Characterization of a Three Wavelength Photoacoustic Soot Spectrometer (PASS-3) and a Photoacoustic Extinctiometer (PAX)

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(Manuscript received 20 October 2014, in final form 30 December 2014)

Abstract

Laboratory experiments were conducted for characterizing the performance of two commercially available instruments employed for the measurement of light absorption and scattering coefficients of aerosols at $\lambda = 405, 532,$ and 781 nm (using three-wavelength photoacoustic soot spectrometer; PASS-3) as well as at 375 nm (using photoacoustic extinctiometer; PAX) based on photoacoustic spectroscopy and reciprocal nephelometry, respectively. The calibration factors (conversion factors from the readout to real values) associated with scattering measurements, estimated using gaseous molecules, mono-disperse polystyrene latex and ammonium sulfate particles, and/or poly-disperse ammonium sulfate particles, are in good agreement with one another, typically within 5 %, 5 %, and 10 % at 375, 405, and 781 nm, respectively. In contrast, a significant particle size dependency was observed for the calibration factors at 532 nm, which is possibly because of a combination of differences in the polarization states of the lasers relative to the scattering planes and large truncation angle. Considering the estimated effective truncation angle, the typical uncertainties in calibration factors for scattering when measuring non- or weakly light-absorbing particles, with volume-based geometrical diameters of less than 700 nm, were estimated to be 12 %, 7 %, 34 %, and 17 %, at 375, 405, 532, and 781 nm, respectively. The typical uncertainties in the calibration factors for absorption measurements, which were determined using poly-disperse propane soot particles, were estimated to be 6 %, 4 %, 8 %, and 11 %, at 375, 405, 532, and 781 nm, respectively. The calibration factors for absorption determined by the poly-disperse soot particles at 375 and 405 nm were 48 % and 36 % smaller than those by light absorption of NO$_2$ molecules possibly because of NO$_2$ photolysis, although good agreement was observed at 532 nm. These results suggest that the photolysis effect should be taken into account when light absorption by NO$_2$ is used for calibration at 375 and 405 nm.

Keywords photoacoustic spectrometer (PAS); reciprocal nephelometer; absorption coefficient; scattering coefficient; aerosol optical property; calibration
1. Introduction

Atmospheric aerosols, both from natural and anthropogenic origins, are known to modify the energy balance of the Earth’s atmosphere. Aerosols directly modify the energy balance by the absorption and scattering of solar radiation. Moreover, because they can act as cloud condensation nuclei, they modify the physical properties of clouds (Boucher et al. 2013), thereby indirectly modifying the energy balance. Black carbon (BC) is considered to be the most potent light absorbing material in the visible region of the spectrum (Bond et al. 2013). Light absorbing organic carbon (brown carbon or BrC) and mineral dust may also act as sources of significant absorption, especially in the ultraviolet (UV) and shorter visible wavelength regions (Moosmüller et al. 2009; Andreae and Gelencser 2006; Wagner et al. 2012). Because the optical properties of such particles depend on wavelength, particle size and shape, morphology, coating, and refractive index (or chemical composition), accurate in situ measurements of the wavelength dependence of the optical properties of aerosols are required.

Recently, several instruments have been developed on the basis of photoacoustic spectroscopy (PAS) to allow the direct in situ measurement of the light absorption of particles suspended in air (Arnott et al. 1999, 2000, 2005, 2006; Lack et al. 2006, 2012; Lewis et al. 2008; Ajtai et al. 2010; Haisch et al. 2012; Gyawali et al. 2012; Sharma et al. 2013). The three-wavelength photoacoustic soot spectrometer (PASS-3, Droplet Measurement Technologies, Inc.) is a commercial instrument based on a prototype originally developed at the Desert Research Institute and the University of Nevada, Reno (Lewis et al. 2008) to measure absorption ($b_{abs}$) and scattering ($b_{sca}$) coefficients typically at $\lambda = 405$, 532, and 781 nm. Recently, the PASS-3 has been applied to both laboratory and observational studies of aerosol optical properties (Cross et al. 2010; Flowers et al. 2010a; Nakayama et al. 2012, 2013, 2014; Lan et al. 2013; Metcalf et al. 2013; Chakrabarty et al. 2013; Liu et al. 2014; Guo et al. 2014; Holder et al. 2014; McMeeking et al. 2014).

During PASS-3 operation, the air being sampled is continuously introduced into an acoustic resonator, where it is irradiated by laser light at $\lambda = 405$, 532, and 781 nm amplitude-modulated at slightly different frequencies ($\Delta f \sim 5$ Hz) around the acoustic resonance frequency ($f_0 \sim 1500$ Hz). Radiation absorption by aerosols and gaseous components in the sampled air results in the generation of pressure waves in the resonator if the energy of the absorbed radiation is transferred to the surrounding air. By detecting the standing wave corresponding to each modulation frequency using a microphone located at a pressure anti-node, $b_{abs}(\lambda)$ values are determined (Arnott et al. 1999; Lewis et al. 2008). In addition, during the absorption measurements, $b_{sca}(\lambda)$ values are measured by detecting scattered light using a cosine-weighted sensor positioned at the center of the acoustic resonator that functions as a reciprocal nephelometer (Abu-Rahmah et al. 2006; Lewis et al. 2008).

For advanced measurement systems, such as those described here, instrument characterization may be needed to be made by the user, because detailed characterizations cannot always be provided by the manufacturer. Only a few reports concerning the performance of the PASS-3 are currently available (Cross et al. 2010; Flowers et al. 2010b; Sharma et al. 2013). Cross et al. (2010) reported that the mass specific absorption coefficient at $\lambda = 532$ nm for denuded soot measured by the PASS-3 is in good agreement with that measured by a single-wavelength photoacoustic spectrometer developed at NOAA (Lack et al. 2006). They applied the “closure method” for PASS-3 calibration (Cross et al. 2010, supplemental information; hereafter referred to SI), which is similar to the calibration method used by Lewis et al. (2008) for their two-wavelength photoacoustic instrument at 405 and 870 nm. The sensitivity of the scattering measurements was initially examined using high concentrations of poly-disperse ammonium sulfate (AS) particles by comparing the obtained scattering coefficients with the extinction coefficient, which is determined from the changes in the intensity of light passing through the acoustic cell with and without the particles using the Beer-Lambert law. The sensitivity of the absorption measurements was then examined using high concentrations of poly-disperse, strongly light-absorbing aerosols (such as soot particles generated by a kerosene lamp or spherocarbs) by comparing the observed absorption coefficients with the difference between the extinction and calibrated scattering coefficients. In addition, Cross et al. (2010, SI) conducted an absolute calibration of absorption using low concentrations of NO₂. They reported that the derived calibration factors were consistent with those obtained by the closure calibration described above, with slopes of $0.97 \pm 0.22$ and $1.02 \pm 0.18$ at $\lambda = 405$ and 532 nm, respectively, where the calibration factors were used to convert the readout values of absorption coefficients, after correcting the bias from...
airflow carrier, to real absorption coefficients. Flowers et al. (2010b, SI) adopted similar calibration methods and reported that the closure and absolute calibrations of absorption agreed within 4% and 3% at $\lambda = 405$ and 532 nm, respectively, using smoldering cardboard particles and kerosene soot particles for the closure calibration and low concentrations of $\text{NO}_2$ for the absolute calibration.

Although calibration factors for scattering measurements potentially depend on particle size owing to truncation error, to our knowledge, no experimental study has so far been conducted to characterize particle size dependence of the calibration factors for the scattering measurements of the PASS-3. If the calibration factor for scattering measurements depends on particle size, the calibration factor for absorption measurements, determined using the close measurements, may also be influenced by the particle size used for the calibrations. Further, because possible interference from $\text{NO}_2$ photolysis at ~417 nm during the calibration of the photoacoustic signal has recently been reported for a multi-wavelength photoacoustic nephelometer developed by Sharma et al. (2013), further investigations are required for studying relations between the calibration factors determined using $\text{NO}_2$ light absorption and those obtained using other techniques.

Recently, another commercially available instrument, a photoacoustic extinction meter (PAX, Droplet Measurement Technologies, Inc.), has been developed for measuring $b_{\text{abs}}(\lambda)$ and $b_{\text{scat}}(\lambda)$ at a single wavelength chosen by the user based on techniques similar to those applied in the PASS-3. However, to date, no experimental study has reported the performance of the PAX. In the PAX, a reciprocal nephelometer that measures scattering coefficients is separated from the photoacoustic cell and the sampling inlet is placed between them. A cosine sensor different than that used in the PASS-3 is positioned at the center of the reciprocal nephelometer. While the standard wavelength employed in the PAX unit is 870 nm, we chose 375 nm to study the light absorption properties of BrC in the UV region. The laser radiation with a wavelength of 375 nm is amplitude-modulated around the acoustic resonance frequency ($f_0 \sim 1500$ Hz), which is similar to that of the PASS-3.

In the present study, laboratory trials were conducted to characterize the performance of the PASS-3 (at $\lambda = 405$, 532, 781 nm) and PAX (at $\lambda = 375$ nm), focusing, in particular, on the effect of particle size on the calibration factors as well as the consistency of the calibration factors obtained using different methods. Note that, although information on the long term stability of calibration factors and the effect of transportation of the instruments on these factors can be important in some cases, these factors are beyond the scope of this study.

2. Experimental

In this study, a series of laboratory-generated aerosols, including polystyrene latex (PSL) spheres, AS, and propane soot particles, were measured with the PASS-3 (at $\lambda = 405$, 532, 781 nm) and PAX (at $\lambda = 375$ nm) with or without size selection. The typical configurations of the apparatus employed during particle measurement with and without size selection are shown in Figs. 1a and 1b, respectively.

For the experiments incorporating mono-disperse particles, procedures similar to those used in our previous studies were adopted (Nakayama et al. 2010a, b). PSL particles with diameters of 203, 299, 400, 499, 600, 707, or 903 nm (Thermo Scientific) or aqueous solutions of AS (Wako Chemicals) were nebulized using an atomizer with synthesized, filtered air. The particles thus generated were dried using diffusion dryers incorporating silica gel and then passed through a differential mobility analyzer (DMA) (TSI, model 3081) and an aerosol particle mass analyzer (APM) (Kanomax, model 3601) to obtain mono-disperse particles. In this configuration, the APM was used to remove multi-charged particles that were passed through the DMA. The size selected particles were subsequently mixed with dilution air and then introduced into the PASS-3, PAX, and a condensation particle counter (CPC) (TSI, model 3772) to measure $b_{\text{abs}}(\lambda)$ and $b_{\text{abs}}(\lambda)$ values at $\lambda = 405$, 532, and 781 nm, $b_{\text{abs}}(\lambda)$ and $b_{\text{abs}}(\lambda)$ values at $\lambda = 375$ nm, and particle number concentrations ($N_p$), respectively (Fig. 1a). The ratio of the sample and sheath flows of the DMA remained constant at a value of 0.10, and the $\lambda$ parameter, which characterizes the classification performance of the APM (Tajima et al. 2011), was maintained at either 0.32 or 0.50.

In the experimental trials employing poly-disperse particles, AS aqueous solution was nebulized by an atomizer and then dried using diffusion dryers with silica gel. Soot particles generated during propane combustion (Takenaka Co.) were also used in these trials. The resulting soot particles were dried using the diffusion dryers with silica gel, and then passed through a heater maintained at 300°C to remove volatile materials such as organic compounds (Kondo et al. 2009). The design of the heater, consisting of a stainless steel tube and electronic jacket heaters, was
similar to that reported by Kondo et al. (2009); details of the heater have been provided in Guo et al. (2014). Then, the particles were introduced into the PASS-3 and PAX, as well as a scanning mobility particle sizer (SMPS) (TSI, 3934) that measured particle size distribution between 17.2 and 1000 nm at 5-min intervals (Fig. 1b).

Blank readings were obtained from the PASS-3 and PAX by passing the sample through a particulate filter (Balston) for 2–6 min every 5–12 min (Figs. 1a, b). The typical laser power levels at $\lambda = 375, 405, 532$, and 781 nm after modulation were 93, 133, 99, and 184 mW, respectively. In the present study, 60 s averages of the $b_{\text{abs}}$ and $b_{\text{sca}}$ data were typically used for analyses after subtracting the background signal, except for the Allan variance analyses where 2 and 1 s data averages were used for the PASS-3 and PAX, respectively. The sampling flow rates of the PASS-3, PAX, CPC, and SMPS were typically 1.0, 1.0, 1.0, and 0.2 lpm, respectively.

Gaseous calibrations of the PASS-3 and PAX using CO$_2$ (> 99.995 %, Japan Fine Products), HFC-134a (CH$_3$FCF$_3$) (> 99.6 %, Mono-taro Co.), and an NO$_2$/air mixture (prepared by diluting 201 ppm NO$_2$/air (Japan Fine Products) with synthesized, filtered air) were also conducted. All the experimental trials were conducted at room temperature (293 ± 5 K).

3. Results and discussion

3.1. Instrumental stability and detection limit

The Allan variance analysis is a useful tool for evaluating the stability and precision of this type of instrument (Werle et al. 1993; Lack et al. 2006; Sharma et al. 2013). Eight sets of 8 h data (64 h of data in total) measuring filtered air were used for this analysis, after accounting for the calibration factors described in the following sections. Figure 2 shows the average of eight Allan plots for $b_{\text{abs}}(\lambda)$ and $b_{\text{sca}}(\lambda)$ at $\lambda = 375, 405, 532$, and 781 nm. From Fig. 2, the typical Allan deviations (\(\sigma_A\)) for $b_{\text{abs}}(\lambda)$ and $b_{\text{sca}}(\lambda)$ at $\lambda = 375, 405, 532$, and 781 nm for a 60 s integration interval were estimated to be 0.82(0.81), 0.55(0.15), 1.20(0.18), and 0.71(0.61) Mm$^{-1}$, respectively. Sharma et al. (2013) reported the Allan deviation for $b_{\text{abs}}(\lambda)$ (and $b_{\text{sca}}(\lambda)$) at 405, 532, and 781 nm, based on their PASS-3 instrument for 60 s integration time.
to be 0.4(0.2), 8(1.7), and 0.3(0.8) Mm$^{-1}$, respectively. Therefore, the Allan deviations for $b_{\text{abs}}(\lambda)$ and $b_{\text{sca}}(\lambda)$ at 405 and 781 nm determined in the present study were in good agreement with those reported by Sharma et al. (2013), while those for $b_{\text{abs}}(532$ nm) and $b_{\text{sca}}(532$ nm) were smaller by factors of 6–10. Sharma et al. (2013) reported minimum detection limit for $b_{\text{ext}}(532$ nm) to be 16500 Mm$^{-1}$ for 60 s integration time, where $b_{\text{ext}}(532$ nm) was calculated from changes in the light intensity passing through the cell in the presence and absence of particles. Figure 2c shows the averaged Allan plots for laser power measured simultaneously in the present study. The typical Allan deviation for laser power at 532 nm for 60 s integration time corresponds to $b_{\text{ext}}(532$ nm) of 1200 Mm$^{-1}$, which is one order of magnitude smaller than the detection limit reported by Sharma et al. (2013). The higher stability of laser power at 532 nm compared than that for the PASS-3 used by Sharma et al. (2013) is a plausible source of the smaller deviations for $b_{\text{abs}}(532$ nm) and $b_{\text{sca}}(532$ nm).

The minimum in the Allan plot represents the optimum integration time, and it is evident that the $\sigma_A$ values for $b_{\text{abs}}(\lambda)$ at $\lambda$ = 405, 532, and 781 nm decreased with integration time up to ~600 s. In contrast, the $\sigma_A$ values for $b_{\text{sca}}(\lambda)$ at $\lambda$ = 405, 532, and 781 nm started to increase at shorter integration times of approximately 120, 60, and 30 s, respectively, due to signal drift. The more pronounced drifts associated with $b_{\text{sca}}(532$ nm) and $b_{\text{sca}}(781$ nm) are possibly due to a greater drift of the laser power at 532 and 781 nm, as shown in Fig. 2c. $\sigma_A$ values for both $b_{\text{abs}}(375$ nm) and $b_{\text{sca}}(375$ nm) measured using the PAX instrument were found to decrease with longer integration times of up to > 1000 s. Although the $\sigma_A$ values for $b_{\text{sca}}(375$ nm) obtained at shorter integration times (<
100 s) were significantly larger than those for $b_{sca}(\lambda)$ at other wavelengths, variance was reduced when longer integration times were adopted.

In the present study, similar to our previous studies (Nakayama et al. 2012, 2013, 2014), blank measurements were conducted using a particulate filter for 2–6 min every 5–12 min as a substitute for the automated zeroing function of the instruments, with the aim of minimizing the effects of signal drift. Subsequently, $b_{abs}(\lambda)$ and $b_{sca}(\lambda)$ values were calculated at 5–12 min averages by subtracting the average absorption/scattering coefficients measured during the two blank measurement periods immediately before and after the sampling period. Typical detection limits for 10 min average values were estimated, assuming that blank measurements were conducted for 3 min at 10-min intervals using a particulate filter. Using the same data that was used for the Allan variance analysis, the differences between the average absorption/scattering coefficients during the sampling period (7 min) and those during the two blank measurement periods (3 min) before and after the sampling period were calculated. Figure 3 presents the histograms of replicate calculation data for the differences associated with 64 h data by applying a 0.25 Mm$^{-1}$ bin width. Eight sets of 8 h data were used for these calculations.

3.2. Calibrations for scattering measurements

a. Rayleigh scattering of CO$_2$ and HFC-134a

The Rayleigh scattering of gaseous molecules, such as CO$_2$ and hydrofluorocarbons, has been commonly applied to the calibration of integrated nephelometers (Bodhaine et al. 1991; Anderson et al. 1996) and reciprocal nephelometers (Peñaloza 1999; Abu-Rahmah et al. 2006). In the present study, filtered air and filtered calibration gases (pure CO$_2$ or HFC-134a) were alternately introduced to the PASS-3 and PAX every 5–6 min. Because the scattering coefficients at $\lambda = 781$ nm from PASS-3 did not stabilize after
several minutes of changing the calibration gas, only the scattering coefficients at \( \lambda = 375, 405, \) and 532 nm were analyzed. By comparing the differences in the scattering coefficients obtained for air and CO\(_2\) (or HFC-134a) from the PASS-3 and PAX with those reported in the literature, calibration factors \( f_{\text{sca,x}}(\lambda) \), \( X = \text{CO}_2 \) or HFC-134a and \( \lambda = 375, 405, 532 \) nm for the gaseous calibration of scattering measurements were determined by the relationship:

\[
[f_{\text{sca,x}}(\lambda) - f_{\text{sca,air}}(\lambda)] = f_{\text{sca,x}}(\lambda) [b_{\text{sca,x}}(\lambda) - b_{\text{sca,air}}(\lambda)],
\]

where \( b_{\text{sca,x}}(\lambda) \) and \( b_{\text{sca,air}}(\lambda) \) are the scattering coefficients obtained for X and air from the PASS and PAX instruments, and \( f_{\text{sca,x}}(\lambda) \) and \( f_{\text{sca,air}}(\lambda) \) are the scattering coefficients for X and air reported in the literature. In the present study, a value of 13.8 ± 0.1 Mm\(^{-1}\) was assumed for \( f_{\text{sca,air}}(\lambda = 532 \) nm and STP condition (0°C, 1 atm) based on previous theoretical studies (Bucholtz 1995; Anderson et al. 1996). The \( f_{\text{sca,air}}(\lambda) \) values at \( \lambda = 375 \) and 405 nm were then calculated using the \( \lambda^{-4} \) scaling of Rayleigh scattering, while the \( f_{\text{sca,CO}_2}(\lambda) \) and \( f_{\text{sca,HFC-134a}}(\lambda) \) at each wavelength were calculated using Rayleigh light scattering multipliers of 2.61 and 7.25 times the value of air, respectively (Air Resource Specialists, Inc. 2005).

The 1σ relative uncertainties of the \( f_{\text{sca,CO}_2}(\lambda) \) and \( f_{\text{sca,HFC-134a}}(\lambda) \) values at \( \lambda = 375, 405, \) and 532 nm were calculated using eight sets of filtered air and CO\(_2\) (HFC-134a) measurements to be 4(5), 3(2), and 4(2) %, respectively (Table 1). The ratio of these calibration factors, i.e., \( f_{\text{sca,HFC-134a}}(\lambda)/f_{\text{sca,CO}_2}(\lambda) \), at \( \lambda = 375, 405, \) and 532 nm were then determined to be 0.97 ± 0.06, 0.98 ± 0.04, and 0.93 ± 0.06, respectively (Table 2). The slightly smaller average values than unity may be caused by the uncertainties in the Rayleigh light scattering multipliers.

b. Mono-disperse PSL and AS particles

The particle size dependencies of the sensitivity of the scattering measurements from the PASS-3 and PAX were examined using both mono-disperse PSL and AS particles. Mono-disperse PSL particles with mobility diameters \( (D_m) \) of 203, 299, 400, 499, 600, 707, and 903 nm and AS particles with \( D_m \) of 200, 300, 400, 500, 600, 700, 800, and 900 nm were selected using a combination of the DMA and APM (Fig. 1a). The observed scattering coefficients \( b_{\text{sca,PSL}}(\lambda) \) were determined by subtracting the average scattering coefficients obtained during the two blank measurement periods before and after the sampling period from those acquired during the sampling period. By comparing the \( b_{\text{sca,PSL}}(\lambda) \) values with those calculated by Mie theory \( b_{\text{sca,Mie}}(\lambda) \) using the particle diameter selected by the DMA–APM system and the particle number density obtained from the CPC, particle size dependent calibration factors \( f_{\text{sca,Y}}(\lambda, D_m) \), \( Y = \text{PSL or AS} \) for the scattering measurements were calculated as

\[
b_{\text{sca}}(\lambda) = f_{\text{sca,Y}}(\lambda, D_m) b_{\text{sca,PSL}}(\lambda).
\]

During Mie calculations using the BHMIE algorithm (Bohren and Hoffman 1983), the real part of the refractive index \( (RI, m = n - ki) \) of 1.64 ± 0.02, 1.63 ± 0.02, 1.60 ± 0.02, and 1.58 ± 0.01 at \( \lambda = 375, 405, 532, \) and 781 nm, respectively, was used for PSL particles based on the values reported by Matheson and Saundersson (1952), Nikolov and Ivanov (2000), Pettersson et al. (2004), Baynard et al. (2007), Abo Riziq et al. (2007), Lang-Yona et al. (2009), and Washenfelder et al. (2013), while values of 1.53 ± 0.01, 1.54 ± 0.01, 1.53 ± 0.01, and 1.52 ± 0.01 at \( \lambda = 375, 405, 532, \) and 781 nm, respectively, were used for AS particles based on the reported values of Toon et al. (1976), Pettersson et al. (2004), Abo Riziq et al. (2007), Diar et al. (2008), Nakayama et al. (2010c), and Washenfelder et al. (2013).

Figure 4 show the examples of correlation plots between the \( b_{\text{sca,Mie}}(\lambda) \) and \( b_{\text{sca,PSL}}(\lambda) \) values of PSL particles with diameters of 299, 499, and 707 nm. The slopes in Fig. 4, which represent \( f_{\text{sca,PSL}}(\lambda, D_m) \), increased significantly with increasing particle diameter at \( \lambda = 532 \) nm, while the particle size dependencies of the slopes were minimal at \( \lambda = 375, 405, \) and 781 nm within the range of diameters plotted. Three to five similar experimental trials were conducted for

| Table 1. Relative (± 1σ) uncertainties used to determine the calibration factors for scattering and absorption measurements |
|-----------------|-----------------|-----------------|-----------------|
| Calibration factor | Wavelength (nm) |
|------------------|-----------------|-----------------|-----------------|
| \( f_{\text{sca,CO}_2}(\lambda) \) | ± 4 % ± 3 % ± 4 % |
| \( f_{\text{sca,HFC-134a}}(\lambda) \) | ± 5 % ± 2 % ± 2 % |
| \( f_{\text{sca,polyAS}}(\lambda) \) | ± 2 % ± 2 % ± 3 % ± 2 % |
| \( f_{\text{abs,polySoot}}(\lambda) \) | ± 6 % ± 4 % ± 8 % ± 6 % |
| \( f_{\text{abs,NO}_2}(\lambda) \) | ± 2 % ± 2 % ± 2 % ± 2 % |
| a) Obtained using the Rayleigh scattering of CO\(_2\) (Eq. 1). |
| b) Obtained using the Rayleigh scattering of HFC-134a (Eq. 1). |
| c) Obtained using poly-disperse AS particles (Eq. 6). |
| d) Obtained using poly-disperse soot particles (Eq. 8). |
| e) Obtained using absorption of NO\(_2\) (Eq. 10). |
The calibration factors at \( \lambda = 532 \) nm determined for mono-disperse PSL and AS particles increase significantly with increasing diameter from \( \sim 200 \) to \( \sim 700 \) nm and then decrease with further increases in diameter from \( \sim 700 \) to \( \sim 900 \) nm, while the correction factors determined for PSL and AS particles with diameters approximately 200 nm are consistent with those determined using the Rayleigh scattering of gaseous molecules, within the estimated uncertainties (Fig. 5). These results indicate that the sensitivity associated with the PASS-3 scattering measurement at \( \lambda = 532 \) nm undergoes significant change with varying particle diameters. No significant particle size dependence is observed at 781 nm with average (\( \pm 1 \sigma \)) \( f_{\text{sca},Y}(781 \text{ nm}, D_m)/f_{\text{sca},\text{PSL}}(781 \text{ nm}, D_m = 299 \text{ nm}) \) values of 1.04 \( \pm 0.14 \) for \( D_m \leq 707 \) nm (Fig. 5). It is also noted that the average \( f_{\text{sca},Y}(781 \text{ nm}, D_m)/f_{\text{sca},\text{PSL}}(781 \text{ nm}, D_m = 299 \text{ nm}) \) value for the AS particles (1.10 for \( D_m \leq 700 \) nm, Table 2) is slightly larger than that for the PSL particles (0.98 for \( D_m \leq 707 \) nm, Table 2), and that the average \( f_{\text{sca},Y}(781 \text{ nm}, D_m)/f_{\text{sca},\text{PSL}}(781 \text{ nm}, D_m = 299 \text{ nm}) \) values for both the AS and PSL particles with \( D_m \) \( \sim 900 \) nm (1.23 and 1.16, respectively) are slightly larger than those obtained for the smaller particles (Fig. 5).

Reciprocal nephelometer has the potential to exhibit particle size-dependent sensitivity, especially in the case of larger particles, if the detectable angular range is relatively small and/or the deviation of cosine sensor response is non-negligible (Mulhol-
land and Bryner 1994; Peñaloza 1999; Abu-Rahamah et al. 2006). A schematic configuration of the reciprocal nephelometer is shown in Fig. 6. The lower limits of the truncation angles ($\theta_{\text{min}}$) for the PASS and PAX instruments, as estimated from their respective geometric configurations and assuming identical responses of cosine sensors and ideal laser alignment, with photo-detectors and laser beams with infinite areas, are 5° and 6°, respectively. In addition, the polarization state of the laser contributes to the particle size-dependency of the sensitivity. In the PASS-3, the polarization state of the laser at 532 nm is perpendicular to the scattering plane, whereas the polarization state is parallel to the scattering plane at 781 nm. Although the polarization state of the laser at 405 nm is typically parallel to the scattering plane, the angle can be varied from instrument to instrument because the laser is screwed into place. For the PASS-3 used in the present study, the polarization is rotated by approximately 15° from the scattering plain. The polarization state of the 375 nm laser of the PAX is 45° to the scattering plane.

The effective truncation angles ($\theta'(\lambda)$) of the PASS-3 and PAX were estimated to minimize the sum of the squares residuals between the normalized $f_{\text{sca,Y}}(\lambda, D_m)$ values in Fig. 5 and those simulated using the following equations, with the assumption that the cosine sensors exhibit ideal responses within the detectable angular range and that the detectable angular range is the same in both forward and backward directions, as well as assuming ideal laser alignment and infinite areas for the photo-detectors and laser beams (Mulholland and Bryner 1994; Peñaloza 1999; Abu-Rahmah et al. 2006):

Fig. 4. Correlation plots between scattering coefficients at (a) 375, (b) 405, (c) 532, and (d) 781 nm obtained for PSL particles with diameters of 299 (red circles), 499 (green triangles), and 707 nm (blue inverted triangles) during measurements with the PASS-3 and PAX and those calculated using Mie theory (see Eq. (2) in the text). The blue, green, and red lines are the results of linear least-squares fitting of data for particle diameters of 299, 499, and 707 nm, respectively. The slopes of the black solid and dashed lines represent the $f_{\text{sca,CO}_2}(\lambda)$ and $f_{\text{sca,HFC-134a}}(\lambda)$, respectively, which were obtained on the same day.
Fig. 5. Particle size dependencies of averaged calibration factors for scattering measurements at $\lambda =$ (a) 375, (b) 405, (c) 532, and (d) 781 nm, normalized to $f_{sca,X}(\lambda)$ (average of $f_{sca,CO_2}(\lambda)$ and $f_{sca,HFC-134a}(\lambda)$) at $\lambda = 375$, 405, and 532 nm or $f_{sca,PSL}(\lambda, D_m = 299$ nm) at $\lambda = 781$ nm. Red filled circles and blue open triangles represent the results obtained by the measurement of mono-disperse PSL and AS particles, respectively. Solid lines indicate the results of simulations calculated using Eq. (3) or (4) with an optimal effective truncation angle ($\theta' = 8°$, 5°, 21°, and 19° at $\lambda =$ 375, 405, 532, and 781 nm) chosen to minimize the sum of squared residuals between observation and simulation. Dashed lines indicate the results of simulations calculated using Eq. (3) or (4) at ±5° deviation from the optimal effective truncation angle. Orange and sky blue lines in panel (c) indicate the results of simulations for PSL and AS particles, respectively, when the polarization state of the 532 nm laser is assumed to be parallel to the scattering plane.

Fig. 6. Schematic configuration of a reciprocal nephelometer. The value of $d$ represents the minimum distance between the cosine sensor and the laser beam. The $L_{sca}$ and $\theta'$ term represent the maximum effective detectable distance of the laser beam and the minimum effective detectable scattering angle (or effective truncation angle), assuming that the cosine sensor exhibit an ideal response within the detectable angular range and the detectable angular range is the same in both the forward and backward directions, as well as assuming ideal laser alignment and infinite area for the photo-detector and laser beam.
where \( I_x(x, \theta, m_Y) \) is the scattering intensity function for a single particle with size parameter \( x = \pi D/\lambda \), where \( D \) is the geometric particle diameter) and complex RI \( m_Y \) (\( Y = \text{PSL} \) or \( \text{AS} \)), \( I_\lambda(\theta) \) is the scattering intensity function for Rayleigh scattering by gaseous molecules, and \( I_{\text{PSL}299}(x, \theta, m_{\text{PSL}}) \) is the scattering intensity function for a single PSL particle with a diameter of 299 nm. For spherical particles, the geometric diameter is equal to the mobility diameter such that \( D = D_m \). The BHMIE algorithm (Bohren and Hoffman; 1983) incorporating the same refractive index value, which was used to determine \( b_{\text{sca}M\text{ie}I}(\lambda) \) in Eq. (2), was used for calculating scattering intensity functions. In these calculations, the \( \theta'(/\lambda) \) values were assumed to be greater than the \( \theta'_{\text{min}} \) values estimated from the geometrical configurations. It should be noted that the estimated \( \theta'(/\lambda) \) values do not necessarily represent the actual geometrical truncation angle because of the possible differences between assumed and actual conditions in the response of cosine sensor, symmetry of detectable angle, and laser alignment.

These calculation results determined the optimal effective truncation angles (\( \theta'(/\lambda) \)) at \( \lambda = 375, 532, \) and 781 nm to be 8°, 21°, and 19°, respectively. The estimated optimal effective truncation angle at 405 nm was smaller than the \( \theta'_{\text{min}} \) value (5°) when the polarization state of the laser at 405 nm was assumed to be parallel to the scattering plane. If the polarization is rotated from the scattering plain, optimal effective truncation angle would become even smaller. Therefore, we decided to use the \( \theta'_{\text{min}} \) value (5°) as the effective truncation angle at 405 nm in the simulation. The particle size dependency of the normalized \( f_{\text{sca}XY}(\lambda, D_m) \) values simulated using Eq. (3) or (4) along with the optimal effective truncation angles are indicated by solid lines in Fig. 5. To demonstrate the sensitivity of the truncation angle to the particle size dependency of the normalized \( f_{\text{sca}XY}(\lambda, D_m) \) values, simulation results at ±5° of the obtained optimal effective truncation angles are also included, as shown by dashed lines in Fig. 5. Note that the uncertainties in the normalized \( f_{\text{sca}XY}(781 \text{ nm}, D_m) \) values are larger compared to the range of simulation results at ±5° of the obtained optimal effective truncation angles (Fig. 5d). Therefore, the uncertainties in the estimated effective truncation angles values at 781 nm should be larger than those at other wavelengths.

Both the large effective truncation angle (21°) and polarization states of the laser would contribute to the observed large particle size dependence of the correction factor at \( \lambda = 532 \text{ nm} \). If the polarization state of the 532 nm laser is assumed to be parallel to the scattering plane, the maximum values of the normalized correction factors for PSL and AS particles calculated using Eq. (3) with \( \theta'/(532 \text{ nm}) = 21° \) are estimated to be 1.36 and 1.48, respectively (orange and sky blue lines in Fig. 5c). These values are significantly smaller than the corresponding values (1.89 and 2.06 for PSL and AS particles) obtained when the polarization state of the 532 nm laser is perpendicular to the scattering plane. These results suggest that the difference in the polarization state at 532 nm and other wavelengths contributes to the observed large particle size dependence of the calibration factor. It should be noted that optimal effective truncation angles, which are remarkably large, are obtained at \( \lambda = 532 \) and 781 nm compared to the angle at \( \lambda = 405 \text{ nm} \), even though the same photo-detector was used for all the scattering measurements of the PASS-3. Although the reason for this discrepancy is unclear, the non-ideality of laser alignment at 532 and 781 nm as well as the wavelength dependence of the cosine sensor response might contribute to the difference. In addition, the possible contributions of light scattering from cell wall cannot be ruled out. Further studies are required to clarify the source of this discrepancy. For the PAX instrument at 375 nm, the optimal effective truncation angle of 8° is close to the lower limit of truncation angles (\( \theta'_{\text{min}} = 6° \)).
c. Poly-disperse AS particles

The calibration factors for scattering measurements were also determined based on the closure method using high concentrations of poly-disperse AS particles (Fig. 1b). In this method, the obtained scattering coefficients were compared with the extinction coefficients determined from changes in the light intensity passing through the acoustic cell in the presence and absence of particles using the Beer-Lambert law (in Mm–1);

\[ b_{\text{ext,obs}}(\lambda) = (1/L_{\text{path}}) \ln \left( I_0/I \right) \times 10^6, \quad (5) \]

where \( L_{\text{path}} \) is the path length of the lasers in the cell (0.2486 and 0.354 m for the PASS-3 and PAX, respectively), and \( I_0 \) and \( I \) are the light intensities passing through the cell in the presence and absence of particles, respectively. The uncertainties in the \( L_{\text{path}} \) values are estimated to be \(< 1\%\). The calibration factors \( (f_{\text{sca,polyAS}}(\lambda)) \) for the scattering measurements are determined as follows (Lewis et al. 2008; Cross et al. 2010, SI):

\[ f_{\text{sca,polyAS}}(\lambda) = f_{\text{sca,polyAS}}(\lambda) b_{\text{sca,obs}}(\lambda). \quad (6) \]

Two series of experimental trials were conducted using poly-disperse AS particles with volume-based geometric mean diameters \( (D_{v,\text{AS}}) \) between 215 and 473 nm (volume-based geometric standard deviation, \( \sigma = 1.66 \pm 0.05 \)) and 210 and 349 nm \((\sigma = 1.74 \pm 0.08)\). Figure 7 shows the correlation plots between the \( b_{\text{ext,obs}}(\lambda) \) and \( b_{\text{sca,obs}}(\lambda) \) of poly-disperse AS particles with \( D_{v,\text{AS}} \) values ranging between 215 and 473 nm. Considering the uncertainties in the linear least-squares fitting for the two sets of experimental data and in the laser path lengths, the relative uncertainties of the \( f_{\text{sca,polyAS}}(\lambda) \) at \( \lambda = 375, 405, 532, \) and 781 nm, derived from the slopes of these plots, were estimated to be 2\%, 2\%, 3\%, and 2\%, respectively (Table 1).

The averages of the ratio of obtained \( f_{\text{sca,polyAS}}(\lambda) \) values to \( f_{\text{sca,X}}(\lambda) \) (average of \( f_{\text{sca,CO}_2}(\lambda) \) and \( f_{\text{sca,HFC-134a}}(\lambda) \)) for two series of experiments are listed in Table 2. The calibration factors obtained with poly-disperse AS particles, \( f_{\text{sca,polyAS}}(\lambda) \) at \( \lambda = 375 \) and 405 nm were in good agreement with those determined from the Rayleigh scattering of gaseous molecules, with average \( f_{\text{sca,polyAS}}(\lambda)/f_{\text{sca,X}}(\lambda) \) ratios of 1.00 ± 0.12 and 1.04 ± 0.12, respectively. In contrast, the \( f_{\text{sca,polyAS}}(532 \text{ nm}) \) values were significantly larger than the \( f_{\text{sca,X}}(532 \text{ nm}) \), with average \( f_{\text{sca,polyAS}}(532 \text{ nm})/f_{\text{sca,X}}(532 \text{ nm}) \) ratio of 1.45 ± 0.06. These results are consistent with the data obtained using the mono-disperse PSL and AS particles (Section 3.2.b). The average ratio of the obtained \( f_{\text{sca,polyAS}}(781 \text{ nm}) \) to \( f_{\text{sca,PSL}}(781 \text{ nm}, D_m = 299 \text{ nm}) \) determined on the same day was 1.11 ± 0.07. This ratio was also consistent with the average \( f_{\text{sca,AS}}(781 \text{ nm}, D_m)/f_{\text{sca,PSL}}(781 \text{ nm}, D_m = 299 \text{ nm}) \) value for mono-disperse AS particles with diameters smaller than 700 nm (1.10 ± 0.13, Table 2).

d. Estimation of truncation error

Because the truncation error (or sensitivity) of the nephelometer depends on the complex RI values of the particles, the possible range of the truncation errors when measuring sub-micron sample particles is estimated. By assuming that the calibrations of the scattering measurements were performed using poly-disperse AS particles with \( D_{v,\text{AS}} = 300 \text{ nm} \) and a log-normal size distribution \((\sigma = 1.7)\) and that the sample particles are homogeneous and spherical, the ratio of \( f_{\text{sca,polyAS}}(\lambda, D_{v,\text{AS}} = 300 \text{ nm}) \) to the actual calibration factors for the sample particles \( (f_{\text{sca,polyS}}(\lambda, D_{v,S})) \) may be calculated using the following equation:

\[ \frac{f_{\text{sca,polyAS}}(\lambda, D_{v,\text{AS}} = 300 \text{ nm})}{f_{\text{sca,polyS}}(\lambda, D_{v,S})} = \frac{\int_0^\infty f_{\text{sca,AS}}(\lambda, D, m_{\text{AS}}) Q_{\text{sca,AS}}(x, m_{\text{AS}}) \left( \frac{\pi D^2}{4} \right) N_{\text{AS}}(D) dD / \int_0^\infty Q_{\text{sca,AS}}(x, m_{\text{AS}}) \left( \frac{\pi D^2}{4} \right) N_{\text{AS}}(D) dD}{\int_0^\infty f_{\text{sca,S}}(\lambda, D, m_{\text{S}}) Q_{\text{sca,S}}(x, m_{\text{S}}) \left( \frac{\pi D^2}{4} \right) N_{\text{S}}(D) dD / \int_0^\infty Q_{\text{sca,S}}(x, m_{\text{S}}) \left( \frac{\pi D^2}{4} \right) N_{\text{S}}(D) dD} \quad (7) \]

where \( D_{v,S} \) and \( D_{v,\text{AS}} \) are the volume-based geometric mean diameters for the sample and AS particles, \( f_{\text{sca,AS}}(\lambda, D, m_{\text{AS}}) \) and \( f_{\text{sca,S}}(\lambda, D, m_{\text{S}}) \) are calibration factors for the mono-disperse sample and AS particles with a diameter of \( D \) (calculated in the same manner as the numerator of Eq. 3), \( Q_{\text{sca,AS}}(x, m_{\text{AS}}) \) and \( Q_{\text{sca,S}}(x, m_{\text{S}}) \) are the scattering efficiencies for a single sample and AS particles with size parameter \( x \) and complex RI \( (m_{\text{S}} \text{ and } m_{\text{AS}} \text{ for sample and AS, respectively}) \), and \( N_{\text{S}}(D) \) and \( N_{\text{AS}}(D) \) are the number concentrations of the sample and AS particles in size bin \( dD \) with a mean diameter of \( D \) in a unit volume.
The $f_{\text{sca,polyS}}(\lambda, D_{v,S})$ and $f_{\text{sca,polyAS}}(\lambda, D_{v,AS})$ terms are equivalent to the average correction factors for mono-disperse samples and AS particles weighted by the total scattering coefficients for the particles in each size bin.

In these calculations, the optimum effective truncation angles estimated in Section 3.2.b are used for $\theta'(\lambda)$. The sample particles are assumed to consist of poly-disperse spheres with log-normal size distributions and $D_{v,S}$ between 200 and 700 nm ($\sigma = 1.5$), which corresponds to number-based geometric mean diameters ranging between 122 and 427 nm. Two types of particles are assumed, with complex RI values of (A) $n = 1.35–1.65$ (varying in 0.05 steps) and $k = 0.000–0.010$ (varying in 0.002 steps), representing non- or weakly light-absorbing particles such as inorganic and organic aerosols, and (B) $n = 1.7–2.0$ (varying in 0.05 steps) and $k = 0.7–1.2$ (varying in 0.1 steps), representing strongly light-absorbing particles such as soot particles. For each size distribution, a total of 42 calculations were performed for both type A and B particles.

Figures 8 and 9 present the calculated $f_{\text{sca,polyAS}}(\lambda, D_{v,AS})/f_{\text{sca,polyS}}(\lambda, D_{v,S})$ values for weakly and strongly light-absorbing particles, respectively, as a function of $D_{v,S}$. For both particles types, the $f_{\text{sca,polyAS}}(\lambda, D_{v,AS})/f_{\text{sca,polyS}}(\lambda, D_{v,S})$ values at all the four wavelengths decreased with increasing particle size of the samples from 1.00–1.16 to 0.70–0.97, and the rates of decrease were largely dependent on the wavelength. These simulations indicate that, when a calibration factor obtained with poly-disperse AS particles with a $D_{v,AS}$ value of 300 nm is used, the subsequently obtained scattering coefficients for weakly light-absorbing particles with a $D_{v,S}$ of 700 nm can be underestimated by 6 ± 1%, 2 ± 1%, 23 ± 4%, and 5 ± 4% at $\lambda = 375, 405, 532,$ and 781 nm.
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nm, respectively, while the coefficients for strongly light-absorbing particles may be underestimated by 12 ± 1%, 5 ± 1%, 22 ± 1%, and 14 ± 1% at these same wavelengths. Interestingly, the truncation errors for strongly light-absorbing particles are larger than those for weakly light-absorbing particles at \( \lambda = 375, 405, \) and 781 nm, while the truncation errors are comparable at \( \lambda = 532 \) nm. Relatively large truncation errors are associated with weakly light-absorbing particles for which real portion of the RI value \((n)\) is smaller, especially at \( \lambda = 532 \) and 781 nm (Fig. 8). In case of the strongly light-absorbing particles (Fig. 9), both \( n \) and \( k \) values do not significantly contribute to the particle size dependency of the truncation within the examined ranges of \( n \) and \( k \) values, except at \( \lambda = 532 \) nm, at which relatively larger truncation errors are observed for particles with smaller \( k \) values. Typical truncation errors for particles with \( D_{v,S} \) values less than 500 or 700 nm are estimated from the 5th and 95th percentiles of the \( f_{\text{sca,polyAS}}(\lambda, D_{v,AS})/f_{\text{sca,polyS}}(\lambda, D_{v,S}) \) values, and are summarized in Table 3.

As listed in Tables 1 and 2, the calibration factors for scattering coefficients can be determined from the Rayleigh scattering of gaseous molecules, mono-disperse PSL and AS particles, and/or poly-disperse AS particles with typical relative uncertainties of approximately 5 %, 5 %, and 10 % at \( \lambda = 375, 405, \) and 781 nm, respectively. Although a significant particle size dependency of the calibration factors at \( \lambda = 532 \) nm was evident during the trials using mono-disperse PSL and AS particles, the lower limit calibration factor can be determined using Rayleigh scattering of gaseous molecules and/or mono-disperse PSL and AS particles with a diameter of 200 nm, with typical relative uncertainties of ≤ 10 %. By combining the uncertainties in the determination of the calibra-
tion factors with the truncation errors estimated in this section, the typical overall uncertainties of the calibration factors for the scattering measurements of non- or weakly light-absorbing particles with \( \overline{D}_{v,S} \) less than 500(700) nm were estimated to be 9(12) \%, 6(7) \%, 23(34) \%, and 13(17) \% at \( \lambda = 375, 405, 532, \) and 781 nm, respectively, while those for strongly light-absorbing particles with \( \overline{D}_{v,S} \) smaller than 500(700) nm were estimated to be 10(17) \%, 7(10) \%, 26(31) \%, and 13(23) \%, at \( \lambda = 375, 405, 532, \) and 781 nm, respectively. It should be noted that, if the calibration was conducted using gaseous scattering or monodisperse particles, the obtained calibration factors should be corrected to the values of poly-disperse AS particles with a volume-based geometric mean diameter of 300 nm. Otherwise, the uncertainties in the scattering measurements, especially at 532 nm, become larger.

The truncation correction factors estimated for commonly used commercial integrated nephelometers (e.g., model 3563, TSI) are from a few to 15 \% depending on the scattering Ångström exponent and RI of particles when measuring submicron particles (Anderson et al. 1998, Massoli et al. 2009, Müller et al. 2009; Bond et al. 2009). The truncation errors estimated in the present studies are comparable with the values at 375, 405, and 781 nm, but larger at 532 nm. Note that, if the truncation errors for the PASS-3 and PAX can be adequately corrected using scattering Ångström exponent (and possibly RI value), the uncertainties in the scattering measurements will be substantially reduced.

3.3. Calibrations for absorption measurements

a. Poly-disperse propane soot particles

To determine the calibration factors for absorption measurements \( (f_{\text{abs}}(\lambda)) \) based on the closure method, high concentrations of poly-disperse soot particles, were generated by the combustion of propane and introduced into the PASS-3 and PAX instruments (Fig. 1b). The observed absorption coefficients \( (b_{\text{abs}}^{\text{obs}}(\lambda)) \) were determined by subtracting the
averages of absorption coefficients obtained during the two blank measurement periods before and after the sampling period from those measured during the sampling period. The $b_{\text{abs}}^{\text{obs}}(\lambda)$ values were compared with the differences between extinction coefficients ($b_{\text{ext}}^{\text{obs}}(\lambda)$) determined using Eq. (5) and calibrated scattering coefficients ($f_{\text{sca}}(\lambda)b_{\text{sca}}^{\text{obs}}(\lambda)$) based on the equation (Lewis et al. 2008; Cross et al. 2010, SI):

$$b_{\text{ext}}^{\text{obs}}(\lambda) - f_{\text{sca}}(\lambda)b_{\text{sca}}^{\text{obs}}(\lambda) = f_{\text{abs,polySoot}}(\lambda)b_{\text{abs}}^{\text{obs}}(\lambda),$$

where $f_{\text{sca}}(\lambda)$ is the calibration factor for scattering measurements, and $f_{\text{abs,polySoot}}(\lambda)$ is the calibration factor for absorption measurements obtained using this method.

In the present study, the calibration factors for poly-disperse AS particles with $D_{V,AS}$ of 300 nm ($\sigma = 1.7$), $f_{\text{sca,polyAS}}(\lambda)$, were substituted for $f_{\text{sca}}(\lambda)$ in Eq. (8). The $f_{\text{sca,polyAS}}(\lambda)$ values at 375, 405, and 532 nm were estimated from $f_{\text{sca}}(\lambda)$, whereas the value at 781 nm was estimated from $f_{\text{sca,PSL}}(\lambda)$ by taking the truncation error into account and applying the simulation described in Section 3.2.d. During these calculations, both the $f_{\text{sca}}(\lambda)$ and $f_{\text{sca,PSL}}(\lambda)$ values determined within two days were used to minimize the influence of long term variations of the calibration factors, if any.

Three series of experimental trials were conducted using poly-disperse soot particles with volume-based geometric mean diameters ($D_{V,Soot}$) ranging between 395 and 541 nm ($\sigma = 1.55 \pm 0.02$, “Run 1”), 470 and 602 nm ($\sigma = 1.52 \pm 0.02$, “Run 2”), and 399 and 436 nm ($\sigma = 1.59 \pm 0.07$, “Run 3”). Figure 10 shows the correlation plots between the $b_{\text{ext}}^{\text{obs}}(\lambda) - f_{\text{sca}}(\lambda)$ and $b_{\text{abs}}^{\text{obs}}(\lambda)$ values of poly-disperse soot particles during “Run 1.” The slopes in Fig. 10 represent the $f_{\text{abs,polySoot}}(\lambda)$ values. A linear relationship between $b_{\text{ext}}^{\text{obs}}(\lambda) - f_{\text{sca}}(\lambda)b_{\text{sca}}^{\text{obs}}(\lambda)$ and $b_{\text{abs}}^{\text{obs}}(\lambda)$ was observed in all the data sets, with the exception of the 375 nm data in which $b_{\text{abs}}^{\text{obs}}$ was saturated above 55000 Mm$^{-1}$. This phenomenon was also observed with the 375 nm data for $b_{\text{abs}}^{\text{obs}}(375 \text{ nm}) > 55000 \text{ Mm}^{-1}$ during “Run 2,” although no data for which $b_{\text{abs}}^{\text{obs}}(375 \text{ nm}) > 55000 \text{ Mm}^{-1}$ were obtained during “Run 3.” Therefore, only values below 55000 Mm$^{-1}$ were used for the determination of $f_{\text{abs,polySoot}}(375 \text{ nm})$. The uncertainties for strongly light-absorbing particles with $D_{V,Soot}$ smaller than 700 nm estimated in Section 3.2.d (17, 10, 31, and 23 %, at $\lambda = 375$, 405, 532, and 781 nm, respectively) were adopted as the uncertainties associated with $f_{\text{sca}}(\lambda)$ during the soot particle measurements. The typical overall uncertainties in the determination of $f_{\text{abs,polySoot}}(\lambda)$ at $\lambda = 375$, 405, 532, and 781 nm were 6 %, 4 %, 8 %, and 6 %, respectively, by considering the uncertainties in the linear least-squares fitting of the three sets of experimental data, as well as in the laser path lengths and the $f_{\text{sca}}(\lambda)$ values (Table 1). The propagation of uncertainties from $f_{\text{sca}}(\lambda)$ to $f_{\text{abs,polySoot}}(\lambda)$ were relatively minimal because the ratios of scattering ($f_{\text{sca}}(\lambda)b_{\text{sca}}^{\text{obs}}(\lambda)$) to total extinction ($b_{\text{ext}}^{\text{obs}}(\lambda)$) values were small for the poly-disperse soot particles used in the calibrations, which are, on average, 0.22, 0.20, 0.18, and 0.12 at 375, 405, 532, and 781 nm, respectively.

To examine the contributions of particle size to the correction factors for absorption, 5 min average $f_{\text{sca,polySoot}}(\lambda)$ values were calculated and compared with $D_{V,Soot}$ values obtained by the SMPS at 5-min intervals. Typical detection limit values for 5 min

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Table 3. Typical truncation errors for scattering measurements$^{a)$

| $D_{V,Soot}$ (nm)$^{b)$ | RI$^{c)$ | Wavelength (nm) |
|-------------------------|---------|-----------------|
|                         | $n$     | 375  | 405  | 532  | 781  |
| 200–700                 | 1.35–1.65 | 0.0–0.01 | ± 4 % | ± 1 % | ± 13 % | ± 3 % |
| 200–700                 | 1.35–1.65 | 0.0–0.01 | ± 7 % | ± 2 % | ± 24 % | ± 7 % |
| 200–500                 | 1.7–2.0  | 0.7–1.2 | ± 5 % | ± 2 % | ± 16 % | ± 3 % |
| 200–700                 | 1.7–2.0  | 0.7–1.2 | ± 12 % | ± 5 % | ± 21 | ± 13 % |

a) Estimated from 5th and 95th percentiles of the $f_{\text{sca,polyAS}}(\lambda, D_{V,AS} = 300 \text{ nm})/f_{\text{sca,polyS}}(\lambda, D_{V,S})$ calculated using eq. (7), assuming that calibration for scattering measurements was conducted using the poly-disperse AS particles with $D_{V,AS}$ value of 300 nm in log-normal size distribution ($\sigma = 1.7$).

b) Range of $D_{V,Soot}$ values for poly-disperse sample particles in log-normal size distribution ($\sigma = 1.5$).

c) Assumed ranges of complex RI values of the sample particles (see text for detail).
average $b_{\text{ext}}(\lambda)$ data at $\lambda = 375$, 405, 532, and 781 nm during these trials were estimated at 1300, 1700, 1100, and 2200 Mm$^{-1}$ using the 2σ values of the laser power during the filtered air measurements and the drift between neighboring filtered air measurements. Only the $b_{\text{ext}}(\lambda)$ data, whose were more than three times those of the detection limit values, were applied during this analysis. Figure 11 shows the particle size dependencies of the 5 min average calibration factors for absorption measurements obtained using poly-disperse soot particles ($f_{\text{abs,polySoot}}(\lambda, D_{v,Soot})$) for “Runs 1 through 3,” normalized to the optimal $f_{\text{abs,polySoot}}(\lambda)$ values determined from the correlation plots between $b_{\text{ext}}^{\text{obs}}(\lambda) - f_{\text{sca}}(\lambda)b_{\text{sca}}^{\text{obs}}(\lambda)$ and $b_{\text{abs}}^{\text{obs}}(\lambda)$. The results demonstrated that no significant particle size dependency of $f_{\text{abs,polySoot}}(\lambda, D_{v,Soot})$ was observed at all four wavelengths within the particle size range examined.

Absorption Ångström exponents (AAE) are often used (Bond and Bergstrom 2006, Andreae and Gelencsér 2006, Moosmüller et al. 2011) to investigate wavelength dependence of absorption coefficients. The AAE value between $\lambda_1$ and $\lambda_2$ can be calculated using the equation:

$$\text{AAE}(\lambda_1, \lambda_2) = -\ln\left[\frac{b_{\text{abs}}^{\text{obs}}(\lambda_1)}{b_{\text{abs}}^{\text{obs}}(\lambda_2)}\right] / \ln(\lambda_1/\lambda_2).$$  (9)

AAE values close to 1 in the vicinity of visible wavelengths have been reported for fresh soot particles based on laboratory experiments and field observations (Bond and Bergstrom 2006; Andreae and Gelencsér 2006, and references therein). In the present study, propane soot particles were passed through a heater maintained at 300°C; thus, most organic and inorganic materials should have been removed prior to measurements (Kondo et al. 2009; Nakayama et al. 2014). Therefore, the observed soot particles were expected to have AAE values close to
1. Figure 12 shows the wavelength dependencies of the calibrated average absorption coefficients for poly-disperse propane soot particles for the trials in which data at all four wavelengths are available. The lines in Fig. 12 indicate the results of the least-squares fitting to the log–log plots. The AAE values for Runs 1, 2, and 3 were determined to be 0.93 ± 0.24, 1.14 ± 0.19, and 1.27 ± 0.19, respectively, from the slope of Fig. 12. Thus, the obtained AAE values are all close to 1 and are consistent within the uncertainties estimated based on the anticipated errors in both the fitting and the $f_{\text{abs,polySoot}}(\lambda)$ values. In addition, the fitting lines are in good agreement with all the other data, with the exception of the value obtained at $\lambda = 532$ and 781 nm for Run 1. The smaller AAE value associated with Run 1 implies that the $f_{\text{abs,polySoot}}(781 \text{ nm})$ value used for this trial was overestimated. If it is assumed that the AAE value does not change between the experimental runs, and assuming a linear relationship for the log–log plots, a larger uncertainty (of 11 %, compared to the typical uncertainties of 6 % otherwise applied), must be employed when determining the $f_{\text{abs,polySoot}}(781 \text{ nm})$ values for the Run 1 data. Except the results obtained at 781 nm, these results suggest that the actual calibration factors at each wavelength likely lie within the estimated accuracies. The estimated uncertainties for the absorption measurements using the PASS-3 and PAX (4–11 %) were comparable with those reported for other PAS instruments developed at NOAA (5–10 %) (Lack et al. 2006, 2012).

b. Absorption by NO$_2$ molecules

NO$_2$ molecules strongly absorb light below $< 600$ nm (Sander et al. 2011). The calibration factors for absorption at 375, 405, and 532 nm were determined by comparing the measured absorption coefficients...
(b_{abs,NO2}^{obs}(\lambda)) are the calibration factors for absorption measurements obtained using this method. The filtered air and filtered NO2/air mixture, prepared by diluting 201 ppm NO2/air with synthesized air in different dilution ratios, were alternately introduced to the PASS-3 and PAX every 4–6 min. The b_{abs,NO2}^{obs}(\lambda) values were determined from the differences in the observed absorption coefficients for air and NO2/air. Because the contribution of the difference between the Rayleigh scattering of air and NO2/air should be negligible at the concentrations used in the present study, the observed extinction coefficients can be directly compared with the observed absorption coefficients.

Figure 13 presents typical correlation plots between b_{ext}^{obs}(\lambda) and b_{abs}^{obs}(\lambda) for NO2 samples, in which linear relationships can be observed for all the three wavelengths. Although saturation was observed in the case of the 375 nm data with b_{abs}^{obs}(375 nm) > 55000 Mm^{-1} when measuring propane soot particles (Fig.10), this effect was not observed when measuring NO2 for b_{abs}^{obs}(375 nm) values as high as 64000 Mm^{-1}. The relative uncertainties of the f_{abs,NO2}(\lambda) values, determined from the slopes of the plots and considering the uncertainties in the linear least-squares fitting of the three sets of data as well as laser path lengths, were estimated to be 2% for all the three wavelengths (Table 1). The slopes of the black dashed lines in Fig. 13 indicate the f_{abs,polySoot}(\lambda) value determined on the same day. The obtained f_{abs,NO2}(\lambda) value is in good agreement with the value of f_{abs,polySoot}(\lambda) at 532 nm, but is significantly larger than the f_{abs,polySoot}(\lambda) values at 375 and 405 nm. On the basis of the three experimental data sets, the ratios of these calibration factors, f_{abs,polySoot}(\lambda)/f_{abs,NO2}(\lambda) at \lambda = 375, 405, and 532 nm were determined to be 0.52 ± 0.04, 0.64 ± 0.09, and 1.00 ± 0.08, respectively (Table 2).

The f_{abs,polySoot}(\lambda)/f_{abs,NO2}(\lambda) ratios at 375 and 405 nm were less than 1, which can be explained by assuming that a portion of the energy absorbed by NO2 molecules is applied to NO2 photolysis rather than heating the surrounding air, as was suggested in a previous study (Sharma et al. 2013). Although the theoretical wavelength threshold for NO2 dissociation is 397.8 nm, significant photo-dissociation still occurs at longer wavelength (up to ~420 nm), primarily due to the contributions of the internal vibrational and rotational energies of NO2 molecules (Roehl et al. 1994). The quantum yields of NO2 photolysis at 375 and 405 nm are reported to be 1.0 and 0.37, respectively (Sander et al. 2011). The 1-f_{abs,polySoot}(\lambda)/f_{abs,NO2}(\lambda) value at 405 nm (0.36 ± 0.09), which potentially represents the contributions of the photolysis to total light absorption, was in excellent agreement with the quantum yield value. The small 1-f_{abs,polySoot}(\lambda)/f_{abs,NO2}(\lambda) value at 375 nm (0.48 ± 0.04) compared to the unity quantum yield may be partly explained by the formation of internally and/or translationally excited NO and O(\text{3P}) in NO2 photolysis. Using their multi-wavelength photoacoustic nephelometer with supercontinuum laser as a light source, Sharma et al. (2013) found that b_{abs} values estimated around 417 nm from the photoacoustic signal were reduced by approximately 30–40 % compared to b_{ext} values determined using the Beer-Lambert law as well as b_{abs} estimated from the absorption cross section in the HITRAN database.
In contrast, no significant difference was observed in the vicinity of 542 nm. The results at 405 and 532 nm obtained in the present study for the PASS-3 are consistent with the results of Sharma et al. (2013). The observed agreement between $f_{\text{abs,NO}_2}(\lambda)$ and $f_{\text{abs,polySoot}}(\lambda)$ at 532 nm supports the reliability of the calibration method using poly-disperse soot particles.

Cross et al. (2010, SI) and Flowers et al. (2010b, SI) used low concentrations of NO$_2$ for the absolute calibrations of $b_{\text{abs}}$ at 405 and 532 nm. They reported that the results of the absolute calibration agreed with those of the closure calibrations at both the wavelengths. However, it is difficult to discuss the consistency between our result and their results at 405 nm because it is unclear that they considered the photolysis effect in their comparisons.

4. Summary

The performances of the PASS-3 (at $\lambda = 405, 532, 781$ nm) and PAX (at $\lambda = 375$ nm) to measure absorption and scattering coefficients, $b_{\text{abs}}(\lambda)$ and $b_{\text{sca}}(\lambda)$, have been characterized based on laboratory experiments. The results of Allan variance analyses of the $b_{\text{abs}}(\lambda)$ and $b_{\text{sca}}(\lambda)$ data suggest that frequent blank measurements are important for reducing the effect of signal drift, especially in the case of $b_{\text{sca}}(\lambda)$ at $\lambda = 405, 532$, and 781 nm. Typical detection limits for 10 min average $b_{\text{abs}}(\lambda)$ (and $b_{\text{sca}}(\lambda)$) values at 375, 405, 532, and 781 nm were estimated to be 1.3(1.7), 1.0(0.4), 1.9(0.5), and 0.7(0.8) Mm$^{-1}$, respectively.

The Rayleigh scattering of gaseous molecules, such as CO$_2$ and HFC-134a (except for $\lambda = 781$ nm), comparison with Mie theory for the scattering of mono-disperse PSL and AS particles with diameters ranging between 200 and 909 nm, and the closure method using high concentrations of poly-disperse AS particles were all assessed as calibration methods during scattering measurements. The calibration...
factors for scattering measurements, $f_{\text{sc}}(\lambda)$, at $\lambda = 375$, 405, and 781 nm determined using these methods are in good agreement with each other, within approximately 5 %, 5 %, and 10 % (with the exception of calibration at 781 nm using the Rayleigh scattering of gaseous molecules), suggesting that these methods can be reasonably used. In contrast, a large particle size dependency was observed for the $f_{\text{sc}}(532 \text{ nm})$ values, possibly because of a combination of the differences in the polarization states of the lasers relative to the scattering planes and the large truncation angle. By taking into account the effective truncation angles estimated from the observed particle size dependency as well as the uncertainties in the determination of the calibration factors, the typical overall uncertainties of the $f_{\text{sc}}(\lambda)$ values when measuring non- or weakly light-absorbing particles with $D_{v,S}$ values less than 500(700) nm were estimated to be 9(12) %, 6(7) %, 23(34) %, and 13(17) %, at $\lambda = 375$, 405, 532, and 781 nm, respectively, while the uncertainties for strongly light-absorbing particles were estimated to be 10(17) %, 7(10) %, 26(31) %, and 13(23) %, at the same wavelengths.

High concentrations of poly-disperse propane soot particles and NO$_2$ molecules were also examined as potential calibration methods for absorption measurements. It was found that the calibration factors ($f_{\text{abs}}(\lambda)$) for absorption measurements at 375, 405, 532, and 781 nm can be determined with typical overall uncertainties of 6 %, 4 %, 8 %, and 11 %, respectively, using poly-disperse propane soot particles. Moreover, it was found that the $f_{\text{abs}}(\lambda)$ values obtained using the poly-disperse propane soot particles at 375 and 405 nm were 48 ± 4 and 36 ± 9 % smaller than those determined by the light absorption of NO$_2$ molecules, respectively, likely due to the influence of NO$_2$ photolysis. These results suggest that the photolysis effect should be taken into account when light absorption by NO$_2$ is used for the calibration of absorption measurements at 375 and 405 nm. In contrast, the $f_{\text{abs}}(532 \text{ nm})$ determined by the light absorption of NO$_2$ molecules is in good agreement with that determined using the poly-disperse propane soot particles (within 8 %), suggesting that the absorption measurements of the PASS-3 at 532 nm can be calibrated using these methods. Although we examined only two instruments, the procedures described in the present study may also be useful for the calibrations of other nephelometers and photoacoustic spectrometers.

Acknowledgments

We would like to thank N. Toriyama, R. Fujimori, H. Sasago (Nagoya Univ.), H. Fujii (Kyoto Univ.), K. Kita (Ibaraki Univ.), and J. W. Walker (Droplet Measurement Technologies, Inc.) for their technical supports and fruitful discussions. This work was partly supported by the Global Environment Research Fund of the Japanese Ministry of the Environment (RF-1008), the Grant-in-Aid for Scientific Research (KAKENHI 25701001, 26281007) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), the Steel-Foundation for Environmental Protection Technology, and by the Toyoaki Scholarship Foundation. The authors have no conflict of interest relevant to the content of this article.

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