A STUDY OF SMOKE AGING EXAMINING CHANGES IN SMOKE PARTICULATE SIZE

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ABSTRACT

The activation time of ionization smoke detectors compared to photoelectric smoke detectors has resulted in a debate over which detector provides the best protection for people and property. Smoke detector activation times vary as a function of distance from a fire source as well as the type of burning (i.e. smoldering vs. flaming). Ionization and photoelectric smoke detectors have been shown to respond differently to variables such as: smoke velocity, smoke temperature, optical density, particle size, particle number concentration, and refractive index. Reports have concluded that as the particles age they grow in size, resulting in the primary change in detector activation times. However, it remains unclear if the change in smoke detector response is due solely or even primarily to the changing particle sizes in the smoke aging process.

Calculations were conducted to replicate the agglomeration process. One set of calculations identified changes to number concentration as it relates to changes in particle size while the mass of the smoke concentration is kept constant. The minimum and maximum UL 217 obscuration rates for smoke detector activation were used in a second set of calculations to establish the number concentration at detector activation. The number concentrations were then utilized to find the average distance between each particle. The velocity, due to Brownian motion, of the particles was calculated accounting for temperature. The results established the relationship between temperature, number concentration, and time as it relates to the agglomeration process due to Brownian motion.

This paper presents the collected laser scattering of various aerosols, including calibration aerosols as well as fire-generated aerosols. Laser scattering has been used to find many of the properties of soot particles, including particle size. The laser scattering measurements were made at two linear polarizations, vertical (VV) and horizontal (HH). The scattering angles ranged from 20 to 155 degrees and used a laser source with a wavelength of 632.8 nm. A bench top experimental setup was constructed to measure the intensity of light scattered by assorted aerosols at the various angles. The bench top setup was constructed of a Helium Neon laser, as the light source, with a Photo Multiplier Tube (PMT) mounted on a rotational stage, as a receiver of the scattered light. A glass control volume (125cm³) was mounted in the path of the laser to contain the aerosol. To evaluate the operation of the laser scattering setup, experiments were performed using two test
aerosols of known particle size and optical properties. The collected laser scattering results of the calibration aerosols were then compared to the Mie scattering theory. The Mie theory fits the size range expected from smoke and has been shown to accurately predict the scattering from aerosols. Comparisons of the calibration tests, to the results calculated using the Mie theory indicated that the scattering setup was working properly. Smoke from a heptane pool fire, and flaming polyurethane was then introduced into the glass control volume. Measurements made over a period of time to obtain scattering changes due to smoke aging. The results were analyzed to determine changes to smoke particulate size over time. The Mie theory was adjusted using a lognormal distribution to generate the curves expected from a polydisperse aerosol, typical of smoke. The collected data was examined using a combination of the Mie theory and various particle-sizing techniques including dissymmetry ratio and polarization ratio to examine the changes to the laser scattering over time.

The overall changes in scattering over time indicate that particle transformations are occurring due to smoke aging. The dissymmetry ratio and polarization ratio both indicate changes to the particle size. The number concentration supports the findings of particle growth with decreases in number concentration during the period of growth. The scattering indicates that the larger particles depart the control volume possibly due to deposition or sedimentation. The agglomeration and deposition of the larger particles decreases the number concentration and no further agglomeration is seen. The experimental data supports the general trend produced from the calculations.
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NOMENCLATURE

A  Amplitude[mW] or Area [m2]
B  collision frequency function [#/s]
c  speed of light [m/s]
C  scattering cross section [m²]
D  distance [m]
Dg  geometric mean number diameter [m]
d  diameter [nm]
dd  droplet diameter [nm]
dp  particle diameter [nm]
dm  molecule diameter [nm]
dc  volume equivalent diameter of aggregate [nm]
Df  fractal or Hausdorff dimension [-]
E  electric field [Newtons/Coulomb]
fv  soot volume fraction [-]
g  asymmetry factor [-]
G  geometric cross section [m²]
H  magnetic field [coulombs/ms]
i  Mie Intensity coefficient [-]
I  light Intensity [W/m²]
Ix  moment of Inertia [g/nm²]
k  wave number, 2π/λ [nm⁻¹]
kext  extinction coefficient [m⁻¹]
km  specific extinction coefficient[m²/g]
K  Boltzmann Constant [1.38 × 10⁻²³ Joules/Kelvin]
L  Length [m]
m  refractive index of soot, [n + ik] or mass [g]
n  real part of refractive index of soot [-]
N_A  Avagadro's number [6.02x10²³ mol⁻¹]
N_p  number of primary particles per unit volume [#/m³]
N_t  total number concentration [#/m³]
N  number concentration [#/m³]
N_f  final number concentration [#/m³]
N_o  initial number concentration [#/m³]
N_g  geometric mean of number of primary particles per aggregate [#]
O_u  percent obscuration [%/m]
O_d  percent obscuration at distance d [%]
P  pressure [psig]
P_n  Legendre Polynomials
Q  volumetric optical cross section [nm]
Q_ext  extinction efficiency [-]
Q_sca  scattering efficiency [-]
r  radius [nm]
rc  electric resistivity [Nm²/coulomb³]
ri  distance of each primary particle from the center of mass of aggregate [nm]
\( R_g \) radius of gyration of an aggregate [nm]
\( R \) ideal gas constant [8.3145 Joules per mole Kelvin]
\( S_1 \) Complex scattering amplitude [-]
\( S_2 \) Complex scattering amplitude [-]
\( T \) temperature [C]
\( t \) time [s]
\( V \) Volume [cm\(^3\)]
\( V_s \) scattering volume [mm\(^3\)]
\( v \) velocity [m/s]
\( x \) size parameter \([2\pi r/\lambda]\) or particle size [nm]

Greek
\( \varepsilon \) permittivity \([\text{Coulomb}^2/\text{Newton-m}^2]\)
\( \eta \) viscosity of the liquid [Pascal second]
\( \theta \) scattering angle from forward direction [degrees]
\( \kappa \) imaginary part of refractive index of soot [-]
\( \lambda \) wavelength of light [nm]
\( \gamma \) electrical permittivity \([\text{coulombs}^2/\text{Nm}^2]\)
\( \nu \) kinematic viscosity [Pascal second]
\( \rho \) density [g/cm\(^3\)]
\( \rho_s \) soot density [g/cm\(^3\)]
\( \rho_p \) particle density [g/cm\(^3\)]
\( \rho_m \) molecular density \([2.687 \times 10^{25} \text{ m}^{-3}]\)
\( \sigma_g \) geometric standard deviation (GSD) [-]
\( \tau \) monochromatic transmittance [-]
\( \phi \) azimuth angle [degrees]
\( \pi \) Pie (approximately 3.14159) [-]
\( \mu \) magnetic permeability \([\text{Ns}^2/\text{coulomb}^2]\)
\( \Gamma \) coagulation coefficient [cm\(^3\)/s]

Subscripts
\( p \) distance
\( abs \) absorption
\( sca \) scattering
\( ext \) extinction
\( e \) emitted
\( pp \) scattering for vertically (horizontally) polarized incident and scattering directions, either vv or hh
\( s \) soot
\( f \) fractal
\( g \) gyration or geometric
\( p \) primary
\( inf \) ambient condition
\( t \) total
\( r \) rate
\( o \) intial
m  mass

Abbreviations
MMD  Mass Median Diameter
CMD  Count Median Diameter
GSD  Geometric Standard Deviation
1.0 DOCUMENT ORGANIZATION

The text of this document is divided into two sections. The first section (Chapters 1-4) gives an overview of the work completed and its contribution to fire research and the field of fire protection engineering. This section sets the context for the second section, a series of appendices that constitute the core of this thesis. Appendix A entitled A STUDY OF SMOKE AGING EXAMINING CHANGES IN SMOKE PARTICULATE SIZE, is a paper that describes the experimental setup of a laser light scattering system. The laser scattering system was used to collect experimental data to support calculations outlined in the paper that compute the agglomeration process. The paper presents the results and describes the analysis of the data collected by the scattering system, including adjustments to the Mie theory to account for the polydisperse nature of smoke aerosols. Appendix B through Q gives additional information, relevant to this MS Thesis and Appendix A.

1.1 Guide to Appendices

Appendix A: A STUDY OF SMOKE AGING, EXAMINING CHANGES IN SMOKE PARTICULATE SIZE

This appendix is a paper describing the laser light scattering setup and theoretical calculation used to measure particle size changes over time. The paper presents calculation conducted to replicate the agglomeration process. The collected laser scattering of various aerosols, including calibration aerosols and fire-generated aerosols, follows the calculations. The measurements were made at two linear polarizations, VV and HH, and scattering angles ranging from 20 to 155 degrees using a laser source with a wavelength of 632.8 nm. The aerosols were then compared to the Mie scattering theory. The theory was adjusted using a lognormal distribution to generate curves expected from polydisperse aerosols typical of smoke. The collected data was examined using a combination of the Mie theory and various techniques including dissymmetry ratio and polarization ratio to examine changes in laser scattering over time, specifically looking at particle size changes. The changes to the particle size and aerosol number concentration were used to support the calculations conducted.

Appendix B LITERATURE REVIEW AND BACKGROUND ON SMOKE

This appendix describes smoke particulates and presents information on assorted smoke properties. The appendix includes sections on smoke growth, structure, and optical properties. The appendix defines particle size and distribution, concluding with sections on the sedimentation, deposition, thermophoresis, and agglomeration of smoke particulate.

Appendix C SMOKE DETECTOR REVIEW

This appendix explains the inner workings of smoke detectors, specifically ionization smoke detectors and photoelectric smoke detectors. The appendix identifies
the need for testing of the smoke aging process, describing specific cases of recorded detector activation in both full-scale experimental tests and bench top tests. The appendix ends with testing that has occurred to examine specific aspects of detector sensitivity to variables, such as particle size.

Appendix D UL 217
This appendix describes the Underwriters Laboratories standard smoke detector test UL217, including the obscuration limits set by the test procedure. The UL standard was used as a starting point for the calculations conducted in Appendix A. The appendix includes the Bouguer-Lambert’s law as well as test methods for measuring the obscuration with optical density meters (ODM) and the various parameters associated with obscuration measurements.

Appendix E PARTICLE SIZING METHODS
This appendix describes the numerous particle sizing techniques and some of the assumptions and limitations of each technique. The appendix concludes with why laser light scattering was chosen as the particle sizing method.

Appendix F LASER LIGHT SCATTERING THEORY
This appendix explains the concept behind laser light scattering theories and some of the assumptions and limitations of each theory. This appendix also contains a brief background on the electromagnetic theory including the Maxwell equations. The appendix indicates the relationship between the electromagnetic theory and the Mie scattering theory that was chosen for analysis of the light scattering results.

Appendix G MIE THEORY
This appendix includes the equations used for calculating the Mie coefficients of the scattering theory used to find the scattering intensity. The appendix outlines important values and variables, relating the Mie scattering theory to the electromagnetic theory.

Appendix H FORTRAN PROGRAM
This appendix presents the FORTRAN program used to calculate the Mie coefficients from the Mie theory. The Mie coefficients are used to find the scattering intensity of a sphere at a given angle. Sections include validation of the FORTRAN program.

Appendix I MODIFICATIONS TO THE MIE THEORY
This appendix outlines the adjustments made to the Mie theory. The adjustments include compensation for the assumption of a solid spherical particle made by the theory, introducing the fractal equation. The appendix also introduces an adjustment to the theory to compensate for the polydisperse distribution of smoke aerosols.

Appendix J METHODOLOGY AND EXPERIMENTAL SETUP
This appendix provides a methodology and experimental set up constructed to collect light scattering for the purpose of measuring size changes. A description of each
component used in the experimental set up and it influence on the collection of scattered light is included.

Appendix K AEROSOL GENERATION
This appendix provides information pertaining to the generation and delivery of a calibration aerosol. A description of each component and its role in producing a consistent monodisperse aerosol is included.

Appendix L PROCEDURE
This appendix provides a procedure to maintain consistency through the calibration tests and smoke aerosol testing.

Appendix M PSL CALIBRATION
This appendix provides the results from the calibration tests, and analysis of the calibration results. The analysis of the calibration aerosol scattering resulted in a calibration constant that adjust the scattering signal for changes due to the polarization of light as well as errors in the scattering set up. The calibration testing also established the sensitivity and reliability of the apparatus.

Appendix N DATA RESULTS AND ANALYSIS
This appendix provides the data results and analysis from smoke samples taken from flaming polyurethane and heptane pool fires. The laser scattering results were examined by looking at the overall changes in the scattering curve over time, the polarization ratio, and the dissymmetry ratio. These were related to the number concentration and compared to calculations conducted to replicate the agglomeration process and support the experimental findings.

Additional material supporting the thesis can be found in the attached CD including raw data collected from the laser scattering apparatus.

2.0 THESIS OVERVIEW
There is some ambiguity in the ability to detect aged smoke. The purpose of this study is to prove or disprove if particle size increases, due to Brownian motion in the ceiling jet. This study will focus on the particulates produced by the combustion process and the particulate’s change in size. A better understanding of the factors that influence detection as well as a better understanding of the particulate aging process will increase the ability to detect fire in it’s incipient stage.

Smoke detectors activate when they identify one, or a combination of, fire properties, or signatures. The four primary signatures for fire detection are convective heat, flame radiation, gas emissions, and smoke. Photoelectric and ionization smoke detectors are designed to respond to a single signature, smoke. Photoelectric detectors use
a beam of light to sense the presence of smoke while ionization detectors use ions created from the decay of a radioactive element.

The increase in the size of smoke particles due to smoke agglomeration has been depicted as the cause for a delayed detection in ionization smoke detectors. Agglomeration is defined as the action or process of collecting in a mass, heap, or cluster of usually distinct elements. This is not to be confused with coagulation. Coagulation occurs when two particles collide and form a single particle whose volume is the sum of the volumes of the original two particles. Agglomerates by definition can be dismantled into the units from which it is made. Although both will be referred to within this thesis it should be noted that there is a distinct difference. Many individuals have interpreted work in the area of smoke detection to support the idea that the increase in the size of smoke particles due to smoke agglomeration is the cause for a delayed detection in ionization smoke detectors. One topic that has remained unclear, however, is weather smoke agglomeration continues to occur in the ceiling jet. The purpose of this study is to examine laser light scattering from poly- and monodisperse aerosols, as a function of time. Comparing the laser light scattering results collected over time to the calculated theoretical results of the Mie theory will indicate changes in particle size due to agglomeration. The changes in particle size and changes in number concentration collected during the tests will then be compared to calculations conducted to replicate the agglomeration process.

The test set-up consists of an optical table. The table established a flat vibration isolated surface to conduct the laser measurements, and as a result defined the scattering plane. The scattering plane is defined to be the plane in which the incident and scattering beams lie: for our experiments this is a horizontal plane. The laser was a Helium Neon (HeNe) Laser with a linear polarization ratio greater than 500:1 and operates at a wavelength of 633 nm. Linear polarization is when the intensity of the electric field vector is constant, and its direction of oscillation is constant. In order to measure size changes using the Mie scattering theory linear polarization of the laser light is required. The laser beam was also modulated to a frequency by passing it through a light chopper attached to a lock-in amplifier. Incorporating an optical chopper and lock-in amplifier permits rejection of all but the laser wavelength, or laser light scattered by the aerosol of interest. The beam then passes through a polarization rotator to control the direction of
polarization of the beam. The beam then becomes focused on the center of the control volume using a lens. The light scattering of the laser beam appears as a red line of light with a few bright spots arising from the larger particulate. The scattered laser light is collected by a receiver at angles ranging from 20 to 155 degrees for both vertically (VV) and horizontally (HH) polarized light. The receiver is made up of a number of components including a Photo Multiplier Tube (PMT) mounted on a rotational stage. The rotational stage moves the receiving optics along an arc path ranging from 20 degrees to 155 degrees with a diameter of 0.508 meters (1 ft 8 in.). A variable iris diaphragm in front of the collecting lens defines the solid angle of scattered light the detector receives. The detectors solid angle limits both the smallest size that can be measured and the accuracy of the particle size measurement. A collecting lens, a dichroic sheet polarizer, a pinhole, and a PMT with a narrow band filter follows the iris diaphragm. A slight reduction of the intensity of the incident beam occurs at all elements along the optical train. The PMT collects the signal that is then sent to a lock-in amplifier that is attached to the chopper. Once the signal is amplified it is recorded by the data acquisition system and saved for post processing and analysis.

The reliability of the system was established by separately testing two sets of monodisperse polystyrene latex (PSL) calibration spheres. The first aerosol to be tested was comprised of 500 nm PSL spheres. Introducing the PSL spheres into the glass scattering volume and collecting the light scattered at various angles concludes the calibration experiments. The collected data is then processed correcting for the chopper amplification, and the sin dependence due to the changing control volume size as the rotational stage moves from side to side. This can be corrected for by simply multiplying the detector signal by sin of the angle \((\sin(\theta))\) the scattered light was collected at. A calibration function is determined by normalizing the detected signal by the theoretical values for the given sphere size. The calibration function corrects for small error effects produced by each component of the optical train.

Once the monodisperse aerosol measurements were recorded and analyzed, and the test setup demonstrated the capability to accurately measure particle size, smoke was produced and tested. Smoke produced from a flaming fire of polyurethane and a heptane pool fire was examined. Polyurethane blocks \((1\text{ in}^3)\) were ignited in a small pan to produce smoke while heptane smoke was produced with a 100% by volume heptane pool
fire. The smoke was collected and contained within the glass control volume and left to age 15 minutes. Laser light scattering was collected throughout the 15 minutes to examine changes to the smoke particles. The scattering signal was collected and saved for analysis.

The scattering data was processed and examined for changes due to smoke aging, specifically changes in particulate size. The analysis included examination of the overall scattering curve shape, and comparisons to the Mie theory using the polarization ratio and dissymmetry ratio sizing techniques to find changes in particle size. The changes in particle size were then compared to number concentration measurements taken. The results were then compared to calculations reproducing the agglomeration process. The Mie theory was adjusted to compensate for the polydisperse nature of smoke using a log-normal distribution.

3.0 CONCLUSIONS

- As demonstrated by previous work done by Mullholand and Bukowski particle growth must be significant to effect detector activation. Calculations using UL 217 imply that the increase in particle size needed to significantly effect detector activation and reverse the alarm sensitivity between ionization detectors and photoelectric detectors would result in a significant decrease in number concentration if the mass were constant.

- Calculations of the Brownian motion shows that particle motion decreases forming and asymptote at 500nm. The calculations form a relationship between temperature, particle size, and number concentration that gives stagnation points were agglomeration due to Brownian motion will not occur if the temperature it to low, the particle size is to large, or the number concentration is to low.

- By examining the scattering curve created by smoke particles over a range of time steps, changes to the curve shape imply an ongoing aging process where increases in particle size are taking place.

- Using the Mie theory in conjunction with particle sizing techniques such as the polarization ratio and dissymmetry ratio, reveal a change in particle size. The particles are shown to grow larger over time, this is also supported by the
obscuration measurements demonstrating a decrease in number concentration supporting calculation conducted to replicate the agglomeration process.

- Smoke detection is dependent on a number of variables that form a web of dependence upon one another. These include temperature, charge, size, color, velocity, and refractive index. Size changes significant enough to effect detector activation are shown to occur. The large particles, however, are produced during a specific stage of smoke aging when the conditions are right for agglomeration, possibly temperature dependant. The larger particles then depart from the observed volume and the concentration of particles returns to the smaller size range.

### 3.1 Significant Contributions

Light scattering is fascinating because of its diagnostic of particle size and morphology, which relates to detector activation. The paper presents the results of smoke aging tests, calculations replicating the agglomeration process, and the design of a model for predicting the laser scattering from a polydisperse aerosol. The results of the laser scattering tests were compared to the theoretical results of the adjusted Mie theory. Using particle-sizing techniques such as the polarization ratio and dissymmetry ratio, the results indicated a change in particle size over time. Extinction measurements validated the size changes seen by confirming a drop in particle number concentration confirming trends produced by calculations replicating the agglomeration process. The test results also supported other trends replicated by the calculations conducted depicting the process of agglomeration. These results represent a piece of the overall effects that occur in the smoke plume and ceiling jet. Smoke detector activation is dependent on a number of smoke properties such as smoke velocity, smoke temperature, optical density, particle density, condensation, particle size, particle shape, number concentration, smoke distributions, smoke color, electrical charge, and refractive index. Many of these properties form a matrix of dependence upon one another complicating the significance one property has over another as it relates to detector activation.
3.2 Recommendations for Future Research

Because of the limited time and resources associated with any thesis there remains numerous unanswered questions and concepts that deserve exploration. This section highlights some of the many questions that stemmed from this paper.

A complete calibration and validation of the adjusted theory as it applies to polydisperse aerosols is needed. The collected scattering from a mixture of PSL sphere sizes, creating a polydisperse aerosol, could be tested. The scattering results can then be compared to the ensemble-averaged results of the Mie theory to provide a more reasonable result that can be expected from smoke. The results can then be calibrated and validated for a polydisperse aerosol.

Testing of various smoke properties and their influence on detection should be conducted. One such property is the electric charge the particles carry. A report by Cable and Sherman stated: “If smoke particles have already agglomerated with other smoke particles and become large, and possibly neutralized any charge polarities, they would be less prone to attach to an ionized air molecule in an ionized chamber.” However, there is no supporting experimental data in the paper to support this claim. Along similar lines, examining the affect of humidity, or condensation around particles should further be tested. The scattering measurements from steam can also aid in the characterization of this nuisance alarm. The testing of additional smokes, and possible nuisance aerosols, is a logical next step. Eight different UL/EN style test fires should be tested in the bench top light scattering apparatus. These standard test fires are used in the certification of smoke detectors. They include a flaming liquid hydrocarbon pool fire, a flaming wood crib fire, a flaming polyurethane foam fire, a flaming paper fire, a smoldering wood fire, a smoldering polyurethane foam fire, a smoldering paper fire, and a smoldering cotton wick fire. The fires represent the corresponding standardized test in fuel configuration.

Once the bench top tests are complete the scattering system should be relocated into a full-scale configuration. At this point, full scale testing would occur to measure laser scattering, temperature, optical density, and detector activation. These full-scale tests would also be subject to the affects of fire location and the aerosols path of travel.

A more robust model for calculating the Mie coefficients for scattering of a polydisperse aerosol can be created. The model developed would be similar to the one introduced in this thesis, however, a variety of theories, such as Rayleigh, Mie, RDG,
RDG-FA Geometric optics, could be implemented. The results of the theories can then be multiplied by the distribution calculated. Distributions can include normal, log-normal, Junge, and exponential. The inputs would include, size, wavelength, refractive index of the aerosol, refractive index of the medium, GSD, average mean value, number concentration and particle size. This would create a very robust and useful tool for aerosol studies.

As a result of any work done examining smoke, it is the hope that the final outcome will be a better ability to detect the presence of a fire, providing life safety as well as protection to property and continued operation.
APPENDIX A  A STUDY OF SMOKE AGING EXAMINING CHANGES IN SMOKE PARTICULATE SIZE
ABSTRACT

The size of a soot particle has an effect on smoke detector alarm activation. It is the purpose of this paper to identify changes to soot particle size and examine if those size changes effect smoke detector alarm times in the ceiling jet. Changes in particle size has been attributed to delays in detector activation, however, little evidence exists to support that particle size changes occur in the ceiling jet where detector activation occurs. This paper presents the results from laser scattering experiments and calculations conducted to support and validate the experimental findings. The laser scattering from various aerosols was collected, over time, to examine changes in particle size due to agglomeration in the smoke aging process. The laser scattering measurements were made at two linear polarizations, vertical (VV) and horizontal (HH), and scattering angles ranging from 20 to 155 degrees. A laser with a wavelength of 632.8 nm was used as a light source. The aerosol laser scattering results were then compared to the results from the Mie scattering theory. The Mie scattering theory was adjusted using a lognormal distribution to generate theoretical light scattering curves expected from a polydisperse aerosol typical of smoke. The collected data was examined using a combination of the Mie theory with various particle sizing techniques, including dissymmetry ratio and polarization ratio, to look for changes in laser scattering indicating changes in particle size.
INTRODUCTION

There is some ambiguity in the ability to detect aged smoke. The increasing size of smoke particles due to smoke agglomeration has been depicted as the cause for delayed detection when using ionization smoke detectors [1]. One topic that has remained unclear, however, is whether smoke agglomeration continues to occur in the ceiling jet. The purpose of this study was to examine if changes in smoke detector activation times are the result of smoke agglomeration. Examining the laser light scattering from poly- and monodisperse aerosols, as a function of time, and comparing the laser light scattering results to theoretical results would indicated if a change in particle size due to Brownian motion had occurred. Brownian motion in the governing phenomenon resulting in agglomeration for particles under 1000 nm in size [2]. This study focused on the particulates produced by the combustion process and the particulate’s aging process. A better understanding of the factors that influence detection as well as an increased understanding of a particulates aging process will increase the ability to detect fire at its incipient stage.

Detector activation has been documented in numerous tests ranging, from full-scale house burns to bench top testing [3, 4, 5]. Detector response time is often measured from the time of ignition to detector activation, however, when two detectors of differing modes (i.e. photoelectric and ionization) are placed side-by-side, the difference between the two detectors activation times can be compared. This can create a misconception of which detector is more suitable for egress and life safety, if a proper analysis is not conducted. The differences between activation times for ionization and photoelectric smoke detectors has been shown to vary with smoke source and distance to that source [6]. Ionization detectors contain an ionization chamber, which contains a source of alpha radiation positioned between two electrodes [7]. The alpha radiation source emits positively charged particles. These ions, which are charged gas molecules, are then attracted to the oppositely charged electrodes on either side of the chamber and produce a small current flow across the chamber. Interference of this flow of ionized molecules causes a reduction in current leading to alarm activation [7]. Photoelectric detectors work on the principle of light scattering. The light source and the photocell are at an angle to each other. Under normal circumstances the photocell will not receive laser light from the light source. In fire conditions, smoke enters into the chamber and scatters the light, some
of which strikes the photocell increasing the alarm voltage [7]. When the alarm threshold is reached, the alarm is triggered.

Tests have been conducted that demonstrate that ionization detectors respond slower than photoelectric detectors in certain situations and vice versa, attributing these differences to various smoke characteristics such as velocity, number concentration, neutralization of the charged particles, and temperature [1, 8 - 10]. The smoke detector methodologies, ionization and photoelectric, react differently to the characteristics of smoke due to their individual methods of operation and the response will potentially vary with the smoke aging process. Smoke aging, as defined in this paper, encompasses all the changes smoke undergoes after leaving the flame front. The delay in detection may not be due solely to the larger particle size associated with smoke aging. The time of alarm is more likely due to a combination of soot properties that change during smoke aging and is not limited to only changes in size but includes such changes as temperature, condensation, concentration, etc. A more impartial and scientific characterization of detector activation may use obscuration, particle size, and smoke velocity over time to better describe changes to the atmosphere and its tenability.

Smoke detector activation is affected by various smoke characteristics. There is a void in distinguishing the significance each of these characteristics has on detector activation in relation to one another. Significant work has been completed on individual variables and their effect on detection. Mulholland has reported results for detector sensitivity to monomer-sized particles, as shown in Figure 1 [11]. Bukowski has also examined various detectors sensitivity to particle size, Figure 2 [12]. However, the graphs are quite different, due to the fact that the particle mass concentration was kept constant in Figure 2 while the number concentration remains constant in Figure 1. The graphs of detector sensitivity to particle size produced by Mulholland and Bukowski demonstrate that ionization and photoelectric detectors, react quite differently to particle size and significant particle growth is needed to effect sensitivity enough to factor into substantial changes in alarm time.

The purpose of this study is to determine if changes in particle size is significant once smoke has traveled from the fire plume. A single variable, smoke particulate, test was designed to examine smoke agglomeration though the process of Brownian motion. The results will demonstrate whether Brownian motion continues to occur in the field far
from the fire influencing particle size as it approaches the smoke detector. The results will help define the significance of agglomeration, through Brownian motion, on detector activation.

**SMOKE AGING AND AGGLOMERATION**

Smoke consists of both solid and liquid particulates, as well as gaseous products [13]. In the combustion process, nucleation is the initial stage of smoke growth where elementary particles are produced inside the flame [13]. Elementary particles then agglomerate forming small clusters [14]. The clusters continue to agglomerate with cluster-cluster collisions until the particles pass through the soot burnout zone, where the particle size decreases as the number concentration increases [15]. If the soot is not consumed in the oxidation region and escapes the flame tip to the overfire region, the particulate may travel out of the flame forming a plume. It is within the overfire region that smoke particles may begin to “age”.

Soot particles are constructed of nearly constant primary particle diameters, with a large variation in the number of primary particles per aggregate [13]. Smoke particles can form various structures with the aggregated primary particles and, although the soot structure is complex, recent work shows that it can be characterized as mass fractal-like in nature [16]. The number concentration of particles in the over-fire region is initially very high, allowing the particles to collide and agglomerate. However, the particles travel with the plume that is entraining air, cooling and therefore rapidly decreasing the particle number concentration [17]. It is after this stage of smoke transport in the fire plume that smoke reaches the ceiling forming a ceiling jet. It is generally in the ceiling jet where point source smoke detector activation would occur and is the stage of smoke transport that is of interest in this paper.

This study examines the characteristics of smoke over time in order to distinguish particle morphology, especially changes to particle size. Particles can change size due to either coagulation or agglomeration. Coagulation is when two particles collide and form a single particle whose volume is the sum of the volumes of the two original particles. Soot particles have been shown to agglomerate rather than coagulate during the smoke aging process [18]. Agglomeration is the collection of particles in a cluster of usually distinct elements [18]. Smoke agglomeration is caused by the collision of smoke particulates due
to either Brownian motion, hydrodynamic, electrical, acoustic, or gravitational forces [18].

This paper focuses of agglomeration due to Brownian motion. During Brownian motion the soot particle is struck by surrounding molecules. Since the impacts of the molecules on the particle are asymmetric, the particles will drift. This movement of a particle is known as Brownian motion. The agglomeration process due to Brownian motion is dependant on number concentrations, temperature, and time. The number concentration is directly related to the distance a particle must travel before colliding with a neighboring particle and agglomerating. The higher the concentration the higher the rate of agglomeration. The temperature influences molecular movement. The higher the temperature the faster a molecule will travel. This fast molecular movement increases Brownian motion increasing the rate of agglomeration. The amount of agglomeration increases with time, often confused with distance when referring to detectors, however, it is not the distance but the amount of transport time that affects Brownian motion. Using calculations and bounding the upper and lower limits of temperature, number concentration, and time will demonstrate the conditions needed for agglomeration due to Brownian motion. By establishing the limits needed to sustain the agglomeration process with calculations and supporting the calculations with experimental data, investigating changes to particle size and number concentration, a better understanding of the process can be extracted.

Brownian motion in gases with a high particle concentration can result in many particle collisions and the formation of larger particles. The agglomeration of particles rapidly decreases the number concentration. In the initial region of a fire plume, a high number concentration of particles, N, with a fixed volume, V, and soot density, $\rho$, are expected. The mass of the total particle concentration can be calculated via Eq 1.

$$M_{\text{soot}} = N\rho \left(\frac{4}{3}\pi\right)\left(\frac{d}{2}\right)^3 = \frac{1}{6}\pi N\rho d^3$$  

Eq. 1

where $M_{\text{soot}}$ is the total mass of the soot concentration, d is the diameter of each particle and the volume $V = 4\pi r^3/3 = \pi d^3/6$.

Consider a fixed volume of particles, which are colliding and agglomerating. Since the mass (or density) of particles remains constant, $(Nd^3)_{\text{initial}} = (Nd^3)_{\text{final}}$. This
equation demonstrates that if particle size were to double, the particle number concentration must decrease by a factor of eight. Therefore particle agglomeration, with the combined effect of entrainment and deposition would quickly decrease the number concentration as the particles travel within the smoke plume. Agglomeration is significant in the plume of a fire lowering the number concentration [19]. However, in this stage of smoke transport it has no effect on spot type smoke detector activation.

The process of agglomeration can be further illustrated by using the obscuration limits at which all smoke detectors must activate. The values given by UL 217 represent the minimum and maximum obscuration limits at which a smoke detector must activate [5]. These obscuration limits are typically given as optical density per unit length. The obscuration limits for detector activation and basic smoke properties allow the smoke particle number concentration to be calculated at typical detector activation obscurations. Knowing the minimum and maximum number concentrations needed to activate a spot type smoke detector will assist in determining whether agglomeration due to Brownian motion can occur at the obscuration levels needed for detection. Table 1 contains the minimum and maximum smoke obscuration limits at which detector activation must occur as prescribed by UL 217 [5].

Table 1: Visible Smoke Obscuration Limits taken from UL 217.

<table>
<thead>
<tr>
<th></th>
<th>%/ft (%/m)</th>
<th>OD/ft (OD/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>4.0 (12.5)</td>
<td>0.0177 (0.0581)</td>
</tr>
<tr>
<td>Min</td>
<td>0.5 (1.6)</td>
<td>0.0022 (0.0072)</td>
</tr>
</tbody>
</table>

The extinction coefficient (K) can be calculated from the optical density limits set in Table 1. The extinction coefficient is the product of the extinction coefficient per unit mass, K_m, and the mass concentration of the smoke aerosol (m), as shown in Eq. 2.

\[ K = K_m m \] Eq. 2

K_m values of 7.6 m^2/g and 4.4 m^2/g for flaming and smoldering sources, respectively, have been found to be a reasonable estimate of the extinction coefficient per unit mass [9]. The mass concentration can be calculated using the extinction coefficient per unit mass for flaming and smoldering fires and the minimum and maximum obscuration limits. Assuming an average particle diameter of 500 nm and taking the
density to be similar to graphite (2.0 g/cm³) the volume and weight of each particle can be calculated [21]. Dividing the mass concentrations for the obscuration limits by the weight of each average particle gives an expected number concentration for flaming and smoldering fires at the UL 217 prescribed obscuration levels.

Table 1: Number concentrations from UL217 prescribed obscuration levels assuming ρ = 2.0 g/cm³ and d = 500nm

<table>
<thead>
<tr>
<th>Source</th>
<th>Km (m²/g)</th>
<th>Obscuration UL217 (OD/m)</th>
<th>Mass concentration (g/m³)</th>
<th>Number concentration (particles/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flaming Source</td>
<td>7.6</td>
<td>0.0072</td>
<td>0.002179</td>
<td>1.7 x 10¹⁰</td>
</tr>
<tr>
<td>Smoldering Source</td>
<td>4.4</td>
<td>0.0072</td>
<td>0.003764</td>
<td>2.9 x 10¹⁰</td>
</tr>
<tr>
<td>Flaming Source</td>
<td>7.6</td>
<td>0.0581</td>
<td>0.017583</td>
<td>1.34 x 10¹¹</td>
</tr>
<tr>
<td>Smoldering Source</td>
<td>4.4</td>
<td>0.0581</td>
<td>0.030371</td>
<td>2.3 x 10¹¹</td>
</tr>
</tbody>
</table>

Once the number concentration associated with each obscuration level and mode of burning was established. The average distance between each particle could be determined. The distance between each particle will determine the temperature and time needed for each particle to travel and collide into one another. Using the total number concentration and the area the soot occupies the linear distance a particle must travel before striking another particle can be calculated.

Table 2: Particle travel distance before possible contact with another particle.

<table>
<thead>
<tr>
<th>Source</th>
<th>Number concentration (particles/m³)</th>
<th>Total volume occupied by smoke (m³)</th>
<th>% of volume occupied by particles</th>
<th>Volume occupied per particle (m³)</th>
<th>Distance traveled (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flaming Source</td>
<td>1.7 x 10¹⁰</td>
<td>1.118 x 10⁻⁹</td>
<td>1.118 x 10⁻⁷</td>
<td>5.88 x 10⁻¹¹</td>
<td>3.89 x 10⁻⁴</td>
</tr>
<tr>
<td>Smoldering Source</td>
<td>2.9 x 10¹⁰</td>
<td>1.90 x 10⁻⁹</td>
<td>1.90 x 10⁻⁷</td>
<td>3.45 x 10⁻¹¹</td>
<td>3.26 x 10⁻⁴</td>
</tr>
<tr>
<td>Flaming Source</td>
<td>1.34 x 10¹¹</td>
<td>8.76 x 10⁻⁸</td>
<td>8.76 x 10⁻⁷</td>
<td>7.46 x 10⁻¹²</td>
<td>1.95 x 10⁻⁴</td>
</tr>
<tr>
<td>Smoldering Source</td>
<td>2.3 x 10¹¹</td>
<td>1.50 x 10⁻⁸</td>
<td>1.50 x 10⁻⁷</td>
<td>4.35 x 10⁻¹²</td>
<td>1.63 x 10⁻⁴</td>
</tr>
</tbody>
</table>
The distance a particle travels is dependent on the force a molecule striking the soot has. The temperature directly affects the rate and force at which a molecule strikes a particle. As the temperature rises, a soot particle is more likely to be struck by surrounding molecules due to the greater movement of those molecules. The average displacement of a particle, \( r^2 \), making a random walk can be calculated using Eq. 3.

\[
\langle x^2 \rangle_{\text{ave}} = \left( \frac{RT}{3' r \eta N_A} \right) t
\]

Equation 3

where \( x^2 \) is the motion of a particle, \( R \) is the Ideal gas constant, \( T \) is the temperature of the hot gases, \( r \) is the particle radius, \( \eta \) is the viscosity, \( N_A \) is Avagadro’s number, and \( t \) is time. Figure 4 illustrates the effect temperature has on the movement of particulates. The larger movements occur for small particles.

The calculations demonstrate the effect particle concentration; particle size, time, and temperature have on the agglomeration process. The decline in concentration due to agglomeration, as well as decreases in temperature and number concentration, due to entrainment, all play a role in slowing or stopping the agglomeration process. The calculations indicate that given enough time the particles will travel and agglomerate. The smaller the particle and higher the concentration needed to obtain the UL 217 obscuration for smoke detector activation and faster the particle will move and agglomerate. Through obscuration measurements and light scattering measurement the changes in particle size and number concentration due to agglomeration will be collected and compared to the calculations. The light scattering will be analyzed using a combination of the Mie theory with particle sizing techniques.

**MIE THEORY**

Laser light scattering is well documented and a variety of theories exist containing various assumptions including, particle size, and particle shape. Light scattering was chosen to size the soot particle because of it non-intrusive nature and its use in characterizing soot particulate [22]. There are three basic size regions that define which theory will apply [23]. The regions are defined by the ratio of particle diameter, \( d \), to the wavelength, \( \lambda \), of the incident light. Mie scattering was assumed because it lies in the medium size range (60 nm to 2630 nm for a 633nm wavelength laser) well with in the soot size range and the theory is well documented [9]. The Mie theory assumes spherical
monodisperse particles that made it ideal for the calibration procedure used in this study [24]. The equations for calculating the scattering intensity using the Mie coefficients calculated from the Mie theory are listed below in equations 4 and 5. The intensity, $I_s$, in W/m$^2$ is calculated using equation 4 or 5, where $I_o$ is the incident light. The calculated intensity value in equation 4 is the amount of scattered laser light per particle, therefore the concentration of particles in the control volume must be considered when calculating the total intensity as seen in equation 5.

$$I_s = I_o \frac{\lambda^2}{8\pi^2 l^2} (i_\perp, i_\parallel)$$  \text{Equation 4} \\

$$I_{s\text{total}} = I_o \frac{\lambda^2 N_0 V_s}{8\pi^2 l^2} (i_\perp, i_\parallel)$$  \text{Equation 5} \\

where

$V_s$ is the scattering volume

$N_0$ is the concentration

$l$ is the length from the scatterer to the receiver

$i$ is the Mie coefficient either parallel or perpendicular

$I_o$ is the incident source laser intensity

$I_s$ is the scattered laser intensity.

The Mie theory inputs include the wavelength of the laser light, which is a known 632.8 nm. The refractive index of the median, assumed to be 1.00 even though the medium could be Air, CO$_2$, CO, or a mixture of all three. A rough sensitivity analysis was conducted to see differences due to a changing refractive index of the medium and little change was noted. The refractive index of the particle is the third variable and assumed to be, 1.75 or 1.57 to provide a reasonable range for soot values [2, 25]. The final input is the variable of particle size.

The Mie coefficient ($i$) for parallel or perpendicular scattering is calculated from the Mie theory. Calculating the Mie coefficients using the Mie theory can be quite complex. The analysis was conducted using the method developed by Bohren and Huffman [26]. This method was shown to accurately produce the Mie scattering coefficients through a number of validation exercises [27].
EXPERIMENTAL SET-UP

As demonstrated in the previous section, global considerations indicate that the dilute nature of fire plumes reduces the occurrence of soot agglomeration in the far field of fire, where smoke detector actuation occurs. There are a number of methods used for sizing particulates, including physical processes, imaging, and light scattering. Light scattering was chosen for our sizing technique because it is un-intrusive, and its use has been well documented [28]. Figure 5 is a diagram of the test apparatus. The test set-up consisted of an optical table, which established a flat, vibration isolated surface to conduct the laser scattering measurements and a defined horizontal scattering plane. The light source was a Helium Neon (HeNe) laser with a linear polarization ratio greater than 500:1, operating at a wavelength of approximately 633 nm. Passing the laser beam through a light chopper attached to a lock-in amplifier modulated the laser beam. The lock in amplifier was connected to the output of the PMT and the light chopper, so that phase-sensitive detection could be utilized. Incorporating phase sensitive detection permits rejection of all light but that modulated by the chopper, allowing for higher resolution. The beam then passed through a polarization rotator to control the direction of polarization of the beam. The beam was then focused on the center of the control volume using a lens.

The receiving components of the test setup consisted of a photo multiplier tube (PMT) mounted on a rotational stage. The rotational transition stage moved the receiving optics along a circular path ranging from 20 degrees to 155 degrees centered on the control volume. A variable iris diaphragm in front of the collecting lens defined the solid angle of scattered light incident on the detector. The iris diameter was kept at a constant 10 mm during testing. Reducing the size of the iris will increase the accuracy of the apparatus, however, to small of an iris opening can reduce the signal to noise ratio. The solid angle bounds the smallest particle size and accuracy of the measurement. A collecting lens, a sheet polarizer, a pinhole, and a PMT with a narrow band filter followed the iris diaphragm. The signal from the PMT was directed to a lock-in amplifier, and then to a data acquisition system.

The accuracy of the apparatus was determined during the calibration exercises using monodisperse aerosols. Calculating the error associated with each angular
measurement and comparing it to the change in intensity between two particle sizes established the accuracy. The error associated with each angular measurement is a function of the iris opening and the particle size. As the particle size increases the light scattered from the particle begins to fluctuate due to interference patterns created by the scattered light. These fluctuations increase the slope of the scattering curves between any two given angular points. The larger the iris opening the larger the angle of scattering the detector receives. When the particles are small the detector receives a signal intensity with a low slope, decreasing the error and increasing the ability to differentiate between particle sizes. As the particle size increases, the error increases and the ability to distinguish independent scattering intensities decreases.

**AEROSOL GENERATION**

The laser light scattering system was calibrated by measuring the light scattered from polystyrene latex spheres (PSL) flowing through the control volume. The calibration was performed as a function of angle. The scattered intensities from the PSL aerosol can be quantified, because the properties of the aerosol are known. Using the design of Hinds [29], a nebulizer was developed to produce an aerosol of small particles by removing larger spray droplets through impaction within the device. Monodisperse PSL spheres were placed in a nebulizer with water and supplied with air at 15 psi. After nebulization, the liquid was removed from the solid particulate with a diffusion dryer producing an aerosol of known size. Once the particles leave the diffusion dryer, they entered a 3-liter volume for final mixing. The aerosol flow was then introduced into a glass vessel, which contained the smoke and housed the control volume.

Liquid suspensions of monodisperse polystyrene latex (PSL) spheres were chosen for the purpose of calibrating the laser scattering system because the majority of these PSL spheres have uncertainty in their mean size of less than 1% and relative standard deviations for their size distributions of less than 2%. Sphere sizes of 500 nm and 1000nm were chosen for their similarity to smoke particulate sizes. Properties of the PSL spheres used in this study are listed in Table 2.
Table 2: List of properties for the 500 nm and 1000 nm PSL calibration spheres.

<table>
<thead>
<tr>
<th></th>
<th>1000nm PSL</th>
<th>500nm PSL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certified mean Diameter (nm)</td>
<td>993 +/- 21</td>
<td>491 +/- 4</td>
</tr>
<tr>
<td>Standard deviation (nm)</td>
<td>10</td>
<td>6.3</td>
</tr>
<tr>
<td>Microsphere composition</td>
<td>Polystyrene</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>Polymer density (g/cm³)</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>Index of refraction</td>
<td>1.59</td>
<td>1.59</td>
</tr>
<tr>
<td>Approximate concentration (% solids)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hydrodynamic Diameter (nm)</td>
<td>N/A</td>
<td>495-530 (PCS)</td>
</tr>
</tbody>
</table>

**PSL CALIBRATION**

The reliability of the system and a scattering calibration factor (C) was established by separately testing the two PSL sphere sizes. The calibration experiment was conducted by collecting the laser scattering signal at angles ranging from 20 to 155 degrees using both vertically (VV) and horizontally (HH) polarized light. The collected data was then processed, correcting for the scattering signal amplification and angular dependence on the scattering volume. A calibration factor is determined by normalizing the detected signal with the theoretical signal for these spheres assuming Mie scattering.

The collected and calibrated data from 1000 nm PSL spheres for VV and HH scattering can be seen in Figure 6 and Figure 7. It can be seen that the VV scattering curve undulate significantly due to interference patterns caused by the scattered light [30]. It can be seen that the collected 1000 nm experimental data follows the trend of the theoretical Mie curve but does not attach itself to the curve. This phenomenon was also found by Grasso et al. [30]. The 1000 nm spheres produced a slightly different calibration factors for HH and VV. Small differences noted in the calibration values between the VV and HH polarization for each PSL sphere size is believed to be due to the PMTs affinity for one form of polarization over the other. The change seen in the calibration factors between 500 nm and 1000 nm is believed to be due to the change in particle size resulting in a slightly different number concentration produced from the nebulizer and within the control volume. The calibration factors for both 500nm and 1000nm PSL spheres do not change the shape of the curves themselves but rather adjust the scattering intensity compensating for losses in the optics. The calibration factors do not reflect the overall error of the system but are rather a correction to the amplitude. The two calibration
factors were averaged giving a single calibration factor applicable over the given size range.

The high angles (i.e. greater than 120°) of the calibration data collected for the 500 nm PSL sphere did not correspond well with the theoretical Mie curve. These points were present for both polarizations VV and HH over all tests involving the 500 nm PSL spheres. The difference between the experimental and theoretical data points are due to the failure of the Mie theory to describe the experimental data in the high scattering angle region that starts near 120 degrees and proceeds in the backscattering direction. Grasso et al identifies the failure of the Mie theory to describe the experimental data in the high scattering angle. The failure is due to the effect of the reflections at the surface of the glass control volume. In this study, reflection of the beam were reduced, but not completely eliminated, by cutting holes 180 degrees apart in the glass cylinder so the source laser light could pass uninterrupted through the glass volume walls. Observations by Grasso et al. [30] confirm the observed deviations from theory seen at angles greater than 120 in the 500 nm scattering curve, these deviations were not as apparent with the larger 1000 nm particle sizes.

The experimental error determined by averaging the repeated calibration tests indicates the ability of the scattering system to measure changes in size. The deviation created by averaging the repeated test must be small enough to differentiate the scattering points from one time step, source, or PSL sphere size to the next. The error for each point is dependent on the iris opening and particle size. This is seen with the larger PSL spheres where the error bars are elongated due to the iris opening combined with the large fluctuations of scattering intensity associated with larger particles. The calibration of the laser light scattering system identified the limitations of the test setup, but validated its use as an instrument for collecting laser scattering measurements and the general particle sizing of aerosol particulate. The HH scattering of the 500 nm PSL spheres generated an error of approximately 22% while the VV generated approximately 31% error. The percent error for the 1000 nm PSL spheres was significantly higher, as expected, with HH producing approximately a 64% error and VV a 92% error. Taking into consideration the expected changes to intensity with particle size and the error associated with those changes it becomes clear that the apparatus improves in accuracy as the particle size decreases, and even thought the error associated with the larger particle
size is significant the scattering intensity are to distinct to be confused for one another. For the purposes of identifying agglomeration as it relates to smoke detector activation it can be seen in the figures produced by Mulholland and Bukowski that a significant change in particle size (i.e. 100nm to 1000nm) needs to occur to reverse the detector sensitivity. The calibration procedure has demonstrated the ability of the apparatus to identify this significant size change.

**SMOKE PRODUCTION**

Following calibration of the optical system, smoke was produced and tested on the bench top setup. Two different smokes were tested, polyurethane and heptane. Smoke from the polyurethane was produced from a 16 cm³ block ignited in a small pan. The smoke was collected in a smoke box where it was then pumped into the glass control volume. Smoke was also produced and collected from heptane pool fires in a similar manner. To ensure a constant smoke yield, the heptane was maintained at a constant level within the pan to ensure a steady burning rate. The smoke was again collected in the smoke box from which it was then pumped into the glass control volume. Extinction measurements were conducted throughout the testing to determine the number concentration with in the glass control volume. Once a steady flow of smoke was established, the pump would then be shut off with the smoke contained within the control volume that was then left, undisturbed, to age for 15 minutes. Laser light scattering was collected throughout the 15 minutes to examine changes to the smoke particles. A time span of 15 minutes was chosen as upper bounds of the expected duration of smoke transport in the ceiling jet before detector activation.

**RESULTS**

Scattering data from the two different smokes was collected and averaged over three tests for each angular point for both vertically (VV) and horizontally (HH) polarized light. The data was then processed adjusting for the chopper amplification, angle dependence, and the calibration factors. The data was averaged in 30-second intervals to produce slices of the scattering curve over the 15-minute time span. The data, displayed in Figure 8, has been normalized to the 90 degree vertically (VV) polarized data point for easy comparison. It can be seen that the shape and intensity of the curves changes over time. This is a clear indication that smoke aging is occurring. Further more,
as the time passes the curves begin to oscillate. This has been shown to occur due to interference patterns caused by the scattering of larger particles implying an increase in particle size over time. The 90-degree VV and HH points were compared to the Mie theory over time. This method is similar to the polarization ratio sizing technique [60]. The ratio of various light intensities has been used as indicators in distinguishing types of smoke as well as particle size [25]. The polarization ratio is the ratio of the VV scattering intensity to the HH scattering intensity at 90°. The dissymmetry ratio is the ratio of VV scattering intensity at two points 90° apart from each other (i.e. 45° and 135°). The smoke was examined for size changes using both the polarization ratio and dissymmetry ratio. Following a similar procedure to that outline earlier the number concentration was calculated using the obscuration measurements collected from the PMT, Figure 20.

**ANALYSIS AND DISCUSSION**

The data analysis can be broken into two sections. The first section was a direct problem, which was typified by the calibration, in that a given particle of specific shape size and composition, which is illuminated by a beam of specified irradiance, polarization, and frequency determines the field of scattering. The smoke testing is representative of the inverse problem where by suitable analysis of the scattering field, a description of the particle and particle distribution responsible for the scattering can be determined.

Applicable to monodisperse particles, the Mie Theory was adjusted in an effort to fit the collected laser scattering results from the polydisperse distribution of smoke particulates. This was done by cataloging the calculated Mie theory results for aerosols ranging in size from 5 nm to 1000 nm in increments of 5 nm. The chosen size range of 5 nm to 1000 nm coincides with the size range of the Mie theory and various smoke particulate sizes, bounding the lower limit. The 5 nm size is well below the expected smoke aggregate size, and smoke particles are known to grow larger than 1000 nm, however, the range in size was believed to be adequate to capture size changes due to agglomeration. A particle size of 1000 nm is also the transition point where the particles become too large to be governed by Brownian motion and outside the range of the systems calibration [2]. Two scenarios were made in order to calculate the Mie coefficients incorporating two refractive index values for soot particulate, 1.75-.5i and
The Mie intensity coefficients were calculated for vertical and horizontal polarized light. A log-normal distribution was assumed. The shape of the distribution was changed using the Geometric Standard Deviation (GSD) and average mean size. The resulting distribution values for each particle size were multiplied by the calculated Mie coefficients for each angle and summed to produce the scattering coefficients \((i_{\text{pol,y},y})\) and \((i_{\text{pol,HH}})\) expected from the polydisperse aerosol for each angle. The distribution is shaped by its own set of variables including GSD. Establishing a GSD range of 1.1 (monodisperse) to 2.3 Figure 9 (polydisperse), encapsulates a wide range of smoke distributions. The average size along with the GSD was changed to fit the experimental laser scattering points at 90 degrees. Slices providing the averaged intensity of scattering over 30 second intervals of the light scattering can be seen in figure 8. The curves differ between each time step indicating changes to the smoke particulate. Specifically the curves become more undulating indicating changes in particle size. The curves also provide the points for calculating the polarization ratio using the VV and HH intensity at 90 degrees and the dissymmetry ratio. Figure 10 and 11 provide the changes in particle size over time produced by applying the Mie theory accounting for monodisperse and polydisperse smoke distributions and changes in the refractive index using the polarization ratio sizing technique. All four results analyzing the heptane results which compensate for changes in distribution and refractive index, Figure 10, demonstrate the same trend. However, the results using a refractive index of 1.75 and monodisperse distribution (1.1) show a slightly lower particle growth. The polyurethane results differ slightly with the results using a refractive index of 1.75 and monodisperse distribution (1.1) showing no particle growth while results using a refractive index of 1.73 and polydisperse distribution of 2.3 producing more inconsistent larger particle sizes at the beginning and end of testing as well as a double peak. Averaged values are used to represent the particle size however a distribution of 2.3 results in a large particle size range so the results represent trends in particle growth not the exact particle sizes present. The figures indicate a significant growth in particle size between 400 and 600 seconds. The change in particle size would be expected to occur at the initial stages of the testing once the smoke was secured in the glass control volume and left to age. However, the growth in particle size is substantially delayed possibly indicating a change in the dynamics influencing smoke agglomeration. The large particles remain in the control
volume for a significant period of time (~200 seconds). The larger particles then leave the control volume possible due to deposition or sedimentation. Unfortunately the dynamics occurring within the control volume could not identified to establish the changes occurring to promote the growth of the particles or cause the sudden loss of the larger particles. These dynamic forces may or may not exist for extended duration within a ceiling jet.

The graphs in Figure 8 represent 30 second averages of the data taken at 360 seconds and 480 seconds. The graphs demonstrate the significant change in scattering seen during this time interval. The change in laser scattering intensity at the 90 degree HH value changes by a factor of 10 (0.01 at 360 seconds to 0.1 at 480 seconds). This change in intensity is greater than the error established in the calibration of the apparatus signifying a change in light scattering intensity due to changes in particle size.

The dissymmetry ratio is the ratio of two angle intensities of similar polarization, separated by 90 degrees. Light scattering at angles of 50 and 140 degrees were used to establish the dissymmetry ratio, Figure 12. The dissymmetry ratio demonstrated similar trends to those seen by the application of the Mie theory. Again an increase in the ratio indicating an increase in particle size was seen between 400 and 600 seconds supporting the findings of the polarization ratio.

Obscuration measurements were collected to find changes to the number concentration. The PMT was placed in line with the laser path along with neutral density filter stacked to reduce the intensity of light and damage to the PMT. Following Lambert-Bougers law [33]

$$k_{ext} = \frac{\ln\left(\frac{I_c}{I_o}\right)}{L}$$  \hspace{1cm} \text{Equation 6}

$I_c$ is the intensity of light exiting the soot
$I_o$ is the intensity of light initially, or with out any aerosol in the path of the laser.
$L$ is the path length through the aerosol
$k_{ext}$ is the extinction coefficient in m$^{-1}$.

Where
\[ k_{\text{ext}} = k_m m \]  
Equation 7

\( k_m \) is the specific extinction coefficient in \( \text{m}^2/\text{g} \)

\( m \) is the mass in \( \text{g/m}^3 \).

The changes in number concentration support the agglomeration process. When the number concentration and changes to particle size graphs are compared on the same time scale it can be seen that the number concentration drops at approximately the same time as the increase in particle size, Figure 14. These finding also support the general finding of the calculations conducted. The number concentration within the control volume was similar to the one calculated using the UL 217 limits for detector activation. This would imply that the dynamics that affected the particle growth would have to occur in the ceiling jet for similar growth to occur. Because of the similar number concentrations similar average particle travel distances can be assumed. The duration of the scattering test was significantly long enough to expect detection to occur, however, the temperature would be lower than expected within a ceiling jet lowering the agglomeration rate.

CONCLUSIONS

- As demonstrated by previous work done by Mullholand and Bukowski particle growth must be significant to effect detector activation. Calculations using UL 217 imply that the increase in particle size needed to significantly effect detector activation and reverse the alarm sensitivity between ionization detectors and photoelectric detectors would result in a significant decrease in number concentration if the mass was to remain constant.

- Calculation of the Brownian motion shows that particle motion decreases forming and asymptote at 500nm. The calculations identifies the relationships between temperature, particle size, and number concentration that gives stagnation points were agglomeration due to Brownian motion will not occur if the temperature it to low, the particle size is to large, or the number concentration is to low.

- By examining the scattering curve created by smoke particles over a range of time steps, changes to the curve shape imply an ongoing aging process where increases in particle size are taking place.
• Using the Mie theory in conjunction with particle sizing techniques such as the polarization ratio and dissymmetry ratio, reveal a change in particle size. The particles are shown to grow larger over time, this is also supported by the obscuration measurements demonstrating a decrease in number concentration. General trends demonstrated by the calculations are supported by the experimental results.

• Smoke detection is dependent on a number of variables that form a web of dependence upon one another. These include temperature, charge, size, color, velocity, and refractive index. Size changes significant enough to effect detector activation are shown to occur. The large particles, however, are produced during a specific stage of smoke aging when the conditions are right for agglomeration. The larger particles then depart from the smoke and the concentration of particles is returned to the smaller size range.
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28 H Y Chen, M F Iskander, and J E Penner: Light Scattering and Absorption by Fractal Agglomerates and Coagulations of Smoke Aerosols Modern Optics, 37, 171-181 (Also UCRL-100084.)


Figure 1: Detector Sensitivity versus Particle Diameter reproduced from testing performed by Mulholland.
Figure 2: Detector sensitivity versus particle diameter with constant mass concentration reproduced from testing performed by Bukowski [].

Figure 2: Detector sensitivity versus particle diameter with constant mass concentration reproduced from testing performed by Bukowski [].
Figure 3: Calculated number concentration for the minimum and maximum optical density necessary for smoke agglomeration as set by UL217. A particle density of 2.0 g/cm³ was used for calculating the number concentration.
Figure 4: Particle motion based on the Brownian movement of smoke particles. Particles size range up to 1000 nm for temperatures ranging from 100 to 1000 degrees Celsius.
Figure 5: Diagram of laser scattering test apparatus.
Figure 6: Graph of the calibration curve for 1000nm PSL spheres. The theoretical curve was produced using Mie theory and the information from the manufacturer of the 1000nm calibration aerosol. The experimental data was the collected scattering of HH laser light.

Figure 7: Graph of the calibration curve for 1000nm PSL spheres. The theoretical curve was produced using Mie theory and the information from the manufacturer of the 1000nm calibration aerosol. The experimental data was the collected scattering of VV laser light.
Figure 8: Averaged 30 second time step of collected laser scattering for 360 seconds (6 minutes) and 480 seconds (8 minutes) for heptane smoke.
Figure 9: Figure of Log-normal distribution for a GSD of 2.3.
Figure 10: Results for heptane smoke using the Mie theory Polydisperse distribution for distributions of 1.1 and 2.3 and refractive indices of 1.75-0.5i and 1.57-0.56i.
Figure 11: Results for polyurethane smoke using the Mie theory Polydisperse distribution spreadsheet for distributions of 1.1 and 2.3 and refractive indices of 1.75-0.5i and 1.57-0.56i.
Figure 12: The dissymmetry ratio calculated from the collected scattering intensities of polyurethane smoke. The spike between 400 and 500 seconds indicates the soot particles are growing larger in size.
Figure 13: The corresponding number concentration from three tests of heptane smoke produced from a pool fire. The number concentration assumes a density of 2.0 g/cm$^3$ and a diameter of 500nm. The graph shows a decrease in number concentration between 400 and 500 seconds.

Figure 14: Graph comparing the change in number concentration to change in particulate size during a heptane pool fire. Similar results were seen for the polyurethane tests.
**B.1 Smoke Growth**

Smoke consists of both solid and liquid particulates, as well as gaseous products. The gaseous products depend on the fuel being burned and can include H2O, CO2, CO, HCL, and HCN. In the combustion process nucleation is the initial stage of smoke growth. Elementary particles 20 to 30 nm in size are produced in the nucleation stage. These elementary particles are produced when coagulation occurs between PAH (Polycyclic Aromatic Hydrocarbons), CHS (Condensed Hydrocarbon Species), carbonaceous soot, and acetylene [1]. The elementary particles then agglomerate through additional collisions forming small clusters. The clusters continue to agglomerate with cluster-cluster collisions until the particles pass through the soot burnout zone in the flame where oxidation of the particles occurs. The soot burnout zone increases from about 10% to 50% of the visible flame length as the soot concentration increases [2]. The particle size decreases as the number concentration increases while passing through the soot burnout zone [3]. Flames begin to emit soot when the soot temperature in the oxidation zone falls below 1300K [2]. If the soot is not consumed in the oxidation region and escapes the flame tip to the overfire region, the particulate may travel out of the flame and form a smoke plume. The minimum laminar axisymmetric diffusion flame height, at which smoke just escapes from the flame tip, is known as the smoke point. The smaller the value of the smoke point the greater the tendency for soot to form in the flame [4]. Smoke emission characteristics of fuels have been expressed for decades by the smoke point value. It is within the overfire region that smoke particles begin to age and may agglomerate. Water (H2O) in the form of steam, a product of combustion, cools and can condense on the outer edge of the soot particles. The condensation increases the particle size and changes the optical properties of the soot. It is at this point in the smoke aging process when detector activation occurs. The particle formation process, nucleation, within the flame is assumed to be complete. It should be understood that smoke aging is not limited to only changes in size but encompasses all of the changes that the particles undergo from the over fire region to the far field.
B.2 Smoke Structure

Smoke consists of small primary particles that are similar to elemental carbon, in that they have a chemical structure comparable to impure graphite [5]. The density of soot can range from 1.82 to 2.05 g/cm³, where as pure graphite has a density of 2.0 g/cm³ [5]. The soot particles are constructed of nearly constant primary particle diameters and can be as large as 60nm in size, with a large variation in the number of primary particles per aggregate [6]. The smoke particles can form wispy open structures with the aggregated primary particles and, although the soot structure is complex, recent works shows that it can be characterized as mass fractal-like in nature [7]. The fractal power law that is applicable to soot aggregates is in equation 8:

\[ n = k_f \left( \frac{R_g}{d_p} \right)^{D_f} \]  

Equation 9

- \( R_g \) is the radius of gyration
- \( d_p \) is the diameter of the primary particles
- \( D_f \) is the fractal or Hausdorff dimension
- \( k_f \) is the prefactor
- \( n \) is the number of primary particles in the aggregate

This fractal power law applies to soot generated in the laboratory for values of \( n \) as small as 10 or less [8].

B.3 Smoke Particle Size

Smoke particles are described by particle size (\( \mu \)m or nm), number concentration (particle/cm³), and mass concentration (g/cm³). Smoke can also be characterized by the size distribution. Most naturally occurring aerosols have a lognormal distribution. Smoke particulate size is usually characterized by the distribution or range of sizes because of the tendency of smoke to be a polydisperse aerosol. A monodisperse aerosol has particles of one size, resulting in a Geometric Standard Deviation (GSD) of 1. For most practical purposes, a GSD of 1.2 or less is accepted as monodisperse [9]. However, most naturally occurring aerosols are polydisperse, with GSDs in the 2 range [10]. The lognormal size distribution is widely used for describing the size distribution of aerosols, including both flaming and non-flaming smoke. The form of the distribution is the same as the normal
distribution except that the GSD, and geometric mean number is replaced with the log of the GSD and log of geometric mean number so that one has

$$f_g(x) = \frac{1}{(2\pi)^{\frac{1}{2}}\ln\sigma_g} x^{-1} \exp\left(-\frac{\ln D_g^2}{2\ln\sigma_g^2}\right)$$  
Equation 10

$D_g$ is the geometric mean number

$\sigma_g$ is the geometric standard deviation (GSD)

$x$ is the particle size

The aerosol size distribution range can be viewed as an addition of several lognormal distributions based on a model classification by Whitby [11]. These distributions include coarse mode (aerosol mass aerodynamic diameter larger than 3 um), fine mode (between 1 and 3 um), accumulation mode (from 0.1 to 1 um) and nuclei mode (below 0.1 um) [11]. The size ranges designate transitions regimes in particle behavior due to changes in size. For example, Brownian motion will cease once the soot particles grow beyond 1000 nm [12]. The determination of the aerosol size distribution is a very important aspect involved in both measuring and in modeling aerosol dynamics. Additional distributions have also been used to characterize smoke particles such as the exponential scaling distribution and the Junge distribution.

**B.3 Smoke Deposition, Sedimentation, and Thermophoresis**

Smoke loss due to diffusion, sedimentation, and thermophoresis to the walls and ceilings plays a major role in forming the smoke size distributions. Soot particles are removed from the atmosphere through deposition, particle diffusion, and particle settling. Deposition has been studied with mathematical models available for predicting deposition rates. The major property to be considered is particle size and it’s influence on impaction, sedimentation, and diffusion. Inertial impaction is the mechanism that causes particles moving in an air stream to be able, because of excessive mass, to follow the air-stream around a bend. The larger the particle the greater the chance of depositing by impaction. Impaction is relatively an unimportant form of deposition for particles smaller than 0.5 microns in size [13].

The effect of gravity on suspended particles causes them to fall, a process known as sedimentation. Sedimentation also becomes relatively unimportant for particles less
than 0.5 microns in size [13]. Larger particles fall faster and, for all particles, the greater the residence time the greater the likelihood of deposition by sedimentation.

Diffusion is characterized by Fick’s law that states diffusion is the net transport of particles from a region of higher concentration to a region of lower concentration. Depending on the size regime diffusion or gravitational settling will have more of an impact on the size distribution. Important known factors in smoke agglomeration are: initial size of the particles, concentration of the particulates, and time or rather velocity of the smoke gasses.

**B.4 Smoke Agglomeration due to Brownian Motion**

Smoke agglomeration is the collision of smoke particulates in the atmosphere due to either Brownian motion or hydrodynamic, electrical, acoustic, or gravitational forces. Mulholland stated in his graduate lecture series that agglomeration is described best when considering “the motion of a single smoke or dust particle. The particle is “bombarded” by molecules, and because of its small size, more molecules will be hitting the particle from one side than the other at any one instant [13]. This imbalance at the molecular level is the cause of the very erratic particle motion.”[13]. This irregular movement of the particle is known as Brownian motion, which is the primary cause of agglomeration. Brownian motion in high particle concentration causes particle collision and results in the formation of larger particles. Three morphologies of this process are the straight chain, randomly branched chains, and closely packed clusters. The mechanism of agglomeration is very crucial in the development of the size distribution in the atmosphere.

The Smoluchowski equation, normally expressed in terms of particle volume coordinates, describes the collision of the particles in the atmosphere. In aerosols, as stated earlier, the time rate of change of the particle size distribution is of primary interest. When considering two types of particles, with volume, \( v_i \) and \( v_j \) the rate of collision between \( i \) and \( j \) particles is \( N_{ij} \). For spherical particles, each particles diameter has a unique volume. The collision of two particles leads to the growth of a new particle with the summed volume of the two combined particles. The concentration of particles \( i \) is \( N_i \) and that of \( j \) is \( N_j \). \( B_{ij} \), the collision frequency function, is defined as:

\[
N_{ij} = B_{ij}(v_i, v_j, T, P, \text{ect.}) N_i N_j \quad \text{Equation 11}
\]
A new particle, k, is formed with each collision. The volume of k is $v_k = v_i + v_j$. The rate of formation of the k particle is,

$$\frac{1}{2} \sum_{i+j=k} N_{ij} \quad \text{Equation 12}$$

The rate of loss of particle k, due to collision with other particles is,

$$\sum_{0}^{\infty} N_{ik} \quad \text{Equation 13}$$

Then,

$$\frac{dN_k}{dt} = \frac{1}{2} \sum_{i+j=k} N_{ij} - \sum_{i=k}^{\infty} N_{ik} = \frac{1}{2} \sum_{i+j=k} \beta(v_i, v_j)N_iN_j - N_k \sum_{i=1}^{\infty} \beta(v_i, v_j)N_i \quad \text{Equation 14}$$

This is known as the Smoluchowski equation. The equation converts the problem of determining the progression of a variety of particle sizes to the problem of determining the collision frequency function, $\beta_{ij}$.

For nanoparticles (particles smaller than 1 µm) Brownian motion governs the collision frequency [12]. As stated earlier, agglomeration increases at higher particulate concentrations, and the total number of particles, or number concentration, decreases rather quickly in the initial portion of a smoke plume [14]. Mulholland has characterized this change in number concentration through calculations using a coagulation coefficient $\Gamma$ (cm$^3$/s) where,

$$\frac{dN}{dt} = -\Gamma N^2 \quad \text{Equation 15}$$

so

$$N_f = \frac{N_o}{1 + \Gamma N_o t} \quad \text{Equation 16}$$

$N_o$ is the initial number concentration

$N_f$ is the final number concentration
t is the time duration

Although most think of agglomeration taking place over a ceiling jets distance, it can be seen from the equation that agglomeration is more dependent on time rather than on linear distance. With less buoyant force in a plume, such as in a smoldering source versus a flaming source, more time is needed for the soot particles to reach the detectors.

**B.5 Soot Optical Properties**

The refractive index of soot is one of the most significant properties involved in calculating particle size. The refractive index of soot is influenced by material, hydrogen to carbon ratio (H/C ratio), wavelength, density, and changes in temperature (known as the schlieren effect). Accurate determination of the optical properties also requires knowledge of the smoke composition, morphology, and quantity of soot. Therefore, the changing characteristics of smoke, through smoke aging, are expected to have an important effect in predicting it’s optical characteristics. The complex refractive index can be written as $m = n + ik$ where $n$ and $k$ are often referred to as the optical constants.

$$m = n + ik = c\sqrt{\frac{\varepsilon\mu}{\varepsilon_o\mu_o}}$$

Equation 17

c is the speed of light

$\varepsilon$ is the permittivity

$\mu$ is the permeability.

The subscript o corresponds to free space. The refractive index of various soot, under various conditions are listed in Table 17 and Table 24.

Table 3: Refractive index used for computations of soot aggregate optical properties. The table was reproduced from Koylu U.O., Emission, Structure and Optical Properties of Overfire Soot from Buoyant Turbulent Diffusion Flames, (1992)

<table>
<thead>
<tr>
<th>Refractive index</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33+0.11i</td>
<td>Iskander et al. (1989)</td>
</tr>
<tr>
<td>1.75+0.29i</td>
<td></td>
</tr>
<tr>
<td>1.38+0.275i</td>
<td>Ku and Shim (1992)</td>
</tr>
<tr>
<td>1.7+0.1i</td>
<td></td>
</tr>
<tr>
<td>1.33</td>
<td>Chen et al. (1990, 1991)</td>
</tr>
<tr>
<td>1.33+0.11i</td>
<td></td>
</tr>
<tr>
<td>1.75+0.29i</td>
<td></td>
</tr>
<tr>
<td>1.75+0.5i</td>
<td>Nelson (1989)</td>
</tr>
</tbody>
</table>
Table 4: Literature values of the complex refractive index of flame-generated smoke taken from a paper entitled Coupled Dipole Calculation of Extinction Coefficient and Polarization Ratio for Smoke Agglomerates written by George W. Mulholland and Raymind D. Mountain. NIST, Gaithersburg, MD

<table>
<thead>
<tr>
<th>Date of Publication</th>
<th>Wavelength (nm)</th>
<th>Refractive Index</th>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1969 (24)</td>
<td>650</td>
<td>1.57+0.44i</td>
<td>Acetylene</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>1.56+0.52i</td>
<td>Propane</td>
</tr>
<tr>
<td>1980 (25)</td>
<td>488</td>
<td>1.7+0.7i</td>
<td>8 um carbon sphere</td>
</tr>
<tr>
<td>1981 (26)</td>
<td>633</td>
<td>1.9+0.55i</td>
<td>NA</td>
</tr>
<tr>
<td>1983 (27)</td>
<td>633</td>
<td>1.7+0.8i</td>
<td>NA</td>
</tr>
<tr>
<td>1987 (28)</td>
<td>633</td>
<td>1.85+0.40i</td>
<td>Toluene</td>
</tr>
<tr>
<td></td>
<td>633</td>
<td>1.85+0.39i</td>
<td>Methane</td>
</tr>
<tr>
<td>1990 (29)</td>
<td>540</td>
<td>1.77+0.63i</td>
<td>Propane, 100mm above burner</td>
</tr>
<tr>
<td>1993 (30)</td>
<td>633</td>
<td>1.53+0.38i</td>
<td>Propane</td>
</tr>
</tbody>
</table>

NA = Not Available

The soot index of refraction of 1.57-0.56i used in the data analysis was first used by D’Alessio et al. as a value close to the determined value for soot produced by propane-air flames [15]. A refractive index of 1.75-.5i was also used in the analysis as an upper limit bound taken from the tables 3 and 4.
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APPENDIX C SMOKE DETECTOR REVIEW
**C.1 Smoke Detectors**

To better comprehend how smoke aging effects detection, the method of detector operations is examined for both ionization and photoelectric smoke detectors. Although each detector type responds to the aerosol component of smoke, each does so based on different operating principles and thus responds to different characteristics of the aerosol itself. As a result, the response of the detectors to a given smoke can be quite different. Ionization detectors contain an ionization chamber, Figure 15.

![Figure 15: View of the inside of a Maple Chase smoke detector (cover removed)](image)

This chamber is made up of a source of alpha radiation positioned between two electrodes. The alpha radiation source emits positively charged particles. These ions, which are charged gas molecules, are then attracted to the oppositely charged electrodes.
on either side of the chamber and produce a small current flow across the chamber. Interference of this flow of ionized molecules causes a reduction in current leading to alarm activation, as shown in Figure 16 [1].

![Diagram of an ion detector under alarm conditions](image1)

**Figure 16**: Diagram of an ion detector under alarm conditions

The exact mechanism causing the reduction in current involves one or more of the following [2].

1) The attachment of a molecule from the smoke aerosols to the charged gas molecules reduces the ion’s velocity and thereby reduces current.
2) The attachment of a molecule from the smoke aerosol to the charged gas molecule reduces its mobility and allows air currents to carry the charged ion out of the chamber before reaching the electrode reducing the current.
3) Smoke aerosols in the chamber enhance positive and negative ion recombination, which decreases the concentration of charged gas molecules (ions) in the chamber reducing the current.

Photoelectric detectors work on the principle of light scattering. The light source and the photocell are at an angle to each other. Under normal circumstances the photocell will not receive laser light from the light source as shown in Figure 17.

![Representation of a photoelectric detector in non-fire conditions](image2)

**Figure17**: Representation of a photoelectric detector in non-fire conditions [1].
In fire conditions, smoke enters into the chamber and scatters the light, some of which strikes the photocell increasing the alarm voltage. When the alarm threshold is reached, the alarm is triggered.

Smoke detectors may be one of the most thoroughly tested pieces of fire related equipment. Detector activation has been documented in numerous tests ranging, from full-scale house burns to bench top tests. Smoke detector activation can be measured in a number of ways. Detector response time is often measured from the time of ignition to detector activation. When two detectors are placed side-by-side, the difference in detector activation time between the two detectors is used as a measure of detection time. This time difference in activation between the two detectors has been shown to vary with distance. This can create a misconception of which detector is more suitable for egress and life safety if a proper analysis is not conducted. A more scientific characterization may use obscuration, particle size, or smoke velocity, to better describe the atmosphere and its tenability. A tenability analysis would provide significant information regarding detector response as it applies to life safety. The sensitivity of the detectors can also be manipulated to obtain various results, however, manufacturers preset sensitivity levels in an attempt to give the fastest response while minimizing false alarms.

The delay in detection of aged smoke by ionization detectors is the subject of a paper written by Eugene Cable and Philip Sherman [2]. The paper has been used to establish a basis for opinions used in court cases involving ionization detectors. Examples of various fires where a delay in detection of the fire is documented, as well as a number of tests that demonstrate the conditions for delayed detection are discussed within the paper. Numerous tests have been conducted that have been interpreted and used to demonstrate that ionization detectors respond slower than photoelectric detectors. One test is the ITT Research Institute tests at Gary Indiana Laboratories in 1977. In this test, various detectors, detector sensitivities, and spacings where tested in a long corridor and a large room [2]. These tests were later published in a Federal Emergency Management Administration (FEMA) summary report. NASA tested Condensation Nuclei Fire Detectors (CNFI), ionization detectors, and photoelectric detectors in a large room. The Fire Detection Institute tested ionization detectors, measuring the optical density at the time of alarm [2]. Test by Heskestad for the National Bureau of Standards (NBS) examined ion detectors in an apartment [2]. The Indiana Dunes Tests placed a number of
detectors in a dwelling and examined the response times [2]. Further details of the tests are within the Sherman Cable paper. The Sherman Cable paper attributes the delay in detection to smoke agglomeration and, more specifically, the larger particle size.

A consequence of smoke, most commonly associated with detection, is optical density. Optical density, or obscuration, is a term used to describe the reduction of light transmitted across some path length due to the density of the smoke present in a given volume. The optical density of smoke refers to the physical properties of smoke that causes a decrease in the amount of incident light transmitted through it. There are several methods of quantifying this decrease in light transmission. The basis for optical density, or light extinction measurements is Bouguer’s Law. This relates the intensity of the incident monochromatic light of wavelength $\lambda$, $I_o$, and the intensity of the light, $I_e$ transmitted through a path length $L$ of the smoke, equation 18.

\[
\tau_{\lambda} = \ln \frac{I_e}{I_o} = -K_{\text{ext}}L \quad \text{Equation 18}
\]

$K_{\text{ext}}$ is the extinction coefficient

$I_o$ is the Initial intensity of light

$I_e$ is the exiting intensity of light

$L$ is the path length

$\tau_{\lambda}$ is the transmittance
Figure 18: Detector Sensitivity versus Particle Diameter from testing performed by Mulholland, x-axis is particle size, y-axis is sensitivity.
There is a need to distinguish the importance of each of the aging affects, and prevalence of each variable as it relates to smoke detector activation. Mulholland has reported results for detector sensitivity to monomer-sized particles, as shown in Figure 18. While Bukowski has also examined various detectors sensitivity to particle size, Figure 19. It is clear the graphs are quiet different, due to the fact that the mass concentration in Bukowski’s work was kept constant while the number concentration in Mulhollands was kept constant. The sensitivity tests of Mulholland and Bukowski demonstrate that ionization and photoelectric detectors react differently to particle size. However, the graphs do not demonstrate the sensitivity to detectors have relative to other factors such as velocity or temperature. There are many approaches used in predicting the activation time of smoke detectors. In 1975, Heskestad tested a detector’s sensitivity to flow velocities and suggested a way of characterizing the difficulty smoke has entering some detectors [3]. The entry characteristic of a detector was measured in a sensitivity test tunnel where alarm points were measured at several test velocities. The entry was
described by a value, L, the characteristic length. The characteristic length is the transport delay for smoke to move from the outside of the detector to the sensor [3].

In 1977 Delichatsios and Heskestad proposed a temperature correlation where activation occurs after a 13 °C temperature rise at the detector location. Recent literature has suggested that temperature rise at activation values of 4 °C or 5 °C provide good agreement with experiments in which current detectors were installed on a ceiling 2.4 m high. Another approach is the critical velocity concept, where the detector will activate as long as a critical ceiling jet velocity is present in the detector’s region.

Detector activation has been attributed to various smoke characteristics such as velocity, number concentration, neutralization of the charged particles, and temperature changes. The two smoke detectors, ionization and photoelectric, react differently to the characteristics of smoke due to their individual method of operation.

REFERENCES:
2) E. A Cable, P.R. Sherman, The Ionization Smoke Detector and Smoke Aging, Presented to John Titus, Professor FP 552 WPI and John D. White, Deputy Chief Fire Marshal, Boston Fire Department, June 24, 1986 WPI.
APPENDIX D UL 217
D.1 UL 217

Currently smoke detectors are evaluated on their ability to respond to smoke of a certain optical density. As a result, optical density has become a primary criteria used in predicting a detector’s response. UL 217 is widely known as the standard for smoke detector testing. UL 217 defines a detector’s sensitivity as the relative degree of response of a detector. A high sensitivity denotes response to a lower concentration of smoke versus a low sensitivity under identical smoke build-up conditions. The sensitivity test sets visible obscuration limits a detector must activate at, before manufacturing and installation, Table 20.

Table 5: Visible Smoke Obscuration Limits

<table>
<thead>
<tr>
<th></th>
<th>%/ft</th>
<th>%/m</th>
<th>OD$^a$/ft</th>
<th>OD/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>4.0</td>
<td>12.5</td>
<td>0.0177</td>
<td>0.0581</td>
</tr>
<tr>
<td>Min</td>
<td>0.5</td>
<td>1.6</td>
<td>0.0022</td>
<td>0.0072</td>
</tr>
</tbody>
</table>

The test method states standards for the testing environment including the ambient temperature, humidity, barometric pressure, and air velocity within the test compartment. Various tests are conducted to determine the limits of a detector’s reliability. These tests include the battery, humidity, temperature, corrosion, jarring, vibration, static discharge, and dust.

The light extinction is measured to determine the obscuration, where obscuration is:

$$O_u = \left[1 - \left(\frac{T_s}{T_c}\right)\right] \times 100 \quad \text{Equation 19}$$

$O_u$ is the % obscuration per meter
$T_s$ is the aerosol density meter reading with smoke
$T_c$ is the aerosol density meter reading with clean air
$d$ is the distance in meters
$O_d$ is the % obscuration at distance $d$ where
The ratio of optical density per meter to mass concentration is termed particle optical density (POD). POD is shown to be a relatively constant property for each mode of burning, i.e., smoldering and flaming combustion. For each of the two modes of burning POD is approximately 3400 kg/m² for flaming and 1900 kg/m² for non-flaming.

The monochromatic transmittance $\tau_\lambda$, given by the ratio between the intensity of the emerging ($I_e$) and the Incident ($I_o$) beams, is related to the extinction coefficient $K_{ext}$ through Bouguer-Lambert’s law as follows:

$$\tau_\lambda = \ln \frac{I_e}{I_o} = -K_{ext}L \quad \text{Equation 21}$$

or

$$\frac{I_e}{I_o} = e^{-K_{ext}L} \quad \text{Equation 22}$$

$L$ is the path length in the medium that is producing the extinction.

$K_{ext}$ is the extinction coefficient

$e$ is the natural exponential function

Both scattering and absorption contribute to the extinction of the beam. In most practical cases, scattering can be neglected so the extinction and absorption coefficients practically coincide ($K_{ext} = K_{abs}$) and depend on the refractive index. The specific extinction $\sigma_{ext}$ is obtained by dividing $k_{ext}$ by the mass concentration, $c_m$, of smoke aggregates.

The UL 217 standard for smoke detection activation establishes the minimum and maximum obscuration rates for detector activation. The values can be used to establish expected number concentrations at detector activation. The number concentrations can then be used to calculate the particle travel distances need for agglomeration.
APPENDIX E PARTICLE SIZING METHODS
### E.1 Particle Sizing Methods

Interest in the transport and the continuous transformations of soot particles in the overfire region stems from the need for greater detection efficiency. One particular aspect of interest is particle size. There are a number of methods used for sizing particulates, including physical processes, imaging, and light scattering. Table 6 lists some of the various methods used for sizing and examining aerosols.

Table 6: Listing of various testing methods.

<table>
<thead>
<tr>
<th>Physical</th>
<th>Imaging</th>
<th>Light Scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieving</td>
<td>Photography</td>
<td>Absolute Intensity</td>
</tr>
<tr>
<td>Sedimentation</td>
<td>Microscopy</td>
<td>Intensity Ratio</td>
</tr>
<tr>
<td>Impactors</td>
<td>Holography</td>
<td>Duel Beam</td>
</tr>
<tr>
<td>Thermophoresis</td>
<td>PIV</td>
<td>Visibility</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phase Doppler</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DCW</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Projected Grids</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow Doppler</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pulse Displacement</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polarization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diffraction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DLS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PCS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Transmission</td>
</tr>
</tbody>
</table>

The first method, physical processes, can be accomplished through sieving, sedimentation, impactors, and thermophoresis. The direct sampling of the particles is an intrusive technique that can affect the structure and the various properties of the soot. Some of the physical methods are based on the fact that soot deposition rates on cold targets immersed in a hot plume are dominated by particle thermophoresis. Thermophoretic deposition is driven by the presence of a temperature gradient created by a cold surface inside the hot flow field of a particle-laden gas [1]. This gradient can be established by introducing a probe surface into the hot gasses.

The second method, imagining, includes photography, microscopy, Transmission Electron Microscopy (TEM), holography, and Particle Image Velocimetry (PIV). The physical and imaging methods were discarded due to a variety of reasons including the information desired, sensitivity, and effect on smoke processes.
The third method is laser light scattering. Laser light scattering is widely used for analyzing and sizing soot. It has considerable appeal because it is un-intrusive, allowing observation of the soot field without intervening in the chemical or physical processes. The properties that make the laser a useful tool include its monochromatic nature, and spectral power. Spectral power describes the intensity per unit wavelength band of the laser. For most lasers the range of wavelengths is confined to one frequency or to a small frequency interval, making the laser nearly monochromatic. This means that large amounts of power can be concentrated in narrow wavelength bands. An extensive search of particle sizing techniques was conducted. Many techniques were scrutinized and eliminated. Laser-based techniques were chosen, specifically laser scattering because of its non-intrusive nature, sensitivity to particle size changes, and its similarity to light scattering detectors. However, laser scattering is characterized by its own set of issues, such as light scattering by a single or group of particles, focused beam effects, sample volume size, and light intensity profiles. Focused beam effects can cause changes to the particulate through heating, however, there are no physical changes to the particulate due to the low power of the laser used in this thesis. This corresponds to an elastic scattering, where the word elastic signifying no change of wavelength and a unintrusive process as mentioned earlier.

Laser scattering can be categorized into two sub-categories, Single Particle Counters (SPC) and Ensemble. Ensemble measures a large distribution or group of particles. When considering the interaction of light with an aerosol it is usually assumed that only single scattering occurs, but it is well acknowledged that multiple scattering occurs and increases with cluster size and number density. Therefore, when considering whether SPC or Ensemble scattering is preferred, the possibility of multiple scattering must be considered. Single scattering is the scattering by well-defined separate particles. The extension of the single scattering theory to multiple particles can be performed at two levels. The simplest level occurring at low concentrations. Complications can arise at high concentrations where multiple scattering and particle interaction effects become significant. There are rigorous multiple scattering calculations for determining the effects of multiple scattering. A simple and conclusive test to determine the absence of multiple scattering is to measure the intensity of a beam passing through the soot sample. Ensemble methods are generally restricted to extinctions in laser power of less than 50%
to avoid complications due to multiple scattering effects [2]. Multiple scattering also seems to be sensitive to structure in the cluster than that describable by the fractal dimension and hence may allow quantification and measurement of the structure [3]. However, the agglomerates can be assumed to be spherical particles [4].

Small amounts of smoke do not require multiple scattering calculations. The volume and concentration of smoke within the smoke detector chamber is relatively small. There is no need for the complex corrections for multiple scattering and multiple scattering effects would not greatly influence the response time of the detectors. Along those lines the experimental control volume is also quite small and will contain low concentration, therefore no multiple scattering adjustments will be conducted.

REFERENCES:


APPENDIX F LASER LIGHT SCATTERING THEORY
F.1 Laser Light Scattering Theory

Scattering applications range from one end of the electromagnetic spectrum to the other. Laser light scattering is well documented and a variety of theories exist containing various assumptions. The light scattering theory describes how light transmitted from one source to one receiver becomes scattered by a particle or aerosol. Two angles characterize the direction of scattering. The first angle theta, \( \theta \), is created by two lines on the horizontal plane of scattering. The laser beam creates the first line as it travels to the scatterer from the source; the second line is created as the scattering beam travels to the receiving optics. The second angle is the azimuth angle \( \phi \). The azimuth angle represents the vertical scattering angle received by the detector, Figure 20.

Figure 20: Coordinate system for scattering from agglomerates of small spheres.
Many theories are available depending on the assumptions that can include particle size, particle shape, light source and various particle properties. There are three basic size regions that can define which theory will apply. The regions are defined by the ratio of particle diameter (d) to the wavelength of the incident light. In general, these regions correspond to small, medium and large particles within the following limits:

\[
\begin{align*}
d/wavelength & < 0.1 \\
0.1 & < d/wavelength < 4.0 \\
d/wavelength & > 4.0
\end{align*}
\]

For larger particulate, or particles that are large compared to the wavelength of radiation, the scattering processes are commonly described by reflection, refraction, and diffraction. For particles that are of the order of wavelength in size or smaller, the processes cannot be distinguished and are referred to as scattering only. However in general all the deflection phenomena and absorption are grouped under the heading of scattering.

Fraunhofer diffraction, Geometrical optics, Fresnel diffraction, are some of the theories not described within this paper. However it is worth mentioning a few as background into some of the concepts and assumptions behind laser scattering.

Rayleigh Scattering applies to particles very small compared to the wavelength of the laser (d/wavelength < 0.1). Rayleigh scattering technique can supply information such as concentration, density, temperature, and flame thickness in a flow field [1].

The Rayleigh-Debye-Gans (RDG) theory assumes that Multiple scattering effects within each aggregate are negligible, however, RDG scattering theory can be modified to account for the actual soot morphology. This is known as RDG-FA or Rayleigh-Debye-Gans for Fractal Agglomerates. This elaborate theory has been shown to yield all physical soot parameters, such as, sphere diameter, soot volume fraction, fractal dimension, and aggregate size distribution when multi-angle scattering data is available, ie. every 10 degrees between 30 and 150 degrees. [1]

The Mie Theory lies in the medium size range (0.1 < d/wavelength < 4.0) well within the smoke particle size range. The theory assumes spherical monodisperse particles and is considered a single particle counter. These attributes made the theory ideal for the calibration of the experimental laser scattering test set up and applicable to the soot particle sizing.
G.1 Maxwell Equations

Light is a transverse wave, with the electric and magnetic fields varying in orientation, Figure 21.

Figure 21: Diagram of light as a transverse wave, broken into its two electromagnetic components.

A light wave carries electromagnetic energy and thereby can interact with a light detector, such as a Photo Multiplier Tube (PMT). The magnitude and direction of the electromagnetic energy at all points in space is given by the poynting vector $\mathbf{S}$. $\mathbf{S}$ is equal to $\mathbf{E}$ times $\mathbf{H}$ where $\mathbf{E}$ and $\mathbf{H}$ are the electric and magnetic field respectively. Energy flows in the direction in which the wave advances and flows the right hand rule.

$$\left(\mathbf{S}\right) = \mathbf{E} \times \mathbf{H} \quad \text{Equation 23}$$

The most important property of the scattering wave is it’s intensity ($I$) or energy flux per unit area in units of $\text{W/m}^2$. In optics this is called the irradiance. The magnitude of $(\mathbf{S})$ is the irradiance or intensity of the beam.

In 1865, Maxwell unified and extended the laws of Faraday, Gauss, and Ampere [2]. This was an outstanding achievement by Maxwell because electric and optical phenomena were linked and has since been known as Maxwell’s electromagnetic theory of light. Maxwell’s theoretical treatment resulted in a predicted propagation velocity of electromagnetic waves in a vacuum, $c=1/(\varepsilon\mu)^{1/2}$. In contrast, a wave moving through a material medium travels at a speed $v=1/(\varepsilon_o\mu_o)^{1/2}$. Here $\varepsilon$ is the permittivity and $\mu$ is the permeability of the medium. The absolute index of refraction ($m$) is then defined by:
\[ m = n + ik = c \sqrt{\varepsilon \mu} = \sqrt{\frac{\varepsilon \mu}{\varepsilon_0 \mu_0}} \quad \text{Equation 24} \]

The fundamental equations of electromagnetic theory, Maxwell’s equations, can be used to describe the interaction of electric and magnetic fields within any isotropic medium. Maxwell’s 4 fundamental equations are listed below in equations 22 through equation 25.

\[ \nabla \times H = \gamma \frac{\delta E}{\delta t} + \frac{E}{r_e} \quad \text{Equation 25} \]

\[ \nabla \times E = -\mu \frac{\delta H}{\delta t} \quad \text{Equation 26} \]

\[ \nabla \cdot E = 0 \quad \text{Equation 27} \]

\[ \nabla \cdot H = 0 \quad \text{Equation 28} \]

\( E \) is the Electric intensity in Newtons per Coulomb
\( H \) is the magnetic intensity in Coulombs per meter second
\( r_e \) is the electrical resistivity in Newton meter squared second per Coulomb squared
\( \gamma \) is the electrical permittivity measures in Coulomb squared per Newton meter squared
\( \mu \) is the magnetic permeability in Newton seconds squared per coulomb squared

The solution to these equations reveals how radiation waves travel within a material and what the interaction is between the electric and magnetic fields. By knowing how the waves move in each of two adjacent media and applying coupling relations at the interface between the media, the relations governing reflection and absorption are formulated [3].
REFERENCES:


APPENDIX G MIE THEORY
**G.1 Mie Theory**

The measured optical properties of soot can be used to determine the soot particle properties using results from Maxwell’s electromagnetic theory [1]. In 1908, Gustav Mie originally applied the electromagnetic theory to derive properties of the electromagnetic field when a monochromatic wave is incident upon a spherical surface. The exact solution of the Maxwell equations for an absorbing particle of arbitrary size is possible only for the sphere and is known as the Mie theory.

The Mie intensity coefficients (i perpendicular and i parallel) refer to the intensity of light vibrating perpendicular and parallel to the scattering plane through the direction of propagation of the incident and scattered beams. The non-dimensional values are used in equation 26 to find the scattering intensity of a solid spherical particle. The scattered intensity, $I_s$, in watts per meter squared is calculated in equation 29.

$$I_s = I_o \frac{\lambda^2}{8\pi^2 l^2} \left( i_\perp, i_\parallel \right) \quad \text{Equation 29}$$

where $i$ is the Mie intensity parameter

$I_o$ is the incident light

$l$ is the distance from the center of the particle to the receiver

$\lambda$ is the wavelength of the laser

The scattering intensity in equation 21 is the amount of scattered laser light per particle at a specific angle, therefore the concentration of particles in the environment must be considered when calculating the total intensity as in equation 30.

$$I_{\text{total}} = I_o \frac{\lambda^2 N_o V_s}{8\pi^2 l^2} \left( i_\perp, i_\parallel \right) \quad \text{Equation 30}$$

$V_s$ is the scattering volume

$N_o$ is the concentration

The Mie intensity coefficients, (i) perpendicular and parallel, are calculated using the scattering amplitudes $S_1$ and $S_2$ as seen in equation 31.
\[ i_{11} = S_{11} + S_{12} = |S_2|^2 \]  
Equation 31

\[ i_{\perp} = S_{11} - S_{12} = |S_1|^2 \]

The formulas for the scattering amplitude are listed along with the other Mie scattering quantities in the equations below.

\[ Q_{\text{ext}} = \frac{2}{x^2} \sum_{n=1}^{N} (2n + 1) \text{Re}(a_n + b_n) \] (extinction efficiency)  
Equation 32

\[ Q_{\text{sca}} = \frac{2}{x^2} \sum_{n=1}^{N} (2n + 1)(|a_n|^2 + |b_n|^2) \] (scattering efficiency)  
Equation 33

\[ g = \frac{4}{x^2 Q_{\text{sca}}} \sum_{n=1}^{N} \left[ \frac{n(n + 2)}{n + 1} rE(a_n a_{n+1} + b_n b_{n+1}) + \frac{2n + 1}{n(n + 1)} \text{Re}(a_n b_n) \right] \] (asymmetry factor)  
Equation 34

\[ S_1(\mu) = \sum_{n=1}^{N} \frac{2n + 1}{n(n + 1)} \left[ a_n \tau_n(\mu) + b_n \tau_n(\mu) \right] \] (complex scattering amplitude)  
Equation 35

\[ S_2(\mu) = \sum_{n=1}^{N} \frac{2n + 1}{n(n + 1)} \left[ a_n \tau_n(\mu) + b_n \tau_n(\mu) \right] \] (complex scattering amplitude)  
Equation 36

where \( Q_{\text{sca}} \) and \( Q_{\text{ext}} \) are the scattering and extinction efficiency of the particles in the aerosol and

\[ Q_{\text{sca}} = \frac{C_{\text{sca}}}{G} \]

\[ Q_{\text{ext}} = \frac{C_{\text{ext}}}{G} \]  
Equation 38

\[ Q_{\text{abs}} = \frac{C_{\text{abs}}}{G} \]

\( C \) is the scattering cross section of the spherical particle

\( G \) is the geometric area of the sphere.

Conservation of energy states that \( C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}} \) in units of area therefore \( Q_{\text{ext}} = Q_{\text{sca}} + Q_{\text{abs}} \).  
\( g \) is the asymmetry parameter. For a particle that scatters light the same in all directions or isotropically, \( g \) vanishes. \( g \) also vanishes if the scattering is symmetric about a scattering angle of 90 degrees. If the particles scatters more light towards the forward
direction away from the laser source, $g$ is positive, $g$ is negative if the scattering is
directed more towards the back direction or back towards the laser source.

The equations for $S_1$ and $S_2$ contain the functions $\pi_n$ and $\tau_n$ which are angle dependent.
$P_n$ is the Legendre Polynomials

$$\pi_n(\cos \theta) = \frac{1}{\sin \theta} P_n'(\cos \theta)$$
$$\tau_n(\cos \theta) = -\sin \theta \frac{P_n'(\cos \theta)}{d(\cos \theta)}$$

The equations for $S_1$ and $S_2$ also contain the complex valued Mie coefficients $a_n$ and $b_n$.
$a_n$ and $b_n$ depend on $(x)$ where $x=k_0R$, and the complex refractive index. They are
expressed in terms of spherical Bessel functions.

$$a_n = \frac{m \psi_n(mx)\nu'_n(x) - \psi'_n(mx)\psi_n(x)}{m \psi_n(mx)\xi'_n(x) - \psi'_n(mx)\xi_n(x)}$$
$$b_n = \frac{\psi_n(mx)\nu'_n(x) - m \psi'_n(mx)\psi_n(x)}{\psi_n(mx)\xi'_n(x) - m \psi'_n(mx)\xi_n(x)}$$

where

$$x = k_n R$$
$$\psi_n(z) = z j_n(z)$$
$$\xi_n(z) = z h_n^{(1)}(z)$$

are Riccati-Bessel functions. There are several algorithms for the calculation of $a_n$ and $b_n$.
These are discussed by, Bayuel and Jones [2] as well as Bohren and Huffman. [1]

The full relations indicating how the intensity and state of polarization of the scattered
light depend on the intensity a state of the polarization of the incident light are contained
in the matrix equation

$$\begin{bmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{bmatrix} = \frac{1}{k_0^2 r^2} \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{bmatrix} \begin{bmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{bmatrix}$$

Equation 42
where $S_{ij}$ form the elements of the Stokes Matrix. When we examine scattering intensity we need a means of describing all the polarization states and their relationships. This is achieved through the Stokes matrix, which relates four intensities defined by

$$I = E_{\|}^*E_{\|} + E_{\perp}^*E_{\perp}$$
$$Q = E_{\|}^*E_{\perp} - E_{\perp}^*E_{\|}$$
$$U = E_{\|}^*E_{\|} + E_{\perp}^*E_{\perp}$$
$$V = E_{\|}^*E_{\perp} - E_{\perp}^*E_{\|}$$

where (*) means it’s a complex conjugate

For our purposes the matrix elements can be eliminated to show the polarized state of the laser beam

$$\begin{bmatrix}
I_s \\
Q_s \\
U_s \\
V_s
\end{bmatrix} = \frac{1}{k^2 r^2}
\begin{bmatrix}
S_{11} & S_{12} & 0 & 0 \\
S_{12} & S_{11} & 0 & 0 \\
0 & 0 & S_{33} & S_{34} \\
0 & 0 & -S_{34} & S_{33}\end{bmatrix}
\begin{bmatrix}
I_i \\
Q_i \\
U_i \\
V_i
\end{bmatrix}$$

Equation 44

where $I, Q, U,$ and $V$ are the Stokes parameters, therefore

$$S_{11} = \frac{1}{2}(|S_2|^2 + |S_1|^2)$$

Equation 45

$$S_{12} = \frac{1}{4}(|S_2|^2 - |S_1|^2)$$

Equation 46

$$S_{33} = \frac{1}{2}(S_2^*S_1 + S_2S_1^*)$$

Equation 47

$$S_{34} = \frac{i}{2}(S_1^*S_2 - S_2S_1^*)$$

Equation 48

The poyting vector ($S$) determines the energy flux in the wave.

$$\vec{S} = \frac{1}{2} \text{Re}(\vec{E} \times \vec{H}^*)$$

Equation 49

which becomes

$$\vec{S}_{scat} = \frac{1}{2} \left( \frac{\varepsilon_{\infty}}{\mu_{\infty}} \right) \frac{E_o^2}{k_o^2 r^2} |A(\theta, \phi)|^2 \vec{r} = \frac{I_o}{k_o^2 r^2} F(\theta, \phi) \vec{r}$$

Equation 50
The degree of polarization is defined by

\[
POL = \frac{S_{12}}{S_{11}} = \frac{i_\perp - i_{\parallel}}{i_\perp + i_{\parallel}} \quad \text{Equation 51}
\]

REFERENCES:

2) A.R. Jones, Light Scattering for Particle Characterization, Progress in Energy and Combustion Science 25 1-53

3) T.T. Charalampopoulos and H. Chang, Agglomerate Parameters and Fractal Dimension of soot using Light Scattering -Effects on Surface Growth


**H.1 FORTRAN Program**

The Mie theory calculations are complex and time consuming, therefore, a FORTRAN program was used in order to calculate the results. The FORTRAN program uses the refractive index of the surrounding medium, the refractive index of the scatterer, the particle radius (µm), and the laser wavelength (µm) as input variables. Frequently it is desirable to change from the particle radius, to the size parameter, x, where

\[ x = \frac{2\pi r}{\lambda} \]  

Equation 52

The program outputs the size parameter, as well as the scattering efficiency, and the extinction efficiency. The polarization, S₁₁, S₃₃, and S₃₄ values verses angle are also displayed in a table. The input and output values are displayed in an output file as seen in section I.3 FORTRAN output file.

The program was taken form Bohren, and Huffman Absorption and scattering of light by small particles. After the program was written by Brohren and Huffman an extensive study was published by Wiscombe [1]. The program was modified in the light of Wiscombe’s work. In the program convergence of the series is not determined by iteration. Instead, slightly more than x terms are sufficient for convergence, where x is the size parameter. Thus, the series in the program are terminated after NSTOP terms, where NSTOP is the integer closest to equation 53.

\[ x + 4x^{1/3} + 2 \]  

Equation 53

**H.2 FORTRAN output file**

Below is the output file produced from the FORTRAN program listed above for a particle with a radius of 265 nm a refractive index of 1.33-0.0000001 scattering light with a wavelength of 500nm.

```plaintext
SPHERE SCATTERING PROGRAM

REFMED = 1.0000  REFRE = 0.133000E+01  REFIM = 0.100000E-06
SPHERE RADIUS = 0.265  WAVELENGTH = 0.5500
SIZE PARAMETER = 3.027

QSCA = 0.178785E+01  QEXT = 0.178785E+01  QBACK = 0.912854E-01
```

91
Checks on the program has been thoroughly conducted and there are several independent verifications that can be conducted. For example, the extinction efficiency ($Q_{ext}$) and the scattering efficiency ($Q_{sca}$) must not be negative. $Q_{ext}$ must be greater than $Q_{sca}$ except for nonabsorbing spheres, in which case they are equal. Polarization (POL), the degree of polarization, must vanish for scattering angles 0 and 180. Also the 4X4 scattering matrix elements must satisfy equation 54.

$$\left(\frac{S_{12}}{S_{11}}\right)^2 + \left(\frac{S_{33}}{S_{11}}\right)^2 + \left(\frac{S_{34}}{S_{11}}\right)^2 = 1 \quad \text{Equation 55}$$

S represents a real number amplitude in a transformation matrix. $S_{12}$ the last remaining element of the matrix can be calculated using equation 56 or equation 57.
\[
\frac{S_{12}}{S_{11}} + \frac{S_{33}}{S_{11}} + \frac{S_{34}}{S_{11}} = 1 \quad \text{Equation 56}
\]

\[
S_{11}^2 = S_{12}^2 + S_{33}^2 + S_{34}^2 \quad \text{Equation 57}
\]

Once \( S_{12} \) is calculated, the Mie Coefficients, \( i \), vibrating perpendicular and parallel to the plane through the directions of propagation of the incident and scattered beams can be calculated using equation 53 and equation 54. The polarization can also be recalculated and compared to the FORTRAN polarization output as a check using equation 55.

\[
i_{\|} = S_{11} + S_{12} = |S_2|^2 = HH \quad \text{Equation 58}
\]

\[
i_{\perp} = S_{11} - S_{12} = |S_1|^2 = VV \quad \text{Equation 59}
\]

\[
POL = -\frac{S_{12}}{S_{11}} = \frac{i_{\perp} - i_{\|}}{i_{\perp} + i_{\|}} \quad \text{Equation 60}
\]

As an additional check for the FORTRAN program, an example in Absorption and Scattering of light by small particle written by Bohren and Huffman was recreated. The example used a water droplet with a size parameter of 3, illuminated by visible light of wavelength 0.55 um. At this wavelength the complex refractive index of water is 1.33 + i10^{-8}. A size parameter of \( x=3 \) corresponds to a droplet radius of about 0.26 um.
Figure 22: Graph of the polarization ratio from a water droplet. The water droplet example was used as a check of the FORTRAN against the results previously published in Absorption and Scattering of light by small particle written by Bohren and Huffman.
Figure 23: Graph of the Mie intensity coefficients from a water droplet performed as a check and compared to previously published results.

The results from the FORTRAN program match those produced from the example noted in the book, Figure 22 and Figure 23. The water droplet example was used as a check of the FORTRAN against the results previously published in Absorption and Scattering of light by small particle written by Bohren and Huffman.

The FORTRAN was used to calculate the Mie scattering results, vertical and horizontal polarization, for particles ranging in size from 5nm to 1000nm in increments on 5nm. Two separate groups of results were calculated for the two index of refraction used, 1.57-0.65i and 1.75-0.5i. Figure 24 and Figure 25 display the Mie intensity coefficient values for VV and HH. Figure 24 contains the results for particles ranging from 100nm to 500nm in increments of 100nm and Figure 25 contains the results for the
particles ranging in size from 600nm to 1000nm in increments of 100nm. The results were displayed on two separate graphs and in increments of 100nm to reduce the graph clutter. The graphs clearly show that each particle size, when everything else is constant, has a distinct Mie Intensity coefficient for each angle. This results in a distinct scattering curve for each particle size, if all other variables are kept constant.

Figure 24: Mie Intensity Coefficient values, VV and HH, for sizes ranging 100 nm to 500 nm. The above graphs show the changes of the Mie intensity coefficient with change in size parameter. In order to validate the results of the FORTRAN program numerous iterations were run for various scenarios.
Figure 25: Mie Intensity Coefficient values, VV and HH, for sizes ranging 600 nm to 1000 nm. The above graphs show the changes of the Mie intensity coefficient with change in size parameter. In order to validate the results of the FORTRAN program numerous iterations were run for various scenarios.

The results displayed above in Figure 24 and Figure 25 are again displayed in Figure 26 and Figure 27. Figure 26 and Figure 27 are 3-dimensional depictions of the Mie intensity coefficients. Figure 26 represents the horizontally polarized values and demonstrates the deep trough at the small particle sizes, associated with Rayleigh scattering.
Figure 26: A graph showing the Mie Coefficient (HH) values verses angle and size.
Figure 27 represents the vertically polarized values. It should be noted that the intensity values are non-dimensional values and represent the shape of the scattering intensity for a given particle size.
Figure 28: Graph of the polarization ratio for a PSL sphere of 500 nanometers calculated using the Mie theory.

As an additional check of the FORTRAN program, the results graphed above were used to calculate the polarization ratio of each PSL sphere. Figure 28 is an example of the polarization ratio calculated for a sphere with a size parameter of 4.963. Repeating the process, Excel can be used to produce a surface graph of the polarization intensity from 0 to 180 degrees verses the size parameter. The final product is a three dimensional graph of the polarization amplitude. On the back side of the graph where the size parameter is small, hence the particle size is small, it can be seen that the polarization is Rayleigh like in that the intensity distribution is evenly distributed on each side of the 90 degree mark with the lowest intensity at 90. The results roughly match the results seen in
Figure 29: A graph of the results of a number of tests for various size parameters equally spaced apart. The results are given in polarization intensity at angles ranging from 0 to 180 degrees. The results match the results seen in Light Scattering by nonspherical particles: Theory, Measurement, and Applications written by Michael L. Mishchenko, Larry D Travis, and Joop W Hovenier.
Finally the Mie intensity coefficients and related outputs were produced for the 500 nm and 1000nm PSL spheres used in the calibration aerosol, Figure 30 and Figure 31 for future comparison.

Figure 30: Graph of Mie intensity coefficients for 500 nm Polystyrene latex spheres.

Figure 30: Graph of Mie intensity coefficients for 500 nm Polystyrene latex spheres.
Figure 31: Graph of Mie intensity coefficients for 1000 nm Polystyrene latex spheres.

Although this was not a check of the FORTRAN program the curves did match the experimental curved collected from the laser scattering apparatus.

**H.3 Program**

Below are the listed command lines for a FORTRAN program. This FORTRAN program as well as being listed here is listed in the back of Bohren and Huffman’s book.

```fortran
1 PROGRAM CALLBH (INPUT=TTY,OUTPUT=TTY,TAPE5=TTY)
2C
3C CALLBH CALCULATES THE SIZE PARAMETER (X) AND RELATIVE REFRACTIVE INDEX (REFREL) FOR A GIVEN SPHERE REFRACTIVE INDEX, MEDIUM REFRACTIVE INDEX, RADIUS, AND FREE SPACE WAVELENGTH. IT THEN CALLS BMIE, THE SUBROUTINE THAT COMPUTES AMPLITUDE SCATTERING MATRIX ELEMENTS AND EFFICIENCIES.
4C
5C COMPLEX REFREL,S(200),S2(200)
6C WRITE (5,11)
7C REFMED = (REAL) REFRACTIVE INDEX OF SURROUNDING MEDIUM
8C REFMED=1.0
```

103
16C  REFRACTIVE INDEX OF SPHERE = REFRE + I*REFIM
17C
18  REFRE=1.55
19  REFIM=0.0
20  REFREL=CMPLX(REFRE,REFIM)/REFMED
21  WRITE (5,12) REFMED,REFRE,REFIM
22C
23C  RADIUS (RAD) AND WAVELENGTH (WAVEL) SAME UNITS
24C
25  RAD=.525
26  WAVEL=.6328
27  X=2.*3.14159265*RAD*REFMED/WAVEL
28  WRITE (5,13) RAD,WAVEL
29  WRITE (5,14) X
30C
31C  NANG = NUMBER OF ANGLES BETWEEN 0 AND 90 DEGREES
32C  MATRIX ELEMENTS CALCULATED AT 2*NANG - 1 ANGLES
33C  INCLUDING 0, 90, AND 180 DEGREES
34C
35  NANG=11
36  DANG=1.570796327/FLOAT(NANG-1)
37  CALL BHMIE(X,REFREL,NANG,S1,S2,QEXT,QSCA,QBACK)
38  WRITE (5,65) QSCA,QEXT,QBACK
39  WRITE (5,17)
40C
41C  S33 AND S34 MATRIX ELEMENTS NORMALIZED BY S11.
42C  s11 IS NORMALIZED TO 1.0 IN THE FORWARD DIRECTION
43C  POL=DEGREE OF POLARIZATION (INCIDENT UNPOLARIZED LIGHT)
44C
45  S11NOR=0.5*(CABS(S2(J))**2+CABS(S1(J))**2)
46  NAN=2*NANG-1
47  DO 355 J=1,NAN
48  AJ=J
49  s11=0.5*CABS(S2(J))*CABS(S2(J))
50  S11=S11+0.5*CABS(S1(J))*CABS(S1(J))
51  S12=0.5*CABS(S2(J))*CABS(S2(J))
52  S12=S12-0.5*CABS(S1(J))*CABS(S1(J))
53  POL=-S12/S11
54  S33=REAL(S2(J)*CONJG(S1(J)))
55  S33=S33/S11
56  S34=AIMAG(S2(J)*CONJG(S1(J)))
57  S34=S34/S11
58  S11=S11/S11NOR
59  ANG=DANG*(AJ-1.)*57.3958
60  355 WRITE (5,75) ANG,S11,POL,S33,S34
61  65 FORMAT (//,1X,"QSCA= ",E13.6,3X,"QEXT = ",E13.6,3X,
62    "QBACK = ",&.E13.6)
63  75 FORMAT (1X,F6.2,2X,E13.6,2X,E13.6,2X,E13.6,2X,E13.6)
64  11 FORMAT ("SPHERE SCATTERING PROGRAM"//)
65  12 FORMAT(5X,"REFMED = ",F8.4,3X,"REFRE = ",&.E14.6,3X,
66    3*REFIM = ",&.E14.6)
67  13 FORMAT (5X,"SPHERE RADIUS = ",&.F7.3,3X,"WAVELENGTH = ",&.F7.4)
68  14 FORMAT (5X,"SIZE PARAMETER = ",&.F8.3//)
70  STOP
71  END
72C
SUBROUTINE BHMIE CALCULATES AMPLITUDE SCATTERING MATRIX
ELEMENTS AND EFFICIENCIES FOR EXTINCTION, TOTAL SCATTERING
AND BACKSCATTERING FOR A GIVEN SIZE PARAMETER AND
RELATIVE REFRACTIVE INDEX

SUBROUTINE BHMIE (X,REFREL,NANG,S1,S2,QEXT,QSCA,QBACK)
DIMENSION AMU(100),THETA(100),PI(100),TAU(100),PI0(100),PI1(100)
COMPLEX D(3000),Y,REFREL,XI,XI0,XI1,AN,BN,S1(200),S2(200)
DOUBLE PRECISION PSI0,PSI1,PSI,DN,DX
DX=X
Y=X*REFREL
C
SERIES TERMINATED AFTER NSTOP TERMS
XSTOP=X+4.*X**.3333+2.0
NSTOP=XSTOP
YMOD=CABS(Y)
NMX=AMAX1(XSTOP,YMOD)+15
DANG=1.570796327/FLOAT(NANG-1)
DO 555 J=1,NANG
AMU(J)=COS(THETA(J))
C
LOGARITHMIC DERIVATIVE D(J) CALCULATED BY DOWNWARD
RECURRENCE BEGINNING WITH INITIAL VALUE 0.0 + I*0.0
AT J = NMX
D(NMX)=CMPLX(0.0,0.0)
NN=NMX-1
DO 120 N=1,NN
RN=NMX-N+1
120 D(NMX-N)=(RN/Y)-(1./(D(NMX-N+1)+RN/Y))
DO 666 J=1,NANG
PI0(J)=0.0
666 PI1(J)=1.0
NN=2*NANG-1
DO 777 J=1,NN
S1(J)=CMPLX(0.0,0.0)
777 S2(J)=CMPLX(0.0,0.0)
RICCATI-BESSEL FUNCTIONS WITH REAL ARGUMENT X
CALCULATED BY UPWARD RECURRENCE

PSI0=DCOS(DX)
PSI1=DSIN(DX)
CHI0=-SIN(X)
CHI1=COS(X)
APSI0=PSI0
APSI1=PSI1
XI0=CMPLX(APSI0,-CHI0)
XI1=CMPLX(APSI1,-CHI1)
QSCA=0.0
N=1
200 DN=N
RN=N
FN=(2.*RN+1.)/(RN*(RN+1.))
PSI=(2.*DN-1.)*PSI1/DX-PSI0
APSI=PSI
CHI=(2.*RN-1.)*CHI1/X - CHI0
XI=CMPLX(APSI,-CHI)
AN=(D(N)/REFREL+RN/X)*APSI - APSI1
AN=AN/((D(N)/REFREL+RN/X)*XI-XI1)
BN=(REFREL*D(N)+RN/X)*APSI - APSI1
BN=BN/((REFREL*D(N)+RN/X)*XI-XI1)
QSCA=QSCA+(2.*RN+1.)*(CABS(AN)*CABS(AN)+CABS(BN)*CABS(BN))
DO 789 J=1,NANG
JJ=2*NANG-J
PI(J)=PI1(J)
TAU(J)=RN*AMU(J)*PI(J) - (RN+1.)*PI0(J)
P=((-1.)**N)
S1(J)=S1(J)+FN*(AN*PI(J)+BN*TAU(J))
T=(-1.)**N
S2(J)=S2(J)+FN*(AN*TAU(J)+BN*PI(J))
IF(J.EQ.JJ) GO TO 789
S1(JJ)=S1(JJ) + FN*(AN*PI(J)*P+BN*TAU(J)*T)
S2(JJ)=S2(JJ)+FN*(AN*TAU(J)*T+BN*PI(J)*P)
789 CONTINUE
PSI0=PSI1
PSI1=PSI
APSI1=PSI1
CHI0=CHI1
CHI1=CHI
XI1=CMPLX(APSI1,-CHI1)
N=N+1
RN=N
DO 999 J=1,NANG
PI1(J)=((2.*RN-1.)/(RN-1.))*AMU(J)*PI(J)
PI1(J)=PI1(J)-RN*PI0(J)/(RN-1.)
999 PI0(J)=PI(J)
IF (N-1-NSTOP) 200,300,300
QSCA=(2./(X*X))*QSCA
QEXT=(4./(X*X))*REAL(S1(1))
QBACK=(4./(X*X))*CABS(S1(2*NANG-1))*CABS(S1(2*NANG-1))
RETURN
END

REFERENCES
APPENDIX I MODIFICATIONS TO THE MIE THEORY
I.1 Mie Theory Modification

The Mie Theory assumes scattering from a single spherical particle. As stated earlier, smoke particles are not solid spheres and are usually not in an aerosol of monodisperse particles. To compensate for the assumptions of the Mie theory an effective diameter of the equivalent sphere becomes;

\[ \frac{d_e}{d_p} = N^{\frac{1}{3}} \]  \hspace{1cm} \text{Equation 61}

\( d_e \) is the volume equivalent diameter of the aggregate
\( d_p \) is the primary particle diameter
\( N \) is the number of primary particles in the aggregate

The number of primary particle can also be calculated using the radius of gyration (\( R_g \)) using equation 72.

\[ N = k_f \left( \frac{R_g}{d_p} \right)^{D_f} \]  \hspace{1cm} \text{Equation 62}

\( k_f \) is the prefactor (range 5.8-9.4)
\( R_g \) is the radius of gyration
\( D_f \) is the fractal dimension.

It is usually the case in scattering experiments that a large number of scatterers are simultaneously illuminated. Modifications to the Mie theory were not made to compensate for the agglomerate shape of the particulate. Because of the large number of particulate being illuminated the averaged scattered intensity is similar to a sphere. The results from the Mie theory can be used in calculating the scattering intensity from multiple particles as well as polydisperse ensembles. If the concentration is low enough to avoid multiple scattering, then a sample containing (N) scattering particles is illuminated and the intensity scattered by the cloud is (N) times that scattering by a single particle, Equation 61 and Equation 62.

\[ I_s = I_e \frac{\lambda^2}{8\pi^2l^2} \left( \frac{I}{l^{1/2}} \right) \]  \hspace{1cm} \text{Equation 63}
i is the Mie intensity coefficient

\[ I_{\text{total}} = I_o \frac{\lambda^2 N V}{8\pi^2 l^2} (i_{\perp}, i_{\parallel}) \]  \hspace{1cm} \text{Equation 64}

\( V_s \) is the scattering volume (approximately 15mm³)
\( N \) is the number concentration

This greatly simplifies the interpretation of the experiment: the total intensity measured is simply the sum of the intensity from each individual scatterer.

With a solution of monodisperse, non-interacting spheres, the observed intensity pattern is the same as the scattering intensity pattern of a single sphere, showing the same scattering intensity at various scattering angles. If the spheres are polydisperse the oscillations observed in the single sphere scattering pattern can be rapidly damped out.

When spherical particles of different sizes are present in the measurement volume it is necessary to integrate the Mie intensity coefficients over the size distribution. In the case of the scattering measurement from an ensemble of clusters the same applies. The aggregation process produces a size distribution that changes with time, and the collected scattering intensity will be the sum of the light scattered from each cluster in the size distribution. For example, if you had in 5nm particle and collected the scattering intensity at 90 degrees, the intensity could be value \( y \). If you had three 5 nm particle the collected intensity would then be \( 3y \). If you had a 5 nm particle scattering \( y \), 20 nm particle scattering \( z \) and 100 nm particle scattering \( w \), the collected scattering intensity would then be \( y+z+w \). Because of the undulating nature of the Mie scattering coefficients, especially at the larger sizes, this approach to measuring the polydisperse nature of the smoke aerosols results in an averaging effect seen in Figure 13. The figure shows the polarization intensity pattern for various size parameters over angle, similar to Figure 32. However, the intensities are averaged over a size range given by a normal distribution with a GSD of 2.3.
Figure 32: The graph of the averaged polarization for an example polydisperse aerosol with a GSD of 2.3.
J.1 METHODOLOGY, EXPERIMENTAL SET-UP

The purpose of this section is to describe the experimental plan and experimental setup. The experimental plan outlines the guidelines and safety procedures to ensure the successful, repeatable, and safe collection of data. The experimental bench top setup was where laser light scattering measurements were recorded. The objective of the experimental tests was to obtain data related to the process of smoke aging, specifically changes to particulate size. Collecting and recording the signal produced by the scattering of laser light from smoke aerosols along with the optical density completed the sizing measurements.

The optical density measurements were recorded through the use of a laser extinction system. The particle size measurements were recorded with an apparatus for measuring the light scattered by smoke as a function of the scattering angle and linear polarization. The test setup consisted of three major components: laser conditioning, receiving optics, and data acquisition.

The test setup was mounted on a 48” by 96” by 8.4” Veer optical table. The table included vibration isolation legs, a 1” grid of ¼-20 holes, 1/8” thick ferromagnetic steel skin with antireflective coating, and a 1’ by 1’ square hole cut into the surface. The 1’ by 1’ square hole was specially inserted to let smoke or gas pass through from under the table to the surface where the measurements were taken. The table helped establish a flat vibration isolated surface to conduct the laser measurements. This allowed for a defined scattering plane. The scattering plane is defined to be the plane in which the incident and scattering beams lie. For these experiments the scattering plane is horizontal.

The laser conditioning component of the test setup consists of a Melles Griot Helium Neon (HeNe) Laser with a power output of 5.0 mW and a beam diameter of 0.80 mm. The beam has a linear polarization ratio greater than 500:1 and operates at a wavelength of 633 nm. Linear polarization is when the intensity of the electric field vector is constant and the direction of oscillation is constant. In order to find particle size using the Mie theory linear polarization is needed. The orientation of the linear polarized light affects the amount of light scattered by the particles. A graph of the scattered light intensity to degree of polarization through air can be seen in Figure 33.
Figure 33: Graph of the scattered light intensity to degree of polarization through air. It can be seen the polarization rotator lens was slightly misaligned in the holder. This misalignment was compensated for during testing.

The laser beam was modulated to a frequency of 1200 Hz as it passed through a Model SR 540 optical chopper made by Stanford Research Systems, Inc. The SR 540 optical chopper was used to square-wave modulate the intensity of the optical signal. The unit can chop light sources at rates from 4Hz to 3.7kHz. Incorporating an optical chopper permitted the rejection of all but the laser wavelength of interest. The beam then passed through a polarization rotator to control the direction of polarization of the beam. The polarization rotator made it easier to shift from VV to HH rather than moving the orientation of the laser. The beam then became focused on the center of the control volume using a lens with a focal length of 15mm. The control volume had two holes inserted 180 degrees apart in the glass vessel to allow the laser to pass through while minimizing reflections off the glass surface. The laser light scattering from the aerosol appeared as a red line of light with a few bright spots arising from larger particles.

The receiving component of the test setup consisted of a Photo Multiplier Tube (PMT) mounted on a rotational stage. The rotational transition stage moved the receiving optics along an arc path ranging from 20 degrees to 155 degrees with a diameter of 0.508
meters (1 ft 8 in.) The rotational transition stage consisted of a linear transition stage and mounting rod. The mounting rod was a steel beam that passed directly under the control volume and was securely attached under the glass control volume by a pivot bolt assembly. The mounting beam was also attached to a secure pin centrally located to the linear transition stage. The pin could move along the axis of the mounting beam. As the linear stage moved, the receiving optics traveled in a circular path, Figure 6.

Figure 34: Top view diagram of rotational stage with receiving optics (yellow) attached to the mounting beam (black).

A variable iris diaphragm in front of the collecting lens defined the solid angle of scattered light the detector receives. The detectors solid angle limited the smallest size that can be measured and the accuracy of the particle sizing measurement. It is possible to choose a very small solid angle to collect almost pure degree scattering signal, but this can result in a signal weaker than the noise level. Thus, there was a trade off between signal to noise ratio and accuracy in sizing.
A collecting lens, a dichroic sheet polarizer, a pinhole, and a Photo Multiplier Tube (PMT) with a narrow band filter followed the iris diaphragm. A slight reduction of the intensity of the incident beam occurred at all elements along the optical train. The polarization filter reduced unwanted light from outside sources by only allowing the chosen polarized light to pass. A lens focused the light past the pinhole to the PMT reducing any arrent light from entering the PMT. A narrow band filter mounted to the PMT filtered out any light without a wavelength of 633nm. Unwanted light was produced by the lights in the lab as well as from reflections from unwanted particles, such as dust. It would not be cost effective to try and remove all of the dust in the test lab, however, darkening the test lab and building a light tight “black box” around the receiving optics of the test setup reduced the amount of stray light.

The PMT was a Hamamatsu R316 standard 1 1/8 inch side-on photo multiplier tube attached to a Hamamatsu HC 123-01 Regulated HV supply for high voltage power. The photo multiplier is a very versatile and sensitive detector of radiant energy in the ultraviolet, visible, and near infrared regions of the electromagnetic spectrum. The basic radiation sensor is the photo cathode and is located inside a vacuum envelope. Photoelectrons are emitted and directed by an appropriate electric field to an electrode or dynode within the envelope. A number of secondary electrons are emitted at this dynode for each impinging primary photoelectron. These secondary electrons are directed to a second dynode and so on until a final gain of around $10^7$ is achieved. An anode that provides the signal current collects the electrons from the last dynode. The particular PMT used has a cathode sensitivity at a wavelength of 633 nm of 41 mA/W and an anode sensitivity at a wavelength of 633nm of $4.1 \times 10^5$ A/W. In order to calibrate the output from the photo multiplier tube (PMT), the incident beam from the laser was diminished using neutral density filters. A known and small intensity of the beam entered the PMT, which then measured and recorded the intensity without damaging the PMT. Placing additional neutral density filters in front of the laser provided additional points for a calibration curve of the PMT.

Data acquisition (DAQ) begins once the signal is amplified within the lock-in amplifier that was attached to the light chopper. The signal passed from the lock-in to a National instruments BNC 2140 as it entered the DAQ the data was stored in the
computer. The data was then backed up and saved for processing and analysis. The system was calibrated using PSL spheres of monodisperse sizes of 500 nm and 1000 nm.
APPENDIX K AEROSOL GENERATION
K.1 Aerosol Generation

An important component of aerosol measurements is the production of monodisperse test aerosols for calibration of the particle size measuring apparatus. In aerosol research, monodisperse test aerosols of known size, shape, and density are highly desirable. The characteristics of an ideal aerosol generator are a constant and reproducible output of monodisperse particles. The angular light scattering system was calibrated by measuring the light scattered from polystyrene latex spheres (PSL) flowing through the scattering volume, as a function of angle. The absolute scattered intensities from the aerosol can be determined, because the properties of the aerosol are known. Experimental uncertainties of the calibration procedure are generally dominated by contamination of the scattering volume with room dust, diffusion dryer issues, and scattered light from the optics and other equipment. William C. Hinds proposed a simple way to generate solid-particle aerosols, by nebulizing a liquid suspension containing monodisperse solid particles of a known size [1]. Nebulization is the general name for the process of distributing a liquid into air-borne droplets. A nebulizer is a type of atomizer that produces an aerosol of small particles by removing larger spray droplets by impaction within the device. Nebulizers produce aerosols at concentrations of 5-50 g/m³ with MMDs of 1-10µm and GSDs of 1.5-2.5. Compressed air at a supply pressure of 5-50 psig exits from a small tube or orifice at high velocity. The low pressure created in the exit region by the Bernoulli effect causes liquid to be drawn from a reservoir into the air stream through a second tube. The liquid exits the tube and is accelerated in the air stream until it breaks into droplets. The spray stream is directed onto an impaction surface, where large droplets are deposited and drain back to the liquid reservoir. The operation principles are the same for most nebulizers, but the geometry of the components differs with each device. Most nebulizers produce a maximum particle number concentration of $10^{12}$-$10^{13}$/m³. The nebulizer used was from Gemini Scientific Corp. After nebulization, the liquid is removed from the aerosol concentration of PSL spheres using a diffusion dryer. This produces a solid monodisperse particle aerosol. The diffusion dryer is designed as a general-purpose aerosol dryer that has minimal aerosol loss. The drier consists of two 500 mm long concentric cylinders formed by an inner wire screen and plastic tube cylinder (10 mm diameter) and a clear plastic outer cylinder (70
mm ID) that contains a volume of silica gel (dry-rite). As wet aerosol flows through the empty inner cylinder, water vapors diffuse through the wire screen and into the silica gel. Particle loss is minimized because the particles do not come in contact with the silica gel. The silica gel is easily regenerated in an oven at 120 degrees Celsius.

Problems can arise in the generation of monodisperse aerosols. The first is when more than one sphere is present in a droplet when it is formed. When the droplet dries, the resulting particle is a cluster or chain of spheres. The empty droplets creates the second problem. Some of these empty droplets have a significant percentage of stabilizer in the liquid. When these “empty” droplets dry out the stabilizer forms a residue particle. Scattering can be corrected for the residue particles and cluster of spheres by calculating the number of doublet, triplets, etc [1].

Liquid suspensions of monodisperse polystyrene latex (PSL) spheres were chosen for the purpose of calibrating the laser scattering system. The PSL spheres are available in a wide range of sizes. For example, Duke Scientific, sells spheres from 20nm to 1mm, with more than 100 sizes between 0.002µm and 100µm. The spheres are part of a series of monodisperse polymer micro spheres with calibrated mean diameter traceable to the standard meter through the National Institute of Standards and Technology (NIST). The majority of these have uncertainty in their mean size of less than 1% and relative standard deviations for their size distributions of less than 2%. They are sold in 15-mL vials containing 0.5, 1, 2, or 10% solids in aqueous suspension. The water contains 0.02 or 0.2% stabilizer (surfactant and dispersant) to prevent coagulation in the liquid. Sphere sizes of 500 nm and 1000nm were chosen for their similarity to smoke particulate sizes.

The density of the spheres is 1.05 g/cm³, as seen in the Table 3.

Table 3: Properties of PSL spheres used for calibration of experimental setup.

<table>
<thead>
<tr>
<th>Sphere Size</th>
<th>1000 nm</th>
<th>500nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certified mean Diameter (nm)</td>
<td>993 +/- 21</td>
<td>491 +/- 4</td>
</tr>
<tr>
<td>Standard deviation (nm)</td>
<td>10</td>
<td>6.3</td>
</tr>
<tr>
<td>Microsphere composition</td>
<td>Polystyrene</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>Polymer density (g/cm³)</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>Index of refraction</td>
<td>1.59</td>
<td>1.59</td>
</tr>
<tr>
<td>Approximate concentration (%)</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
The suspension is prepared by adding about 2 ml of the concentrated suspension to 50 ml of particle free water. Compressed air at 15 psi is introduced to the nebulizer filled with the solution. The aerosol travels through a 10 mm diameter tube until it reaches the diffusion dryer. Once the particles leave the diffusion dryer they pass by a two-way air filter to balance the pressure in the system before entering a 3-liter mixing volume for final mixing. The flow is then introduced into the glass control volume where the laser light scattering measurements are taken. Finally the aerosol passes through the pump and is exhausted out a duct.

REFERENCES
APPENDIX L PROCEDURE
1.1 Procedure:

Pre-test procedures consist of an initial walk through of the lab, this is to ensure that the lab is clean, and everything is in its appropriate spot. The receiving optics are then moved to the desired angle to be measured, at this point all optics should be cleaned and correctly positioned. The black box is put in place covering the receiving optics. Signs should be posted to inform others that testing is about to occur. The system is then activated by turning on the precision power supply to the PMT, before the power supply is turned on and attached to the PMT it should be checked to assure that it is delivering the appropriate voltage. Checking the voltage will assure the secondary power source to the PMT and the PMT are not overloaded. Because of its sensitivity the PMT needs time to warm up and stabilize as does the amplifier and attached light chopper. Power is initiated to the laser by turning the key on the control box. The shutter on the laser can be opened, the beam should now pass through the control volume into the beam dump. A beam dump is used to catch the laser minimizing reflections and scattering that could produce arrant light, it also gives the beam a finite length as a safety concern. Once the data acquisition system is activated it will record a data signal from the PMT. The test can now begin and various particulate can pass through the control volume for measurement.

Once the measurements are complete the shutter to the laser should be closed, and the power to the laser shut off in order to protect the sensitive PMT. The valve to any of the gas bottles used should be closed and excess gas in the system will flow out into the hood. Next, the power source to the PMT is shut off. Finally, the chopper and amplifier can be shut off. This concludes the test. However, any data files should now be saved and backed up on a separate computer.

Once the monodisperse aerosol measurements were recorded and analyzed, smoke was produced and tested on the bench top setup. At this point the data acquisition system in activated and the pump is turned on. After one minute has passes (the DAQ will be measuring the scattering from air) the fuel source is ignited. The first smoke to be tested was that produced from a flaming fire of polyurethane. 1in$^3$ polyurethane blocks were ignited in a small pan, the smoke traveled up a glass tube (diameter) into a smoke box. After 1 minute of smoke running through the glass control volume the pumps are
shut off and the smoke is left to age for approximately 15 minutes. The fire is extinguished or left to burn out after the pump is shut off. And after fifteen minutes the DAQ is stopped and the pumps are turned on to clear the glass control volume as well as any remaining smoke within the tubing and smoke box. The second smoke was produced from a 100% by volume heptane pool fire. To ensure a constant smoke yield the heptane was placed in a 1000ml plastic separator funnel located approximated 2 ft above a ceramic Buchner funnel 35 to 40 mm in diameter, both from Cole-Parmer. The two funnels were attached though tubing with a valve to control the flow of heptane. When the valve was opened the heptane was gravity fed into the ceramic funnel creating a small pool (35 to 40 mm in diameter). The pool was ignited and the valve was positioned in such a way that a constant pool level of heptane was maintained. The smoke then traveled up the glass tube, and into a smoke box, from the smoke box the particulate was immediately removed to the glass control volume by a pump. Once a steady state pool fire was established and a constant scattering was maintained the pump was shut off, and the smoke was left in the control volume to “age” as the fire was extinguished. Once the measurements were completed the smoke was pumped out into an exhaust hood.

It is understood that agglomeration and aging effects such as thermophoretic deposition and diffusion do occur in the time it takes the smoke to travel from the source through the smoke box and tubing to the glass control volume. However, the concern of this report is to examine agglomeration and aging in the ceiling jet, and the minimal time it takes to travel that distance is assumed to be negligible.
APPENDIX M PSL CALIBRATION
**M.1 PSL Calibration**

The reliability of the laser scattering system was established by separately testing two Polystyrene Latex (PSL) sphere sizes. The first aerosol tested was made up of 500 nm polystyrene latex spheres. The calibration exercise was conducted by measuring the scattering signal at angles ranging from 20 to 155 degrees for both vertically (VV) and horizontally (HH) polarized light. The collected data was then processed correcting for the chopper amplification and the control volumes dependence on angle. The volume dependence can be corrected for by multiplying the scattering signal by the angle ($\sin \theta$). A calibration function can be determined by normalizing the scattering signal by the theoretical results for the given sphere sizes. The calibration function corrects for detector effects, and small error effects of the optical train.

The collected and calibrated data from 500 nm PSL spheres for VV and HH scattering can be seen in Figure 35 and Figure 36 respectively. The curves demonstrate good agreement with the theoretical Mie curves validating the experimental set up. The calibration factors for the HH and VV scattering of 500 nm particles was $2.455 \times 10^{11}$ and $4.21 \times 10^{11}$, respectively.
Figure 35: Graph of the calibration curve for 500nm PSL spheres. The theoretical curve was produced using the Mie FORTRAN program and the information from the manufacturer of the 500nm calibration aerosol. The experimental data was the collected scattering of HH laser light.
Figure 36: Graph of the calibration and experimental horizontally polarized light scattering curve for 500nm PSL spheres. The theoretical curve was produced using the Mie FORTRAN program and the information from the manufacturer of the 500nm calibration aerosol. The experimental data was the collected scattering of VV laser light.

Once calibration was conducted with the 500 nm PSL spheres, larger 1000 nm PSL spheres was tested. The collected data from the 1000 nm scattering was processed the same way as the 500nm data. The 1000 nm had slightly different calibration factors for HH and VV, with HH at $3.41 \times 10^{11}$ and a factor of $9.03 \times 10^{11}$ for VV. The relatively slight change seen in the calibration factors between 500 nm and 1000 nm could be due to changes in number concentration or the change in particle size itself.

The collected and theoretical data from 1000 nm PSL spheres for VV and HH scattering can be seen in Figure 37 and Figure 40. Figure 37 shows the experimental and theoretical curves produced for vertically polarized light interacting with 1000 nm spheres. It can be seen that the theoretical curve generated is significantly more undulating than the horizontal curve for the 500 nm particles. The increased fluctuations in intensity seen in the 1000 nm results are due to increase interference patterns caused
by the larger size particles. It can be seen that the collected experimental data for the 1000 nm particles follows the trend in the theoretical Mie curve but does not attach itself as well as the 500 nm data. This phenomenon is seen else where in literature in “Particle sizing with simple differential light scattering photometer. Homogeneous spherical particles” by Vincenzo Grasso, Fortunato Neri, and Enrico Fucile. The paper explains the two high points in the 500nm results and the smoothing seen in the 100nm results.

Figure 37: Graph of the calibration curve for 1000nm PSL spheres. The theoretical curve was produced using the Mie FORTRAN program and the information from the manufacturer of the 1000nm calibration aerosol. The experimental data was the collected scattering of VV laser light.

“A rough qualitative agreement is obtained for the data sets, indeed all the structures that are visible in the experimental data are present in the Mie calculation at nearly the same angular value. However, as one can see from the figure, pure Mie theory fails to describe the experimental data in the high scattering angle region that starts near 120 degrees and proceeds the the backscattering direction. These differences between measured and calculated scattered intensity, recently noted in a similar experiment by Suparno et all and taken explicitly into account by Schnablegger and Glatter, was explained as the effect of the reflections at the surface of the cell that contains the sample. We agree with this interpretation, but we show that it can be calculated and also that it is not the only complication affecting the experimental results. Indeed from the figure and from the
experimental results obtained by Suparno et al. it appears evident that something acts to flatten the experimental curves and this cannot be an effect that is due to only the reflected beam. “

**Figure 1.** Schematic illustration of the interference between waves by different particles and how it determines the overall scattered field.

Figure 38: Schematic Illustration of the interference between waves by different particles and how it determines the overall scattered field. Figure taken from Light Scattering from Simulated Smoke Agglomerates by Raymond D Mountain and G.W. Mulholland.

**Figure 39.** Measured Scattering pattern and calculated Mie Intensity for 303nm (top) and 993 nm (bottom) particles diameters. Taken from Particle sizing with a simple
differential light-scattering photometer: Homogeneous spherical particles by Vincenzo Grasso, Fortunato Neri, and Enrico Fucile

Figure 40: Graph of the calibration curve for 1000nm PSL spheres. The theoretical curve was produced using the Mie FORTRAN program and the information from the manufacturer of the 1000nm calibration aerosol. The experimental data was the collected scattering of HH laser light.

Acceptable results were obtained from the calibration of the monodisperse aerosols with the laser scattering system demonstrating the ability to measure various particle sizes. The laser scattering systems ability to differentiate particle size decreases as the particle size increases.
N.1 Data Results and Analysis

The data analysis is broken into two sections. The first is a direct problem in that a given particle of specific shape size and composition, which is illuminated by a laser beam of specified irradiance, polarization, and frequency determine the field of scattering. The next section is typified by the inverse problem where by suitable analysis of the scattering field, a description of the particle or particles responsible for the scattering can be determined.

N.2 Direct Problem

The direct problem is typified by the calibration exercise, where a know particle in terms of shape, size, and refractive index was introduced to the control volume and illuminated by a beam of specific intensity, frequency and polarization. The calibration calculations were conducted for the 500nm and 1000nm PS1 spheres. One calibration constant, C, corresponded to the VV light while the other the HH. The numbers were slightly different between VV and HH for 500 and 1000 nm so the average was calculated. A C value of $2.93 \times 10^{11}$ and $6.62 \times 10^{11}$ for HH and VV respectively were calculated. The numbers are different due to the PMTs affinity to VV light over HH light. The calibration measurement using the 500 nm and 1000nm particles not only find the calibration factors, validate the FORTRAN but serve as a check of the scattering setup.

The calibration factors were used to properly adjust the scale of the scattering curves and do not change the shape of the curves themselves. These numbers do not reflect the overall error of the system but are rather a correction to the amplitude. A better indicator of error is the error bars on the graph. The changing shape of the scattering implies that the particle size is changing, as does the ratio of the light intensities at 90 degrees.

Once the calibration numbers were calculated from the calibration aerosols, the numbers were applied to the experimental scattering results obtained from the heptane pool fire as well as the polyurethane flaming fire. The resulting numbers were then used to produce the overall scattering curves as well as the polarization ratio and dissymmetry ratio.
N.3 Indirect Problem

In an effort to match the laser scattering collected from the polydisperse size distribution present in smoke aerosols a spreadsheet was configured to adjust the Mie theory. The spreadsheet consisted of the calculated FORTRAN results for aerosols ranging in size from 5 nm to 1000 nm in increments of 5 nm. In order to generate the scattering curves the first step is to establish a size range. The chosen size range was 5 nm to 1000 nm well within the range of smoke particulate. The 5 nm is well below what a smoke aggregate would be and although smoke particles are known to grow larger than 1000 nm the scattering system was calibrated for this size and the range in size is large enough to capture size changes. Even if the smoke particles were to grow larger than 1000 nm the growth will be captured. The Mie theory is bounded by a size range of 0.1< d/wavelength<4.0 or 63 nm to 2500 nm for a laser with a wavelength of approximately 633 nm. The size will also be characterized by the distributions. The distribution is shaped by its own set of variables including size, geometric standard deviation (GSD), and average size. Most smokes have a GSD of 2.3, establishing a range of 1.1 monodisperse to 2.3 polydisperse should encapsulate any distributions seen. Two models were made in order to change the Mie coefficients to incorporate two refractive index values, 1.57-0.65i and 1.75-.5i. These values were chosen from literature because of their range and usability. The Mie intensity coefficient (VV and HH) were placed into an excel spreadsheet where a log-normal distribution was calculated. The distributions could be changed using the GSD and average mean size. The resulting distributions were multiply by the calculated Mie coefficients and summed to produce the total scattering expected from an aerosol.

The next factor is the refractive index although the refractive index was known for the PSL spheres (1.59) the soot’s refractive index was assumed using literature results. A refractive index of 1.75.5i and 1.57-.65i was used. The final parameter was the wavelength of the laser light a known 632.8 nm. The refractive index of the median was also assumed to be 1.00 and although the medium could be Air (1.0002926), CO2 (1.00449-1.000450), CO (1.000340), or a mixture of all three, the refractive index of all those gasses is relatively 1.0. A rough sensitivity analysis was conducted to see the differences due to changing the refractive index of the medium. Little to no change was noted.
Figure 41: Figure of Log-normal distribution for a GSD of 1.1 and an average particle size of 500 nm
Figure 42: Figure of Log-normal distribution for a GSD of 2.3 and an average particle size of 500 nm

The number concentration was measured using the laser, with neutral density filters stacked in front of the PMT to protect it from relatively high power. Obscuration measurements were made to find the approximate number concentration and the possibility of multiple scattering. The PMT was placed in line with the laser path along with neutral density filter stacked to reduce the intensity of light on the PMT and prevent any damage.
Figure 43: The corresponding number concentration from three tests of heptane pool fire. The number concentration assumes a density of 2.0 g/cm³ and 500 nm diameter.
Following Lambert-Bougers law

\[ k_{\text{ext}} = \frac{\ln \left( \frac{I_e}{I_o} \right)}{L} \quad \text{Equation 65} \]

$I_e$ is the intensity of light exiting the soot
$I_o$ is the intensity of light initially, or without any aerosol in the path of the laser.
$L$ is the path length through the aerosol
$k_{\text{ext}}$ is the extinction coefficient in m$^{-1}$.

Where

\[ k_{\text{ext}} = k_m m \quad \text{Equation 66} \]

$k_m$ is the specific extinction coefficient in m$^2$/g
$m$ is the mass in g/m$^3$.

$k_m$ is usually accepted to be 7.6 for flaming and 4.4 for smoldering. However, Mulholland recently introduced a value of 8.5 with fuels ranging from 11.6 (fuel oil) 20 5ml to 5.3 (Acetylene turbulent diffusion burner 5kW to 10 kW).

The number concentration varies significantly depending on the specific extinction coefficient used. $k_m$ values listed above assume soot is carbon, has a primary soot diameter (dp) much less than the wavelength of light and a fractal dimension less than 2. where

\[ N = k_f \left( \frac{R_g}{d_p} \right)^{D_f} \quad \text{Equation 67} \]

$D_f$ is the fractal dimension assumed to be less than 2.
$k_f$ is the prefactor constant assumed to be 2.2 (lit).
$d_p$ the particle diameter
$N$ the number of primary particles in the aggregate.
$R_g$ the radius of gyration that is defined as
\[ R_g = \sqrt{\frac{I_x}{A}} \quad \text{Equation 68} \]

A is the area
I_x is the moment of Inertia
The equation for the moment of inertia is different depending on the shape of the object. however

\[ I_x = \frac{1}{2}mr^2 \quad \text{Equation 69} \]

where
m is the mass
r is the radius.

Conceptually, the radius of gyration is the distance that, if the entire mass of the object were all packed together at only that radius would give you the same moment of inertia. This implies that the radius of gyration is calculated for a tightly packed aggregate sphere of primary particles.

The number concentration was also measured using the data already collected. The intensity of light scattered at 90 degrees was collected and examined over time. Because

\[ I_{\text{scat}} = I_o \frac{\lambda^2 N_o V_x}{8\pi^2 I^2} \left( i_\perp, i_\parallel \right) \quad \text{Equation 70} \]

If the scattering intensity collected at any one time is compared to any other time step then

\[ \frac{I_{\text{scat},o}}{I_{\text{scat},f}} = \frac{N_o i_o}{N_f i_f} \quad \text{Equation 71} \]

and because the possible change in the Mie coefficient (i) is so insignificant in comparison to the Intensity of the scattered light a rough number concentration can be calculated.

V_f is the volume fraction and

\[ N_o \times V_{\text{particle}} = V_f \quad \text{Equation 72} \]
\[ V_{\text{particle}} = \frac{4}{3} \pi \left( \frac{d}{2} \right)^3 \]  
Equation 73

**N.4 Mathematical Analysis:**
A mathematical analysis of smoke agglomeration was conducted to calculate the probability of two soot particles coming in contact with one another, the volumetric relationship to number concentration as the particles agglomerate, and the use of smoke obscuration to calculate a smoke particle ratio of particle size to distance to the next particle. The motion of the particulate is calculated using Einstein’s equation for Brownian motion and the probability of one particle striking the next is tabulated. These calculations were conducted to support the experimental findings as well as assist in the visualization process of agglomeration.

If you have N number of particles with a fixed volume of \( \frac{4\pi r^3}{3} \) and a soot density \( (2.00 \text{ g/cm}^3) \). Multiplying the density times the volume equals the mass. If the particle were to agglomerate and double in size while the soot mass remained constant then the equation \( N_0 d_0 = N_d d_f \) demonstrates that for ever double in size the particle number must decrease three fold. This quickly decreases the number concentration as demonstrated by the graph below.

Using UL217 to set the limits of smoke obscuration for a active detector, this gives the values of 1.6% and 12.5% per meter.

**Table 7: Visible Smoke Obscuration Limits**

<table>
<thead>
<tr>
<th></th>
<th>%/ft</th>
<th>%/m</th>
<th>OD°/ft</th>
<th>OD/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>4.0</td>
<td>12.5</td>
<td>0.0177</td>
<td>0.0581</td>
</tr>
<tr>
<td>Min</td>
<td>0.5</td>
<td>1.6</td>
<td>0.0022</td>
<td>0.0072</td>
</tr>
</tbody>
</table>

Calculating the equivalent number concentration using Mulholland’s smoke obscuration equations gives the number concentrations on the order of \( 10^{10} \). Multiplying the number concentration by the volume per particle gives the total volume occupied by the smoke and a true percentage of the volume the smoke occupies with in the box.
compared to a smoke obscuration percentage. Taking the total concentration divided by the total area the smoke occupies (1 m³) you can obtain a volume per particle, or the volume a particle has to itself within the total area. Dividing the average volume each particle occupies by the volume of each particle gives the smoke distance ratio. The cubed root of the volume ratio gives the linear distance to the next particle or the smoke distance ratio. These numbers are on the order of 100’s as seen in the graph below.

Einstein’s equation for Brownian motion can be used to calculate the distance moved by the soot particle due to the forces created by molecular bombardment. Factor such as Fluid viscosity, temperature, and particle size play important roles in the particle movement.

A drunken sailor calculation for random movement was conducted to calculate the probability of two particles crossing path at the same time for a given time durations. Total number of collisions is

\[
\frac{\#}{s} = \rho_m^2 d_m^2 \sqrt{\frac{2\pi}{hn}} \quad \text{Equation 74}
\]

or

\[
\frac{\#}{s} = \frac{\pi}{\sqrt{2}} \rho_m^2 d_m^2 \bar{v} \quad \text{Equation 75}
\]

\(\rho_m\) is the molecular density
\(d_m\) is the diameter of the molecule
\(\bar{v}\) is the average velocity

Factors in calculated collision include particle size, room size, velocity, and duration of time (t). Using UL217 minimum and maximum obscuration to find amount of smoke for a smoldering and flaming fire source. 12.5 %/m obscuration corresponds to 30,404.495 µg/m³ and 17,602.649 µg/m³ for smoldering and flaming combustion, respectively. While 1.6%/m obscuration corresponds to values of 3,733.36 µg/m³ and 2,161.55 µg/m³ for smoldering and flaming combustion, respectively. These values were calculated using \(K_m\) specific extinction coefficients of 4.4 m²/g for smoldering and 7.6 m²/g for flaming.
Figure 44: Graph shows the distance ratio each particle has verses particle size for temperatures ranging from 100 C to 1000C and time interval of 60 to 360 seconds.
Figure 45: Graph of calculated particle concentration for the minimum and maximum UL 217 obscuration levels required for detection assuming smoldering and flaming combustion extinction coefficient values taken from the SFPE handbook.
Figure 46: Motion of a free particle due to Brownian Motion at temperatures of 100 and 1000 degrees Celsius.

N is the number of particles

Sphere volume ($V_s$) is $V_s = \frac{4\pi r^3}{3} = \frac{\pi d^3}{6}$  \hspace{1cm} \text{Equation 76}

Therefore the soot volume is $V_{soot} = N\left(\frac{4}{3}\pi\right)\left(\frac{d}{2}\right)^3$  \hspace{1cm} \text{Equation 77}

And soot mass can be calculated using $M_{soot} = N\rho\left(\frac{4}{3}\pi\right)\left(\frac{d}{2}\right)^3 = \frac{1}{6}\pi N \rho d^3$  \hspace{1cm} \text{Equation 78}

Keeping soot mass constant $\left(Nd^3\right)_{\text{initial}} = \left(Nd^3\right)_{\text{final}}$ \hspace{1cm} \text{Equation 79}
By calculation the mass of one particle, using the density of graphite and a calculated volume (V) from the particle size (d), the total number of particles can be calculated for a specific obscuration, by dividing the amount of soot (µg/m³) from mulhollands extinction calculation by the mass of each particle to give the particles per meter cubed (part/m³). Multiplying the number of particles by there volume will give the total volume of smoke particulate, taking the square root of the total area occupied by smoke particulate by the total area gives the ratio of one smoke particulate to the next.

Einstein’s 1905 paper used kinetic theory to show results in three dimensions for a spherical particle being bombarded by the (smaller) molecules of a liquid in which the particle was immersed. The number of collisions of the particle is directly proportional to time, the size of the particle, the viscosity of the liquid in which the particle is immersed and the temperature. Einstein’s equation for the average location of a particle making a random walk in a liquid is

$$\langle r^2 \rangle_{ave} = \left( \frac{RT}{3r\eta N_A} \right)t \quad \text{Equation 80}$$

R is the ideal gas constant
r is the radius of the particle
\( \eta \) is the viscosity of the liquid
N_A is Avagadro’s number
t is the time duration.

The displacement, r, is the magnitude of a 3-dimensional location vector and appears in the equation as the average of the square of displacement.

Calculating the molecular weight of various molecules using

Hydrogen (H) = 1.00794
Oxygen (O) = 15.9994
Carbon (C) = 12.011
Nitrogen (N) = 14.0067
Clorine (CL) = 35.453
\[ MW_{\text{mix}} = \sum_i X_i MW_i \]  
\text{Equation 81}

and

\[ E = \frac{mv^2}{2} = \frac{3KT}{2} \]  
\text{Equation 82}

\( m \) is the mass
\( v \) is the velocity
\( K \) is the Boltzmann Constant
\( T \) is the temperature.

And the mean squared displacement is \( r^2 = 6KTBt \)

\( B \) is the mobility of the particle which is inversely proportional to the medium viscosity \( \eta \) and size of the particle.

The velocity of the soot particle due to Brownian molecular collisions can be found by

using the ratio of mass to velocity \( \frac{m_{\text{particle}}}{m_{\text{molecule}}} = \frac{v_{\text{particle}}}{v_{\text{molecule}}} \)  
\text{Equation 83}

To determine whether a collision has occurred between a pair of particulate is to simply simulate the movement of the objects, and calculate mathematically whether they overlap. If they do overlap, a collision has occurred. Unfortunately, this is not entirely practical at the nanoscale. The difficulty lies in the fact that particles are not moving in straight lines, rather they are following a Brownian motion random-walk that are approximated as a Gaussian probability distribution. The intensity of the Brownian motion, or chaotic motion is increased with an increasing temperature. Mulholland wrote that it was possible to “freeze” the coagulation process due to the dilution of the smoke though the introduction of air. This would lower the number concentration halting the agglomeration process. As the plume rises further growth due to agglomeration is said to “freeze” due to dilution by air and any continued growth of the particles will occur primarily as a result of condensation.
Slices providing the averaged intensity of scattering over 30 second intervals of the light scattering can be seen below. The curves differ between each time step indicating changes to the smoke particulate. Specifically the curves become more undulating indicating changes in particle size. The curves also provide the points for calculating the polarization ratio using the VV and HH intensity at 90 degrees and the dissymmetry ratio. Figures below provide the changes in particle size over time produced by applying the Mie theory accounting for monodisperse and polydisperse smoke distributions and changes in the refractive index using the polarization ratio sizing technique. All four results analyzing the heptane results which compensate for changes in distribution and refractive index demonstrate the same trend. However, the results using a refractive index of 1.75 and monodisperse distribution (1.1) show a slightly lower particle growth. The polyurethane results differ slightly with the results using a refractive index of 1.75 and monodisperse distribution (1.1) showing no particle growth while results using a refractive index of 1.73 and polydisperse distribution of 2.3 producing more inconsistent larger particle sizes at the beginning and end of testing as well as a double peak. Averaged values are used to represent the particle size however a distribution of 2.3 results in a large particle size range so the results represent trends in particle growth not the exact particle sizes present. The figures indicate a significant growth in particle size between 400 and 600 seconds. The change in particle size would be expected to occur at the initial stages of the testing once the smoke was secured in the glass control volume and left to age. However, the growth in particle size is substantially delayed possibly indicating a change in the dynamics influencing smoke agglomeration. The large particles remain in the control volume for a significant period of time (~200 seconds). The larger particles then leave the control volume possible due to deposition or sedimentation.

Unfortunately the dynamics occurring within the control volume could not identified to establish the changes occurring to promote the growth of the particles or cause the sudden loss of the larger particles. These dynamic forces may or may not exist for extended duration within a ceiling jet.

The graphs in Figures 53 to 55 represent 30 second averages of the data. The graphs demonstrate the significant change in scattering seen during this time interval. The change in laser scattering intensity at the 90 degree HH value changes by a factor of 10 (0.01 to 0.1). This change in intensity is greater than the error established in the
calibration of the apparatus signifying a change in light scattering intensity due to changes in particle size.

The dissymmetry ratio is the ratio of two angle intensities of similar polarization, separated by 90 degrees. Light scattering at angles of 50 and 140 degrees were used to establish the dissymmetry ratio. The dissymmetry ratio demonstrated similar trends to those seen by the application of the Mie theory. Again an increase in the ratio indicating an increase in particle size was seen between 400 and 600 seconds supporting the findings of the polarization ratio.

Obscuration measurements were collected to find changes to the number concentration. The PMT was placed in line with the laser path along with neutral density filter stacked to reduce the intensity of light and damage to the PMT. Following Lambert-Bougers law

\[
k_{ext} = \ln\left(\frac{I_c}{I_o}\right) / L \quad \text{Equation 84}
\]

\(I_c\) is the intensity of light exiting the soot
\(I_o\) is the intensity of light initially, or with out any aerosol in the path of the laser.
\(L\) is the path length through the aerosol
\(k_{ext}\) is the extinction coefficient in m\(^{-1}\).

Where

\[
k_{ext} = k_m m \quad \text{Equation 85}
\]

\(k_m\) is the specific extinction coefficient in m\(^2\)/g
\(m\) is the mass in g/m\(^3\).

The changes in number concentration support the agglomeration process. When the number concentration and changes to particle size graphs are compared on the same time scale it can be seen that the number concentration drops at approximately the same time as the increase in particle size. These finding also support the general finding of the calculations conducted. The number concentration within the control volume was similar to the one calculated using the UL 217 limits for detector activation. This would imply that the dynamics that affected the particle growth would have to occur in the ceiling jet.
for similar growth to occur. Because of the similar number concentrations similar average particle travel distances can be assumed. The duration of the scattering test was significantly long enough to expect detection to occur, however, the temperature would be lower than expected within a ceiling jet lowering the agglomeration rate.

Figure 47: Experimental results from Polyurethane fire. VV scattering intensity collected from angle ranging from 18 to 142 over a 15 minute time span.
Figure 48: Experimental result for Polyurethane. Intensity of scattering collected at angles ranging from 18 to 142 over a 15 minute time span.
Figure 49: Dissymmetry ratio calculated using the scattering collected from heptane soot particles. A peak between 400 and 600 seconds coincides with findings produced from the polarization ratio particle sizing technique applied to the same set of data.
Figure 50: Results from polarization ratio particle sizing technique when applied to the scattering results of heptane.

Figure 51: Results from polarization ratio particle sizing technique when applied to scattering from polyurethane smoke.
Figure 52: Number concentration results graphed with polarization ratio results to demonstrate the time relationship between the rise in particle size with the decrease in number concentration.
Figure 53: Slice of 30 seconds averaged and normalized to the 90VV points. Mie theory was then best fit to the curve using a polydisperse distribution.
Figure 54: Slice of 30 seconds from heptane smoke and best fit to the results from the polydisperse model.
Figure 55: Slice of 30 seconds from heptane smoke and best fit of the polydisperse model.
Figure 56: Cross section of 30 seconds of heptane results and best fit of the polydisperse model.

Additional data can be seen in the Attached CD.