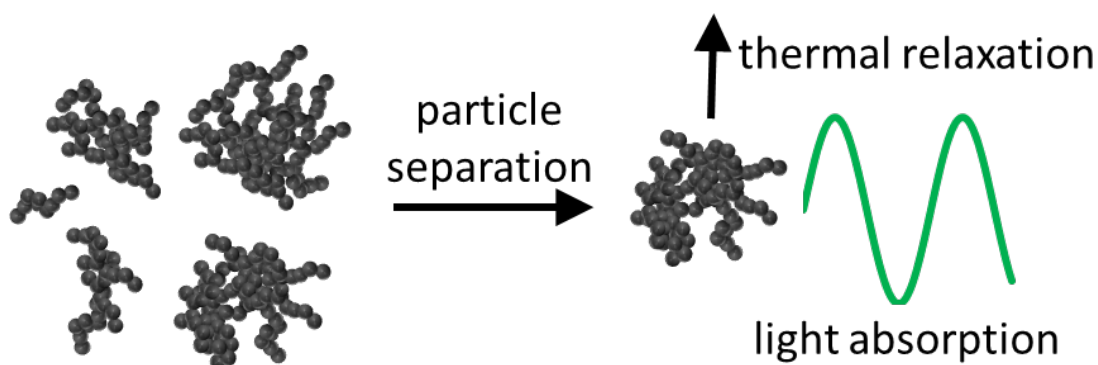


NIST Interlaboratory Study of Aerosol Absorption Measurements using Photoacoustic Spectroscopy

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NIST Technical Note 1989

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April 2018



U.S. Department of Commerce
Wilbur L. Ross, Jr., Secretary

National Institute of Standards and Technology
Walter Copan, NIST Director and Undersecretary of Commerce for Standards and Technology

National Institute of Standards and Technology Technical Note 1989
Natl. Inst. Stand. Technol. Tech. Note 1989, 29 pages (April 2018)
CODEN: NTNOEF

This publication is available free of charge from:
<https://doi.org/10.6028/NIST.TN.1989>

Abstract

The National Institute of Standards and Technology coordinated an interlaboratory study for laboratories that use photoacoustic spectroscopy to measure and report aerosol absorption. This report describes the design and results for the NIST Interlaboratory Study of Aerosol Absorption Measurements using Photoacoustic Spectroscopy from twelve participating laboratories using a material that was characterized and distributed by NIST on June 12, 2017. Participants were requested to provide measurement results by August 30, 2017. The participating laboratories reported 4,569 aerosol absorption cross sections as a function of particle size, particle mass and wavelength. The results indicate that for laboratories with access to electrical mobility-only selection, measurements should be made for $D_m \geq 400$ nm, where deviations of measured absorption cross-section are ≤ 10 % of measurements made with electrical mobility and mass selection. The results also indicate that multiple wavelength measurements should be performed using a single photoacoustic cell to eliminate variation in measurement parameters, if possible.

Key words

Aerosol, absorption, photoacoustic spectroscopy, PAS

Disclaimer

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Definition of variables, terms, and units used in this report

CB = carbon black

CPC = condensation particle counter

DMA = differential mobility analyzer

C_{Abs} = absorption cross-section (m^2)

$C_{\text{Abs,Dm}}$ = absorption cross-section (m^2) of mobility selected aerosol

$C_{\text{Abs,Dm \& mp}}$ = absorption cross-section (m^2) of mobility and mass selected aerosol

CV = coefficient of variation

D_f = mass-mobility scaling exponent

D_m = particle mobility diameter (nm)

$D_m \& m_p$ = selection by particle mobility and particle mass

k_0 = mass scaling prefactor (g)

MAC = mass-specific absorption coefficient ($\text{m}^2 \text{g}^{-1}$)

m_p = particle mass (g)

N = number of measurements

P = particle number density per unit volume ($\# \text{cm}^{-3}$)

PAS = photoacoustic spectroscopy

q = particle net charge

SP2 = single particle soot photometer

Z_p = electrical mobility (nm)

α_{Abs} = absorption coefficient (m^{-1})

λ = wavelength (nm)

μ_{geo} = geometric mean aerosol diameter (nm)

σ_{geo} = geometric standard deviation

γ = drag slip correction

σ = standard deviation

\bar{x} = average

Introduction

Quantifying the amount of light absorbed by suspended nano- and micro-particles (aerosols) in the Earth's atmosphere allows a better understanding of their impact and role in energy distribution and balance. It is currently estimated that absorption of light by highly absorbing aerosol produced during the incomplete combustion of carbonaceous materials represents the second largest positive radiative forcing after CO₂ [1].

In-situ measurements of aerosol light absorption are typically made using photoacoustic spectroscopy (PAS) where a microphone is used to detect the pressure wave generated from the thermal relaxation of light absorbed by a particle. Absorption coefficients, α_{Abs} , measured by the spectrometer are the quotient of the particle absorption cross-section (C_{Abs}) and the particle number density (P), or $C_{\text{Abs}} = \alpha_{\text{Abs}}/P$; P can be measured using a condensation particle counter (CPC) or other comparable technique. Aerosol C_{Abs} are reported in units of m² and most often as function of particle size (or mobility diameter, D_m). Recent developments in the field of mass-based aerosol metrology have enabled particle selection and reporting as a function of particle mass (m_p) for aerosol that has also been D_m selected [2, 3].

The aerosol community recognizes the need for instrumental intercomparisons, but such comparisons have been limited by the lack of suitably characterized and transferrable nanomaterials that mimic the chemical and/or physical properties of materials observed in the atmosphere [4]. Thus, the field has focused its efforts on measurements of co-located instrumentation analyzing a common aerosol stream to: 1) gain a better understanding of the correlations between measurement techniques and 2) quantitatively compare similar instrument designs and methods [5-8].

This study describes the first intercomparison of laboratories reporting a measurand (C_{Abs}) in which: 1) the participants were not co-located, 2) all measurements were performed using a common method (PAS) and 3) a transferrable, aerosolizable, and well characterized nanomaterial was supplied to all the participating laboratories for use. The material was first characterized at the National Institute of Standards and Technology (NIST) and has a C_{Abs} similar to highly absorbing carbonaceous aerosol observed in the atmosphere.

The participants in this NIST-coordinated study measured C_{Abs} using photoacoustic spectroscopy and an appropriate particle counting method for aerosol classified by particle mobility only (D_m -only) or by particle mobility and particle mass (D_m & m_p). The material used to measure C_{Abs} was distributed by NIST to all participant for measurement. The goals of this study were two-fold:

- To determine interlaboratory variability of C_{Abs} measurements of D_m & m_p selected aerosol, where C_{Abs} is reported on a per mass basis.
- To determine interlaboratory variability of C_{Abs} measurements of D_m -only selected aerosol, where C_{Abs} is reported on a per particle mobility basis.

Potential contributors to the intercomparison were identified by their publication record in peer-reviewed literature and were invited to participate (See "Letter Describing Intercomparison to Potential Contributors" in the Appendix). All participants measured

aerosol C_{Abs} using their self-identified best practice methods involving a photoacoustic spectrometer and a suitable particle counting technique for aerosol that was selected by D_m - only and/or D_m & m_p . The methods used for aerosol selection were determined by the instrumentation available to each participating laboratory (see “Cover Letter Distributed to Participants” in the Appendix). The data was reported as a function of D_m , wavelength (λ), and m_p , if available. Participants reported their data to NIST, using a standardized reporting template, where it was compiled, evaluated for consensus values, and summarized using results from all laboratories. An anonymized report was distributed to each participating laboratory at the end of the intercomparison (see “Report to Participants” in the Appendix).

Interlaboratory Study: Measurement of Aerosol Absorption using Photoacoustic Spectroscopy

1. Aerosol characterization and selection

The C_{Abs} of D_{m} -only and $D_{\text{m}} \& m_{\text{p}}$ selected aerosolized water-soluble carbon black (CB, Cab-o-Jet 200, Cabot Corporation, Billerica, MA) was measured. The spectral properties of CB closely mimic materials observed from the incomplete combustion of carbonaceous fuels with $C_{\text{Abs}} \propto \lambda^{-1}$ [9, 10].

Individual units of aqueous CB were distributed to participants in 0.42 mL aliquots at a mass concentration of (21.73 ± 0.04) g of solid material per 100 g of sample. Three vials were distributed to each participating laboratory to ensure sufficient material was available for analysis. Participants were instructed to dilute the aliquots to 100 mL using distilled water to form the aqueous suspension that would be used for analysis. Each laboratory atomized the prepared solution to form a CB aerosol that produced particles with $(30 < D_{\text{m}} < 700)$ nm, see Fig. 1a. The particle mobility diameter is approximately log-normally distributed, therefore the mean $\log(D_{\text{m}})$ is the geometric mean of D_{m} defined here as μ_{geo} (nm) and the geometric standard deviation (σ_{geo}). The aerosol distribution varied between laboratories and could be divided into two groupings based on reported μ_{geo} shown in Table 1. Of the 11 laboratories that reported mobility data, three laboratories had a mean μ_{geo} of 99.0 ± 5.2 (1 σ) nm and a geometric standard deviation (σ_{geo}) of 2.06 ± 0.20 (1 σ). The remaining eight laboratories had an average μ_{geo} of $147.6 \text{ nm} \pm 14.0 \text{ nm}$ and $\sigma_{\text{geo}} = 1.80 \pm 0.13$.

Table 1. Aerosol geometric mean diameter (μ_{geo}) and geometric standard deviation (σ_{geo}).

Lab #	Mean mobility (μ_{geo} , nm)	σ_{geo}
2 ^a	—	—
4	95.8	2.19
12	96.3	2.17
10	105.0	1.83
3	120.6	1.61
8	131.4	1.79
9	147.0	1.73
5	148.0	1.87
6	152.0	1.92
1	157.6	2.01
7	158.0	1.79
11	163.0	1.69

^a No mobility data was received from Lab #2.

Using a differential mobility analyzer (DMA), participants could select a D_{m} from the aerosol stream. Some participants were also able to select m_{p} from D_{m} -selected aerosol to report m_{p} as a function of D_{m} , see Fig. 1b. Other laboratories measured m_{p} using a single particle soot photometer (SP2, see triangles in Fig. 1b). The SP2 measures soot incandescence to determine the particle mass and does not measure the particle mass directly. The measured m_{p} as a function of D_{m} show that the measured m_{p} is within a few percent for all D_{m} , with the exception of one laboratory (Lab #4, see blue circles in Fig. 1b), which also had the lowest

μ_{geo} and σ_{geo} , suggesting that m_p and particle morphology may be a function of the particle size distribution between the two μ_{geo} groupings.

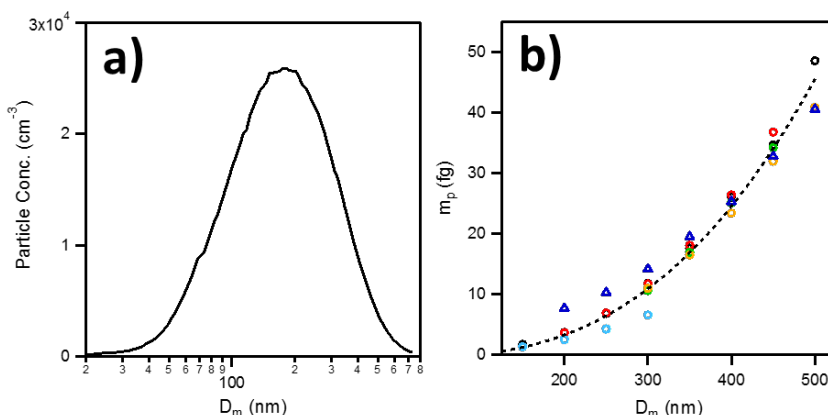


Figure 1. Measured D_m and m_p properties of CB aerosol.

a) Measured aerosol number density ($\# \text{ cm}^{-3}$) as a function of mobility diameter, D_m (nm), for the material used in the intercomparison. b) Measured particle mass (m_p , in femtograms, fg) as function of D_m from intercomparison participants. Masses measured using an aerosol mass analyzer are shown by circles and a single particle soot photometer (SP2) are shown by triangles.

The relationship of m_p as a function of D_m can be described using:

$$m_p = k_0 \left(\frac{D_m}{250 \text{ nm}} \right)^{D_f} \quad (1)$$

where $k_0 = (6.53 \pm 0.45) \times 10^{-15} \text{ g (fg)}$ is the m_p at 250 nm and $D_f = 2.81 \pm 0.12$ is the mass-mobility scaling exponent. The D_f is related to particle morphology, where $D_f = 3$ is consistent with spherical particles [2, 3, 11].

A technical challenge associated with the measurement of aerosol C_{Abs} is the isolation of a singular subset of particles from an aerosol distribution. Particle size selection is typically made by selection of a particles electrical mobility (Z_p) using a DMA. This mobility diameter (D_m), defined as the diameter of a spherical particle with the same electrical mobility as those being measured, is a function of the particle's electro-motive force (which is a function of charge) and drag force, as described in Eq. 2:

$$Z_p \propto \frac{q\gamma}{D_m} \quad (2)$$

where q is the net particle charge, and γ is the drag-slip correction for non-solid and/or non-spherical particles. Multiple solutions exist for a single Z_p depending upon net charge ($q \geq 1$) and its drag force (particle morphology), thereby impacting the selection of a single D_m from a particle distribution.

Further particle selection can be achieved using mass-based classification methods that can isolate particles of known m_p from D_m selected aerosol. Mass-based selection is typically made using an aerosol particle mass analyzer, or other similar instrument, reducing the

impact of multiply charged particles from the selected distribution [2, 3]. This is particularly important for aerosol spectroscopy as particles at $q > 1$ (larger D_m) adversely impact the measured C_{Abs} , due to the non-linear relationship of C_{Abs} with D_m . Lastly, selection of particles with known m_p facilitates the reporting of C_{Abs} on a per mass basis, allowing for better quantitative comparability between laboratories and materials, and also enables metrological traceability to the international system of units (SI).

Mass-based measurements facilitated the determination of the presence, quantity and spectral impact of particles bearing multiple charges within a D_m selected distribution, see Table 2. These results show that more than 20 % of the measured C_{Abs} for $D_m \leq 350$ nm is derived from multiply charged particles ($q > 1$), as measured from the ratio of reported $C_{Abs,Dm}$ (C_{Abs} of D_m selected aerosol) to $C_{Abs,Dm\&mp}$ (C_{Abs} of $D_m\&m_p$ selected aerosol). This observation is also supported by measurements using a single particle soot photometer (SP2), where multiply charged, higher D_m particles account for > 2.5 % of the total number density (P) for $D_m \leq 350$ nm. For laboratories with D_m -only selection available, CB absorption measurements should be made at $D_m \geq 400$ nm where relative deviations in C_{Abs} are ≤ 10 % of those using both $D_m\&m_p$ selection.

Table 2. Average ratio of C_{abs} for D_m and $D_m\&m_p$ selected aerosol and percentage of multiply charged particles ($q > 1$) as determined using an SP2. Uncertainty is 1σ of average values

D_m (nm)	$C_{Abs,Dm}/C_{Abs,Dm\&mp}$ (5 laboratories)	% $q > 1$ using D_m -only selection
150	2.50 ± 0.17	-
200	2.02 ± 0.09	26.0
250	1.62 ± 0.02	11.6
300	1.35 ± 0.01	5.2
350	1.21 ± 0.01	2.5
400	1.10 ± 0.01	1.2
450	1.06 ± 0.01	0.4
500	1.02 ± 0.01	0.1

2. Measurement of CB C_{Abs} for $D_{\text{m}} \& m_{\text{p}}$ selected aerosol

Five participating laboratories selected particles by $D_{\text{m}} \& m_{\text{p}}$. Two additional laboratories reported C_{Abs} for D_{m} -selected particles with subsequent analysis to determine m_{p} and $q = 1$ and reported C_{Abs} on a per mass basis. C_{Abs} was measured as a function of $D_{\text{m}} \& m_{\text{p}}$ and λ . Wavelengths reported for $D_{\text{m}} \& m_{\text{p}}$ selected aerosol were $\lambda = (385, 405, 532, 660, 785, \text{ and } 880) \text{ nm}$. All participating laboratories with mass-reporting (7 laboratories) reported C_{Abs} at $\lambda = (405 \text{ and } 532) \text{ nm}$ enabling comparability across all laboratories, see Figs 2a and 2b. Reported uncertainties represent 1σ from multiple ($N = 3$ to 20) technical replicate measurements as reported by each participating laboratory.

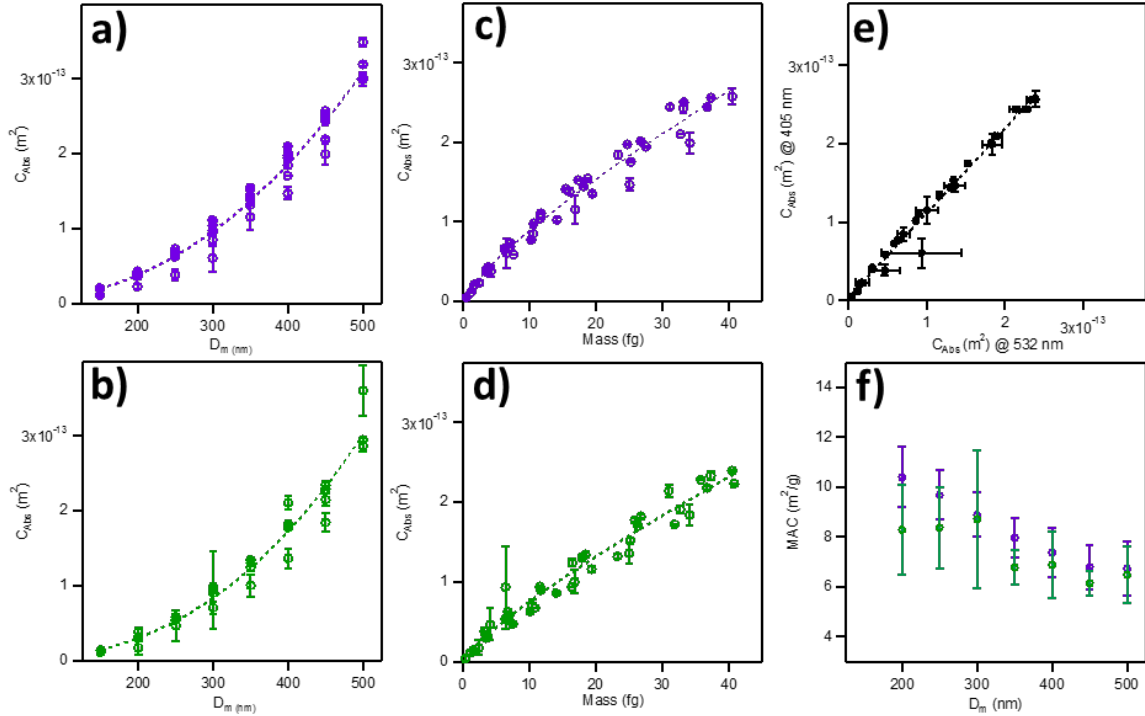


Figure 2. Measured CB properties for $D_{\text{m}} \& m_{\text{p}}$ selected aerosol (7 laboratories).

Measured C_{Abs} as a function of D_{m} for ($150 \leq D_{\text{m}} \leq 500$) nm at a) $\lambda = 405 \text{ nm}$ and b) $\lambda = 532 \text{ nm}$. Measured C_{Abs} as a function of m_{p} for ($150 \leq D_{\text{m}} \leq 500$) nm at c) $\lambda = 405 \text{ nm}$ and d) $\lambda = 532 \text{ nm}$. e) Correlation of C_{Abs} at $\lambda = (405 \text{ and } 532) \text{ nm}$. f) Measured mass absorption coefficients ($\text{MAC} = C_{\text{Abs}}/m_{\text{p}}$) at $\lambda = 405 \text{ nm}$ (violet) and $\lambda = 532 \text{ nm}$ (green). Dashed lines in a) through e) represent best fits of the data using a power law (a, b, c, d) or linear (e) relationship.

The relationship between C_{Abs} as a function of D_{m} was fit for ($150 \leq D_{\text{m}} \leq 500$) nm using a power law for $\lambda = (405 \text{ and } 532) \text{ nm}$.

$$C_{\text{Abs}} = C_{\text{Abs},0} \left(\frac{D_{\text{m}}}{250 \text{ nm}} \right)^{D_{\text{Abs}}} \quad (3)$$

where $C_{\text{Abs},0}$ represents the C_{Abs} at D_{m} at 250 nm and D_{Abs} is the absorption power law scaling exponent. The C_{Abs} is expected to scale with m_{p} , see Table 3.

Table 3. Average C_{Abs} (m^2) at $D_m = 250$ nm and D_{Abs} at $\lambda = (405 \text{ and } 532)$ nm.^a

(7 laboratories)	$\lambda = 405$ nm	$\lambda = 532$ nm
$C_{\text{Abs},0}$	$6.33 \pm 0.26 \times 10^{-14} \text{ m}^2$	$5.28 \pm 0.41 \times 10^{-14} \text{ m}^2$
D_{Abs}	2.29 ± 0.07	2.51 ± 0.14

^a Uncertainties are 1σ .

Figs. 2c and 2d show the relationship of measured C_{Abs} and m_p for D_m & m_p selected aerosol $\lambda = (405 \text{ and } 532)$. The differences in dependencies of m_p and C_{Abs} with D_m are reflected in the power law scaling exponents for each data set resulting in a non-linear correlation between C_{Abs} and m_p . Thus, the data in Figs. 2c and 2d (C_{Abs} as a function of m_p) were fit to a power law ($C_{\text{Abs}} = A * m_p^{\text{Exp}}$) at both $\lambda = (405 \text{ and } 532)$ nm and are shown in Table 4. These data may be used for evaluation of aerosol PAS performance of CB at each λ across this m_p range.

Table 4. Power law fit parameters of C_{Abs} (m^2) as a function of m_p at $\lambda = (405 \text{ and } 532)$ nm for $(150 \leq D_m \leq 500)$ nm with D_m & m_p selected aerosol.^a

(7 laboratories)	$\lambda = 405$ nm	$\lambda = 532$ nm
A	$1.47 \pm 0.13 \times 10^{-14}$	$1.14 \pm 0.13 \times 10^{-14}$
Exp	0.783 ± 0.027	0.816 ± 0.034

^a Uncertainties are 1σ .

The measured C_{Abs} at $\lambda = (405 \text{ and } 532)$ nm were nearly linearly correlated for each participating laboratory ($C_{\text{Abs},405 \text{ nm}}/C_{\text{Abs},532 \text{ nm}} = 1.08 \pm 0.03$, 1σ), as shown in Fig. 2e. Participating laboratories also reported the mass absorption coefficient (MAC , $\text{m}^2 \text{ g}^{-1}$), calculated as $MAC = C_{\text{Abs}}/m_p$. MAC is nearly linear with m_p due to the similar scaling of m_p and C_{Abs} with D_m for both λ . The MAC at these λ is a function of D_m and is shown in Fig. 2f. The MAC is highest at the lowest measured D_m (200 nm), likely due to full light penetration through the particle. At higher D_m , incident light is attenuated due to the compacted spherical morphology of CB, decreasing the reported MAC . For $D_m > 350$ nm the MAC approaches an asymptotic minimum for both λ .

The size dependence of MAC was reported as a function of λ and D_m from each participating laboratory. Fig. 3a and 3b show C_{Abs} and MAC as a function of λ for $D_m = 250$ nm and 450 nm CB aerosol, respectively. The reported C_{Abs} increase with D_m due to the concomitant increase of m_p . The reported MAC was dependent on D_m across all λ , consistent with the observed dependence of MAC as a function of λ , as shown in Fig 2f.

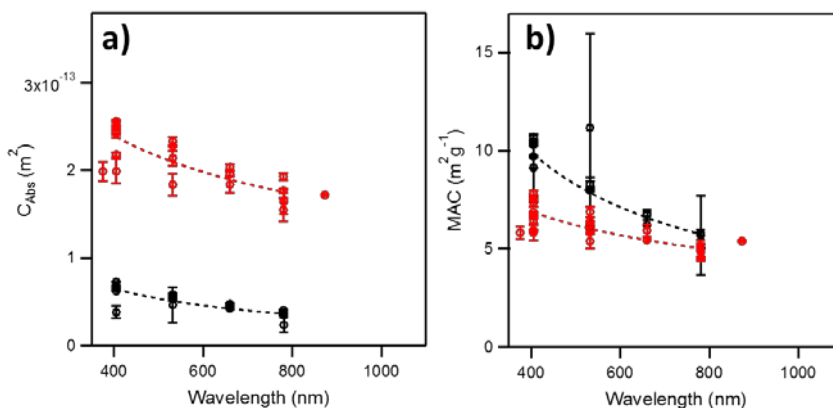


Figure 3. Absorption spectra of D_m & m_p selected CB aerosol.

- a) C_{Abs} as a function of λ for $D_m = 250$ nm (black) and 450 nm (red) CB aerosol.
b) MAC as a function of λ for $D_m = 250$ nm (black) and 450 nm (red) CB aerosol.
Uncertainties are 1σ of technical replicates. Fits are shown to guide the eye.

3. Measurement of CB C_{Abs} for D_{m} -only selected aerosol

All twelve participating laboratories selected particles by D_{m} -only. C_{Abs} was measured as a function of D_{m} and λ . C_{Abs} of D_{m} -only selected aerosol was reported as a function of λ , for $\lambda = (385, 405, 532, 660, 785, 880, \text{ and } 1064) \text{ nm}$. The C_{Abs} of classified D_{m} aerosol was reported at $\lambda = (405 \text{ and } 532) \text{ nm}$ for particles $(200 \leq D_{\text{m}} \leq 500) \text{ nm}$ from eleven participating laboratories. The data was evaluated as a function of D_{m} . Figs 4a and 4b show measured C_{Abs} as a function of D_{m} for mobility selected aerosol at $\lambda = 405 \text{ nm}$ and 532 nm . Reported uncertainties represent 1σ from multiple ($N = 3 \text{ to } 20$) technical replicate measurements as reported from each participating laboratory.

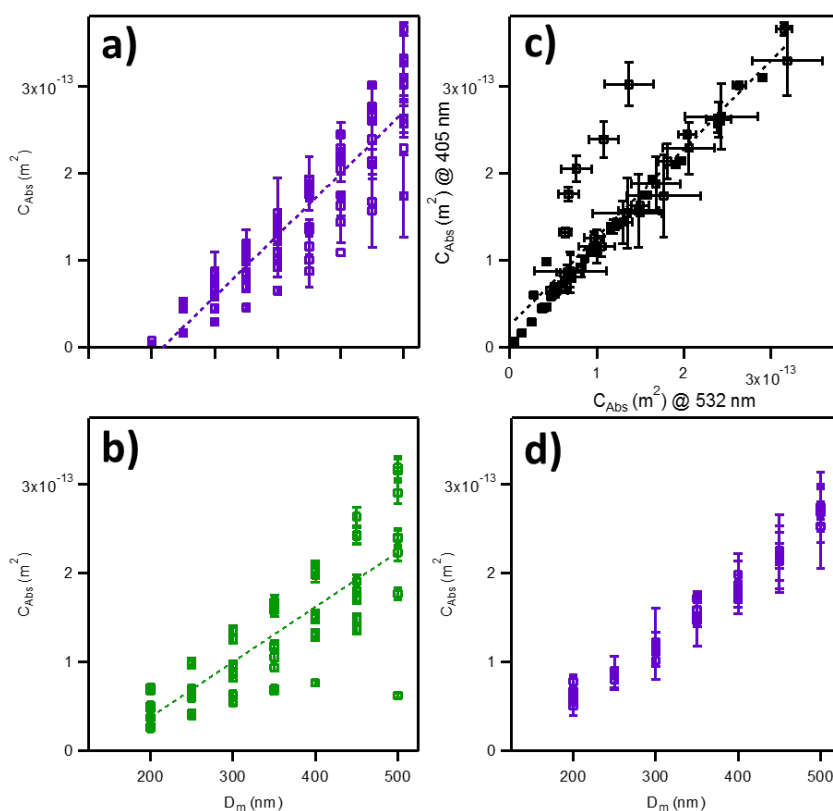


Figure 4. Measured CB properties for D_{m} -only selected aerosol.

Measured C_{Abs} as a function of D_{m} for $200 \text{ nm} \leq D_{\text{m}} \leq 500 \text{ nm}$ at a) $\lambda = 405 \text{ nm}$ and b) $\lambda = 532 \text{ nm}$. Dashed lines show linear line of best fit from all participating laboratories. c) Linear correlation of C_{Abs} at $\lambda = 405 \text{ nm}$ and $\lambda = 532 \text{ nm}$. d) Corrected measured C_{Abs} as a function of D_{m} at $\lambda = 405 \text{ nm}$.

When compared to $D_{\text{m}} \& m_{\text{p}}$ selected aerosol, there is significantly more interlaboratory variability in the reported C_{Abs} at both $\lambda = (405 \text{ and } 532) \text{ nm}$ for D_{m} -only selected CB, likely due to the inclusion of $q > 1$ particles within the output distribution.

With the exception of two laboratories, participants used a single PA spectrometer in the measurement of and reporting C_{Abs} . In laboratories using a single spectrometer, λ was varied by using multiple lasers or other high-powered light sources. This eliminates a source of

intralaboratory uncertainty that may arise from differences in calibration between two or more spectrometers such as: microphone response and sensitivity, spectrometer frequency response to changes in temperature and/or pressure, and uncertainties between using multiple particle counters used to measure P and/or light power meters used to normalize data. The use of a single photoacoustic spectrometer also reduces the uncertainty in the determination of λ -dependent spectral features and eliminates sources of uncertainty in the intra-laboratory correlation between multiple λ . This is illustrated for D_m -only selected aerosol where the reported C_{Abs} at $\lambda = 405$ nm and $\lambda = 532$ nm are correlated, see Fig 4c, $C_{\text{Abs},405 \text{ nm}}/C_{\text{Abs},532 \text{ nm}} = 1.01 \pm 0.06$ (1σ), compared to 1.08 ± 0.03 (1σ) of $D_m \& m_p$ selected aerosol.

One participating laboratory had a significantly higher $\lambda = 405$ nm and $\lambda = 532$ nm ratio (> 2), atypical of all other reported data from laboratories using only D_m -only selection. Importantly, these data were from a laboratory that used multiple spectrometers (one spectrometer at $\lambda = 405$ nm and another spectrometer at $\lambda = 532$ nm), highlighting the importance of developing methods of intralaboratory calibration for aerosol PAS measurements.

The reported C_{Abs} at $\lambda = 405$ nm and 532 nm shown in Fig. 4c shows systematic intralaboratory correlation between measurements. Thus, the reported variability in C_{Abs} can be corrected as a function of D_m for each laboratory to enable a method of interlaboratory comparability. This is demonstrated in Fig. 4d for $\lambda = 405$ nm, where the reported C_{Abs} as a function of D_m for each laboratory has been corrected to the linear best fit of the population, as shown in Fig. 4a at $\lambda = 405$ nm. Additional fit parameters were calculated at $\lambda = 532$ nm and 660 nm, encompassing data from 11 of the 12 reporting laboratories, see Table 5. Importantly, the harmonization is observationally constrained using a linear relationship of C_{Abs} as a function of D_m (see $D_m \& m_p$ C_{Abs} power law dependence with D_m shown in Figs. 2a and 2b), and should not be assumed to be quantitative. As discussed above, D_m -only selection contains $q > 1$ particles for $D_m < 350$ nm, resulting in errors in the reported C_{Abs} .

Table 5. Linear correction fit parameters for D_m -only selected C_{Abs} relative to the population mean.

λ (nm)	Lab #	1	2	3	4	5	6	7	8	9	10	11	12
405	m^a	2.7	1.3	–	-35	–	-8.2	-10.6	-8.56	-20.4	-1.3	24.2	–
	b^b	-1.9	5.7	–	80	–	-0.5	-3.3	13	141	-10.3	-43.6	–
532	m^a	1.5	-2.1	32.2	-30.5	–	-10.8	-16.9	28.3	–	–	16	–
	b^b	-3.5	10.6	-51.2	72	–	-0.1	12.9	-42.7	–	–	-30.4	–
660	m^a	–	–	–	-25.7	–	4.7	-5.7	–	-26.3	–	19.8	-22.2
	b^b	–	–	–	78.4	–	-20.7	-8	–	43.4	–	-34.8	43.4

^a slope = $m \times 10^{-17} \text{ m}^2 \text{ nm}^{-1}$

^b intercept = $b \times 10^{-15} \text{ m}^2$

C_{Abs} for D_m -only classified CB were plotted as a function of λ to construct absorption spectra and are shown in Fig. 5 for $D_m = 250$ nm and 450 nm for comparison to similar data plotted over the same range of λ for $D_m \& m_p$ selected data in Fig 3a. Note the increased intralaboratory uncertainty for D_m -only selected aerosol when compared to $D_m \& m_p$ selected data shown in Fig. 3a.

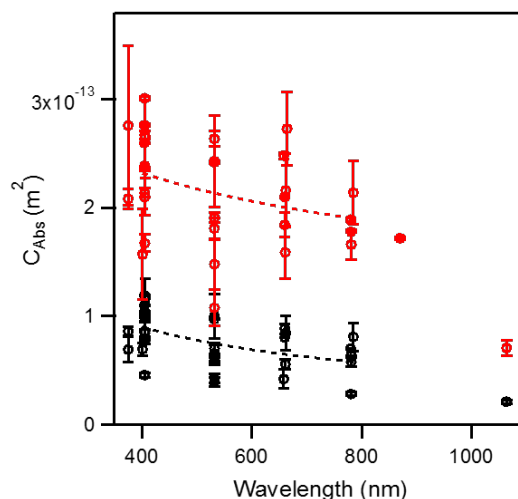


Figure 5. Absorption spectra of D_m -only selected CB aerosol.

a) C_{Abs} as a function of λ for $D_m = 250$ nm (black) and 450 nm (red) CB aerosol. Uncertainties are 1σ of technical replicates. Fits are shown to guide the eye.

4. Comparison of D_m -only and $D_m \& m_p$ selected CB C_{Abs} measurements

The measured C_{Abs} were evaluated by aerosol selection method (D_m -only versus $D_m \& m_p$) at $\lambda = (405, 532, \text{ and } 785) \text{ nm}$, where there was sufficient data for comparability, for $(200 \leq D_m \leq 500) \text{ nm}$. Table 6 shows the coefficient of variation ($CV = 100 \sigma / \bar{x}$) for each method of selection at $\lambda = (405, 532 \text{ and } 785) \text{ nm}$ across all intercomparison participants. The CV of D_m -only selected CB was (25 to 30) %. Selection of aerosol by $D_m \& m_p$ reduced the CV by (2 to 3) times when compared to the same laboratories using only D_m -only selection.

Table 6. CV for D_m -only versus $D_m \& m_p$ selected CB for $\lambda = (405, 532, \text{ and } 660) \text{ nm}$.

	200 nm $\leq D_m \leq$ 500 nm		
	$\lambda=405 \text{ nm}$	$\lambda=532 \text{ nm}$	$\lambda=785 \text{ nm}$
D_m -only (12 laboratories)	25.4 ± 2.5	30.2 ± 6.8	24.8 ± 11.7
$D_m \& m_p$ (7 laboratories)	8.3 ± 3.4	11.3 ± 8.3	7.1 ± 6.3
CV ratio from same 7 labs	2.8 ± 0.7	2.1 ± 0.7	3.6 ± 2.2

5. Interlaboratory comparison of CB C_{Abs}

The consistency of each participant's results were evaluated using "z-scores"

$$z = (x - \bar{x})/\sigma \quad (4)$$

where x is a reported value, \bar{x} is the arithmetic mean of all values reported for the same nominal conditions, and σ is the standard deviation of these values. These normalized measures of relative performance were calculated for each participant as a function of both D_m and λ for D_m -only selected aerosol, see Fig. 6 and Table 7.

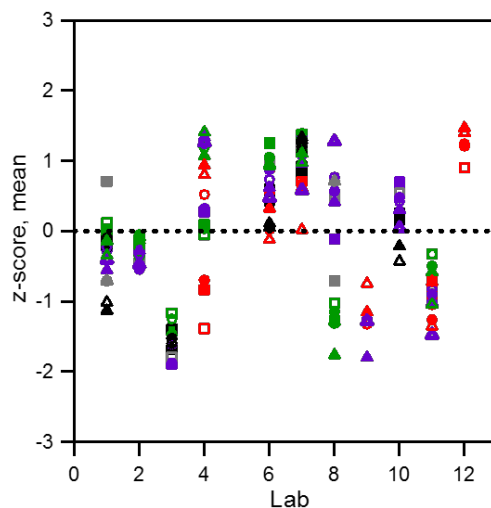


Figure 6. z-scores as a function of D_m for D_m -only selected aerosol.

D_m values are indicated by symbol shape: 200 nm = solid squares, 250 nm = open squares, 300 nm = solid circles, 350 nm = open circles, 400 nm = solid triangles, and 450 nm = open triangles. λ values are indicated by symbol color: $\lambda = 405$ nm, 532 nm, 660 nm, and 785 nm.

The calculated z-scores show that most participating laboratories were systematically biased relative to the reported mean.

Table 7. Calculated z-score for D_m selected aerosol at $\lambda = 405$ nm, 532 nm, and 660 nm for each participating laboratory.

D_m	$\lambda = 405$ nm							$\lambda = 532$ nm							$\lambda = 660$ nm						
	200	250	300	350	400	450	500	200	250	300	350	400	450	500	200	250	300	350	400	450	500
Lab #	Z-score, mean																				
1	-0.08	-0.13	-0.28	-0.23	-0.56	-0.40	1.25	0.02	0.13	-0.05	0.03	-0.14	-0.35	0.92	–	–	–	–	–	–	–
2	-0.22	-0.45	-0.54	-0.33	-0.28	-0.47	1.22	-0.13	-0.18	-0.36	-0.05	-0.09	-0.13	0.91	–	–	–	–	–	–	–
3	-1.89	-1.80	-1.88	-1.60	–	–	–	-1.39	-1.17	-1.48	-1.25	–	–	–	–	–	–	–	–	–	–
4	0.28	-0.05	0.32	1.23	1.33	1.26	1.95	0.09	-0.05	0.03	1.19	1.07	1.41	1.37	-0.84	-1.39	-0.70	0.52	0.93	0.80	2.66
5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
6	0.96	0.96	0.88	0.73	0.62	0.48	1.58	1.26	1.25	1.05	1.04	0.93	0.95	1.22	0.91	0.50	0.08	0.02	0.32	-0.12	2.10
7	1.37	1.24	1.36	1.09	0.97	0.58	1.70	1.13	1.38	1.39	1.30	1.11	0.98	1.38	0.82	0.71	0.67	0.59	0.62	0.02	2.40
8	-0.12	0.47	0.57	0.77	0.41	1.27	0.36	-1.27	-1.02	-1.15	-1.31	-1.77	-1.28	-0.13	–	–	–	–	–	–	–
9	–	–	–	-1.25	-1.80	-1.29	1.03	–	–	–	–	–	–	–	–	–	–	-1.32	-1.15	-0.75	1.89
10	0.69	0.54	0.48	0.42	0.30	0.04	1.39	–	–	–	–	–	–	–	–	–	–	–	–	–	–
11	-0.99	-0.78	-0.90	-0.83	-1.01	-1.48	0.66	-0.72	-0.32	-0.50	-0.33	-0.58	-1.04	0.54	-0.89	-0.72	-1.26	-1.05	-0.72	-1.35	1.36
12	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.90	1.21	1.24	1.47	1.40	–

6. Conclusions

The reported data give guidance to enable quantitative measurements of aerosolized CB and facilitate spectrometer calibration using either D_m -only or $D_m \& m_p$ selection and illustrate the importance of the method used in particle selection for aerosol PAS measurements.

Interlaboratory variability of C_{Abs} is 7% to 11% using $D_m \& m_p$ selection and 25% to 30% for particles selected by D_m -only.

Despite the reported variability in C_{Abs} using D_m -only selection, the results indicate that quantitative measurements of aerosolized CB are possible for $D_m \geq 400$ nm, where differences in reported C_{Abs} are $\leq 10\%$ of measurements made with $D_m \& m_p$ selection.

The reported results indicate that PAS measurements using $D_m \& m_p$ selection were able to be collected across the entire D_m range explored in the study ($200 \leq D_m \leq 500$) nm with $< 10\%$ variation between laboratories for $\lambda = 405$ nm and 532 nm.

The reported results also indicate that for multiple wavelength measurements should be performed using a single photoacoustic cell to eliminate variation in measurement parameters, if possible.

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Appendix: Supplemental Materials

Letter Describing Intercomparison to Potential Contributors



UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
Material Measurement Laboratory
Gaithersburg, Maryland 20899-8300

May 11, 2017

The National Institute of Standards and Technology (NIST) is exploring the preparation of an aerosolizable absorbing carbonaceous reference material with well characterized optical properties. An initial aim is to use this material to assess inter-laboratory variability in photoacoustic spectroscopic measurements as determined by the measurement of absorption cross-sections on a particle mobility and/or mass basis. NIST has conducted intercomparisons for over a century. Such intercomparisons assist the scientific community in assessment and guidance of performance and quantitative understanding. To further this goal NIST is organizing an intercomparison from laboratories with published histories of aerosol photoacoustic spectroscopic measurements. NIST is inviting your laboratory for participation.

The sample to be used in the intercomparison is a water soluble black carbon material with absorption across a broad wavelength region (visible to NIR). The particles produced are amenable to aqueous atomization, drying and mobility selection between 150 nm and 400 nm. Measured optical and experimental data will be collected from each laboratory and recorded in a standardized reporting template. Recorded data will be sent to NIST where it will be used in the intercomparative study. Data reporting and treatment will be kept anonymous and confidential throughout the study. Wavelength selection, sample drying and mobility/mass selection will be dependent on the technical resources available in each laboratory. It is expected that all participants will measure the absorption cross-section of the material using mobility, and if possible, mass selected particles. Participation in the intercomparison requires the use of an atomization source, sample drying (diffusion drier, etc.), mobility selection and mass selection (if available), photoacoustic spectrometer, and a particle counter. Additional guidance will be provided for participants at a later date. Data will be reported as a per particle cross-section (m^2 per particle) and/or as a mass specific absorption cross-section (m^2 per gram) for each mobility diameter measured.

Samples will be dispensed to participating laboratories at the beginning of June 2017 and the aim will be to have all data collection completed within 8 weeks (beginning of August 2017) after the sample is received. The full set of anonymous data will be disseminated to each participant laboratory after completion of the intercomparison. We aim to publish the results in a peer reviewed journal with each laboratory participant listed as co-authors.

Thank you for your consideration and hope you can participate,

Chris Zangmeister Ph.D.
Aerosol Metrology Program
National Institute of Standards and Technology

Cover Letter Distributed to Participants



UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
Material Measurement Laboratory
Gaithersburg, Maryland 20899-8300

June 12, 2017

Thank you for participating in the aerosol photoacoustic absorption intercomparison. Its goal is the assessment of quantitative aerosol photoacoustic absorption measurements by established laboratories using a well-characterized material. Aerosol photoacoustic absorption cross-sections will be determined on a mobility and, if possible, per mass basis.

The sample to be used for the intercomparison is packed in a sealed vial included in the envelope located in the shipping box. Also included is a Material Safety Data Sheet (MSDS) of the material. The particles produced are amenable to aqueous atomization, drying and size selection between 150 nm and 450 nm. Measured optical and experimental data will be collected from each laboratory, recorded in a standardized reporting template that has been sent via email to each participating laboratory.

Each participating laboratory has a published history of aerosol photoacoustic expertise. Thus, it is assumed that, based on prior published experience, each laboratory will utilize its own established best practices in measuring aerosol absorption cross sections. Thus, there is no set procedure, but the following guidelines are provided:

How to use this material. Included are three vials that each contain 0.46 mL of aqueous solution per vial. A single sample vial should be sufficient for all data collection. However, two additional vials are included, if required. To prepare a sample for use, dilute one vial with H₂O to 100 mL total volume. Stirring or sonication is recommended but not required. The solution can be used immediately and is shelf stable at room temperature for over 1 year.

Experiments at NIST conducted using a cross-flow atomizer (e.g. TSI 3076) in conjunction with the prepared solution generates particles with a mean mobility diameter of ≈ 150 nm with a geometric standard deviation of 1.86. It is recommended that the aerosol stream is dried prior to analysis. It was observed that particle absorption of mass/mobility selected particles are not impacted by the method of particle drying. Examples of drying conditions tested at NIST include combinations of multiple diffusion driers in series, Nafion driers, and a tube furnace at 350 °C in conjunction with a diffusion dryer.

Elimination of multiply charged particles and measurements to be made. Spectroscopic measurements should be made in a regime where multiply charged particles ($q = +2$, etc.) are minimized or are not present. NIST has undertaken experiments to understand the mobility regime required for elimination of multiple charged particles from the distribution in the absence of mass selection. Extinction measurements of mass distributions of mobility selected particles indicate that using the aerosol generation conditions described above, mobility diameters ≥ 350 nm do not contain $q = +2$ particles. To ensure measurements minimize the impact of multiple charges, measurements will be made and reported at 350 nm, 400 nm, 450 nm, and 500 nm (if possible). In addition, for data comparison,

measurements will also be made and reported at < 350 nm. Specifically, absorption measurements are to be made for mobility diameters of 200 nm, 250 nm, 300 nm, 350 nm, 400 nm, 450 nm, and 500 nm (if possible).

Particle size distribution should be measured by each laboratory and report measured geometric mean and geometric standard deviation.

Importantly, participating laboratories should make absorption measurements at as many wavelengths as at their disposal. This will enable better comparison among participating laboratories.

In addition to mobility selected measurements, and if laboratory resources are present, perform and report measurements for mass selected aerosol (using an APM, CPMA, etc.) at each mobility diameter (350 nm, 400 nm, and 450 nm) and report data as m^2 per gram.

Reporting data. Reported data will include:

- 1) Geometric mean
- 2) Geometric standard deviation
- 3) Absorption cross section (m^2 per particle) at each particle mobility (200 nm – 450 nm) and at each available wavelength. Report number of measurements at each particle mobility. Report standard deviation across number of photoacoustic measurements.
- 4) If measured, in addition to the above, the mass-specific absorption cross section (m^2 per gram) for each mobility/mass combination and wavelength.

Reported data will be anonymous for each participating laboratory. The full set of anonymous data will be disseminated to each participant laboratory after completion of the intercomparison. The final aim is to publish the results in a peer reviewed journal with each laboratory participant listed as co-authors. Please send reported data via email to cdzang@nist.gov by the end of July 2017. Please contact me if additional time is necessary or if you have questions.

Thank you for participating.

Chris Zangmeister Ph.D.
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Report to Participants



UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
Material Measurement Laboratory
Gaithersburg, Maryland 20899-8300

December 21, 2017

Dear Participants,

Thank you all for your efforts in the initial NIST aerosol photoacoustic spectroscopy intercomparison. The goal for the first aerosol photoacoustic intercomparison was participation from 5 to 7 laboratories. The response from the community was much higher. In all, twelve laboratories from six countries agreed to participate and other laboratories subsequently indicated they would like to participate in future intercomparison studies.

All the data from participating laboratories have been received and the data has been plotted as a function of mobility and wavelength for each measurement. Data sufficient for laboratory intercomparison was received at $\lambda = 385$ nm, 404 nm, 532 nm, 660 nm, 785 nm, and 1064 nm between mobility diameters of 200 nm and 450 nm. Below is a brief synopsis of the data showing C_{abs} (m^2) as a function of λ and particle mobility and z-scores for each laboratory. A more thorough and detailed presentation of the submitted data will be distributed in the next 60 to 90 days and will include λ correlations, the impact of multiple charging on the measured distribution and C_{abs} , mass-specific absorption measurements and comparison of mobility vs. mass-selected absorption measurements. In addition to self- and community-evaluation, an additional end goal will be submission of these data to a peer reviewed journal with all participating laboratories listed as co-authors. Input and suggested locations for submission are encouraged. Please do not distribute these data until the study is finalized and the publication is completed.

Thank you for your participation,

Dr. Chris Zangmeister
Research Scientist
National Institute of Standards and Technology
Gaithersburg, MD 20899 USA

Brief Data Summary:

Figure 1 shows the range in reported C_{abs} as a function of λ at each mobility for all participating laboratories. Typically, the range in C_{abs} at a λ was a factor of 2 to 3 across the laboratories and independent of mobility diameter and λ . The measured wavelength response was fit using a power law (e.g. AAE normalized at 532 nm, $k0$).

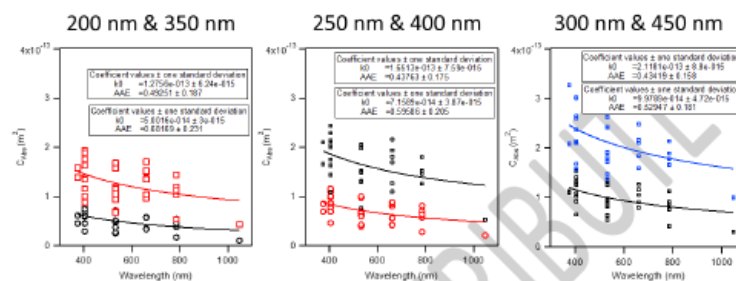


Figure 1. Measured absorption cross-section (C_{abs}) as a function of wavelength for mobility selected particles. Mobility shown at top of each plot and separated in 150 nm to ensure data was well separated in C_{abs} .

Figure 2 shows the same submitted C_{abs} data plotted for each λ as a function of mobility. The line is the linear best fit of the data, α represents the fit slope.

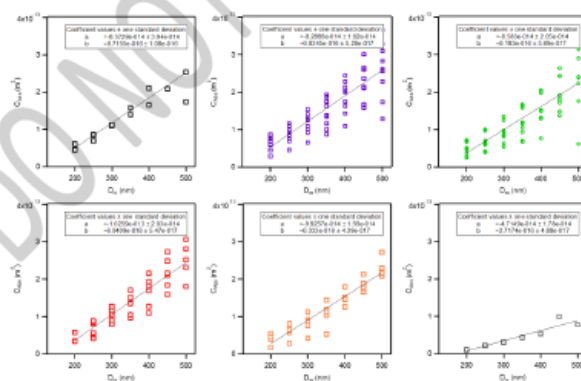


Figure 2. Measured C_{abs} as a function of particle mobility for 385 nm (top left), 404 nm (top middle), 532 nm (top right), 606 nm (bottom left), 785 nm (bottom middle), and 1064 nm (bottom right).

The most quantitative comparative and evaluative method typically used in laboratory intercomparisons is given by the calculation and reporting of a z-score for each participating laboratory. The z-score shows the reported data in terms of differences in units of standard deviations (σ) from the mean (\bar{x}) for each measurement (mobility and λ) to enable data from independent measurements and laboratories to be quantitatively compared. For example, a z-score of 1 means the reported data is 1 standard deviation higher than the population mean for that mobility and λ . Z-scores were determined for each laboratory at each mobility for $\lambda = 404$ nm, 532 nm, 660 nm, and 785 nm, as defined by

$$Z = \frac{C_{Abs}(\lambda, nm) - \bar{x}_{C_{Abs}}(\lambda, nm)}{\sigma(\lambda, nm)},$$

where \bar{x} and σ = mean and standard deviation at a mobility and wavelength, respectively. The laboratory number in Figure 3 is random and is included for each participant laboratory anonymously in the email sent with this summary.

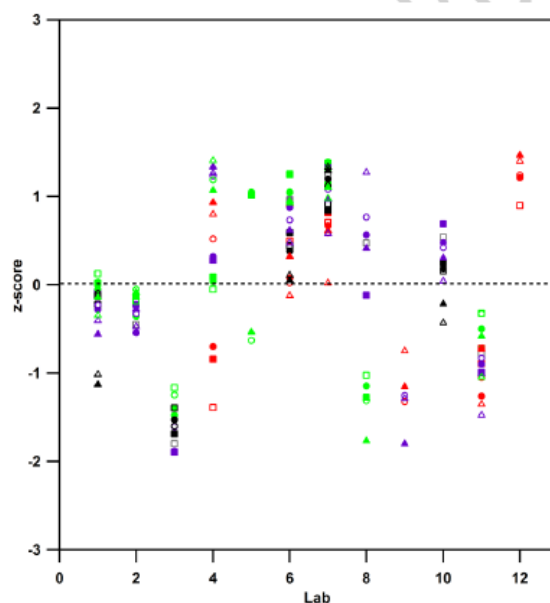


Figure 3. z-score for each reporting laboratory as a function of mobility (200 nm = solid squares, 250 nm = open squares, 300 nm = solid circles, 350 nm = open circles, 400 nm = solid triangles, 450 nm = open triangles) and wavelength ($\lambda = 404$ nm, 532 nm, 660 nm, 785 nm).