Method to measure the size-resolved real part of aerosol refractive index

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Abstract

Knowledge on the refractive index of ambient aerosol can help reduce the uncertainties in estimating aerosol radiative forcing. A new method is proposed to retrieve the size-resolved real part of RI (RRI). Main principle of deriving the RRI is measuring the scattering intensity by single particle soot photometer of size-selected aerosol. This method is validated by a series of calibration experiments using the components of known RI. The retrieved size-resolved RRI cover a wide range from 200nm to 450nm with uncertainty less than 0.02. Measurements of the size resolved real part of the aerosol refractive index can improve the understanding of the aerosol radiative effects.

1 Introduction

Aerosols exert significant influence on the earth energy budget by scattering and absorbing radiation (Ramanathan and Carmichael, 2008). There still remain great uncertainties when estimating the aerosol effective radiative forcing (RF) (Ghan and Schwartz, 2007) and an accurate estimation of the aerosol optical properties can help reduce the RF variations. The optical properties of the ambient aerosol particles are determined by their particle size and complex refractive index (RI, m=n+k*i) (Bohren and Huffman, 2007; Levoni et al., 1997). Despite that the ambient aerosol particle size distribution can be measured with high accuracy (Wiedensohler et al., 2012), an accurate measurement of the ambient aerosol RI remains challenging. The RI is also widely used in remote sensing (Redemann et al., 2000; Dubovik, 2002; Zhao et al., 2017) and atmospheric modelling (Ghan and Schwartz, 2007; Kuang et al., 2015) because the aerosol single scattering albedo (SSA) and aerosol scattering phase function are highly related with the RI. At the same time, a small uncertainty in the real part of the RI (RRI) can lead to great uncertainties when estimating the aerosol RF. Zarzana et al. (2014) finds that a variation of 0.003 in RRI can lead to uncertainties of 1% in RF for non-absorbing ammonium sulfate particles. Moise et al. (2015) estimates that the RF will increase 12% when the RRI varies from 1.4 to 1.5. Valenzuela et al. (2018) also reports an uncertainty of 7% with the uncertainties
of RRI of 0.1 in RRI. Therefore, it is pressing that the uncertainties of the RI be reduced when estimating the RF.

Many methods were proposed to derive the RRI. The RRI can be estimated by linear volume average of the known aerosol chemical components by

$$ n = \sum f_i n_i $$

(1)

where $f_i$ and $n_i$ is the volume fraction and known partial refractive index of $i$th component (Wex et al., 2002; Hand and Kreidenweis, 2002; Hanel, 1968; Liu and Daum, 2008). The aerosol RRI can also be calculated by partial molar refraction approach (Stelson, 1990; Hu et al., 2012) which is essentially consistent with the linear volume method (Liu and Daum, 2008). The ambient aerosol RRI can be derived by synthetically using the radiative transfer calculations and the ground-based solar extinction and scattering measurements (Wendisch and Hoyningen-Huene, 1994, 1992). Sorooshian et al. (2008) developed a method to measure the aerosol RRI based on the differential mobility analyzer (DMA) and an optical particle counters. The RRI is retrieved from the known particle size from the DMA and the aerosol scattering intensity from the Optical Particle Counter (OPC) for aerosol particles larger than 500nm. The Scanning Mobility Particle Sizer (SMPS) and OPC is used in combination to derive the RRI by aligning the particle size distributions in the instrument overlap regions (Hand and Kreidenweis, 2002; Vratolis et al., 2018). The aerosol effective RRI is also retrieved by applying Mie scattering theory to the aerosol particle number size distribution, aerosol bulk scattering coefficient and aerosol absorbing coefficient data (Cai et al., 2011; Liu and Daum, 2000). Spindler et al. (2007) retrieved the aerosol RRI value by using the cavity ring-down spectroscopy to measuring the scattering and absorbing properties of bulk aerosols. Eidhammer et al. (2008) measured the light scattering at different angles and retrieved the RRI. Similarly, the aerosol RRI is retrieved by measuring the aerosol phase function (Barkey et al., 2007). Recently, a method by using the single particle mass spectrometry is proposed to measure the aerosol RRI (Zhang et al., 2015). At the same time, aerosol time-of-flight mass spectrometer is proved to be capable of measuring the aerosol RRI (Moffet et al., 2008). The aerosol RRI can also be retrieved from the Mie spectroscopy by using the optical tweezers in the laboratory (Shepherd et al., 2018).

Up to now, there is no information in the literature of the size-resolved ambient aerosol RRI over the diameter range between 200nm and 500nm where the aerosol scattering coefficients contributes to the total scattering coefficients most (Tao et al., 2017; Kuang et al., 2018). All the instruments
mentioned above can only measure the total equivalent aerosol RRI or aerosol RRI at a given diameter. However, many studies show that aerosol of different diameter shares different properties such as shape (Zhang et al., 2016; Peng et al., 2016), density (Qiao et al., 2018), aerosol hygroscopicity (Wang et al., 2017) and most importantly, the chemical components (Liu et al., 2014; Hu et al., 2012). Thus, there might be significant variations in the aerosol RRI for aerosols of different diameter because the aerosol RRI is highly related to the aerosol density (Liu and Daum, 2008) and chemical components (Stelson, 1990). On the other way round, information of the size-resolved aerosol RRI can help to study the chemical information and the aging process of aerosols among different diameters. Therefore, measurement of the size-resolved aerosol RRI is necessary.

In this study, a novel method is proposed to measure the size-resolved ambient aerosol RRI by using a DMA in tandem with a single particle soot photometer (SP2). The principle of the system is using the SP2 to measure the scattering properties of size-selected aerosols. Knowing the aerosol diameter and corresponding scattering intensity, the size-resolved aerosol RRI can be retrieved based on the Mie scattering theory. This proposed method can measure the ambient aerosol RRI over a wide size range with high accuracy. The measurement system is employed in a field campaign in the North China Plain and the corresponding results are further discussed.

The structure of this manuscript is as follows: section 2 provides the instruments setup and details of the instrument. The method of retrieving the size-resolved aerosol RRI is given in section 3. Section 4 shows the discussions about the uncertainties of the proposed method and field measurements results of the size-resolved aerosol RRI. Conclusions come at the last part.

### 2 Instrument

#### 2.1 Instrument Setup

The instrument setup is schematically shown in fig. 1(a). Firstly, the dried sample aerosols are guided to a X-ray soft diffusion charger and then lead to a DMA (Model 3081, TSI, USA). The quasi-monodisperse aerosols that pass though the DMA at a given diameter are then drawn into a SP2 to measure the aerosol scattering properties with a flow ratio of 0.12 lpm and a condensation particle counter (CPC, Model 3776, TSI, USA) to count the aerosol number concentration with a flow ratio of 0.28 lpm respectively. Thus, the sample flow \( Q_s \) of the DMA is 0.4 lpm. Accordingly, the sheath flow \( Q_{sh} \) of the DMA is 4 lpm. The DMA is set to scan the aerosols diameter from 12.3 to 697 nm.
over a period of 285s and repeats after a pause of 15s. Thus, the combination of DMA, CPC and SP2 can provide the aerosol PNSD and size-resolved RRI every 5 minutes.

On 8th, June, 2018, the measurement system was employed at the filed measurement of AERONET station of BEIJING_PKU (N39°59′, E116°18′) to test the reliability of retrieving the ambient size-resolved RRI. This measurement site locates on the north west of the city of Beijing, China and is about 1.8 km north of the Zhongguancun, Haidian District, which is one of the busiest areas in Beijing. It is surrounded by two main streets: Zhongguancun North Street to the west and Chengfu Road to the south. This site can provide representative information of the urban roadside aerosols (Zhao et al., 2018).

2.2 DMA

When a voltage (V) is applied to the DMA, only a narrow size range of aerosol particles, with the same electrical mobility ($Z_p$) can pass through the DMA (Knutson and Whitby, 1975). The $Z_p$ is expressed as:

$$Z_p = \frac{Q_{sh} \ln(r_1/r_2)}{2nV_L}$$  \hspace{1cm} (2)

where $Q_{sh}$ is the sheath flow rate; $r_1$ is the outer radius of annular space and $r_2$ is the inner radius of the annular space. The transfer function refers to the probability that a particle with a certain electrical mobility can pass through the DMA. For a given $V$, the transfer function is triangular-shaped, with the peaking value of 100% and a half width (HW) of

$$\Delta Z_p = Z_p \frac{Q_a}{Q_{sh}}$$  \hspace{1cm} (3).

The aerosol $Z_p$, which is highly related to the aerosols diameter ($D_p$) and the number of elementary charges on the particle ($n$), is defined as:

$$Z_p = \frac{n e C(D_p)}{3\pi \mu D_p}$$  \hspace{1cm} (4)

where $e$ is the elementary charge; $\mu$ is the gas viscosity coefficient, $C(D_p)$ is the Cunningham slip correction that is defined by:

$$C = 1 + \frac{2\tau}{D_p} \left(1.142 + 0.558e^{-0.999D_p/\tau}\right)$$  \hspace{1cm} (5)

where $\tau$ is the gas mean free path.

Based on the discussion above, the aerosols that pass through the DMA with the same $Z_p$, can have different $D_p$ and different elementary charges.
2.3 SP2

The SP2 is a widely used instrument that can measure the optical properties of every single particle. The measurement principle and instrumental setup of the SP2 have been discussed in detail previously (Stephens et al., 2003; Schwarz et al., 2006) and will be briefly described here. When the sample aerosol particles pass through the continuous Nd:YAG laser beam at 1064nm with power about 1 mW/cm², eight sensors distributed at four directions are synchronously detecting the emitted or scattered light by using avalanche photo-detector (APD) at different angles (45° and 135°). For each direction, the two APDs sample the same signal with different sensitivities to get a wider measurement range. The low gain channels are less sensitive to the measured signal and can be used to measure the stronger signal of larger particles. In accordance, the high gain channels are more sensitive to the measured signal, and can be used to measure the weaker signal of smaller particles. The optical head of the SP2 is shown schematically in fig. 1(b).

In this study, we utilize signals from four channels of the SP2: two of them measure the scattering signals and another two measure the incandescent light between 350 nm and 800 nm. The peak height (H) of the incandescence signals is used to infer whether the sampled aerosol contains the black carbon (BC). If the H of the incandescence signal is larger than 500, the sample aerosol contains the BC and the scattering signals should deviate from the signals of pure scattering aerosol. Those sample aerosols are ruled out when dealing with the aerosol scattering signals.

3 Methodology

3.1 Scattering strength measured by the SP2

From fig. 1(b), the APDs of the SP2 receive signals that were scattered by the sampled aerosols from the directions at 45° and 135°. Thus, the scattering intensity (S) measured by the APD can be expressed as:

$$ S = C \cdot I_0 \cdot \sigma \cdot (PF_{45^\circ} + PF_{135^\circ}) $$

where $I_0$ is the laser’s intensity; $\sigma$ is the scattering coefficient of the sampled aerosol, $PF_{45^\circ}$ and $PF_{135^\circ}$ are scattering phase function at 45° and 135° respectively of the sampled aerosols; and C is constant that is determined by the distance from the aerosol to the APD and the area of the APD. The scattering intensity of the aerosol is recorded as the H of the scattering signals by SP2. Therefore, the SP2 can be used as a powerful tool to measure the scattering signals of the sampled aerosol and the
influence of the BC on the aerosol scattering properties can be avoided. Based on the Mie scattering
theory, $\sigma$, $PF_{45^\circ}$ and $PF_{135^\circ}$ are determined by the size and RRI of the aerosol.

The amount of scattering signals from the sample aerosol varies with the diameter and RRI of the
aerosol (Bohren and Huffman, 2007). The scattering intensity at different aerosol diameter and RRI is
calculated based on equation (6) and shown in fig. 2. The $C$ is assumed to be 1 here. From fig. 2, we
can see that the aerosol scattering intensity increases homogeneously with the increasing aerosol RRI
at a given $D_p$, which makes it possible to retrieve the aerosol RRI when the $D_p$ and the scattering
intensity are known.

Bridging the scattering $H$ values measured by the SP2 scattering channel and the scattering
intensity defined by equation 6 is achieved by calibrating the SP2 with ammonium sulfate. The
instrument setup of the calibration procedure is the same as that described in section 2.2.1. The
diameters of the aerosols passing through the DMA are manually changed from 100 to 450nm with a
step of 10nm. For each diameter, the scattering $H$ value and incandescence signal of every particle are
analyzed. When calibrating, there is no aerosol whose incandescence signal exceeds 1000, which
means that the SP2 works stably and the incandescence signal channel can well distinguish the BC
containing aerosols.

After the calibration, the size-resolved RRI can be retrieved with known aerosol diameter selected
by DMA and the corresponding aerosol scattering $H$ values measured by SP2.

3.2 Multiple Charging

Fig. S2 gives the aerosols scattering $H$ probability distribution under different aerosol diameter.

For each diameter, the distributions of the scattering $H$ may have more than one mode for both the high
gain and low gain channels. The following discussions would give explanation about the multiple
mode distributions of $H$.

For each mode, the number of recorded aerosol particles at a given $H$ is fit by the log-normal
distribution function:

$$N(H) = \frac{N_0}{\sqrt{2\pi}\sigma_\log} \cdot \exp \left[ \frac{(\log(H) - \log(H_0))^2}{2\sigma_\log^2} \right]$$  \hspace{1cm} (7)

Where $\sigma_\log$ is the geometric standard deviation; $H_0$ is the geometric standard mean $H$ and $N_0$ is the
number concentrations for a peak mode. The geometric standard deviation is highly related to the half
width of the transfer function (equation 3) and the $H_0$ is discussed below in detail.
The $H_0$ values of each mode at different diameters are labeled with different markers in fig. 2. The $\sigma_l$ is fitted to be a small range at $1.182 \pm 0.02$ for different mode and different aerosol diameter. In the following discussion, we conclude that the different PH$_0$ values in fig. 3 represent that the aerosols are charged with different number of elementary charges. Based on the Mie scattering theory (Bohren and Huffman, 2007), the scattering intensity increases with increasing $D_p$, which imply that the $H_0$ should increase with the increment of $D_p$. Thus, the black square markers in fig.2 represent the aerosols that are singly charged. At the same time, the relationships between the $H_0$ and $D_p$ can be interpolated. Other colored markers represent that the aerosols have more than one charge. We calculated the corresponding diameter of the aerosols that share the same $Z_p$ but different charges at the given $D_p$ by the DMA ($\bar{D_p}$). Then the corresponding $H_0$ at $\bar{D_p}$ are calculated and shown in dashed line in fig.2. From fig.2, the calculated $H_0$ shows good consistence with the measured $H_0$.

From the discussion above, we conclude that the SP2 detect those ammonium sulfate aerosols with the diameter larger than 160nm. However, the ambient aerosol RRI is always lower than that of ammonium sulfate (Liu and Daum, 2008), thus the lower detecting limit of the ambient scattering aerosols should be larger than 160nm. The measured $H_0$ of the SP2 scattering low gain channel signals are shown in fig. S2. From fig. S2, the same results can be deduced as those of the high gain channel signals.

Fig. 4(a) gives the relationships between the calculated scattering intensity and the SP2 aerosol scattering $H$ at different diameter. When calculating the scattering intensity, the RRI value of ammonium sulfate is set to be 1.521. We can see that the aerosol scattering intensity shows good consistence with the peak height ($R^2=0.9992$).

Furthermore, the RRI of the scattering aerosol at a given diameter can be retrieved using the corresponding scattering $H$.

3.3 Validation of the calibration

Ammonium chloride is used to validate the method of deriving the RRI from SP2. The RRI value of ammonium chloride is 1.642. The scattering $H$ of the ammonium chloride under different diameters are measured and analyzed. Fig. 4(b) shows the comparison between the measured scattering high gain peak height and the theoretical peak height at different aerosols diameter. Results show that the measured peak height and the calculated ones are well correlated with $R^2=0.9994$, which means that
the DMA and SP2 can be used to derived the aerosol RRI with high accuracy.

Fig. S3 gives the corresponding results of the scattering low gain channel. In fig. S3, the relationship between the aerosol scattering peak height of the low gain channel and the scattering strength is determined. At the same time, the comparison between the measured peak height and the calculated peak height shows good consistence too.

4 Results and Discussion

4.1 Field Measurements

Figure 5 shows the measured average probability distribution of the ambient size-resolved RRI and the measured mean PNSD. From fig. 5, we can see that the derived RRI is 1.46 ± 0.02 and doesn’t vary significantly with diameter between 199 nm and 436 nm. The measured aerosol PNSD during the measurement has a maximum of 26400 #/cm³ at 107 nm. Based on the measured PNSD and the measured RRI, the size distribution of the scattering coefficient is calculated based on the Mie scattering theory. The results in fig. 5 show that the measured RRI diameter range covers most of the aerosol that contributes significantly to the aerosol scattering properties. Thus, the derived size-resolved RRI of this range is representative of the ambient aerosols scattering properties.

4.2 Uncertainty analysis

The factors that influence the accuracy of retrieving RRI include the aerosols scattering H measured by SP and the aerosol diameter selected by DMA.

The uncertainties of the selected diameter by DMA is well characterized based on equation 2 and 3. The uncertainties from the DMA transfer function can be avoided by fitting the scattering H using the log-normal distribution function. However, the uncertainties of the measured H from the SP2 remain unknown. The HW of the transfer function is 0.1 times the scanning diameter, which means that the geometric standard deviation of the aerosol PNSD selected by the DMA is estimated to be 1.102. At the same time, the measured geometric standard deviation of the measured H mode by SP2 is 1.182. Thus, the geometric standard deviation of the measured H from the SP2 is estimated to be 1.073, whose corresponding uncertainties is 6.8%.

The uncertainties of the retrieved RRI to the variations in the measured H are analyzed using the Mie scattering theory and the corresponding results are shown in fig. 6. The variations in RRI increase with the increment of RRI but decrease with the increment of the Dp. For most ambient aerosols, the
RRI ranges from 1.4 to 1.5 and corresponds to a variation in RRI of 0.015.

Table 1 lists the retrieved ammonium chloride RRI under different diameter. The absolute difference between the retrieved RRI and theoretical values is always smaller than 0.02 regardless of the particle diameter, which means that the measured RRI is in line with the theoretical one. Thus, we conclude that the uncertainty of the retrieved RRI is within 0.02.

5 Conclusions

Knowledge on the microphysical properties of ambient aerosol is import for better evaluating their radiative forcing. The aerosol RRI is a key factor that determines the aerosol scattering properties.

In this study, a new method to measure the ambient aerosol RRI is developed by synthetically using a DMA in tandem with a SP2. This method can continuously measure the size-resolved RRI over a wide range between 198 nm and 426 nm with an accuracy of 0.02. At the same time, it is free from the influence of the BC containing aerosols.

The basic principle of measuring the size-resolved RRI is to select the aerosols at a certain diameter by the DMA and measure the corresponding scattering intensity by the SP2. The relationship between the aerosols scattering intensity and the peak height of the scattering signal channels are determined by calibrating the SP2 using ammonium sulfate (RRI=1.521).

The method is validated by using the ammonium chloride with the RRI of 1.642 as sample aerosol and the corresponding derived size-resolved RRI is 1.642 ± 0.02.

This instrument is employed at a field measurement at the AERONET PKU stating, the size-resolved RRI of the ambient aerosols is 1.46 and doesn’t show significant variation among the diameter. The corresponding aerosol diameter range, which can be detected by SP2 to derive the RRI, covers most of the aerosol scattering. Thus, the derived size-resolved RRI of this range can be used as a good representative of the ambient aerosols scattering properties.

Data availability. The measurement data involved in this study are available upon request to the authors.
Author contributions. Gang Zhao and Chunsheng Zhao designed the experiments; Gang Zhao and Weilun Zhao conducted the measurements; Chunsheng Zhao and Gang Zhao discussed the results and wrote the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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Figure 1. (a) Schematic of the measurement system. (b) Diagram of SP2 Chamber.
Figure 2. The distribution of the aerosols scattering strength at different Dp and different RRI.
Figure 3. The geometric mean peak height for different diameters of the high gain. The markers gives the measured values and the dotted line shows the theoretically calculated value. Different colors represent the different number of elementary charges.
Figure 4. (a) the relationship between the scattering peak height from the SP2 high gain scattering channel using the ammonia sulfate and (b) the comparison between the measured scattering peak height from SP2 high gain scattering channel using the ammonia chloride and the calculated scattering peak height using the Mie scattering theory. Different colors represents the results at different diameter.
Figure 5. The measured probability of the size-resolved RRI (the filled color), the measured mean PNSD (the full line) and the mean scattering size distribution (the dotted line).
Figure 6. The variation in RRI for different kinds of aerosols that have different diameters and different RRI.
Table 1. The retrieved RRI and the absolute difference between the retrieved RRI and the theoretical RRI for different ammonia chloride diameter.

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<tr>
<th>Dp(nm)</th>
<th>160</th>
<th>170</th>
<th>180</th>
<th>190</th>
<th>200</th>
<th>210</th>
<th>220</th>
<th>230</th>
<th>240</th>
<th>250</th>
<th>260</th>
<th>270</th>
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<td>RRI</td>
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<td>1.650</td>
<td>1.651</td>
<td>1.643</td>
<td>1.656</td>
<td>1.645</td>
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<td>1.634</td>
<td>1.626</td>
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<tr>
<td>Difference</td>
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<td>0.009</td>
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<td>0.008</td>
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