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Final Report

Development of On-line Instrumentation and Techniques to Detect and Measure Particulates

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Abstract

In the 17 quarters of the project, we have accomplished the following milestones — first, construction of the three multiwavelength laser scattering machines for different light scattering study purposes; second, build up of simulation software package for simulation of field and laboratory particulates matters data; third, carried out field online test on exhaust from combustion engines with our laser scatter system.
# Table of Content

Disclaimer ................................................................................................................................... 3  
Abstract ....................................................................................................................................... 3  
Table of Content ......................................................................................................................... 4  
Executive Summary .................................................................................................................... 5  
Experimental methods ................................................................................................................ 7  
1. Two versions of multiwavelength laser light scattering platforms for PM samples ....... 7  
2. The multiwavelength laser scattering microscope setup .............................................. 10  
3. Simulation work ............................................................................................................ 12  
Results and Discussion ............................................................................................................. 13  
1. Results from Construction of the PM monitor .............................................................. 13  
2. Field test results from the online exhaust PM monitor ................................................. 17  
3. Simulation efforts and results from field test monitor .................................................. 24  
4. Discussions on the field test results and simulation results .......................................... 25  
Conclusions ............................................................................................................................... 26  
GRAPHICAL MATERIALS LIST .......................................................................................... 26  
TABLE LIST ............................................................................................................................ 27  
REFERENCES ......................................................................................................................... 28  
BIBLIOGRAPHY ..................................................................................................................... 29  
Quarterly Reports .................................................................................................................... 29  
Conference presentations ........................................................................................................ 29  
Patents ................................................................................................................................... 29  
Papers and Manuscripts ........................................................................................................ 29  
LIST OF ACRONYMS AND ABBREVIATIONS .................................................................... 30  
Appendix: .................................................................................................................................. 30  
Work plan for the 16 quarters of the project ........................................................................... 30
Executive Summary

This report gives a summary of the results and achievements during the project’s 16 quarters period. During the 16 quarters of this project, we constructed three multiwavelength scattering instruments for PM2.5 particulates. We build up a simulation software package that could automate the simulation of light scattering for different combinations of particulate matters. At the field test site with our partner, Alturdyne, Inc., we collected light scattering data for a small gas turbine engine. We also included the experimental data feedback function to the simulation software to match simulation with real field data.

The PM scattering instruments developed in this project involve the development of some core hardware technologies, including fast gated CCD system, accurately triggered Passively Q-Switched diode pumped lasers, and multiwavelength beam combination system. To calibrate the scattering results for liquid samples, we also developed the calibration system which includes liquid PM generator and size sorting instrument, i.e. MOUDI. In this report, we give the concise summary report on each of these subsystems development results.

This final report is organized in two sections with the following topics.

1. Experimental
Based on our unique multiwavelength light scattering system, we built three versions of light scattering instruments.
- Two versions are designed for on-line monitoring of particulates emission from combustion engines. The first one is a table-top demonstration version and uses mono-sized polystyrene PM simulates. The second one is for field test as an on-line exhaust PM2.5 emission monitor.
- The 3rd version is designed for microscope observation and measurement of a single particle.
- A patent was filed for the above instruments.
- A universal platform which integrates up to 10 wavelengths lasers is designed and fabricated.
- A high speed linear CCD detector is constructed to retrieve pulsed and continuous wave laser scattering on PM samples.
- Field test data were collected with a turbine combustion engine at the exhaust line.
- We also built a liquid PM particle generating machine, a MOUDI impactor PM sizing instrument that measures both solid and liquid PM particles, and the results are compared to the simulation results, and help the simulation package to optimize the simulation processes.

2. Simulation and theoretical
We designed a software package that simulate mono-sized PM multiwavelength light scattering.
- The software package first could automate the output with a range of mono-sized PM and wavelength input.
- We also added the experimental data feedback input to the software package that let it output the mono-sized PM distribution and density based on multiwavelength light scattering experimental results.
We tried many ways to bridge the gap between online field particle scattering data and our modeling data. This includes adding density as a variable to the PM particles, and also changing PM compositions, e.g. from carbon soot to carbon soot with partial water or diesel droplet.

We conclude the report with the summary on all the results and future directions.
Experimental methods

1. Two versions of multiwavelength laser light scattering platforms for PM samples

1.1. Table-top multiwavelength scattering system

In the first year, our experimental work results in a table top demonstration of multiwavelength laser scattering.

The lasers used are given in table 1. We first used 8 CW lasers, and then added a pulsed laser operating at 355nm.

Table 1. Laser sources used in the mutiwavelength scattering system

Some more details about the diode lasers we acquired, they come in the following wavelengths and power,

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>635nm</th>
<th>650nm</th>
<th>780nm</th>
<th>810nm</th>
<th>830nm</th>
<th>980nm</th>
<th>532nm</th>
<th>1064nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (mW)</td>
<td>30</td>
<td>40</td>
<td>80</td>
<td>1000</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>200</td>
</tr>
<tr>
<td>Package</td>
<td>TO</td>
<td>Cir. TO</td>
<td>Bare</td>
<td>C-mnt</td>
<td>TO</td>
<td>FC</td>
<td>DP/CW</td>
<td>DP/CW</td>
</tr>
</tbody>
</table>

Note: Cir.TO: Circular output (from Blue sky) in a TO can, C-mnt: C-mount bare chip, FC: Fiber coupled, DP/CW: Diode pumped CW operation (could be modulated at low frequency up to 10kHz)

We also designed our own laser driver and TEC temperature controller for the diode lasers and also the high power pump lasers for the pulsed PQS lasers. These drivers feature flexible current driving capability (from 100mA to over 10A) and fast modulation bandwidth (2MHz). Today, they form the backbone of our optical lab’s driver for any customized system that precludes large commercial LD driver boxes.

Noteworthy here, we have been improving the performance of PQS pulsed lasers, i.e. its pulsing timing precision, pulse energy and UV harmonic conversion efficiency, so that we could add two UV wavelength of 355nm in this setup.

We adopted the beamsplitter scheme (figure 1) for combining the lasers together because of the high efficiency and also the number of lasers is rather limited.

![Figure 1. Schematic for combining 10 multiple wavelength lasers together from UV to NIR for light scattering.](image)

We also measured the angular scattering for multiple particle-standard

1. The standard is Polybead Polystyrene microspheres from Polysciences, Inc (Warrington, PA). The kit includes 5 mono dispersed spheres. We recorded the intensity distribution of scattering for each standard over several concentration levels and over an angular distribution.
of $\pm 40^\circ$. We verified the angular distributions are consistent with Mie theory. Figure 2 gives the table top setup for verifying such scattering results.

Figure 2. Schematic (top) and actual setup (bottom) of the table-top light scattering setup. The Angle of the detector platform could be changed to extend the angle measurement from $\pm 10^\circ$ to $\pm 40^\circ$.

2. We also constructed a water droplet nebulizer (see figure 3) that could generate water particles with mono-sized distribution. *This system is used in the 3rd and 4th year to simulate the PM emission in the exhaust line when water droplets are quite obvious and need to be addressed during low power operation of the turbine engine.*

3. A MOUDI impactor aerodynamic particle sizing machine is also constructed over the past 3 years to measure water droplet particle sizes. This proved to be quite valuable in the end of the project when we need to verify our simulation model on water particulates.
1.2. Online PM monitoring system for combustion engines

We first fabricated the field deployable PM monitor system with USB1.1 system. We then upgraded the system to USB2.0 system which gives much higher frames rate, i.e. from 10 Hz to
150Hz now. For our 9 wavelengths scattering system, this translate into ~17 scans on all 9 wavelengths each seconds. There is still room to further improve the frame rate to 1kHz, and the faster the scan rate, the more responsive and less noisy the system becomes.

Figure 4. Online-PM multiwavelength scattering instrument for field test, installed at Alturdyne test site with a turbine engine. The left side is the receiver with CCD detector and the right side is the multiwavelength transmistter.

2. The multiwavelength laser scattering microscope setup

We found that we could “see” single particles whose size is well below optical resolution if laser scattering signal from a single particle is detected at a large angle from direct incidence. Although this is not a new discoveries as “dark filed microscopy” had already demonstrated this decades ago. But, when we use multiwavelength lasers instead of white light, we would be able to measure the single particles that usually have features below the optical resolution limit of microscopy. The schematic is given in figure 5.
We successfully used this technique to observe and measure paraffin particle growth in our center’s Enhanced Oil Recovery (EOR) research project (figure 5a~5f). We are exploring the applications of this technique to other research field, e.g. biology.

Figure 6a. The darkfield TIR illuminated image right after...
the heated emulsion is deposited on the prism surface, the bright spot is impurity solid stuff not dissolvable at 50°C. 14minutes after the heated emulsion is deposited on the prism surface, the bright spots are the wax formed.

Figure 6b. The bright field image of the emulsion right after deposition on the prism surface.

Figure 6e. The bright field image 14min after the heated emulsion is deposited on the prism surface, one could not distinguish the wax solid from other bright area.

Figure 6c. Half-darkfield TIR microscopy right after deposition
Figure 6f: Half-darkfield TIR microscopy clearly verifies the locations of the solid wax

Figure 6. Study of wax crystallization with TIR illumination. The above images' total width is 160μm.

In the 4th year, we added the scanning imaging function for vertical angle of incidence for laser beams. This function coupled with multiwavelength laser scattering will boost the power of this technique. A US patent is filed for this technology.

3. Simulation work

The simulation work is focused on first building the basic scattering modeling software for PM2.5 mono-sized particulates. We found that for PM2.5 particulates, forward scattering is good enough to gauge the PM sizes if multiple wavelength lasers are utilized. **This proved our project’s principle that multiwavelength scattering could alleviate for the requirements on wide angular distribution measurements for single wavelength scattering scenarios.** We then automate the simulation so that a total of 12 different wavelength laser scattering results could be generated for a mono-sized distribution of particulates.
We also found that even with multiple wavelength scattering with wavelengths ranging from 355nm in the UV to 1064nm in the IR, we still need +/− 10 degree of angular scattering results in order to simulate the size distribution correctly. Our design of multiwavelength scattering instrument therefore had a detector system that guarantee such an angular range of data. After collecting field test data, we found that the online exhaust PM emission has a much more complicated composition than we anticipated. This complication comes in especially under heavy loading conditions, when the soot particulates with different packing densities start to form, the total transmission loss of lasers drop significantly due to high PM concentration, and also complication from water condensation all happen in the exhaust line. We have been trying to bridge the gap between simulation and field test results by including transmission loss factor in the simulation, and adding the channel that detect transmission loss in the instrument. We also included the water simulation capability in the software package (see the next section).

Results and Discussion

1. Results from Construction of the PM monitor

In order to construct the PM monitor we have also conducted research and development in several photonics instruments. These instruments include fast gated CCD system, high power precisely trigger passively Q-switched (PQS) diode pumped lasers, multi-spectral laser source combination system.

1.1. Fast gated CCD system

We have spent a great amount of time in the development of a USB 2.0 based fast gated CCD system. The reasons we developed our own system instead of using commercial ones are:

5.1. Our laser is being pulsed at high speed rate, at over 1kHz rate. The majority of CCD linear array systems are not designed for operating at such high repetition rate.

5.2. The lasers are operating with short pulse widths, usually 10s of microseconds, and the PQS lasers will have pulselength less than 10nanoseconds. At the same time, the background light is always contributing to the total signal. To improve signal to noise ratio, we prefer to shorten the integration window of the CCD detector. We wish to achieve submicrosecond integration and this kind of shutter speed is not available on most non-fast-gated CCD detectors.

5.3. The spectral response of regular windowed CCD detector is above 400nm, and the window could create interference with laser beams. We need to apply special AR coated window to standard CCD detectors to avoid interference buildup.

The system is based on a CMOS based linear photodiode array system. We solved above problems with the following features (figure 6),

1. We developed VHDL code for the CPLD IC (XILINX 9500XL) in the USB-CCD board. This board allows fast trigger at over 1kHz, and collect data from a ADC chip with 1.25MHz sampling rate at 12 to 16 bits resolution.

2. The VHDL code has an onboard integration timing programming capability that allow short integration window as little as 50nsec.

3. Along with vendor, we developed a repeatable process for taking off windows from commercial CCD chips. The default window is made of uncoated BK7
material, and not suitable for UV and could create interference lines. Without the window we could avoid such problems.
1.2. High speed and high power LD driver

The lasers we used in the PM monitor are all based on diode lasers, or diode laser pumped solid state lasers. They require LD driver with high speed and high power capability. We designed a controller with LD with TEC control. The controller is based on Wavelength Electronics LD driver IC (WLD3343) and temperature controller IC (HTC3000). It has a 2MHz modulation bandwidth and current capability up to 10A with connect two boards together, along with 4 of the LD driver chips.
1.3. Prepumping for accurate timing of PQS lasers

We need to precisely trigger the PQS laser at about 100Hz rate when the PM monitor is scanning all 10 wavelength laser systems at 1kHz rate. The traditional free running PQS laser system runs without external trigger, and if use a pump pulse to start a PQS pulse, the delay between the pump pulse and the PQS laser pulse is on the order of dozens of µsec, and the jitter is also several µsec. We improved the timing accuracy of diode pumped PQS lasers. The trick here is the prepumping the PQS crystal at a current level just below PQS threshold. Then, quickly pulse the pump current when a laser pulse is needed. With such technique, we are able to reduce PQS pulse to pulse jitter from ±5µsec to below 100nsec.

![Figure 8. Prepumping reduces pulse jitter to 100nsec in 5 seconds. The bottom trace has a DC offset of 0.94Volt.](image)

The trace at the bottom is the current pulse to the pump laser diode, and the trace above is the PQS laser pulse. Jitter is about 100ns in 5seconds (100 shots accumulated). The DC offset in the pump current helps to reduce the jitter and also the delay between the fire command pulse and the actual laser pulse, i.e. down to 2.5µsec has been demonstrated.

The results we obtained compared favorably to others as shown in table 2.

Table 2. Results of prepumping on PQS laser from previous references and this project.
### References

<table>
<thead>
<tr>
<th>References</th>
<th>Delay (µsec)</th>
<th>Jitter (ns)</th>
<th>Drift(ns)</th>
<th>Memo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q-Peak [4]</td>
<td>40</td>
<td>200</td>
<td>400</td>
<td>Microchip 1mm thick, no mentioning of prepumping, minimal is 40 µsec,</td>
</tr>
<tr>
<td>Brimose [2]</td>
<td>350</td>
<td>500</td>
<td></td>
<td>0.5µsec is the smallest jitter after using prepumping, 2sec histogram</td>
</tr>
<tr>
<td>TH Prepump [3]</td>
<td>20</td>
<td>2800</td>
<td></td>
<td>Cr:+Nd: codoped, 12msec switching time</td>
</tr>
<tr>
<td><strong>This report</strong></td>
<td><strong>2.5</strong></td>
<td><strong>100</strong></td>
<td></td>
<td>5sec average, discrete components ~25mm cavity, 0.4msec switching</td>
</tr>
</tbody>
</table>

#### 1.4. Increase the pulse energy of PQS laser systems

We increased the total pulse energy of PQS laser system by using longer cavity mode and higher feedback output couplers. The original PQS lasers only could output 1.5µJ of pulse energy in about 2 nsec pulse width. We have achieved 10µJ pulse energy at 355nm in about 15nsec pulse in the final PQS laser system. The pulse energy are 50µJ at 532nm and 120µJ at 1064nm.

#### 1.5. Major Conference Presentations, Papers and Patents

We prepared 2 manuscripts for peer review publications that originated from the research in this project. The first one is on the simulation efforts proving that PM2.5 could be detected with limited angular range in the forward direction if multiple wavelengths of lasers are used. The second manuscript was sent to present the laboratory and field test results along with simulation work, both are submitted to “Atmospheric Environment”, ISSN: 1352-2310, Elsevier Publications. Both manuscripts are under review right now.

We also filed a US patent on our microscopy analysis of single particle’s size and other properties with multiple wavelengths of lasers. The patent review process is finished and is now allowed by USPTO. The title of the patent is “Dark field laser-scattering microscope for analyzing single molecules”.

#### 2. Field test results from the online exhaust PM monitor

Our field test at our partner’s internal combustion engine manufacturing facility, Alturdyne (El Cajon, CA), lasted over 2 years, with 2 campaigns over a total of 4 months. We collected 1.4 Gigabyte of data. The first campaign (3.5 months, or 15 weeks) in the summer of 2005 yielded the following results.

**2.1. The field data shows repeatable patterns under the same load conditions and wavelengths. This proves the reliability of the instrument and concept.**

In the first field test campaign in 2005, we already proved that the small forward angular scattering signal pattern is quite repeatable. Shown in figure 9, the scattering signal in a +5.7°~+0.2° and -0.2°~ -3.9° degree angle cone is collected with a 1024 pixel linear CCD; the signal is collected over ~1 minute period while the turbine engine is operating under normal load conditions (160kW). The scatter signal peak amplitudes actually show a ~3% periodical variation every 5 seconds (it took 5seconds to conduct 100 averages), with peaks on both sides
going up and down together. The two side peaks are not symmetric and the asymmetric shape is attributed to CCD’s limited pixel height (200µm), which resulting in asymmetric signal response when the incoming light signal is not in the focal plane and intercepted by the CCD detector plane. Similar repeatable scanning patterns over several minutes time period are observed at other 7 wavelengths (8 wavelengths are available, we use only 1064 or 355nm at one time as they come out from the same pulsed PQS laser source) under different load (figure 10 and 11).

Figure 9. 1 minute small angular scattering data collected at 532nm in the exhaust line of a Cummings turbine engine under normal load conditions.
2.2. The total scattering signal and pattern changes with load and wavelengths are also consistent with theory.

As the load increases from light load (110kW) to normal load (150–160kW) and then to high load (200kW), the scattering patterns also change in the following ways.

A. The amplitude of scattering signal peaks increases dramatically with load, a direct indication of higher PM emission rate.

B. The most obvious change is the shift of the two peaks of the major side wings from closer to the center to further away from the center as the load increases.
This indicates that the size of the dominating particles actually decreases as the load increases.

C. The other obvious change is the sharpening of the two peaks of the major side wings as load increases --- indicating particles with a dominating size is generated at higher throughput. Our simulation efforts were first directed at simulating carbon black particles, but yield inconsistent patterns as we do not have the exact composition information for the soot particulates. The subsequent simulation efforts indicate that we are generating monosized water PM as the dominating species (see explanation in subsection F below), and the center of the PM size changes from ~1.0µm to ~2.8µm as the load increases. Figure 12 shows that the simulation for low load condition emission, where we used a water PM size centered at 1.4µm with a full width at half maximum of 0.4µm, and centered at 668 pixel. This fitting gives least deviation error and is quite repeatable for many repeated scenarios, especially under low load conditions where the emission conditions are not changing dramatically (table 3).

D. The 3rd obvious change, and most obvious under high load condition is the breakup of the simple side wings as the load increases. Based on the emission type, we believe it is related to carbon black soot PMs. It is obvious to our naked eyes.
eyes that under high load conditions the PM emission fluctuates dramatically over the time, and the opacity also increases. This prompts us to simulate the PM scattering results by adding carbon black PMs. However, our simulation efforts have had a hard time when adding carbon black due to the parameters for the carbon black, such as density or packing density, are quite uncertain. We also suspect that there is water inclusion in the carbon black, whose content also changes as load changes. All these uncertainties create large errors in the correlation $R^2$ in the simulation under heavy load conditions.

**E.** The changes of the scattering pattern v.s. wavelengths are also consistent with theory.

![Image](image.png)

**Figure 13.** Above, PM scattering signal under light load (110kW) condition at 650nm.

![Image](image.png)

**Figure 14.** Above, PM scattering signal under light load (110kW) condition at 780nm.
The above three plots and the plot shown in figure 10, are collected under light load conditions (110kW). When the probing wavelength changes to longer wavelength, the angular distribution changes --- spreading to the larger angles, and there are also peak broadening (780nm, figure 9f) and sharpening (980nm, figure 9g) in the longer wavelength scattering, which we first attributed to resonance --- an effect that not associated with carbon black particulates, we later on found that they are related to water PM resonance scattering effects. At first, we were unable to simulate such resonances effects with carbon black or water. We later on (see section 3 below) added this resonance effect in our modeling after verifying with monosized water PM generated in the lab, and we were able to close this gap.

F. The above theoretical simulation results did not match with field test results in a straightforward way. We first failed to simulate the field results, i.e., there is great discrepancy, the R² for longer wavelengths, e.g. 780nm, 8100nm, are as small as 0.8 even at light load conditions. After that, we had to go back to the lab and modified the simulation especially for monosized water PM, and verified first that the monosize water PM could be generated with our neubilizer, and then collect the scattering pattern with our scattering instrument, and then verified the modified simulation software could simulate the results with improve R², see section 3 below.

2.3. Detailed simulation based on standard particles will further analyze the components in the emissions.

We then went back to our lab trying to optimize the simulation model for the data collected (see section 3 for details). We found out that,

A. We need to add transmission attenuation detection in our system in order to account for heavy load conditions when PM sizes is no longer mono-sized, and simulation deviates from experimental results.
B. We need to add UV channel with enhanced power which was not available in the first campaign. This UV channel with extra photons will provide information about soot particulates v.s. water, or the mixed kind of particles.

We also went back to Alturdyne in early 2007, and conducted 1 week of test and collected some data and we are analyzing them. We have 3 major new findings so far,

C. The transmission losses did increase to a significant level. In table 4 below, we list the transmission loss data for 532nm, 650nm and 980nm. It is obvious that we have to include the transmission loss when operating at or above normal conditions.

Table 4. Transmission losses, due to both direct absorption and scattering, at different wavelengths and load conditions

<table>
<thead>
<tr>
<th>Load Conditions</th>
<th>110kW</th>
<th>150kW</th>
<th>180kW</th>
<th>200kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission @ 355nm</td>
<td>63.7%±5.5%</td>
<td>40.5%±13.8%</td>
<td>31.1%±16.1%</td>
<td>27.5%±17.8%</td>
</tr>
<tr>
<td>Transmission @ 532nm</td>
<td>92.4%±2.1%</td>
<td>84.4%±2.8%</td>
<td>75.1%±3.5%</td>
<td>63.5%±5.8%</td>
</tr>
<tr>
<td>Transmission @ 650nm</td>
<td>94.3%±2.2%</td>
<td>86.5%±2.4%</td>
<td>78.6%±3.3%</td>
<td>65.7%±5.2%</td>
</tr>
<tr>
<td>Transmission @ 980nm</td>
<td>90.8%±2.5%</td>
<td>81.9%±2.7%</td>
<td>70.6%±3.5%</td>
<td>52.2%±12.4%</td>
</tr>
</tbody>
</table>

D. The power of the UV wavelength is still quite low especially under above normal load conditions. The transmission is only ~40%±14% at 355nm under normal conditions. This low transmission and large fluctuation in transmission at 355nm prevents us to use the data to provide meaningful scattering simulation. We propose to use this wavelength to probe the increase of carbon soot PM. However, we need to collect some soot PM transmission data first which is currently not available. The transmission loss for 355nm measured with our water PM generated in the lab is much lower --- we constantly getting over 60% transmission for 355nm even under high density of water PM in the neubilizer jet. This indicates that carbon soot could be the main absorber or scattering source for 355nm. In fact, it is obvious to our naked eye that there is substantial amount of black generated in the emission plume under heavy load. However, we do not have a carbon black standard to use as reference for measuring 355nm transmission loss. The carbon black particles often have huge density and size variations because the condition that they were formed is not stable at all, especially under heavy load. Under light and normal load conditions, the carbon black particulates could be formed quite stably, and therefore it is possible to use the transmission loss difference between 355nm channel and other wavelengths channels to monitor carbon soot emission rate --- a very important pollution source for this project. In our current turbine engine, under light and normal load conditions, the dominating emission is water as our simulations confirm; but for diesel engines, the carbon soot emission could be significant and this large transmission loss at 355nm could be used to monitor the total carbon soot emission rate when compared with other wavelengths transmission loss.
3. Simulation efforts and results from field test monitor

Our simulation efforts are divided into two stages in this project. The first stage is to develop the core multiwavelength scattering program that could generate scattering patterns for monosized particulates at different wavelengths. We used Mie scattering model, and developed the software package that was especially tuned for PM2.5 particulates. The second stage is to add different PM parameters to the modeling software, simulating and matching the field experimental results.

3.1. Successful simulation with monosized water droplet modeling

After the first field campaign, we first simulate the PM with regular carbon black (graphite) particulates, and found that if we give one set parameters to match scattering pattern at one wavelength, the simulation would perform poorly at other wavelengths, especially at the place where the field results show broadening side peaks --- our initial simulation results failed. We then discovered that we were simulating with a wrong target --- instead of carbon black, we should be aiming at water in the Cummings turbine engine. Because water particles have special resonance effect, the original first version modeling software failed to include and therefore simulated incorrectly.

We went back to use our water particulate neubilizer and verified with MOUDI dynamic PM sizing instrument that mono-sized water particulates were indeed generated. Then, scattering data were collected with the mono-sized water particulates. We then added the resonance effect in the modeling software and used water particles as the particulates material, and then we were able to match the monosized water droplet scattering data with our modeling software.

Back to the field test data simulation, with the modified model, we are able to achieve better simulation consistency for all wavelengths. Compared to the first modeling software, the resulting optimized PM particles changed both the size and distribution of the particulates.
3.2. Discrepancy at high load conditions

After solving the water problem, we found out that there is also significant discrepancy ($R^2 <0.9$) between field test data and our simulation results, particularly at the heavy load stage, we went onto analyze the discrepancy. We believe that the discrepancy comes because at heavy load conditions, the following factors complicated the simulation efforts:

A. The particulates density increases so that the transmission loss increases to a point that is no longer insignificant in the modeling software, i.e. we have to include the correction for input light power along the beam path due to absorption. Before, we assume a constant light flux along the beam path.

B. The particulates at heavy load now include soot particles that have different packing densities, and also mixture particulates consisted of water and carbon black.

We went back to include these factors in our modeling software. We found that we then need to add density factor along with multiple internal reflection for water particles as well. Such simulation has not been done before in the literature (see QE2 report), particularly because we do not have enough knowledge about the composition of the soot particles. After including this capability, we also need to test it by comparing the simulation results with mono-sized water particulates. This remains the biggest uncertainty in the monitoring system when new freedoms open up in the field tests.

4. Discussions on the field test results and simulation results

The initial field data show repeatable patterns under the same load conditions and wavelengths. This proves the reliability of the instrument and concept. The total scattering signal and pattern change with load and wavelengths are also consistent with theory.

However, there is discrepancy between the simulation and experimentally observed scattering patterns, and the discrepancies are particularly large at heavy load conditions. We attribute this discrepancy to the following factors,

- The composition of the PM particles in the engine exhaust is far more complex than we could simulate, especially during change of engine’s load.
- Gas phase water content and absorption loss is not included in the scattering yet at wavelengths of 800nm and 900nm.

We propose that to solve the discrepancies,

- Multiwavelength scattering lasers’ wavelengths could be tuned to monitor water content, and this should help the determination of water content in the particles. We already have the scattering loss measurement channel installed in our new system, and the difference in loss due to water absorption could be measured if strong enough. We need several lasers with wavelengths around 900nm where water absorption peak is available for differentiation measurement.
- Analyze each single individual particle’s content and structure --- impossible right now but possible with other modern technologies. This is especially true for carbon black particulates under heavy load conditions.
Conclusions

This project is the first major research project we conducted here at PEER Center focusing on particulates study. The major results include the multiwavelength PM scattering simulation software package and experimental setups for both online exhaust and microscopic single particles. We have demonstrated here that although single wavelength scattering pattern collect in the small forward angle could yield a PM size distribution solution to match its pattern, the solution is not unique. With the constraints to match other wavelengths’ scattering patterns, we could narrow down the solutions nicely. However, as even more freedoms open up, e.g. large amount of carbon soot with varying density and composition appear as a new species, the solutions become hard to predict again.

These results lead us to the following research directions here at our center.

1. The application of multiwavelength PM scattering to a variety of PM sources, besides online exhaust. We have demonstrated that it could perfectly measure and simulate mono-sized single component PM particles. Such kind of capability is only possible with circularly enclosed single wavelength laser scattering instruments before. Our instrument is the first that could provide such measurement with laser scattering and without the need to completely circle the sample path. The applications of this technology include chemical engineering process development at PM chemical production facilities, such as pharmaceutical industry, painting and other material production processes. This capability is especially needed for the submicron sized nano PM materials.

2. The application of multiwavelength PM scattering is being applied to single particle scattering study with the help of a microscope. Our instrument is adding a new dimension to the current laser scanning microscopy. Particularly, it could detect particles with dimensions under optical resolution and measure its size. We intend to pursue the ultimate goal of measure single particle’s size down to 50nm size.

GRAPHICAL MATERIALS LIST

Figure 1. Schematic for combining 10 mutiple wavelengths lasers together from UV to IR for light scattering.

Figure 2. Schematic (top) and actual setup (bottom) of the table-top light scattering setup. The Angle of the detector platform could be changed to extend the angle measurement from ±10º to ±40º.

Figure 3. Water aerosol generator (neubilizer)

Figure 4. Online-PM multiwavelength scattering instrument for field test, installed at Alturdyne test site with a turbine engine.

Figure 5. Setup of the laser scattering microscope system
Figure 6. Study of wax crystallization with TIR illumination. The above images’ total width is 160µm.

Figure 7. Top. CPLD pin out on the USB 2.0 board, Middle: Driver and Data collection electronics, and Bottom, the schematic layout of the USB2.0 CCD DAQ board.

Figure 8. Prepumping reduces pulse jitter to 100nsec in 5 seconds. The bottom trace has a DC offset of 0.94Volt.

Figure 9. 1 minute small angular scattering data collected at 532nm in the exhaust line of a Cummings turbine engine under normal load conditions.

Figure 10. PM scattering signal under Light load (110kW) condition, scattering signal amplitude is much weaker.

Figure 11. PM scattering signal under heavy load (200kW) condition, shift to larger angular distribution is obvious.

Figure 12. Simulated (red and green) and field measured (black) scattering signal for PM emission with dominating water PM centered at 1.4µm and a full width half maximum (FWHM) of 0.4µm for diameter size distribution.

Figure 13. Above, PM scattering signal under light load (110kW) condition at 650nm.

Figure 14. Above, PM scattering signal under light load (110kW) condition at 780nm.

Figure 15. Above, PM scattering signal under light load (110kW) condition at 980nm.

Figure 16. Scattering signal for 355nm, pulsed mode, 2µJ/pulse, 15nsec pulse width, note that it is summed over 100 pulses, and the signal to noise ratio is poor.

**TABLE LIST**

Table 1. Laser sources used in the multiwavelength scattering system.

Table 2. Results of prepumping on PQS laser from previous references and this project.

Table 3. Summary of simulated and measured water PM sizes

Table 4. Transmission losses, due to both direct absorption and scattering, at different wavelengths and load conditions
REFERENCES

The list is comprehensive as it includes the key references starting from project inception in October, 2003. The BIBLIOGRAPHY section contains the original papers, commercial publications, and DOE-related reports, respectively, of original technical work completed throughout the project or in progress.


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5. Robert J. Pelham Jr & Fred Chang, Actin dynamics in the contractile ring during cytokinesis in fission yeast, NATURE, VOL 419, 82-86, 2002


10. Masayoshi Nishiyama, Etsuko Muto, Yuichi Inoue, Toshio Yanagida and Hideo Higuchi Substeps within the 8-nm step of the ATPase cycle of single kinesin molecules NATURE CELL BIOLOGY 428-431 VOL 3 2001


Quarterly Reports


Conference presentations

Sheng Wu, Yongchun Tang, “SINGLE MACROMOLECULE IN-VIVO MICRO ANALYSIS: SIZE, MOLECULAR WEIGHT AND SHAPE” American Chemical Society meeting, Anaheim, CA, 2004


Sheng Wu, “Accurate timing of Passively Q-Switched lasers” Security and Defence Symposium, SPIE, Kissimee, FL, 2004


Patents


Papers and Manuscripts

“Dark field multiple wavelength laser-scattering microscope for analyzing single molecules”. Submitted to “Atmospheric Environment”, ISSN: 1352-2310, Elsevier, under revision

LIST OF ACRONYMS AND ABBREVIATIONS

ACS: American Chemical Society  
CCD: Charge-Coupled device  
CLK: Clock  
CW: Continuous wave  
FC: Fiber Coupled  
DP: Diode Pumped  
DPSSL: Diode Pumped Solid State Laser  
EOR: Enhanced Oil Recovery  
Hz: Hertz, unit in frequency  
IR: Infra-red  
ISSN: International Standard Serial Number  
LD: Laser Diode  
MOUDI: Micro-Orifice Uniform Deposit Impactors  
OSA: Optical Society of America  
PEER: Power, Energy and Environmental Research Center, California Institute of Technology  
PM: Particulate matters  
PM2.5: Particulate matters with diameter size less than 2.5µm  
PM10: Particulate matters with diameter size less than 10µm  
PQS: Passively Q-Switch  
TEC: Thermal-electric  
TO: Terminology for semiconductor device package  
UV: Ultra-Violet  
USB: Universal Serial Bus  
VHDL: VHDL (VHSIC hardware description language) is commonly used as a design-entry language for field-programmable gate arrays and application-specific integrated circuits in electronic design automation of digital circuits.

Appendix:

Work plan for the 16 quarters of the project

Planed schedule from the statement of work for the first 3 years (12 Quarters) of the project

<table>
<thead>
<tr>
<th>Task</th>
<th>Technical Milestone</th>
<th>Schedule</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Assembly of the multiwavelength light source</td>
<td>Ready diode &amp; DP chip lasers, drivers</td>
<td>Month 1-6</td>
</tr>
<tr>
<td></td>
<td>Ready beam combination system</td>
<td>Month 1-6</td>
</tr>
<tr>
<td>2. Construction of the PM synthesizer</td>
<td>Verify that monosize PM are generated</td>
<td>Month 1-6</td>
</tr>
<tr>
<td>3. Simulation of Ralyeigh and Mie Scattering</td>
<td>Literature review</td>
<td>Month 1-3</td>
</tr>
<tr>
<td></td>
<td>Computer program that could generate simulated scattering spectrum</td>
<td>Month 1-6</td>
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</tbody>
</table>
4. Laboratory demonstration of instrument

<table>
<thead>
<tr>
<th>Experimental scattering spectrum database for different PM sizes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compare with theory and conventional PM monitoring data</td>
</tr>
<tr>
<td>Month 7-18</td>
</tr>
</tbody>
</table>

5. Application of the PM analyzer to a combustion environment: engine intake area

<table>
<thead>
<tr>
<th>Correlation of our instrument data with conventional PM monitoring data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Month 13-24</td>
</tr>
</tbody>
</table>

6. Application of the PM analyzer to a combustion environment: engine exhaust

<table>
<thead>
<tr>
<th>Correlation of our instrument data with total PM mass emission, new data (PM size and chemical composition) about in-situ PM monitoring</th>
</tr>
</thead>
<tbody>
<tr>
<td>Month 13-24</td>
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</table>

7. Applicability assessment for PM emissions from coal fired power plants

<table>
<thead>
<tr>
<th>Design/modify our PM instrument for smoke stack PM monitoring</th>
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<tbody>
<tr>
<td>Month 24-30</td>
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</tbody>
</table>

8. Instrument design optimization

<table>
<thead>
<tr>
<th>Optimize the instrument during different experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Month 13-36</td>
</tr>
</tbody>
</table>

The following milestones for each quarter are proposed for the extended 4th year.

**1st Quarter --- interpret the data using standard PMs’ scattering data**

We have already successfully generated standard monosized particles in liquid jet form -- simulating the real PM coming out of engines. We are collecting the scattering data for these liquid standards. In the first quarter, using these standard PMs’ multiwavelengths scattering data, we will develop protocols that will let us simulate the field test data that we collected in the last year.

**2nd Quarter --- more data collection and develop field test protocol**

We will continue the simulation and collect more field test data for more detail and better explanation of the results.

**3rd Quarter --- compiling the data, develop protocol and publish the results**

We will compile the data --- sorting them under different conditions (engine load, and PM emission scenarios) and present the simulation data as the same time. We could then develop and recommend the protocols for using the instrument for small turbine engines.

We will present the data to the industrial manufacturers, e.g. Siemens. Because of the
budget limit, we will only be able to give a guideline for establishing the protocols with engines other than the same engine that we have been conducting our experiments.

4th Quarter --- Finish report and share with industrial partners

We will finish the report and share with industrial partners. We will publish our results at professional journals and meetings.