well-suited for simulating dynamic systems. Time-dependent processes that can be described by differential equations, such as aerosol charging, are represented by interconnected block diagrams and a calculated signal 'flows' through the system solving the differential equations for a set of initial conditions.

The birth and death equations can be solved numerically for any given initial charge distribution on the aerosol. Model simulations in this effort were based on the initial condition of all particles having zero charges. For a given set of Eulerian and Lagrangian conditions (the blue boxes in Figure A10), charging results can be considered a steady-state solution as there is currently no random element in this model. When a trajectory ends, charging stops, but if

trajectories were longer duration, for example, if the flow rate through the charger were reduced, then the residence time of the particles would increase, and thus the level of charge would be increased because of longer exposure time to the ions. Charger models without dynamic charging assume plug flow in the application of the birth and death equations and use a constant ion concentration, N_{ion} . They assume that every increment of time exposes all particles to an identical ion concentration. However, there is a spread in the particle residence times in this charger, owing to the swirl of the flow field and lost or unfinished particle trajectories. Before the application of this charging algorithm, the residence time statistics are determined after the trajectories are calculated (see lower purple box in Figure A10). This gives an indication of how uniform the charging is likely to be and what kind of standard deviation the resulting charge distribution may have.

Trajectories are processed in a MATLAB script to a suitable form for inputs in the Simulink code. The COMSOL condition for a particle encountering the charger wall is 'stop' and consequently, lost particle trajectories are identified by zero velocity, however the particle remains visible in the plots so one can determine the location where the trajectory ended. This in itself can give insight into improved charger design. A particle is considered to have exited when the x-coordinate (axial) equals the 0.0209 cm, which is just inside the exit tube of the charger. There is no benefit in simulating the particle motion beyond this, as once it is inside the exit tubing, the flow is strictly in the axial direction and there is no significant electric field to alter its course. No particles are lost there, so if the particle survives to x=0.0209 m (axial downstream location of the exit tube), then it will exit the charger. For the charging algorithm to work, the lengths of the trajectory matrices for a given start point must be the same. That is, n=0 trajectory has a given length and no charging can take place beyond this, therefore higher

charged trajectories are truncated to this length. This particular charger had the non-ideal condition whereby some start points have unfinished trajectories for one or more charge level trajectory (residence time is virtually infinite, compared to the other residence times). This is a numerical artifact, and can potentially be remediated in future work. These particles never reach x=0.0209 m and for reasonable computation time, these trajectories must be shortened to a practical designated length. This length is determined by looking at statistics of exit times of all start points. When ~95% of all particles exit within a certain time, then this duration is chosen for the designated maximum trajectory length. Omitting particles with longer trajectories is not expected to significantly affect the final charge distribution, however this must be investigated with sensitivity studies if applied to other charger geometries as well. Some particles have trajectories which exit early or are lost to the walls may be shorter than other trajectories. These are lengthened with zeros to match the designated trajectory size of the matrix per MATLAB convention. When charging takes place along a shorter (n>0) trajectory, then all charging stops for that level of charge when the trajectory ends. This is currently a source of error in the results as it affects the sum of all charged fractions and the final charge distribution.

The upper purple box in Figure A10 represents MATLAB functions that take COMSOL results and put them in matrix format, creating lookup tables so that the relevant quantities are known at each location (x,y,z) of the particle trajectory. These relevant quantities are: the flow field (variables u,v,w [m/sec], used for Stokes drag on particle), and the electric field (variables Ex, Ey, Ez [V/m], used for Coulombic force on the particle), and the ion concentration (variable c_ion [mol/m³], local Nion is used for charging). The spacing of the lookup table values are currently 0.5 mm apart, giving 42 increments (breakpoints) in the axial direction and 26 rows in

the lateral and vertical directions of this charger. These lookup tables are used in the Simulink charging simulation when the birth and death equations are solved.

The dark purple box outline containing the lavender box in Figure A10 is the heart of the charging model. A MATLAB script wraps around the Simulink code which executes the charging algorithm/population balance solution (lavender) for two levels of its application. For a given starting point, the first use of the charging algorithm is with the COMSOL trajectory time step for the neutral particle trajectory. This is the framework for calculating the charged particle populations successively, which have different trajectories than the neutral particles. Subsequently, the same charging algorithm is used to simulate higher charged species acquiring additional charges, 25 times for each COMSOL trajectory time step (known as minisimulations). These mini-simulations are necessary for the charging calculations, as the time scale for acquiring charge is small, and the fixed step used to march through the solution is very small in relation to the COMSOL trajectory time step. In-between each COMSOL trajectory time step execution of the Simulink charging simulation, the previously calculated higher charged species populations (from the lower charged trajectories) are retrieved and incorporated as the initial conditions for charging the next COMSOL trajectory time step.

Aerosols acquire charges incrementally (integer values of n), so the charging model has no continuous states and therefore a fixed-step discrete solver was chosen. The integration method for Simulink was set to ode3 (Bogacki - Shampine) method, which computes the model's state at the next time step as an explicit function of the current value of the state and the state derivatives. The trajectory time is mapped to the Simulink model, and thus a single step size is used throughout the simulation.

A graphical depiction of the charging algorithm executed for one starting point is shown in Figure A11 with a detailed caption summarizing the process. After all start points have been treated in the same manner, the results are compiled to obtain the overall charge distribution, the average charge, and the charging efficiency. A flow chart of the model is shown in Figure A12. The following pseudo-code also provides an example of the charging algorithm progression:

- Start charging equations at origin or start point with particles 100% neutral. This is designated by 'charged fraction'—say the origin represents 100 particles starting out neutral. Thus the charged fraction is 0 (none charged), and the uncharged fraction is 1 (100% have no charges). After exposure to some ions, then the charged fraction will redistribute between the modeled charged states (which go from n=0 [neutral] to n=max charge [nchgmax]) by the population balance equations. For example, solve the charging equations at each time step (duration of time step) using Nion lookup (this reflects the local ion concentration which varies throughout the charger). So the particle's progress along the trajectory encounters different concentrations of ions and the charging calculations reflect the cumulative exposure to ions during the particle's trip from start point to charger exit.
- For the n=0 trajectory: Store fractions of higher charged species at each Δt for future use as ICs. When complete, the final charge distribution (charged fractions) from the calculations reflects what would happen on the n=0 trajectory if all started neutral and encountered the local Nion all along the neutral particle path. Thus the n=0 fraction is saved as the final answer for number of neutrals remaining at the exit. The higher charged fractions are subject to change, as they have not been subjected to the n=1, n=2,

etc. trajectory paths which have been acted upon by the electric field, however, these charged fractions are the ICs for the next levels of charging.

- Results of the charging simulations are stored in a three dimensional array.
- The charging script orchestrates the Simulink model solution of the charging equations using lookup tables to supply Simulink with the necessary inputs for solving the population balance equations. Evenly spaced times of the trajectory steps are breakpoints (lookup values) which give access to the pertinent information about that instant in the trajectory: where the particle is (x,y,z), which allows the Nion at that location to be determined. Thus it is a time-marching solution along a previously calculated trajectory, which accounts for the cumulative exposure to ions along that path and gives the resulting charge distribution (or charged fractions of all modeled species) for a given start point.
- Following the n=0 trajectory, the charging simulation goes to the trajectory of a particle with one charge (n=1).
- Run charging equations again along n=1 trajectory with n=0 fraction empty (zero). There
 is no need to carry any numbers in the n=0 category because the final answer of the
 neutral population was determined upon finishing the n=0 trajectory. The higher charged
 species charged fractions from the n=0 trajectory are ICs for the n=1 trajectory.
- After the first time step of the n=0 charging results, a charge distribution exists (changed from the 100% neutral state [no population of higher charged species at t=0] to some miniscule charged numbers at n=1 and n=2, however these fractions are still heavily weighted at the n=0 position). This value of the n=0 fraction is what we start with for the ICs of the n=1 trajectory simulations, then add in any other previous charged fractions

(for n=1 there are none other than n=0), then get rid of the previous value (subract out the full amount of the previous IC and add back the fraction of singly charged particles remaining. The rest are saved in the singly charged output matrix to be picked up in higher charged species trajectory initial conditions).

- The Simulink simulation runs for every time step in the nchg (number of charges) trajectory. The simulation goes from the 2nd time step to the 3rd, then 3rd to 4th, etc. with the many mini simulations in-between each, up to the end of the trajectory.
- Each time the ICs are updated with the n=0 charging results for that location—and the old IC's are subtracted out, so that the charging that takes place for that location are strictly based on the fraction of particles that were elevated from neutrals in all previous charging trajectories.
- Then, whatever amount is left for that nchg trajectory at the end of all the minisimulations is the FinalCharge value for this start point. If the start point n=1 trajectory was just simulated, then the charged fraction of singly charged particles is equal to the fraction in the n=1 location of the matrix (n=0 is already done).
- Continue with all trajectories for that start point and end up with a final charge distribution (vector) for that start point.
- Then loop through all the start points in the same manner. End up with a 'FinalCharge' for each start point (around one or two hundred, typically).
- To compile all the charge distribution statistics, assemble all the FinalCharge vectors in a matrix. Take an average of all rows to get the composite final charge distribution for all start points.

- Check for the percentage of particles that are accounted for at the end of all the simulations (the variable checkfraction) and also sum up the CompositeFinalChargeDistribution vector and the answer should get very close to 1, depicting 100% of the charged fraction that initially was all neutral.
- Make histogram of composite final charge distribution or other relevant outputs.



Figure A11. A graphical depiction of the charging algorithm. The colored lines represent particle trajectories, as seen in Figure A9 with charger outline geometry omitted here for clarity (refer to Figure A9 for description of trajectory geometry). From one starting point (red dot on left), particle trajectories are simulated for all charged species under consideration. The red neutral particle trajectory

in the charger is only influenced by the flow field (not the electric field). Trajectories for n=1 through 8 charges are traced with subsequent colors in the scale, so the farthest trajectory from the neutral/red is magenta, representing a particle with n = 8 charges. The spatial deviation of the charged species from the neutral trajectory is the most pronounced in the charging zone (owing the the influence of the electric field), and these deviations affect the value of the local ion concentration which is an input in the population balance equations. Simulink is a numerical tool well-suited to time advancing phenomena. The application of Simulink is to step through the previously calculated particle trajectory and determine the instantaneous local charged species fractions using lookup tables for ion concentrations and flow field (for drag) to get the most accurate solution of the birth and death equations. First the neutral trajectory (n=0) is traversed and charged fractions are obtained corresponding to each trajectory time step. These fractions are recorded and used in the analysis of the trajectory with respect to the higher charged species paths. The neutral trajectory charging simulation ends in an intermediate charge distribution which reflects the final fraction of neutral particles from a particle originating at that start point. The remaining quantities in that charge distribution are subject to refinement with subsequent charging simulations of that start point. All of the fractions of the higher charged species are re-calculated with subsequent Simulink simulations along their respective trajectories. Following the neutral simulation, the singly charged fraction results are refined as the birth and death equations are solved iteratively between each n=1 (singly charged particle) trajectory step until convergence is achieved, thus updating the n=1 species results of the charged fractions all along the trajectory. The final charge distribution (for species n=1 to n_{max}) is also an intermediate result but reflects the final charged fraction for n=1 species. Thus, charged fractions making up the final charge distribution of this starting point are successively determined as each charged species trajectory is traversed. Between each trajectory step, the charging equations are solved 25 times, rearranging the charged fractions between the trajectory time steps until convergence is achieved. At the starting point of the trajectory, 100% of the particles are neutral (represented by the red bar in the histogram above). Colors of the higher charged trajectories correspond to the colored bars in the histograms above (e.g. orange is singly charged, green is triply charged, royal blue is n=6 charges, etc.). Thus from the time progression of the histogram, the levels of charge are rearranged (from all neutral at the starting point, left) to a distribution at the end (right). The sum of all the populations of charged species equals the original population (red bar).



Figure A12. Flow chart of numerical charger model. The 'start' block is the beginning of the charging algorithm, which is completed for all the start points of the trajectories, and enveloped in this process is the solution of the birth and death equations many times for each level of particle charge considered.

Each trajectory is used in the charging algorithm as the particle advances by each trajectory time step from the starting point to the charger exit. At some point, one or more higher charged species may become lost to the walls of the charger either from the flow field or under the influence of the electric field. Thus, the population of that species becomes zero for the remainder of the charging of that particle start point. When these are omitted from the charging, then the species charged fractions do not add up to 1 at the end of the simulation. This is more significant than the inherent numerical error and drains off particles, making accounting more difficult. The overall charging efficiency can be calculated at the end of all charging simulations but the lost or unfinished trajectories must be subtracted out when considering the final charged fraction. Or another approach would be to look at trajectory statistics before any charging takes place and eliminate the lost or unfinished trajectories and just run the remaining trajectories. After all is simulated, then make all the eliminated trajectory fractions zero and the resulting sum of all charged fractions is the charging efficiency (after subtracting off the neutral population first).

A5 Sensitivity Studies

A sensitivity study was performed with the COMSOL model mesh: An important test for model fidelity is to ensure that the solution is independent of mesh size. Therefore successively small COMSOL meshes were tested until pertinent parameters did not change.

An additional sensitivity study was performed for lookup table spacing of nodes. The resolution of the lookup tables are important in order to capture the ion concentration and distance a particle traverses in one time step. If the dimension is too large then values in high gradient areas will not capture the variation. These tables are interpolated for local information at every step along the trajectory. There is a trade-off between file size/memory/speed of

simulation and resolution of lookup tables. After comparing model results with various distances between nodes, the spacing of the lookup table values were set to 0.5 mm apart, which is the largest value after which there is no change in the final charging results.

Sensitivity studies were performed for both time steps in charging scheme: First for COMSOL trajectories in Simulink, and then for the mini-simulations that take place between each COMSOL trajectory time step. A sensitivity study was performed on the time step sizes in the charging algorithm. During model development, once a solution was obtained with an initially small time step for the full particle trajectory, successively larger time steps were simulated to determine when the charge distribution results would change compared to the initial level of refinement. It was determined that 25 population balance loops should be completed between each COMSOL time step to ensure that charging loops had completely captured the effect of the ion concentration gradient between each COMSOL trajectory particle position.

An additional important sensitivity study would be to calculate different numbers of start points of particle trajectories (100, 200, 300, etc.) to see if the final charge distribution changes significantly. Ultimately, this is a function of the initial distribution of start points, which should be evenly distributed geometrically to simulate all possible origins of particles entering the charging zone. Eulerian software packages have a variety of methods to distribute particle start points/initial positions in trajectory tracking simulations.

Conclusions from these sensitivity studies are reliable for this charger geometry, its flow velocities and the gradients in the Eulerian fields. Application of this charging model to other chargers would require sensitivity studies for relevant values of model parameters.
A6 Preliminary Results

The quality of this charging model is dependent on the quality of the Eulerian model and the quality of the calculated trajectories. If a CFD model shows that there is no axial symmetry in the charger, then there will be discrepancies between trajectories, with some significantly longer or possibly unfinished. This is an indication that the geometry is not ideal for a narrow charge distribution—there will likely be a bigger standard deviation in the charge distribution. This scheme is well-suited for laminar flow, in which particles have similar residence times. Particles lost to walls owing to the Coulombic force will not pose a problem, however, particles that swirl around and do not exit will lead to greater uncertainty in the results. The model accuracy is highly dependent on accurate CFD results. This mini-charger model was based on laminar flow and could not be solved for flow rates higher than 0.7 lpm, therefore, only 0.3 lpm results were simulated in order to match the experimental data for this charger (Qi et al. 2008). It is reported that a charge on a monodisperse aerosol naturally has a Gaussian distribution (Gauntt et al. 1981). This would occur in simulations based on the combination coefficients and also the spread of residence times. The more non-ideal the flow patterns in the Eulerian model (ie. the more unfinished trajectories), the less likely the resulting charge distribution will appear Gaussian. A highly desirable feature for future improvement of the model would be to consider diffusion in the particle trajectories. This is a feature of some commercial particle tracking software packages but caution must be exercised in interpreting and accepting results (Robinson et al. 2007). At the very least, the addition of diffusion may give a qualitative picture of potential diffusion losses as a function of size and the relationship to electrostatic losses. Note that ion diffusion was included in the Eulerian simulation (transport of dilute species).

A6.1 Silver 10 nm Particles Simulated at 0.5 lpm Flowrate

Trajectory statistics for silver 10 nm particles, showing residence times for neutrals (n=0) and singly charged (n=1) species are shown in Figure A13. Note that for the n=1 trajectory, 96 out of 150 particles were lost (stuck to the walls of the charger), as noted in the caption in the automatically-generated residence time plot for both charged species. This output corresponds to the left green box in Figure A10. Unfinished trajectories are omitted from this plot, and create difficulties for the accounting and accuracy of the final charge distribution. It can be seen that the majority of the particles have a residence time significantly less than 0.3 seconds.



Figure A13. Trajectory statistics for silver 10 nm particles, showing residence times for neutrals (n=0) and singly charged (n=1) species. This output corresponds to the left green box in Figure A10.



Figure A14. The final charge distribution for the 10 nm silver particles shows that 12% are singly charged and 21% remained neutral (and the rest were lost in the charger).



Figure A15. Experimental results for extrinsic charging efficiency for the mini-charger (from Qi et al. 2008), showing that the 0.3 lpm extrinsic charging efficiency (open circles) is approximately 10%, which is quite good agreement with the model prediction that 12% are singly charged.

After the entire simulation has been completed for all 150 start points, the final charge distribution for 10 nm silver particles is shown in Figure A14. The only relevant species in this charging simulation are singly charged and neutral particles, as can be inferred from Table A3 which has only two non-zero entries for 20 nm silver particles and thus 10 nm particles have

equally sparse combination coefficients. Therefore, the output histogram of charge distribution cannot 'appear' Gaussian. Simulation results predict that 12% of the particles become singly charged and 21% remain neutral (and the remainder [67%] were lost in the charger). This is quite good agreement with the experimental results of the mini-charger, shown in Figure A15. With only two charged species, the charging model works optimally, as there are fewer anomalies of unfinished trajectories which affect the accounting and numerical accuracy of the algorithm.

A6.2 Silver 35 nm Particle Simulation

Figure A16 shows trajectory statistics for NaCl 35 nm particles, with residence times for neutrals (n=0) in the upper left subplot, and charged species up to n=4 (each row from left to right). The average residence time for these trajectories was 0.25 seconds. Figure A17 shows experimental results from Qi et al. 2008 compared to simulation results for the mini-charger with 0.3 lpm flow rate and 35 nm silver particles based on 50 trajectory start points. Ideally, more than 50 start points should be considered, however, these are preliminary results. Both the experimental and predicted distributions appear fairly Gaussian, and the experimental results account for fewer total particles (the charged fractions only account for 52% of particles). The simulation charge distribution accounts for 98% of particles that started trajectories, and demonstrates that for smaller particle sizes, accounting and numerical error are is quite acceptable. A potential explanation for this discrepancy is diffusion losses in the experimental setup, which are not accounted for in the numerical model (in the Lagrangian simulations).



Figure A16. Trajectory statistics for 35 nm silver particles, showing residence times for neutrals (n=0) in the upper left subplot, and charged species up to n=4 (each row from left to right). The average residence time for these trajectories was 0.25 seconds.



Figure A17. Experimental results compared to simulation results for the mini-charger with 0.3 lpm flow rate and 35 nm silver particles based on 50 trajectory start points. Experimental results are from Qi et al. 2008.

A6.3 NaCl 75 nm Particle Simulation

Figure A18 and A19 show particle trajectory statics and the predicted charge distribution of 75 nm NaCl particles, based on 100 start points. This simulation was much more complex as it entailed thirteen charged species (n=0 to n=12). The highly charged species are very quickly lost to the walls of the charger in the electric field, owing to their higher mobilities. For particles with 7 or more charges, 20 or more start points are lost to the walls.



Figure A18. Trajectory statistics for NaCl 75 nm particles, showing residence times for neutrals (n=0) in the upper left subplot, and charged species up to n=12 (going left to right).

The simulation duration for these results was 28.5 hours with the current model. Best practices for speeding up MATLAB and Simulink simulations were subsequently applied which improved future simulation times significantly, up to 35% faster.



Figure A19. The final charge distribution for the 75 nm NaCl particles is not as Gaussian, owing to the loss of higher charged species and unfinished trajectories.

A7 Conclusions and Future Work

The numerical model of a unipolar diffusion charger which includes dynamic charging has been developed with preliminary results showing reasonable agreement in smaller particles sizes, and larger discrepancies for larger particles sizes where higher charged species are relevant. The drawbacks that have been evident in this effort stem mainly from unrealistic CFD and particle tracking results which imply that some trajectories never exit the charger within a reasonable simulation duration. This affects the accounting in the code which attempts to match the initial quantity of particles (100% or neutral fraction of 1.0) with the final charged populations. A more accurate flow field should be pursued and particle diffusion should be considered in the particle trajectories for future work. Improvements can be made in the algorithm to accommodate lost particles in the final accounting. Most real-world charging does not apply to monodisperse aerosols, so model results will not be directly applicable for typical polydisperse conditions. As computing capability increases, this could be considered but would add a significant amount of complexity and computation time.

A different charger geometry would lend itself to more accurate modeling, such as having the inlet, body and outlet coaxial, that is, no turns in flow path through the charger. This would reduce losses and improve accuracy of the particle trajectories and reduce the standard deviation of particle residence times. The practice in this model was to neglect charged species for which beta is less than 1e-17, as the effects were negligible in the charging results. If a different charger has a longer residence time, then higher charge levels are possible and more betas should be included in simulations. If a charger had a much higher ion concentration then higher charge levels are likely, but also the space charge effect will significantly change the charged particle trajectories. This scenario would require two-way coupling of between the electric field and the charged particle population, resulting in a more computationally intensive simulation and requiring a different charging algorithm than what is described in this work.

The modeling approach demonstrated here can be useful in the charger design process, with iterations of geometries and parametric studies varying flow and ion concentrations and other pertinent variables. Simulations can give insight on charger configurations which reduce the geometric standard deviation of the final charge distribution (minimize multiple charging for a given particle size). Many results are evident without using the charging algorithm, as particle trajectories can be simulated to get distributions of residence times.

Interesting future applications of this charging model include exploring alternate pre-existing charge distributions as initial conditions (e.g. Boltzmann, charge distribution on smoke particles,

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etc.). Future use should take advantage of the new collision kernels from Gopalakrishnan et al.

2013a, and the potential for using the distribution of ions outlined in Gopalakrishnan 2013c

should be explored. Other charging equipment or processes with definable geometry and particle

trajectories can benefit from this methodology as well, for example electrostatic precipitators.

Once an Eulerian model of the geometry is created and proven, then the numerical process

described in this appendix can be applied and relevant charge predictions can be obtained.

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Appendix B: Additional Smoke-in-Drums Results

B1 Results for Additional Temperature Conditions and Materials

Additional temperature conditions for the three spherical materials show a similar pattern in the residual plots, with the same conclusions that Kapton and lamp wick are reasonably lognormal, and silicone deviates much more from a lognormal size distribution.



Figure B.1. Smoke particle size distributions from SMPS measurements for a representative Kapton[®] high temperature test (557 °C) with open plot markers for unaged smoke ($d_g = 140$ nm, $\sigma_g = 1.63$) and solid symbols for aged smoke ($d_g = 210$ nm, $\sigma_g = 1.55$). The solid curves represent the non-linear least square fits. A residual plot showing the deviations from the lognormal fits is aligned below the size distribution.

The smoke particle size distribution and residual plot of Kapton high temperature smoke is shown in Figure B.1. SMPS results for lamp wick smoke at the baseline temperature and accompanying residual plot are shown in Figure B.2. SMPS results for silicone smoke at the high temperature condition and the residual plot are shown in Figure B.3.



Figure B.2. Smoke particle size distributions from SMPS measurements for a representative lamp wick baseline temperature test (250 °C) with open plot markers for unaged smoke ($d_g = 146 \text{ nm}, \sigma_g = 2.04$) and solid symbols for aged smoke ($d_g = 227 \text{ nm}, \sigma_g = 1.79$). The solid curves represent the non-linear least square fits. A residual plot showing the deviations from the lognormal fits is aligned below the size distribution.



Figure B.3. Smoke particle size distributions from SMPS measurements for a representative silicone high temperature test (369 °C) with open plot markers for unaged smoke ($d_g = 279$ nm, $\sigma_g = 2.00$) and solid symbols for aged smoke ($d_g = 409$ nm, $\sigma_g = 1.62$). The solid curves represent the non-linear least square fits. A residual plot showing the deviations from the lognormal fits is aligned below the size distribution.

Pyrell smoke particle size distributions for baseline and high temperature conditions are shown

in Figure B.4. Teflon SMPS results for both baseline and high temperature tests are shown in

Figure B.5.



Figure B.4. Smoke particle size distributions from SMPS measurements for representative Pyrell[®] tests. Baseline temperature at left (225 °C) with open plot markers for unaged smoke (d_g = 223 nm, σ_g = 1.93) and solid symbols for aged smoke (d_g = 370 nm, σ_g = 1.68). High temperature at right (234 °C) with open plot markers for unaged smoke (d_g = 253 nm, σ_g = 1.88) and solid symbols for aged smoke (d_g = 364 nm, σ_g = 1.73).



Figure B.5. Smoke particle size distributions from SMPS measurements for representative Teflon[®] tests. Baseline temperature at left (501 °C) with open plot markers for unaged smoke ($d_g = 139 \text{ nm}, \sigma_g = 2.22$) and solid symbols for aged smoke ($d_g = 239 \text{ nm}, \sigma_g = 2.02$). High temperature at right (512 °C) with open plot markers for unaged smoke ($d_g = 248 \text{ nm}, \sigma_g = 2.07$) and solid symbols for aged smoke ($d_g = 369 \text{ nm}, \sigma_g = 1.90$).

A TEM lamp wick particle size distribution of particles collected during ground testing is compared with SMPS results in Figure B.6. Two different smoke tests are compared but the heating temperatures are within 0.6 °C so the pyrolysis can be considered to be similar. For the TEM analysis, 17 images containing 4668 particles were processed. TEM images displayed two types of particles: dark, high contrast particles and smaller lower contrast particles. The faint particles could be an artifact on the TEM grid or be the result of poor image quality. Another explanation could be a secondary particle formation event from the pyrolysis products. For this size distribution analysis, all particles were counted without thresholding, so the small faint particles were included in the totals, which reduced the geometric mean diameter and caused σ_{gn} to be significantly larger than the SMPS results.



Figure B.6. Ground test number and volume distribution for lamp wick aged test (286 °C) from SMPS (circle symbols) and from TEM (square symbols). The open symbols correspond to the number distribution and the closed ones are the volume distribution. The best fit parameters for SMPS are $d_{gn} = 248$ nm, $d_{gv} = 548$ nm, $\sigma_{gn} = 1.75$ and $\sigma_{gv} = 1.59$ and for TEM are $d_{gn} = 123$ nm, $d_{gv} = 812$ nm, $\sigma_{gn} = 2.70$ and $\sigma_{gv} = 1.65$.

The SMPS and TEM volume distributions have a similar spread but do not agree well in the peak location. The largest size bin of this TEM analysis had twelve particles which is considered statistically significant for this type of analysis (Hinds 1999). The SMPS size distribution ends at 1000 nm, but there is no upper size limit for particles in the TEM size distribution. Parameters of TEM size distribution results from ISS flight tests are given in Table 2.1.

B2 Derivation of the Relative Cumulative Moment Formula

The *p* moment cumulative function of a lognormal distribution with d_g and σ_g is defined as:

$$M_p(D) = \frac{1}{\sqrt{2\pi} ln\sigma_g} \int_0^D d^{p-1} exp\left(-\frac{\left(lnd-lnd_g\right)^2}{2\left(ln\sigma_g\right)^2}\right) dd \tag{B1}$$

Using the following new variables, we can simplify the derivation.

$$A = \frac{1}{\sqrt{2\pi} ln\sigma_g}, \quad B = 2(ln\sigma_g)^2, \quad C = lnd_g \quad \text{and} \ L = lnd.$$
(B2)

Thus the simplified form of (B1) is:

$$M_p(D) = A \int_{-\infty}^{lnD} exp\left(pL - \frac{(L-C)^2}{B}\right) dL$$
(B3)

It can be shown that

$$pL - \frac{(L-C)^2}{B} = pC + 0.25p^2B - \frac{1}{B}(L - C - 0.5pB)^2$$
(B4)

Define two new variables to simplify the derivation:

$$\xi = pC + 0.25p^2B$$
 and $\eta = \frac{L - C - 0.5pB}{\sqrt{B}}$ (B5)

From (B4), we have that $dL = \sqrt{B} d\eta$

Now, (B3) can be rewritten as

$$M_p(D) = A\sqrt{B} \int_{-\infty}^{\eta_D} \exp(\xi - \eta^2) \, d\eta = A\sqrt{B} \exp(\xi) \int_{-\infty}^{\eta_D} \exp(-\eta^2) \, d\eta \tag{B6}$$

or, in terms of the error function, we have

$$M_p(D) = \frac{\sqrt{\pi}}{2} A \sqrt{B} exp(\xi) [1 + erf(\eta_D)]$$
(B7)

where
$$\eta_D = \frac{lnD - C - 0.5pB}{\sqrt{B}} = \frac{ln\left(\frac{D}{d_g}\right)}{\sqrt{2}ln\sigma_g} - \frac{1}{\sqrt{2}}pln\sigma_g$$
 (B8)

Next, eliminate all intermediate variables to express $M_p(D)$ in terms of d_g , σ_g and p.

Equation (B7) can be rewritten as:

$$M_p(D) = \frac{1}{2} d_g^p exp\left(0.5(p ln\sigma_g)^2\right) \left[1 + erf(\eta_D)\right]$$
(B9)

It is interesting to see when *D* approaches infinity, what the total *p* moment is. As *D* approaches infinity, η_D approaches infinity too and the error function approaches 1. Thus, the total *p* moment of the lognormal distribution is

$$M_p = M_p(\infty) = d_g^p exp \left[0.5 (p l n \sigma_g)^2 \right]$$
(B10)

Equations (B9) and (B10) are very useful, as they give the absolute value of the *p*th moment, partial or total. The dimension of the *p*th moment is $[L^p]$. However, in many cases, we are interested in the relative value to the total moment or the moment value normalized by the total *p*th moment value. The relative values can tell us how much of the signal is captured in the limited detection range of an instrument. Dividing Eq. (B9) by Eq. (B10), we have

$$M_{p,rel} = \frac{1}{2} [1 + erf(\eta_D)]$$
(B11)

The resulting equation (B11) is simple and useful. Note that in equation (B8), *D* is normalized by d_g . Thus $M_{p,rel}$, the relative cumulative value only depends on three parameters, normalized *D*, σ_g and *p*.

B3 Particle Losses in 55 Gallon Drums

Losses in the 55 gallon drum during sampling has been investigated both analytically and through data analysis. Possible loss mechanisms include inertial deposition, gravitational settling and diffusion.

The dominant loss mechanism for larger particles is inertial deposition (impaction). Turbulent deposition can be calculated for tubes or pipes, based on the Reynolds number of what is assumed to be fully developed turbulent flow (Friedlander, 2000). This geometric assumption is not applicable to a fixed volume of air containing a fan, such as the smoke-in-drums hardware. Additionally, it applies to particles greater than 1 μ m, so this loss mechanism can be considered negligible in this work because the smoke particles of interest have significantly smaller

geometric mean diameters and there was no measurement capability for particles greater than 1 μ m. Therefore this loss mechanism will be neglected without further evaluation.

Gravitational settling of particles in the drum is affected by the fan which was used to prevent stratification of the smoke. Losses from stirred settling (settling with mixing) were calculated based on the following assumptions: The aerosol is vigorously stirred with a uniform concentration throughout the drum; diffusion, resuspension and deposition to the walls are negligible, and each particle has a net velocity equal to its calculated terminal settling velocity (assuming that the turbulent fluctuations affecting the particle velocity in the positive and negative directions cancel each other) (Hinds, 1999). The terminal settling velocity of a particle less than 1 μ m with Re < 1 is given by

$$v_{ts} = \frac{\rho_p d_p^2 g C_c}{18\mu} \tag{B12}$$

where ρ_p is the particle density, g is the acceleration due to gravity (9.81 m²/sec at sea level), C_c is the Cunningham slip correction factor and μ is the viscosity of the surrounding air. For an initial particle number concentration of N_o , the number concentration of an aerosol undergoing stirred settling can be expressed as a function of time, t, by the following expression:

$$N(t) = N_0 \exp\left(\frac{-\nu_{ts}t}{h}\right)$$
(B13)

where h is the height of the drum. Essentially, the particle losses are based on the initial concentration and undergo an exponential decay. These losses were calculated for each bin size of the SMPS data, giving essentially separate losses for many monodisperse aerosols, which, when pieced together across all bins gives size-specific losses from stirred settling for the particle size distribution. Most drums of smoke were measured by only three scans, however,

one test point for unaged lamp wick smoke had six scans, and this larger data set was used to extend this analysis to a longer duration of losses. The initial concentrations were taken from the first SMPS scan, and predicted loss percentages using the above equations ranged from 0.017% for 23.3 nm particles to 3.45% for 982.2 nm particles in a duration of 14 minutes (six scans). This is twice as long as the typical measurement sequence, so applying the calculation to the first three scans only results in predicted losses in number concentration ranging from 0.0082% at 23.3 nm to 1.64% at 982.2 nm in approximately 7 minutes. This is considered negligible.

Losses from diffusion are dominant in smaller particle sizes. The upper limit of losses by diffusion to a wall can be calculated using the following formula (Hinds, 1999) for the cumulative number of particles deposited as a function of time

$$N(t) = 2N_0 \left(\frac{Dt}{\pi}\right)^{1/2} A \tag{B14}$$

where *D* is the diffusion coefficient and *A* is the internal surface area of the container. This assumes a stagnant aerosol with initial uniform concentration N_0 outside the diffusion boundary layer. Calculations for diffusion losses were performed based on the SMPS size distribution of Kapton smoke, which has the smallest geometric mean diameter of the spherical smoke particles evaluated. Formula B14 was used for each size bin of the distribution, with the first (earliest) scan bin population considered as the initial concentration, N_0 . Predicted diffusion losses ranged from 3.6% for 20.9 nm particles, to 0.21% for 661.2 nm particles over a duration of 14 minutes, the time required for three SMPS scans. This is considered to be negligible and does not affect the accuracy of the curve-fitting and lognormal analysis of data for the smoke-in-drums experiment.

In light of the negligible predicted losses mentioned above, evaluation of actual data from the three SMPS scans performed in rapid succession can be performed to determine if loss trends can be observed over that duration, which was typically 14 to 15 minutes. Initial calculations from previous SAME data indicated that for all materials, the aerosol concentration in the drum would be less than 2×10^4 particles/cm³, which is below the rule-of-thumb threshold concentration of 10^6 particles/cm³. Below this level, coagulation can be neglected since it will occur at a very slow rate (Hinds, 1999). Thus it could be assumed that very little aging took place in the drum during the SMPS measurements of unaged smoke. During this time period, coagulation is assumed to be negligible, so reduction in particle concentration for a given bin size is assumed to be from losses to walls.

The 3-scan and 6-scan loss predictions calculated using the above formulas were compared to the actual SMPS particle size distributions and no clear trend of losses could be seen in the data for the entire size range of the data. Comparing the percentage changes between the bin populations of the first and the last scans, there were many negative quantities, indicating that some bins increased in population between the first and the last scans. Several of the highest size bins (from 763.5 nm to 982.2 nm) had 100% losses, but some were 100% or 52% gains in bin population, indicating that there was no uniform loss mechanism to be determined from the data. Considering potential diffusion losses at the smaller range of SMPS data for Kapton smoke (the smallest spherical particles characterized), the bins from 23.2 nm to 101.8 nm varied from 100% losses to 1577% gains, and also showed no clear trend from which a loss time constant could be inferred. Overall, 35 out of 105 bins of particle sizes increased in population by the last scan, compared to the first. Since growth by coagulation is assumed negligible, it can be concluded that the percent changes in the SMPS data can be attributed to the typical statistical nature of

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aerosol measurements. A lab-generated aerosol is often considered 'steady' when concentration measurements are within plus or minus 10%. While losses must have taken place in the smokein-drums experimental setup, these losses amount to negligible quantities in the theoretical calculations, and are within the typical margin of variability in the measured data for the relevant time scale in this experiment.

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