White Paper on PM Light Extinction Measurements

Prepared by EPA Staff for the AAMMS Advisory Meeting, February 24 and 25, 2010

Background: EPA is considering establishing a secondary PM NAAQS designed to reduce the welfare impacts associated with visibility degradation caused by PM.[1] This NAAQS may use a PM light extinction indicator instead of the traditional PM mass concentration. PM light extinction is the fractional loss of light by scattering and absorption by PM per unit of distance through the atmosphere. Gases also contribute to light extinction by both scattering and absorption, but their contributions would not be subject to this secondary PM NAAQS. Light extinction and its component parts (e.g. PM and gaseous light extinction) are measured in inverse distance units, which for convenience is often expressed as inverse megameters (i.e., $1/10^6$ meters and abbreviated Mm^{-1}).

Purpose: The purpose of this document is to identify the overall measurement goal and describe measurement approaches that might be consistent with this goal. It envisions an evaluation process for approving instrumentation for PM light extinction monitoring, thought it does not attempt to describe the process in detail. This document does not include any information on site selection criteria, inlet probe exposure or network design, which will be described elsewhere.

Measurement Goal: The proposed overall goal is to determine by measurement daylight hourly averaged light extinction by PM_{10} (particle with diameter less than 10μm) for 550nm wavelength light[2] under ambient conditions with an overall accuracy and precision $\leq$ 10% (RMS) in a range from $10Mm^{-1}$ to $1000Mm^{-1}$ for relative humidity conditions $\leq$ 90%.

Measurement Options: There are several ways to measure light extinction that can meet the goals above. Table 1 shows the instrumental techniques that can make these measurements, and summarizes their advantages and disadvantages for the purposes of meeting the goal. Some of the instruments directly measure the total light extinction. Others measure either light scattering or light absorption, so their selection would require the use of two instruments to produce light extinction. Note that there are prototype instruments (not explicitly identified in Table 1) that combine two measurement approaches in one device (Kebabian, et al., 2007, Arnott, et al., 2009). Some of the approaches in Table 1 are the basis of commercially available instruments that have been in wide spread use for many years (Beuttell and Brewer, 1949, Hansen, et al., 1984). Other approaches are used in more limited availability research or pre-

[1] The first review draft of the Urban-Focused Visibility Assessment is at http://www.epa.gov/ttn/naaqs/standards/pm/data/20100121UFVAforCASAC.pdf
[2] Humans are most sensitive to light at about 550nm wavelength.

commercial production instruments (Baynard, et al., 2007), some of which show significant promise to mitigate shortcomings of the more commonly available methods (Kebabian, et al., 2007, Arnott, et al., 2009).

Based upon their understanding of the state of technology, EPA staff believes that a combination of currently available integrating nephelometer light scattering and filter transmission light absorption measurement instruments are suitable for meeting the light extinction measurement goals. That is not to say that modifications to these techniques or use of alternative approaches/instrumentation would not ultimately be shown to produce superior monitoring systems. Ideally, the monitoring requirements for a possible future PM secondary NAAQS using a PM light extinction indicator would have the flexibility to permit the use of improved monitoring approaches as they are developed and evaluated.

Method Limitations/Evaluation: In order to be considered for use in making measurements for a secondary PM NAAQS, the performance of candidate methods needs to be evaluated with respect to the measurement goal. Practical limitations of measurement techniques need to be considered in translating the overall goal into general specifications. These can be grouped by topic to organize a discussion of the issues. The topics include wavelength, sample integrity, and measurement biases. The following is a brief discussion of well known method limitations that should be considered in evaluations of candidate measurement systems.

Many instrumental techniques for measuring light extinction, scattering and absorption do not make the measurement at 550nm. Measurements made at other wavelengths can be adjusted using the power law relationship that has light scattering and light absorption proportional to wavelength to the power of -α (i.e. $\lambda^{-\alpha}$). Where α is the Angstrom exponent which can range from 0.5 to 2.5 for particle scattering and from 1 for black carbon to up to 2 or more for brown carbon (Moosmüller, et al., 2009). The closer the wavelength of the measurement of light scattering and absorption is to specified wavelength of 550nm, the less sensitive is the wavelength adjustment to the value of the Angstrom exponent. Some monitoring methods may include multiple wavelengths which provide supplemental information that can help in identifying the types and sources of the PM and can be used to estimate the Angstrom exponent corresponding to each measurement. Assessments of measurement uncertainty should include wavelength adjustment uncertainty.

Except for the open path transmissometer, all of the instrumental approaches being considered for measuring light extinction, scattering and absorption pull air into the instrument to make a measurement. This can have the effect of modifying the particle size distribution thereby biasing the optical measurement. Modifications to the particle size distribution can be caused by loss of larger particles by impaction or smaller particles by diffusion within the sample line or instrument. It can also be caused by changes in the temperature that affect the relative humidity causing hygroscopic particle to shrink in response to lower relative humidity or grow in response to higher relative humidity. The best approach is to minimize particle loss and temperature changes that affect particle size distributions by design (e.g., reduce the number and severity of impaction surfaces in the inlet line and instrument, insulate inlet lines and minimize the effects of sample heating by the light source and electronics) rather than attempting to correct the data for these deficiencies. The uncertainty and biases associated with sample modification should be assessed for the PM conditions where the method is proposed to be used. For example, loss of $PM_{10 - 2.5}$ by impaction contributes little bias in locations where $PM_{10 - 2.5}$ concentrations are small, but may be a significant source of bias where it's concentrations are high. This could lead to different measurement options or requirements depending on monitoring location.

Measurement biases are inherent to several of the methods under consideration. Integrating nephelometers ideally measure the light scattered from 0° (forward scattering) to 180° (backscattering), but most have 5° to 10° truncation at both ends of the range (Moosmüller and Arnott, 2003). Adjustments for this are not an issue for small particles (e.g. $PM_{2.5}$), which scatter light symmetrically, but are more problematic where a significant but unknown fraction of the PM_{10} is from larger particles which have enhanced forward scattering (Müller, et al., 2009, Massoli, et al., 2009). This results in under-measuring the light scattering by large particles, which can be a significant measurement bias where there are high concentrations of $PM_{10 - 2.5}$. Smaller truncation angles would help minimize the effect directly. Another approach would be to separately measure the light scattering from $PM_{2.5}$ and PM_{10} so that the difference between the two measurements can be adjusted separately to account for the $PM_{10 - 2.5}$ truncation biases.

Another well-documented measurement bias is associated with filter transmission methods for monitoring particle absorption (Weingartner, et al., 2003, Virkkula, et al., 2005, Snyder and Schauer, 2007, Chow, et al., 2009). Particles collected by filtration absorb more light than when they were suspended in the atmosphere because the light is subject to a much greater degree of multiple scattering by the filter fibers and other particles that they are in much closer proximity to other particles than when suspended in the atmosphere. Adjustment approaches to account for this effect have been developed (Bond, et al.,1999, Arnott, et al., 2005). One such adjustment approach requires simultaneous PM light scattering measurements as input to the adjustment. Use of the filter transmission approach for light extinction should include an assessment of the effectiveness of adjustment approaches that would be needed in order to meet the overall accuracy/precision goals of the measurement.

The above described measurement issues and any others that affect the ability of methods to meet the overall measurement goals need to be included in an evaluation of any method proposed for use in monitoring for the possible secondary PM NAAQS. This evaluation would necessarily include an error analysis based on documented effects and expected ambient conditions. It would also likely involve laboratory and/or field measurement including intercomparisons with other measurement methods. As has been cited above, the scientific literature includes numerous descriptions of previous efforts to explore these issues. As a result some of the evaluation results and many of the methods needed for conducting such evaluations are already available.

<u>Other Factors:</u> There are a number of practical considerations that will be important in selecting the monitoring approach that will be used for this possible secondary PM NAAQS. These include, instrument reliability, cost (capital and maintenance), availability, ease of use, manufacturer's operator support, etc. Additional factors that may weigh in on the selection of a monitoring approach are alternate uses for the primary and/or supplemental data generated by the approach. For example separate measurements of PM scattering and absorption can be used to determine single particle albedo (used in climate research), can aid in source attribution, and may be of help for PM health effects research. Similarly, multiwavelength scattering and absorption can be used to estimate the Angstrom exponents for climate research and can aid in determining source attribution, for example distinguishing diesel from wood smoke or dust from black carbon (Fialho, et al., 2005 and 2006).

Several of the instruments in Table 1 exist as prototypes, but are not currently available commercially. These include instruments with technical and perhaps cost advantages over the currently available commercial instruments (e.g., photoacoustic versus filter transmission for light absorption or cavity approaches compared to transmissometer for light extinction). Prototypes of these instruments could be included in evaluations, but it is unlikely that commercial instruments would be available in less than a year. Until EPA determines a schedule for deploying a monitoring network it is not clear whether instrumental approaches that are not currently commercially available should be considered.

Some of the instruments listed in the table are already in use by some air quality monitoring agencies for other purposes, for example filter transmission measurement to estimate black or soot carbon concentrations (Allen, et al., 1999, Jeong, et al., 2004) or heated nephelometer for dry light extinction (Chow, et al., 2006). While a decision to approve the use of existing instrumentation would save the procurement costs of new instruments, their use for a secondary NAAQS may be inconsistent with their current use. For example, a monitoring site situated near a freeway or bus terminal with a filter transmission measurement for black carbon is unlikely to be at a good location for visibility monitoring. Also use of heated nephelometers would not be consistent with the measurement goal of ambient PM light extinction monitoring. Aside from the capital cost savings, use of familiar instrumentation may have the benefit of reduced training costs. From a national prospective, the use of already deployed instrumentation should be assessed to determine the potential benefits.

Next Steps: There are a number of reasonable next steps to determining the monitoring approach for a possible secondary PM NAAQS. Which steps are taken and when they are accomplished depends on EPA's information needs and schedule, which is not yet available, so the following is necessarily lacking in specificity.

Cataloging and assessing available information on the monitoring techniques is a reasonable first step. This would expand upon the information in this document, especially that contained in Table 1, by including information on specific instruments (make and model for commercially available instruments), published performance specifications, validation testing, and other operational experience (e.g., feedback from current users). This would include an assessment of each instrument's ability to meet the measurement goal (e.g., including a propagation of errors analysis and performance in past laboratory or ambient intercomparison studies). Some of the descriptive information has been compiled by others in literature review articles (Horvath, 1993, McMurry, 2000, Watson, 2002, Moosmüller, et al., 2009). This step could be completed within two to six months by those who are familiar with ambient optical monitoring.

A reasonable second step would be to sponsor an invitational measurement intercomparison study where instrument manufacturers and/or developers are invited to set up their instruments at one or more common locations, for example a suitable well-equipped state/local air monitoring sites (Park, et al., 2006). The purpose would be to gain firsthand ambient monitoring experience with the operations of candidate instruments and generate a collocated measurement data set for intercomparison of results and assessment of instrument performance. The locations and timing would be selected to provide challenging ambient conditions (e.g., high coarse PM impacts, high humidity, etc.). This step could be completed within six to twelve months with the cooperation of state and local air agencies, and with limited cost if instrument manufacturers covered their own cost to participate.

A final step that might be prudent prior to making a decision on a monitoring approach would be to deploy a modest prototype network (e.g., 10 to 20 sites). It would allow one or a few of the most promising of the methods to be tested for a year by typical state and local agencies prior to a more substantial commitment to a specific approach. It would also generate a light extinction data set more quickly than waiting for a fully deployed national monitoring capability that could be valuable for the next PM NAAQS review cycle. The deployment of a prototype network is a specific recommendation of the CASAC PM subcommittee. The cost and timing to set this up depends on the number of sites, equipment selected and cooperation by the state and local agencies.

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Table 1 Summary of likely candidate light extinction, scattering and absorption methods.

Method	Approach	Advantages	Disadvantages
Extinction Measurements			
Open path transmissometer (Malm, 1979)	Path-averaged light extinction is determined by measuring the amount of light transmitted over a known distance (typically 0.1km to 10km). The measurement range depends on the site path length.	1. No modification of the aerosol due to sample handling. 2. Path-averaged measurements may be more representative than point measurements. 3. Short and long path versions are commercially available. 4. Can measure at selected wavelengths	1. Cannot exclude particles exceeding 10µm diameter, including fog, precipitation, etc. 2. Calibration is problematic for long-path instruments. 3. Siting requirements for long-path instrument can be difficult to meet. 4. Cost can be high (~$25k).
Cavity ring down (CRD) and Cavity Attenuation Phase Shift (CAPS) (Moosmüller, et al., 2005, Kebabian, et al., 2007, Baynard, et al., 2007, Arnott, et al., 2009, Radney, et al., 2009)	Light extinction of sampled air is determined by the rate of decay of light intensity (CRD) or waveform distortion (CAPS) as a pulse of laser light bounces back and forth between mirrors.	1. Can exclude ultra-coarse particles (larger than 10µm diameter). 2. Can be calibrated with well characterized standards.	1. Coarse particle sampling loss is a concern. 2. Relative humidity changes due to sample heating or cooling are a concern. 3. Laser-dependent wavelengths (e.g., 531nm, but not 550nm) 4. Not commercially available at this time.
Scattering Measurements			
Integrating nephelometer (Beuttell and Brewer, 1949, Anderson, et al., 1996, Heintzenberg, et al., 2006, Müller, et al., 2009)	Sampled air is illuminated by a light source and the light scattered between ~0° and ~180° is directly measured.	1. Can exclude ultra-coarse particles (larger than 10µm diameter). 2. Can calibrate with well characterized standards. 3. Several commercially	1. Coarse particle sampling loss is a concern. 2. Relative humidity changes due to sample heating or cooling are a concern. 3. Angular truncation (i.e.,

Method	Approach	Advantages	Disadvantages
		available instruments. 4. Has been used by many researchers for decades in field studies and routine monitoring networks.	doesn't measure all the way from 0° to 180°) causes underestimated coarse particle scattering.
	Absorption Measurements		
Filter transmission (Hansen, et al., 1984, Petzold and Schönlinner, 2004)	Light transmission is measured through a filter while it collects particles from the air. The change in transmission over time is related to the change in light absorption by the particles collected on the filter.	1. Can exclude ultra-coarse particles (larger than 10μm diameter). 2. Several commercially available instruments. 3. Has been used by many for decades in field studies and routine monitoring networks.	1. Multiple light scattering by filter fibers and particles caused by concentrating particles on the filter introduces biases that need to be corrected to give atmospheric PM light absorption. 2. Most of the existing units are single wavelength that measure in the infrared, not near 550nm.
Photoacoustic (Moosmüller, et al., 1997)	Light is pulsed through a sample chamber where absorbing particles convert the light to heat expanding the air at the pulsed frequency that is measured acoustically.	1. Can exclude ultra-coarse particles (larger than 10μm diameter). 2. No corrections needed for multiple scattering effects caused by filtration. 3. Commercial units are available	1. Currently available commercial units are expensive (~$40k). 2. Laser-dependent wavelengths (e.g. available at 531nm, but not 550nm)