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by

William Paul Mason
For Constantine Panageotes:

_Fasooli, fasooli, ghiomeze tor sakooli._
(A bean, a bean, it fills the bag.)

For Jane Woodward Mason and family:

Somewhere ages and ages hence,
Two roads diverged in a wood and I,
I chose the one less traveled by,
And that has made all the difference.

— Robert Frost
ACKNOWLEDGMENTS

I wish to thank my colleagues in the lab and particularly Ben Smith, Nicolo Omenetto, and Ron Whiddon for many stimulating conversations, for the patience of oak, and for sharing insight into the language of nature.

There are more things in heaven and earth, Horatio, than are dreamt of in your philosophies.
— Shakespeare, Hamlet, Act I. Scene V

Special thanks go to Ryan Mohney and Dan Shelby for long hours in the lab and valuable discussions. Thanks to Sue, Sal, and Lily for strong prayers.

And God saw the light, that it was good: and God divided the light from the darkness.
— Genesis 1:4
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# LIST OF ABBREVIATIONS

- **a**: Particle radius
- **$A_{ij}$**: Transition probability
- **$c$**: From Latin *circa*, meaning nearby or approximately
- **$c$**: Speed of light, $3 \times 10^8$ meters / second
- **C**: Constant incorporating partition function $Q(T)$
- **cw**: Continuous Wave
- **d**: Beam diameter
- **D**: Unfocused laser diameter or particle diffusion coefficient
- **$D_0$**: Original droplet diameter
- **DIAL**: DIfferential Absorption LADAR
- **$E_i$**: Energy of upper level
- **f**: Lens focal length
- **$g_i$**: Statistical weight of upper level
- **$h$**: Planck’s constant, $6.6 \times 10^{-34}$ kg · m² / s
- **HEPA**: High Efficiency Particulate-Air
- **$I_{ij}$**: Intensity of LIBS spectral line
- **$I_0$**: Incident intensity
- **K**: Evaporation constant
- **L**: Internal diameter of tubing (4 mm) or resonator cavity length
- **$\lambda$**: Laser wavelength or mean free path (m)
- **$\lambda_{ij}$**: Transition wavelength
- **LADAR**: LAser Detection And Ranging
- **LPM**: Liters Per Minute
- **LTE**: Local Thermodynamic Equilibrium
- **$m_e$**: Electron rest mass
- **M**: Molecular species
- **$\mu$**: Dynamic fluid viscosity or Dipole moment
- **MASER**: Microwave Amplification by Stimulated Emission of Radiation
- **n**: Number of modes
- **$N_c$**: Critical electron density for LTE
\(n_\infty\) Number of particles at large distance

\(n_s\) Nanosecond \((10^{-9}\) second\)

\(P\) Pressure

\(p\) Momentum

\(\rho\) Fluid density \((1.168\) kg/m\(^3\) for air at STP\)

\(\rho_p\) Particle density

\(\rho_\infty\) Vapor density at \(r_\infty\).

\(p_w\) Power (watts)

\(pdf\) Probability distribution function

\(ps\) Picosecond \((10^{-12}\) second\)

\(r\) Focal spot radius

\(\sigma\) Absorption cross section \((m^2)\) or particle diameter \((m)\)

\(T_c\) Critical temperature

\(\Delta \tau\) Pulse width

\(t_{rt}\) Round trip travel time in laser resonator

\(u_s\) Mean fluid velocity = 13.26 m/s in these experiments

\(v\) Kinematic fluid viscosity

\(\Delta v_{fsr}\) Free spectral range

\(Z\) Degree of ionization
Abstract of Thesis Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Master of Science

REAL-TIME PARTICLE DETECTION USING SUB-THRESHOLD LASER INDUCED BREAKDOWN SPECTROSCOPY

By

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May 2007

Chair: Nicolo Omenetto
Major Department: Chemistry

Ambient aerosols play an important role in a variety of processes ranging from semiconductor fabrication and industrial emission monitoring to chemical warfare and the global climate. Though interest in particle detection is not new, advancing technology provides heretofore unavailable methods of particle detection. This work lays a historical foundation for optical development, compares related particle detection techniques, describes related work, and exercises the potential of the PowerChip laser in real time aerosol monitoring. Following the work of Kwabena Amponsah-Manager and David Hahn, this effort relates the versatility and robustness of the PowerChip laser with test chamber and electronics for real-time aerosol monitoring. For particles with finite absorption at 1.06 μm, the PowerChip laser shows itself a stable and reliable laser source. With engineering development such as weatherization and battery power, this instrument could become field portable and remotely operable.
CHAPTER 1
INTRODUCTION

The inflationary growth of lasers and optical spectroscopy comes only after millennia of development. The first optical element officially recognized is the Assyrian Layard/Nimrud lens, dated to 700 BC [BBC, 1999]. However, Robert Temple suggests that lenses existed as early as 3300 BC in Egypt, evidenced by microscopic carving on a knife handle, and in 2500 BC by crystal lenses found in the facial wrappings of a mummy [Temple, 2000]. Euclid (325-265 BC) produced the first known writings on optics [Euclid], and both the Greeks and Romans used crystal and water-filled glass spheres as lenses [Pliny]. The triumph of Archimedes against the armies of Marcellus is oft-quoted as the first use of optics [Dijkstra, 1987]. The veracity of the claim has been debated for centuries, but Aristophanes (c. 448–c. 385 BC) does mention the use of a burning glass to start fires in his play “The Clouds” [Aristophanes, 423 BC]. Ptolemy (AD c. 90–c. 168) measured the changes in the path of light from air to water, air to glass, and water to glass [Hecht, 2001]. Ibn al-Haitlam, known in the West as Alhazen (965–1040), developed the first comprehensive alternative to Greek theory. He knew that light traveled in rays composed of colors and that bodies do not emit visible light, the eyes only receive reflected light, unless from a source such as a lamp or the sun. Further, he realized that light had a large but finite velocity and that refraction occurs because light has different velocities in different media [Lindberg, 1976]. The crystal lenses of 11th century Sweden were comparable in quality to aspheric lenses of the 1950s [Schmidt, et al., 1999]. Rene Descartes developed a theory of light as a wave traveling through the plenum, a forerunner to the luminiferous aether proposed by Robert Hooke in 1678. Isaac Newton championed the particle nature of light, but allowed that particles of light could create waves in the aether to explain diffraction (having been recently demonstrated by Francesco Grimaldi and later by Thomas Young). In 1845, Michael Faraday
found that the polarization of a beam of light would change in a magnetic field as it passed through a polarizing medium. In 1847, he proposed that light was an electromagnetic vibration requiring no medium of propagation. Influenced by Faraday, James Clerk Maxwell ultimately derived the equations describing electromagnetic waves [Maxwell, 1865]. However, the failure of the Michelson-Morley experiment to detect the aether, and the inability to explain blackbody radiation, Einstein’s photoelectric effect, and the constant speed of light regardless of reference frame remained troublesome issues for the wave theory of light. Max Planck in 1900 resolved the blackbody problem by proposing the quantization of energy, giving credence to the notion of light as particles, called photons. The packets of discrete energy were called quanta. Thus was born quantum mechanics. Einstein explained the photoelectric effect by suggesting that the energy of ejected electrons was a function of the wavelength of incoming light, while the number of electrons ejected was a function of the incoming photon flux (photons per unit time and area). The invariance of the speed of light was also solved by Einstein with his Special Theory of Relativity. From the time of Galileo, velocities were considered relative to the velocity of the observer. Einstein’s theory suggested that this was not truly the case [Thornton and Rex, 2002].

Einstein also derived the so-called “Einstein coefficients” for stimulated absorption and emission, the first indication that coherent emission may be possible. In short, if a population inversion can develop with sufficient pumping, coherent radiation will result (Figure 1).

Denoting by subscripts one and two the ground state and first electronic excited state, respectively, the Einstein coefficients describe both stimulated (B) and spontaneous (A) emission and absorption. The overall energy balance for a lasing system in a steady state is given by the change in number of excited atoms through time:

\[
\frac{dN_2}{dt} = A_{12}N_1 + B_{12}\rho(\nu)N_1 - B_{21}\rho(\nu)N_2 - A_{21}N_2
\]  

(1.1)
However, $A_{12}N_1$ can be neglected by the Boltzmann distribution, assuming the laser is operating at room temperature. Once the laser achieves steady state (less than one second), the number of atoms brought to the excited state by pumping is balanced by the de-excitation of atoms through both spontaneous and stimulated emission. Einstein’s derivation of stimulated emission, the $B_{21}$ term, is what initially gave rise to the idea of a laser.

Further development by Nikolay Bosov and Alexander Prokhov laid the theoretical framework to build a device for coherent production of microwaves, now known as the MASER. Charles Townes, J. P. Gordon, and H. J. Zeiger built the first maser at Columbia University in 1953. Townes and Arthur Shawlow went on to describe the theoretical basis for the LASER (using visible light instead of microwaves). Theodore Maiman built the first laser in 1960 [Maiman, 1960]. The advantages of lasers over other sources are manifold, including monochromaticity, coherence, short pulse length, and extremely high intensities. A host of laser types exist, from CO$_2$ gas lasers occupying entire buildings to solid state laser pointers, each with concomitant advantages and disadvantages. Lasers may be broadly defined as continuous wave (cw) or pulsed. While cw lasers are useful for applications such as welding and have been developed to the megawatt level, they are large and costly to operate. Pulsed lasers offer the advantage of short pulsewidths (femtoseconds) and high pulse energies (gigawatts). The femtosecond regime offers a new class of physics under active investigation by many groups. Unfortunately, femtosecond lasers remain prohibitively expensive. The JDS Uniphase (now Teem Photonics) PowerChip laser, a 500 ps solid state system, offers a compact, rugged, and cost effective compromise.
The generation of short pulses is done primarily by three methods: Mode locking, Q-switching, and chirped pulse amplification. Mode locking was the first technique developed and takes advantage of the relation:

\[ \Delta t_p = \frac{2\pi}{N_c} = \frac{1}{\Delta \nu} = \frac{1}{\text{bandwidth}}. \]  

(1.3)

Active and passive mode-locking methods are possible, such as electro-optic modulation (active) or saturable absorbers (passive). Consider the modulator as a weak shutter. By timing it to coincide with the round trip time of the cavity,

\[ \tau = \frac{2L}{c}, \]  

(1.4)

A standing wave develops in the cavity. One packet of photons will bounce back and forth in the resonator, emitting regular pulses and recharged by the pump. The round trip time of flight in the laser cavity determines the inter-pulse separation.

The pulse duration \( \Delta t \) obeys the following relation:

\[ \Delta t = \Delta \nu^{-1}, \]  

(1.5)

for \( \Delta \nu \) the gain bandwidth. For a laser with \( n \) output modes,

\[ L = \frac{n\lambda}{2} \]  

(1.6)

\[ \Delta \nu = \frac{c}{2L} \]  

(1.7)

One obtains short pulses by decreasing cavity length or increasing the number of output modes oscillating in phase. Thus the PowerChip has very short pulses because the cavity length is short - the round trip time of flight in the laser cavity determines the inter-pulse separation. Since the number of modes that can oscillate depends on the Doppler width of the transition and the cavity length, optical modulators inside the resonator can cause active mode locking.
Saturable absorbers achieve passive mode locking, as with the PowerChip. To produce more energetic pulses, Q-switching is used to contain the intensity of emitted photons. Here the energy in the resonator builds up to a threshold determined by optical switches or nonlinear crystals. However, active Q-switching requires significant electrical power and is difficult in practice. In passive Q-switching, the pulse repetition frequency can be changed simply by changing the pump power, which changes the amount of time needed to reach a threshold in the passive switching medium.

Passive mode-locking is possible using a Kerr lens that absorbs low intensity light while passing high intensity transient pulses, leading to mode-locking.

Passive Q-switching depends on the saturable absorber becoming transmissive at a certain threshold of photon intensity and dumping the photons in one large pulse. The setup is the same as for active Q-switching, sans drive electronics (Figure 2).

Electro-optic devices can also be used to “dump” the cavity all at once, a form of Q-switching. For example, Pockels cells will change the path of light in response to a change in applied voltage across certain faces of the nonlinear crystal (e.g. potassium dihydrogen phthalate, or KDP). Thus, the population inversion can be built up and then dumped at will (Figure 3).

Active Q-switching is brought about by controlling a saturable absorber, which controls the quality of the resonator and therefore the transmissivity of the resonator. This change in transmittivity is tantamount to a change in the quality of the resonator, hence the name Q (Quality) -switching [McClung and Hellwarth, 1962]. The pump creates a population inversion with only a small number of photons circulating. When the signal is given, the saturable absorber becomes transparent and the excited atoms relax, falling into phase with the small beam of lasing photons to create a giant pulse that exits the resonator all at once (Figure 4).
Chirped pulse amplification is common with femtosecond lasers and essentially stretches the pulse in time so that it can be amplified without damaging the optical system. The amplified pulse is then recompressed to exit the resonator (Figure 5). Once the pulse leaves the laser, several processes can take place. Overall, they fall into three categories: absorption, scatter, and transmission. The normalized energy distribution equals unity: absorption + scatter + transmission = 1. Working backwards, transmission is the trivial case. The laser must have a backstop of some sort to remove excess photons in the event that an absorbing or scattering body is not present.

Scattering represents a more complicated picture. Perhaps the most well known form of scattering is Rayleigh, in which photons are elastically scattered in preferential directions as a function of frequency to the fourth power, hence blue light is scattered more so than red:

\[ I_{\text{Rayleigh}} \propto I_o \left( \frac{2 \pi c}{\lambda} \right)^4 \quad (1.8) \]

The primary direction of scatter is normal to the incident path, thus the sky overhead appears blue while sunrise and sunset appear red. In Rayleigh scattering, the atom is excited to a virtual state lower in energy than the first excited electronic state and rapidly de-excites, emitting an identical photon in a preferentially radial direction. Rayleigh scattering is dominant in particles of diameter less than or equal to the incident wavelength (Figure 6).

Raman scattering is the inelastic counterpart to Rayleigh scattering and also involves excitation to virtual states. Since the transition probabilities are much smaller than Rayleigh scatter, Raman has very low amplitude. Despite this low intensity, Raman scattering has many important applications such as non-destructive artifact testing.

Now Mie scattering applies primarily to particles of diameter equal to or larger than the incident wavelength and results in preferential scatter along the direction of transmission. Mie
scattering is not highly wavelength dependent, so scattered light appears white, as in clouds and fog.

So far the interactions described have dealt with uncharged particles. Consider now a photon interacting with a charged particle, say, an electron. This interaction is defined by Compton scatter, which does not typically occur with visible wavelength photons because their energy is too low to overcome the atomic binding energy. However, X-ray photons have plenty of energy and can lose energy to electrons:

\[ p = \frac{h \nu}{c} = \frac{h}{\lambda} \quad (1.9) \]

\[ \lambda = \frac{h}{p} = \frac{h}{m_e c} \quad (1.10) \]

\[ \Delta \lambda = \frac{h}{m_e c} (1 - \cos \theta), \quad (1.11) \]

for \( \theta = \) radiation scattering angle. By considering wave theory, \( \Delta \lambda \) can arise due to the Doppler effect [Ditchburn, 1991].

Thomson scatter involves the interaction between a photon and a free charged particle, though only in the plane of polarization of the incident photon. The magnitude of the oscillation varies as \( (\cos \alpha) \), where \( \alpha \) is the angle between the incident light and the observer. Such scattering can give rise to a polarization effect.

Brillouin scatter occurs when light changes its vector due to density changes in its path. Such density changes can arise from acoustic modes (phonons), temperature gradients, or pressure gradients. Brillouin scattering occurs in a Pockels cell when using acoustic shutter frequencies to produce Q-switching.
Photoacoustic scatter is the process wherein light strikes a surface and creates sound waves. Though first noted by Alexander Graham Bell [1881], it was not developed until the 1970s [Rosencwaig and Gersho, 1973]. In essence, the photon source is modulated at an acoustic frequency, say, 1 kHz. The electromagnetic energy excites electrons, which rapidly transfer their energy to the phonons, resulting in acoustic frequency signals.

LADAR is a comparatively new but burgeoning field. Aerosols at large distances (km) can be interrogated by scatter and absorption measurements. Information about particle concentration and composition becomes available upon comparison of retro-reflected scatter at one wavelength versus a different wavelength, a technique known as DIfferential Absorption LADAR or DIAL. While standoff analysis of aerosols is important and continues to grow as a field, interesting physical processes arise when the laser energy is increased to the point where plasma forms.

Plasma composes 99% of the observable universe. Methods for analyzing plasma emission are well characterized, though plasma spectroscopy is still subject to significant background in many situations. Given this, consider now the application of lasers to particle detection by plasma formation, which amounts to looking at the final term, absorption. The basis for LIBS and the present particle detection scheme rests on absorption of laser photons into particles to cause their ionization and emission.

Two years after the first laser was built, F. Brench and L. Cross proposed the theory of LIBS [Brench and Cross, 1962]. In 1967, Moonke and Moenke-Blankenburg built the first LIBS instrument [Cremers and Radziemski, 1989]. Though the complete process of LIBS is still not fully understood, great advances in its application as an atomization/ionization source have been made.
Consider the absorption of photons into a particle. Classically, one may imagine photons of light striking the surface of the particle like bullets hitting a target. The larger the target, the more likely the bullets are to strike. The size of the target is quantified by the absorption cross section $\sigma$. In practice, this is related to but not necessarily the same as the geometrical cross section of the particle. The absorption cross section in essence describes the likelihood of interaction with a photon of given wavelength. A more meaningful analogy is available in terms of resonance. The photon interacts with the outer shell electrons of the atom. The electrons can be seen as point masses vibrating on springs with spring constant $k$ a measure of the strength of the electron's binding energy. Loosely bound electrons will have a small $k$ and will interact with relatively low energy photons. Depending on the energy and number of photons, the electron will excite to a higher energy level and then relax through fluorescence, phosphorescence, or collisional de-excitation. In multiphoton excitation, complete ionization is possible given sufficient photon flux (Figure 7). Since the density of free electrons in most materials at STP is negligibly small, initiation of cascade ionization requires some sort of catalyst such as multiphoton excitation in a laser.

Multiphoton ionization: $n\nu + M \rightarrow M^+ + e^- \quad (1.12)$

Once free, the electron is accelerated by the electric field of the laser, leading to cascade ionization wherein it collides with an atom or molecule and knocks loose another electron, both of which then accelerate in the electric field and repeat the process, forming a geometrically growing electron cascade [Radziemski and Cremers, 1989] (Figure 8).

Again, for LIBS, photons interact with the electrons of the material. The electrons are excited to high temperatures in femtoseconds but transfer the energy to the phonon lattice, resulting in a shockwave and explosive removal of material in a plasma state. In the ns-ps
regime, the laser pulse continues to excite the ejected material as it leaves the surface, heating and ionizing the ejecta to a plasma. This forms an optically opaque plasma with a temperature in excess of 10,000 K. The plasma temperature can be calculated by solving the following equation for temperature [R. Harmon, et al., 2005]:

\[
I_g = C \left( \frac{g_j A_j}{h} \right) \frac{-E}{k_{ij}} e^{\frac{k_{ij}}{T}} 
\]

(1.13)

For ultrashort pulse lasers (< 1 ps) interacting with a solid surface, all the energy is deposited at once into the electron lattice, which transfers the energy to the phonon lattice, resulting in explosive removal of material with virtually no melting, though some researchers have found extensive ionization [Martin, et al., 2002] (Figure 9).

After about 1 \( \mu s \) the shock wave decouples from the plasma, leaving the plasma in local thermodynamic equilibrium [Zeng, et al. 2006]. Thermodynamic equilibrium is defined as a zero gradient for all intensive properties of the system (temperature, chemical activity, pressure, etc.). For a gas, this is tantamount to having a specific Maxwell-Boltzmann distribution. Such a condition is virtually impossible to achieve in LIBS plasma – it is a non-equilibrium phenomenon. However, the approximation suffices for many instances. LTE implies that, though the system parameters vary across space and time, they vary slowly enough to permit the assumption of thermodynamic equilibrium about any given point instantaneously.

Thus, the 58 \( \mu J \) of the PowerChip may or may not allow LTE. One may use the Griem criterion to determine if LTE exists [Yueh et al., 2000]:

\[
N_e (cm^{-3}) >> 30,545 \times 10^{17} \left[ T_e (K) \right]^{1/2} \left( \frac{Z^2}{\lambda (nm)} \right)^3
\]

(1.14)

Given a plasma in LTE, the problem of spatial measurement arises. Though the present effort does not involve LIBS per se, an understanding of the processes at work is instructive.
When an intense ultrashort laser field propagates inside a dielectric medium, it induces a strong polarization field and high density of electrons and holes. This space-time dependent problem is intricate because it involves nonlinear effects such as multiphoton excitation, free carrier absorption, photoemission, electron-phonon interaction, exciton generation, and carrier-carrier interaction, all in the presence of a high intensity field [Audebert, et al., 1994]. Additionally for natural substances, the situation is further complicated by inhomogeneous sample composition and surface irregularities [Harmon, et al., 2005]. Variation in composition manifests as variation in laser-target coupling convolved with surface roughness variation.

Given such difficulties, why bother with LIBS at all? Though LIBS is often touted for little or no sample prep, caution must be exercised in some cases. For example, inhomogeneous matrices can present spectral complexity and create difficulty in interpretation. Further, heavy surface contamination such as grease or dirt can cause wide variation in signal intensities and interference. Surface films and surface roughness can also create skewed results. Bearing these caveats in mind, particle counting and the natural extension to LIBS offer many advantages such as light weight, solid state electronics, no vacuum requirement, and real-time analysis.

Comparison to other techniques shows the usefulness of LIBS as summarized in Table 1:

Armed now with a conceptual understanding of plasma formation and LIBS, the properties of particles may be addressed. For small particles, some transmission and scatter may occur, depending on the shape and composition of the particle. For silicon dioxide (SiO$_2$), we assume that transmission and reflection are negligible. Because the pulse duration is so long (500 ps) relative to the time it takes to eject material from the bulk (femtoseconds), the initial part of the pulse excites electrons and breaks up the particle into clouds of molecules which continue to be irradiated by the later part of the pulse to form a plasma. The emission from this plasma,
Bremsstrahlung, fluorescence, and recombination, can be used for simple particle detection by the photomultiplier tube. The photomultiplier tube is composed of a material that emits electrons when struck by photons of sufficient energy. In the case of the Hamamatsu R 647, the material responds to photons with wavelengths between 300 and 650 nm. The response is controlled in part by the applied voltage, a sensitivity selector of sorts. The price of high sensitivity is an increase in false hits from, for example, cosmic particles or noise fluctuations that are amplified by the high voltage required for sensitive measurements.

Particle detection is desired in a host of applications, from semiconductor fabrication to chemical/biological warfare agent detection and global climate modeling. The following chapter details particle characterization and detection.

Table 1-1: Comparison of Particle Counting Techniques.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Sensitivity</th>
<th>Range</th>
<th>Portability</th>
<th>Ease of Use</th>
<th>Efficiency</th>
<th>Data Complexity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIBS</td>
<td>Low</td>
<td>Moderate</td>
<td>High</td>
<td>Moderate</td>
<td>Low</td>
<td>High</td>
</tr>
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<td>High</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
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</tr>
<tr>
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<td>Low</td>
<td>Moderate</td>
<td>Moderate</td>
<td>High</td>
<td>Low</td>
</tr>
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<td>Moderate</td>
<td>Moderate</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Scatter</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

Figure 1-1: Laser Energy Diagram
Figure 1-2: Passive Q-Switching

Figure 1-3: Active Mode locking

Figure 1-4: Cavity Dumping
Figure 1-5: Chirped Pulse Amplification

Image Credit: http://www.nsu.ru/psj/lector/lotov/terawatt/cpa.gif

Figure 1-6: Rayleigh and Raman Scatter.
Figure 1-7: Multiphoton Excitation

- **Continuum**

- **Virtual State**

- **Incoming electron**
- **Neutral molecule**
- **Positive ion**
- **Two electrons**

Figure 1-8: Cascade electron ionization
Figure 1-9: Laser-material interaction.
CHAPTER 2
PARTICLE DETECTION

The term aerosol derives from the term for hydrosol, meaning a solid (colloid) suspended in liquid (solution). Aerosols are important to many aspects of life, including health, global climate, and military weapons. Epidemiological studies found associations between particulate air pollution and human health [Schwartz, et al., 1996]. People for some time argued that air pollution only sped up the inevitable, killing only those who would soon die anyway. However, though mortality increases as air pollution increases, it is not followed by a deficit when pollution decreases, implying that pollution not only harvests from the vulnerable pool, but recruits new people into the pool. [Zanobetti, et al., 2002].

Aerosols also have an impact on the environment. Their primary effect is to alter the scatter and absorption of solar radiation, leading to either warming or cooling depending on the fraction scattered versus absorbed. The secondary effect manifests by altering the scattering properties and longevity of clouds [Penner, et al., 2001]. Without aerosols in the atmosphere, very few clouds would form [Zalabsky, 1974]. As aerosol number increases in a cloud, water in the cloud is spread over many more droplets, each of which is proportionally smaller. Clouds with smaller droplets reflect more light and last longer, since it takes more time for droplets to coalesce and fall.

According to Raes, et al. [2000], primary particles can be emitted directly into the atmosphere as particles (primary process) or formed in the atmosphere from gas-to-particle conversion (secondary process). Atmospheric aerosols range in size from a few nm to μm in diameter. Once airborne, particles evolve in size and composition through condensation, evaporation, coagulation, chemical reaction, or activation within supersaturated water vapor to
form cloud and fog droplets. Particles smaller than one μm range from 10 – 10,000 cm⁻³, while particles with diameters greater than 1 μm are typically < 10 cm⁻³.

A primary aerosol is emitted into the atmosphere as a particle, whereas secondary aerosols are formed in the atmosphere by gas ➔ particle conversion [Raes, et al., 2000].

Particle formation can be categorized by diameter (φ):

φ > 1 μm = primary formation
φ < 1 μm = secondary formation

Strong overlap exists for particles of diameter 0.1 – 1.0 μm.

Combustion soot is typically 5 – 20 nm, but coagulates rapidly to form fractal aggregates which collapse to more stable structures of tens of nm due to the capillary forces of condensing vapors. Shah et al. [2005] found that lubricating oil was a primary fraction in diesel emission, and increased while the engine was accelerating, versus cruising.

The Kelvin effect plays an important role in particle formation. The equilibrium vapor pressure over a spherical particle increases with decreasing radius of curvature; hence equilibrium vapor pressure above molecular clusters formed by random collisions is much larger than that above a film or flat surface. Consequently, molecular clusters tend to evaporate. Small particles (<1 μm) diffuse to the Earth’s surface, a process that becomes less efficient with increasing φ. For 0.1 < φ < 1 μm, dry removal is very slow, so these particles tend to accumulate in the atmosphere. They are removed mostly by cloud activation and precipitation [Willeke and Baron, 1993].

Particle behavior and composition are weak functions of the particle diameter (Tables 2 and 3).
To develop a new particle detector, consideration of previous devices is important. Important work on the detection of aerosols began with Aitken in the 19th century [Aitken, 1923], who determined that most atmospheric aerosols were less than 100 nm in diameter and ranged from hundreds to tens of millions per mL depending on the cleanliness of the air. Interestingly, the Wilson cloud chamber was developed as a result of Wilson being moved by the sighting of a Brocken specter while working at the meteorological observatory atop Ben Nevis in Scotland. So struck was he that he studied cloud formation and condensation in the laboratory. The result was the cloud chamber, which is also one of the most sensitive particle counters for aerosol measurements. Particle detection methods encompass a range of responses:

- Aerodynamic particle sizer – measures the velocity of particles in accelerating air flow using two laser beams and scatter detectors at various angles.
- Photoacoustic spectroscopy – chopped laser illuminates ambient air. Particles absorb energy from the beam and transfer it as heat to surrounding air. The expansion of heated gas produces a sound wave at the same frequency as the chopper. This acoustic signal is detected by microphone and is proportional to the amount of light absorbed.
• Electrical aerosol analyzer - collects particles according to size dependent mobility in electric field, then detected by deposition of charge on an electrometer.

• Differential mobility particle sizer - classifies particles by their mobility in an electrical field and counts them with a condensation nuclei counter in a range of size bins.

• Scanning mobility particle sizer - a complex version of the Differential Mobility Analyzer (Figure 11), including a radioactive ionization source and Condensation Particle Counter. Because the Condensation Nuclei Counter (CNC) cannot classify particles by size, it is combined with the DMA to give both particle size and number. One drawback of the SMPS is that it can take up to 300 s to obtain size distributions, since the particles need time to form a hydration shell in order to be detected in the chamber. Further, CNCs are overwhelmed by particle concentrations greater than class 1000 environments [Particle Measurement Systems website, 2006].

• Electrical low pressure impactor - offers real time size distribution and concentration measurement from 30 nm to 10 μm. The electric current carried by charged particles into each impactor stage is measured by a sensitive electrometer. One anticipates the difficulty of measuring charged particles at low pressure (requiring some measure of pumping), and interference effects from electronic noise. However, it has the advantage of being able to measure rapid changes in both particle size and concentration.

• Tapered element oscillating microbalance - operates by changing the frequency of oscillation as mass accumulates on the cantilever (Figure 11). As particles accumulate the frequency ω changes as $\omega = \sqrt{\frac{k}{m}}$. The balance lasts for about 3 weeks, with a ½ hour equilibration time before data can be taken.

The classic methods of atomic absorption/emission spectroscopy are well-characterized, but suffer heavy background emission and comparatively low sensitivity. Scattering, absorption, and emission techniques such as Rayleigh, Raman, Fourier-Transform Infrared Absorption, LIBS, LAser Detection And Ranging (LADAR), filter impaction, and mass spectrometry offer a host of techniques for particle detection. While each technique has some advantage and some disadvantage, LIBS offers a few important advantages over other techniques. Mass spectrometry provides high resolution and good limits of detection, but requires the use of vacuum pumps, adding to the cost and bulk of the system, and experiences peak broadening due to excess kinetic
energy [Tolocka, 2004]. Light scattering techniques are effective only to the point at which the particle diameter equals the wavelength. For particles smaller than the wavelength used (below ~300 nm), such techniques are less reliable [Maynard, 2000]. Techniques like LADAR offer remote detection, but have poor sensitivity and minimum detectable particle sizes (~300 nm). CNCs are sensitive, but require periodic refilling with alcohol and are easily saturated in dirty environments. LIBS provides a good detectable size range and good portability, for the price of sensitivity. However, particle focusing could ameliorate this problem [Wu, 2006].

Research has shown a bimodal particle distribution in the atmosphere, while other research has shown that particles in the accumulation region (around 0.1 μm in diameter and smaller) are most harmful to humans. These are also the most difficult to count continuously and the most difficult to filter. Filtration and detection methods are many and wide ranging, from Raman and fluorescence to condensation nuclei counters and impaction.

Having considered particle counting, particle transport bears remark. Particle transport both through the air and through tubing is complex. Physical phenomena such as thermophoresis, turbulence, and adhesion are factors.Velocity focusing, diffusion, and Brownian motion also play into the scheme (Figure 12). Brownian motion of particles results from collision with other particles whose velocity is proportional to the square root of temperature. Equating kinetic energy and the thermal energy gives a relation between velocity and temperature:

\[
\frac{1}{2}mv^2 = \frac{3}{2}k_BT \quad (2.1)
\]

\[
v = \sqrt{3k_BT} \quad (2.2)
\]
Because their mass is so small, Brownian particles do not settle from a given volume; they are kept “afloat” by the thermal motion of the particles around them. In other words, they are perpetually diffusing at a rate given by:

\[ k_B \sqrt{\frac{T}{m}} \]  

(2.3)

Thermophoresis is brought about by temperature gradients in a given volume. Higher temperature will increase the volume between particles, causing cooler particles to move to cooler regions of the gradient. Note that energy must be added to the system to maintain the gradient. Similarly, eddy and turbulence focusing arise from pressure gradients, similar to thermophoresis. In addition to various transport phenomena, particles may adsorb to surfaces by the following two processes:

Electrostriction may arise between particles with a charge or a strong permanent dipole moment. In liquids, such charges will be solvated, but in the gas phase electrostriction can be a significant factor. Electrostriction between two or more particles, usually of opposite sign, is a phenomenon known as accretion.

Simple friction can play a role, such as in HEPA filters, where particles are mechanically trapped by small gaps in a medium. Diffusion and adhesion coexist in a dynamic equilibrium, suggesting that a sudden shift in some relevant parameter (e.g. temperature or pressure) could shift the particle equilibrium and result in a “pulse” of free particles or a sudden shift in average particle diameter. Also, particle concentration decreases with increasing tube length. The rate of decrease depends on several factors, including type of tubing [Willeke and Baron, 1993]. Carranza, et al. [2001] found that particle transport efficiency was greater than 95% for particles from 0.1 to ~1.5 μm in diameter for their system.
Deliquescence, a sharp rise in liquid water content at ~ 55% relative humidity, is a result of the hygroscopicity of particles and is relevant for many salts such as calcium chloride and magnesium chloride. Because the particles are strongly hygroscopic, under high humidity they can absorb enough moisture to dissolve themselves. This could be a factor in situations where particle solutions are created and then dried to form aggregates. The ability of the tower to dry such salts may be questioned.

Clearly a host of physico-chemical processes are at work. Desirous to further develop particle detection capabilities with the PowerChip laser, several experiments were performed. Note here that M.D. Cheng [2003] failed to produce meaningful results from the reference standards while testing the sub-threshold setup similar to the present study. The present work may add further strengthen the overall effort of particle detection with lasers. Though this effort recapitulates much of Cheng, Hahn, and Amponsah-Manager’s work, the use of the PowerChip laser and the discussion of particle distribution (Poisson versus diffusion mediated) may lend insight into the investigation.

LIBS offers some advantages because it can both count particles and characterize them by constituents. Several particle counting systems also provide spectral analysis (e.g. Hahn [1998] and Cheng [2000]). Cheng proposed the use of sub-threshold breakdown for aerosol detection (akin to sub-threshold breakdown in liquids). That is, the laser power is set just below the breakdown threshold of air. When a particle enters the laser focus, the breakdown threshold of air is decreased, causing plasma formation. The tacit assumption is made that the absorption cross section of the particle is greater than that of the background carrier gas. The advantage of using sub-threshold pulses is a reduction in background noise, since a plasma forms only in the presence of particles of nontrivial absorption cross-section. Following this line of work, we
sought to further characterize and expand the capabilities of such a system. The next chapter describes those efforts, including initial development, enhanced chamber setup, aerosol nebulizer and flow gas, and long term measurements.

Figure 2-1: Threshold irradiance versus pulse width.
Figure 2-2: Size range of aerosol physics.
Figure 2-3: Scanning Mobility Particle Sizer.

Electronic driver/recorder

Figure 2-4: Tapered Element Oscillating Microbalance.

Gas particles bouncing against a surface at low velocity

Gas particles bouncing against a surface at high velocity

Figure 2-5: Bernoulli Effect on particle focusing.
CHAPTER 3
EXPERIMENTAL SETUP AND DEVELOPMENT

Manager [2005] worked on particle detection with the JDS MicroChip laser and nebulized solutions of simple salts. Particle focusing occurred by nebulizing and desolvating particles, then passing the air flow through a narrow pipette tip. The stream was interrogated by a 5 kHz MicroChip laser at 50 μJ / pulse. Results were promising but inconclusive. Inspired by the work of Smith, Hahn, Omenetto, Amponsah-Manager, and Cheng, the present study investigated the feasibility of the PowerChip laser for ambient aerosol monitoring at 1 kHz.

The PowerChip laser offers the advantage of relatively high repetition rate, short pulse width, solid state passive Q-switching, air cooling, and short cavity length, yielding essentially single mode output. Again, all of these properties play well into a field portable design as well as complimenting the LIBS detection. The PowerChip laser is amenable to particle detection because its short cavity length allows longitudinal mode spacing greater than the gain bandwidth; it enjoys virtually single mode operation with no frequency beating (Figure 16).

\[
\Delta v_{fr} = \frac{1}{\tau_{rl}} \quad (3.1)
\]

While Amponsah-Manager [2005] worked mostly with solids, some particle sampling was done. This work extends his initial investigation. The test chamber (Figure 17) was built and used in all subsequent experiments. Several modifications were made over time to improve its performance. Light tightness is critical since the PMT is sensitive and low background is desirable. Tightness was improved through the addition of a laser beam tube, black electrical tape around the housing seam, and an aluminum guard ring over the laser entry port. A mirror placed opposite the PMT (in the bottom of the chamber) reflected light towards the PMT to increase signal. In the future, an elliptical mirror with one focus at the laser focus and the other
focus on the PMT might prove a better choice. Lastly, the chamber was wrapped in black felt to further reduce stray room light. Note that a beam expander would improve the focus characteristics (sharper focus), though this might push the system into breakdown regardless of whether a particle was present and would decrease the effective plasma volume. Depending on the desired experimental setup, a variable diameter beam expander could serve as a simple power control. In the limit of perfect system function, particles below a given diameter (all other parameters, e.g. absorptivity, being equal) could be made “invisible” to the system. If the absorption cross section is too small to create a plasma, the particle will pass undetected. Above some minimum diameter, the cross-section will be large enough to form plasma.

The signal passed through an SR 570 amplifier, boxcar, SR 245 signal processor, and out to a computer for data storage and display (Figure 16). Initial tests demonstrated the effectiveness of HEPA filters at reducing the number of events detected in ambient air (Figure 14).

The system measured the emission of light from plasma formed when a particle was struck by the laser pulse and converted to plasma. The number of photons expected for nominal 500 nm diameter, 2% (weight) silicon dioxide particles is given by:

\[
100 \times 10^{-6} \times \frac{2g}{100g} \times \frac{1000 \text{cm}^3}{1L} \times \frac{1g}{\text{cm}^3} = 2 \text{mg silica in 100 \ μL solution.}
\]

\[
0.002g \times \frac{1 \text{particle}}{6 \times 10^{-14} \text{g}} = 2.9 \times 10^9 \frac{\text{particles}}{\text{mL}}
\]

\[
\frac{2.9 \times 10^9 \text{ particles}}{\text{mL}} \times \frac{0.1 \text{mL}}{1 \text{min}} \times \frac{1 \text{min}}{60 \text{sec}} = 4.8 \times 10^6 \frac{\text{particles}}{\text{sec}}
\]

Ambient air traveled through the target chamber by laboratory exhaust flow at roughly 0.2 LPM as measured by a rotometer. If the PMT detected sufficient photons, the signal continued...
through preamplifier, boxcar, and postamplifier before readout on a stripchart or storage in computer memory. Data processing included counting the number of events greater than a certain threshold. Initially this threshold was set at 3 standard deviations (3σ) from the mean, but minor (< 0.05 V) step fluctuations in the background forced a change to the less sensitive but more trustworthy measure of 0.2 V as threshold (Figure 15). This was well above any baseline fluctuations. A power supply regulator (SOLA MCR 1000, Mini/Micro Computer Regulator, catalogue # 63-13-210-05) was installed to eliminate background shifts, but was unsuccessful at doing so. The threshold remained at 0.2 V.

Computer sampling rate:

Expect: \[
\frac{1,000 \text{ shots}}{\text{sec}} \cdot \frac{3,600 \text{ sec}}{\text{hour}} \cdot 24 \text{ hours} = 8.64 \times 10^7 \text{ shots}
\]

Found: \[
3,317 \text{ files} \cdot \frac{15,000 \text{ files}}{\text{sec}} = 4.98 \times 10^7 \text{ shots}
\]

Ratio = 0.576 ~ 58% duty cycle.

This is very repeatable for all runs, leading to the conclusion that it represents the computer writing data to memory, during which time it cannot simultaneously take data.

The amount of light scattered by the particle into the PMT we expect to be negligible compared to the 0.2 V threshold. The following calculation bears this out. Because the particle diameter (500 nm) is less than the laser wavelength (1,064 nm), Rayleigh scatter dominates. Assume a 90° cone of emission circling the equator of the particle normal to the laser beam containing all of the scattered light. Further, assume that approximately one quarter (\(\frac{\pi^2}{4}\) sr) of the emission is detected by the PMT:

For a 58 \(\frac{mJ}{pulse}\) 1064 nm laser,
\[ v = \frac{c}{\lambda} = \frac{3 \times 10^8 \frac{m}{s}}{1.064 \times 10^{-6} \frac{m}{s}} = 2.83 \times 10^{14} \text{ s}^{-1} \]

\[ E_{ph} = h v = 6.6 \times 10^{-34} \frac{kg \cdot m^2}{s} \cdot 2.83 \times 10^{-14} \text{ s}^{-1} = 1.87 \times 10^{-19} J \]

\[ 58 \times 10^{-6} \frac{J}{\text{pulse}} \cdot \frac{ph}{1.87 \times 10^{-19} J} = 3.1 \times 10^{-14} \frac{\text{photons}}{\text{pulse}} \]

\[ \text{Expected Signal} = \frac{P_h}{\text{pulse}} \cdot \text{reflectivity}_{\text{particle}} \cdot \text{attenuation}_{\text{filter}} \cdot \text{Efficiency}_{\text{PMT}} \cdot \text{Gain} \cdot \text{Angle}_{\text{View}} \cdot \frac{\text{Pulses}}{\text{sec}} = \]

\[ \left( 3.1 \times 10^{14} \frac{ph}{\text{pulse}} \right) \cdot (1.0) \cdot (6.3 \times 10^{-6}) \cdot (1.0) \cdot (10^6) \cdot \left( \frac{\pi^2}{4} \right) \cdot \left( \frac{100 \text{ pulses}}{\text{sec}} \right) = 4.9 \times 10^{-11} e^- \frac{\text{sec}}{\text{sec}} \]

\[ \text{Expected Current} = 4.9 \times 10^{-11} \frac{\text{electrons}}{\text{sec}} \cdot \frac{\text{Coulomb}}{1.66 \times 10^{19} \frac{\text{electrons}}{\text{sec}}} = 2.94 \times 10^{-7} A \]

\[ \text{Expected Voltage} = 2.94 \times 10^{-7} A \cdot 50 \Omega = 14.7 \mu V \]

This is well below the 0.2 V threshold for particle hits. Using conservative values for the reflectivity, attenuation, efficiency, and hit rate, we are confident that we do not detect significant scattered light.

Now consider the Reynolds and Knudsen numbers regarding flow characteristics:

\[ \text{Reynolds Number} = Re = \frac{\rho U_s L}{\mu} \quad (3.2) \]

\[ R_e = 1.168 \frac{kg}{m^3} \cdot 13.26 \frac{m}{s} \cdot \frac{0.004 m}{1.78 \times 10^{-5} \frac{kg}{m \cdot s}} = 3480.4 \]
The results suggest that the flow is unstable. This finding prompted a change to a longer drying tube, permitting a lower drying gas flow rate because the particles would have more time to dry.

Knudsen Number \( K_n = \frac{\lambda}{L} = \frac{k_B T}{\sqrt{2}(\pi \sigma^2 P L)} \)  

\[
K_n = \frac{1.38 \times 10^{-23} J}{K} \times 295K \times \frac{L}{2\pi \left(100 \times 10^{-9} \, m \right)^2} \times 50 \times 10^{-9} \, m \times 101,300 \, Pa = 1.8 \times 10^{-5}
\]

Therefore continuum mechanics are valid (for \( K_n < 1 \)), as expected.

Consider now the time \( t_o \) to completely evaporate water:

\[
t_o = \frac{D_o}{K} \quad [\text{Hahn et al., 2001}] \quad (3.4)
\]

Then \( t_o = \frac{(500 \times 10^{-9} \, m)^2}{3.5 \times 10^{-9} \, m} = 7.14 \times 10^{-5} \, s = 71 \, \mu s \).

The lower flow rates should also help reduce effects such as velocity and eddy focusing, plus increase the dwell time within the PMT viewing angle.

The particle dwell time can be calculated as follows:

Dwell time = (Flow rate) (Interaction volume)

\[
= \frac{1 \, \text{min}}{10,000 \, \text{cm}^3} \cdot \frac{60 \, \text{sec}}{1 \, \text{min}} \cdot \pi \cdot \left(0.2 \, \text{cm}^2 \right) \cdot \left(0.2 \, \text{cm} \right) = 1.5 \times 10^{-4} \, \text{sec}
\]

This should provide plenty of time for the detectors, which has a response time of a few nanoseconds.

When the composition of particles is considered, the difficulty of matrix effects comes to bear. Defined as variations in laser-target coupling secondary to variable sample composition...
and surface characteristics [Harmon, et al., 2005], matrix effects can yield transients in plasma emission that could affect the observed hit rate. Indeed, Harmon found that surface roughness is a primary factor in experiment repeatability. The surfaces of aerosols are known to vary greatly from spherical to needle-like [Hinds, 1999].

A final consideration is the distribution of particles, taken to follow a Poisson distribution \( P \):

\[
P(x) = \frac{e^{-\lambda} \lambda^x}{x!} \quad (3.5)
\]

The Poisson distribution assumes no correlations in either space or time, an assumption which may be called into question by point source emission of particles, e.g. from a vehicle passing close to the detector. The diffusion equation may be a more appropriate model. The properties of the diffusion equation are complex, but a brief treatment follows. For a probability distribution function of a single particle \( P \), use the heat equation:

\[
P_t = D \Delta P \quad (3.6)
\]

If the diffusion coefficient \( D \) is not constant but depends on \( P \), then one gets the nonlinear diffusion equation. The random trajectory of a particle subject to the particle diffusion equation is Brownian motion. To treat it, place a particle in \( R = 0 \) at \( t = 0 \) and find the pdf associated with \( R \) to be:

\[
P(R, T) = G(R, T) = \frac{1}{(4\pi D t)^{3/2}} e^{-\frac{R^2}{4Dt}} \quad (3.7)
\]

For \( R^2 = R_x^2 + R_y^2 + R_z^2 \) \quad (3.8)

At \( t = 0 \), \( P(R, T) \) is singular with a pdf for the particle at \( R = 0 \) given by the Dirac delta function. The solution of the diffusion equation subject to this initial condition is the Green Function \( G(R, T) \) given above. This treatment can be extended to a large number
of particles by a decomposition of Green functions giving the time evolution of the particles. Such a decomposition can be generalized to any diffusive process like heat transfer or momentum diffusion, which is the phenomenon at the origin of viscosity in liquids. If the Poisson distribution does not hold, the diffusion equation could serve as a new model [Willeke and Baron, 1993].

Having laid a theoretical foundation, a review of the experiments conducted is indicated. Many experimental series were run to determine the effectiveness of particle detection with the PowerChip laser. The first was with a HEPA filter on ambient outdoor particles. The hit rate showed a marked decrease with installation of the filter, suggesting that the detection system was functioning nominally (Figure 14). A drying tower was assembled and operated using compressed air (Figure 16).

The time responses of the laser beam and the detector were measured to verify that plasma and not scattered light was detected. Because the plasma lifetime is long compared to the laser pulse (microseconds versus picoseconds, respectively), we conclude that plasma, not scatter, is observed. Further, a calculation of expected scatter shows that it should produce a negligible signal at best (Figure 18).

Calculation of Beam waist = \( \omega_0 = r = \frac{2\lambda f}{\pi d} = \frac{2\left(1064\times10^{-9}\right)(0.02m)}{\pi(5\times10^{-3}\ m)} = 2.7\times10^{-6}\ m = 2.7\ \mu m\)

Photon flux: \( \Psi = \frac{P_w \lambda}{\pi^2 \hbar c} = \frac{58\times10^{-6} J}{500\times10^{-12}\ s} \left(1064\times10^{-9}\ m\right) \frac{1064}{s} = 10^{40}\ \text{photon}\)

The expected particle hit rate may be estimated as follows:

For 2% by weight silicon dioxide particles of 500 nm diameter and density = 1.05 \( \frac{g}{mL} \),
\[
\frac{2g}{100g} \cdot 100 \times 10^{-6} \text{ L} \cdot \frac{1000mL}{L} \cdot 1.05 \frac{g}{mL} = 0.0021 \text{ g of silica in 100 } \mu\text{L of solution.}
\]

For the mass of one particle, find the volume:

\[
V = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (250 \times 10^{-7} \text{ cm})^3 = 6.55 \times 10^{-14} \text{ cm}^3
\]

Then find the mass of a single particle:

\[
6.55 \times 10^{-14} \text{ cm}^3 \cdot 1.05 \frac{g}{mL} = 6.9 \times 10^{-14} \text{ g}
\]

To give the total number of particles in 10 mL:

\[
0.002g \cdot \frac{\text{particle}}{6.9 \times 10^{-14} \text{ g}} = 2.9 \times 10^{10} \text{ particles}
\]

Calculate the flow rate using the nebulization rate:

\[
\frac{2.9 \times 10^{10} \text{ particles}}{10mL} \cdot \frac{0.100mL}{\text{min}} \approx 3 \times 10^8 \frac{\text{particles}}{\text{min}} \approx 5 \times 10^6 \frac{\text{particles}}{\text{sec}}
\]

Given a counting efficiency of 1:10^6, this amounts to roughly 5 hits per second.

Experiments were performed using undilute d samples and approximately this rate was observed. A more sensitive detector or higher particle concentrations must be used to see significant hit rates.
Table 3-1: Flow regimes.

<table>
<thead>
<tr>
<th>Reynolds number, $R_e$</th>
<th>Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;2300$</td>
<td>Laminar</td>
</tr>
<tr>
<td>$2300 &lt; R_e &lt; 4000$</td>
<td>Transition</td>
</tr>
<tr>
<td>$&gt;4000$</td>
<td>Turbulent</td>
</tr>
</tbody>
</table>

Figure 3-1: Laser and detection setup. [Reprinted with permission from Xihong Wu]

Figure 3-2: Effect of the HEPA filter.
Figure 3-3: Note Baseline Shift.
Figure 3-4: Drying tower and overall experimental layout.

Figure 3-5: Electronics cart.
Figure 3-6: Target chamber and PMT.

Figure 3-7: Comparison of laser pulse and emission lifetime.
Figure 3-8: Oscilloscope trace of laser pulse.

Figure 3-9: Illustration of near single-mode operation.
Figure 3-10: Diagram to accompany scatter calculation, using a nominal 500 nm particle close to the PMT.
Experimental results over the past 18 months served to characterize and improve system performance, find environmental trends, and determine limits of detection for particle size. Note that the limit of detection for particle concentration is poorly posed because detection with decreasing concentration simply implies a longer time interval between hits, assuming continuous flow. The question is valid and crucial for batch applications.

Styrofoam was tested, but no evidence of interaction was found, so silica powder was used. Long time-series data collection campaigns sought long term environmental effects, as in Tolacka et al. [2004] who found a bimodal particle distribution over 24 hours due to increased human activity in the morning and evening. No such trends emerged in this study, excepting a clear correlation between rainfall and decreased particle counts. Interesting peaks were found, such as transient spikes one order of magnitude higher than surrounding peaks. No satisfactory explanation of their origin was found.

The trials did establish the reliability of the PowerChip and associated electronics for potential field applications to particle monitoring. A test for plasma current (MFP = 40 μm) was unsuccessful. Amponsah-Manager [2005] reported a small current, but did not describe the setup used. The effect of adhesion in tubing was measurable (Figures 19 and 20), but was neglected in the present study.

Tests were conducted using Gelmann filters of varying pore size, though no clear correlations were found. This could be due to dirty filters, fluctuating background signal, or tubing effects.
Figure 4-1: 03 November Outdoor Air Background

Figure 4-2: 03 November Outdoor Air with HEPA Filter.
Figure 4-3: 50 nm Gelman Filter.

Figure 4-4: 20 nm Gelman Filter.
Figure 4-5: Short Tube - Background.

Figure 4-6: Long Tube - Background.
Figure 4-7: 24 hour time series.

Figure 4-8: 24 hour time series.
Figure 4-9: 24 hour time series.

Figure 4-10: 40 hour time series.
The PowerChip laser was used to form plasma on ambient aerosol particles which were detected by a photomultiplier tube and stored to a computer. A variety of subtleties arose in the development of the system, ranging from making the detector housing light-tight to changing the drying tower to make the flow properties more laminar. A 5-day sampling campaign produced no clear environmental cycles and only one correlation; that between rainfall and decreased particle counts. However, PowerChip features such as high repetition rate, short pulsewidth, stable output, and nearly single-mode operation render it useful for many applications including real-time particle monitoring.

By taking long time-series data of ambient air and studying the size and concentration dependence of particle counting, the PowerChip laser shows itself a steady and reliable source for plasma excitation. The PowerChip would be a strong candidate for continuous aerosol monitoring.

Future work may include more precise determination of minimum particle size and improvement in efficiency through, for example, particle focusing [Wu, 2006; Erdmann, et al, 2005] and combination of the laser with an iCCD or other spectrometer to gain spectral identification along with particle counting. Interesting experiments would include using the spectrometer to calculate the plasma temperature to correlate the particle size versus breakdown energy from Weyl [1989]. Lastly, particle beam focusing could dramatically improve particle transport efficiency and, concomitantly, detection efficiency.
APPENDIX
LASER CHARACTERISTICS

Experimental Equipment

JDS Uniphase PowerChip Laser
- 500 picosecond pulsewidth
- 56 μJ/pulse
- 1 kHz repetition rate

Hamamatsu R647 PhotoMultiplier Tube (PMT)
- Diameter = 13 mm
- Wavelength Range = 300 – 650 nm
- Gain = 1.4 x 10^6

BG – 38 filter glued to end of PMT to block laser light
~300–650 nm FWHM transmittance
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BIOGRAPHICAL SKETCH

William Paul Mason was born in Gardner, Massachusetts on 15 May 1973. The youngest of five children, William graduated from Oakmont Regional High School in 1991 and obtained a B.A. in outdoor leadership from Prescott College in 1995. After working as a mountain guide and EMT, he returned to Northern Arizona University to obtain a B.S. in environmental chemistry. Upon graduation he commissioned in the U.S. Air Force and served his first assignment at Kirtland AFB, New Mexico as a scientist. From there, he was selected to obtain a master’s degree and attended the University of Florida.

When not studying, William enjoys outdoor activities ranging from skydiving to cave diving, and is a budding musician with bass guitar and violin.