Analysis of the Mixing State of Airborne Particles using a Tandem Combination of Laser-induced Fluorescence and Incandescence Techniques

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Abstract

We have developed a novel system for real-time measurement of the mixing state of aerosol particles using a tandem combination of laser-induced fluorescence (LIF) and incandescence (LII) techniques. The tandem analysis system comprises two chambers connected in series; particles are analyzed with LIF in the first chamber and LII in the second chamber. We analyzed identical particles using the two methods as judged by the time intervals of detection in the two chambers. This system provides information on the mixing state of fluorescent compounds and black carbon in single particles. Ground-based measurements of ambient particles were performed in Tokyo during October 26–29, 2012. We analyzed 43,881 particles with optical diameters greater than 0.4 μm . The fractions of particles with fluorescent composition, black carbon, and both were 14.2%, 2.3%, and 0.3%, respectively, which indicates the presence of internal mixtures of black carbon and fluorescent species in the ambient air for the first time. Mixtures of biological materials (estimated from fluorescence patterns) and black carbon were also detected. The fluorescence patterns of single particles with and without black carbon were almost identical, suggesting that particles with both black carbon and fluorescent composition might be formed by aggregation in ambient air.

Keywords

Black carbon; Fluorescent particles; Mixing state; Single particles

1. Introduction

Atmospheric aerosols play a significant role not only in solar radiation, through scattering and absorption, but also in agricultural and public health (Finlayson-Pitts & Pitts, 2000). Aerosol particles are made up of a wide variety of components including carbonaceous materials such as black carbon (BC), which has light-absorbing properties, and organic carbon (OC), which has light-scattering characteristics. These components comprise major fractions of atmospheric aerosol particles (Bond et al., 2013). These varieties of atmospheric aerosols influence climate change by heating and cooling the atmosphere. It is important to understand the optical and chemical properties of aerosols to adequately estimate their present and future influence on radiative budgets.

The mixing state of single particles also significantly influences their lifetime, hygroscopicity, optical properties, and cloud nucleating properties in the atmosphere. For example, coatings on biogenic particles, which are of particular interest because of their high ice nucleating abilities and their significant contribution to ambient OC quantities (Despres et al., 2012; Huffman et al., 2013; Möhler et al., 2007; Murray et al., 2012; Tobo et al., 2013), could lead to changes in their characteristics, such as protection of cell viability and high efficiency as cloud condensation nuclei (CCN) (Huffman et al., 2012). On the other hand, enhanced absorption of radiation by coatings has

been reported for BC particles; furthermore, coated particles are efficiently removed by wet deposition compared with non-coated BC particles (Jacobson 2001; McMeeking et al., 2011; Riemer et al., 2010; Weingartner 1997; Zhang et al., 2008). Even if particles are individually pure when initially generated, there are multiple processes that take place in the atmosphere that convert an external mixture to an internal mixture, leading to complexities in estimating the influence of BC properties on climate. Although internally mixed BC particles have been studied (Adachi & Buseck 2008; Cappa et al., 2012; Liu et al., 2013; Moteki et al., 2007; Moteki & Kondo 2007; Shiraiwa et al 2007; Shiraiwa et al., 2008; Ueda et al., 2011), there are still large uncertainties relating to estimating the influence of BC properties on climate due to a lack of detailed measurements of mixing states (Cappa et al., 2012; Möhler et al., 2007).

There are a few established techniques for measuring the mixing state of BC particles. Off-line analyses using electron microscopes are suitable for determining the size, composition, and mixing state of single particles (Abel et al., 2003; Adachi & Buseck 2008; Chen et al., 2006; Takami et al., 2013; Ueda et al., 2011). However, this technique has limitations, such as the difficulty of analyzing volatile samples and low quantitative capabilities. To quantify the chemical, physical, and optical characteristics of BC-containing particles, direct and on-line measurements are required.

Several types of instruments have been developed for real-time measurement. Single particle aerosol mass spectrometry (AMS) with laser ionization provides details of chemical composition including carbon (Gard et al 1997; Murphy & Thomson 1995; Narukawa et al., 2007) but cannot provide quantitative information on BC. Single particle soot photometers (SP2) based on laser-induced incandescence can provide quantitative information on external/internal mixtures of BC and coating thickness (Laborde et al., 2013; McMeeking et al., 2011; Moteki & Kondo 2007; Moteki et al., 2009, 2011; Schwarz et al., 2006, 2010; Shiraiwa et al., 2007, 2008). Although this instrument can measure the coating thickness of BC particles based on the analysis of light scattering and particle incandescence, it cannot directly measure the chemical composition of the coating. Recently, an instrument combining AMS with SP2 was developed, which can measure the chemical composition of particles containing BC (Cappa et al., 2012; Miyakawa et al., 2014; Onasch et al., 2012). While this combined instrument can provide chemical information on BC coatings, it does not provide information of mixing states of individual particles. To obtain more information on the mixing states of particles, it would be better to combine other types of techniques with BC detection.

In this study, we developed a real-time tandem measurement system for suspended single particles by combining the laser-induced fluorescence and incandescence techniques. The fluorescence detection technique has the advantage of being non-destructive, allowing sequential analysis of the same particles. The fluorescence of suspended single particles has been used to identify and classify certain types of organic/biological particles (Pan et al., 2003, 2007, 2009; Pinnick et al., 1995, 1998, 2004; Taketani et al 2013; Kaye et al., 2000, 2005; Kiselev et al., 2013; Toprak, & Schnaiter 2013; O'Connor et al., 2014; Saaria et al., 2014). OC could be directly emitted into the atmosphere from both anthropogenic and natural sources or formed via conversion of volatile precursors. Pöhlker et al., (2012) summarized the fluorescence properties of various types of aerosol particle compositions, including both biological and non-biological compounds. Several instruments have reported real-time monitoring of fluorescence from single particles. Waveband Integrated Bioaerosol Sensor (WIBS) is capable of measuring light-induced fluorescence with two different excitation wavelengths at 280 nm and 370 nm (Kaye et al 2000, 2005). The ultraviolet aerodynamic particle sizer (UV-APS, TSI, Inc.) (Brosseau et al., 2000) uses a pulsed ultraviolet laser (Nd:YAG) at 355 nm for excitation and measures fluorescence in the 420–575 nm wavelength range. These instruments focus on detection of biological fluorophores (tryptophan, NADPH, and/or

riboflavin) with various criteria.⁴⁹ Therefore, on-line fluorescence detection from ambient single particles is of interest as it allows quantification of biological particles.

By detecting BC and/or biological particles based on incandescence and fluorescence signals from single particles, new insights into the mixing of BC and natural sources could be obtained. These mixed particles would have different CCN properties from original ones. Estimating the properties of these particles in the atmosphere would reduce uncertainties in the estimation of the effects of BC properties on climate. Toward this goal, this study aims to build an instrument for the detection of fluorescence and incandescence from the same single particles and to characterize the types of OC fluorophores present as well as the internal/external mixing states of BC particles to understand their optical properties and mixing processes.

2. Experimental

Figure 1 is a schematic diagram of the system used in this study for detection of laser-induced fluorescence (LIF) and incandescence (LII) signals from single particles. Two modules used to detect LIF and LII were combined in this experiment. Each of LIF and LII detection module has been reported previously (Moteki et al., 2011; Miyakawa et al., 2014b; Taketani

et al., 2013). **Figure 2** shows a schematic diagram of LIF module. On the LIF detection module, a 660 nm continuous wave (CW) laser (KLA-STECH, DL-660) with an average power of 50 mW and a 263 nm pulsed UV laser (Photonics industries international: Model DC150-263s) were employed to detect and excite single particles, respectively. The pulse width and energy for the 263 nm UV laser were 50 ns and 15 μ J/pulse, respectively. The two laser beams intersected at the center of the optical chamber, approximately ~3 mm below the exit of the particle injector nozzle and ~3 mm above the outlet nozzle. The particle stream, surrounded by coaxial sheath airflow, passed vertically through the intersection point of the two laser beams. The particles introduced into the optical chamber were first detected by scattering of the 660 nm CW laser beam in the LIF chamber. The light scattered from individual particles at 660 nm was detected using a photomultiplier tube (PMT) (Hamamatsu, R5926) through the optical band pass filter (Semrock, FF01-660/13-25). Particle-size calibration was conducted using polystyrene latex (PSL) particles (Duke Scientific and JSR) of known sizes. The detectable particle size (D_p) range was 0.4–2.5 μ m. Timings to trigger the pulsed UV laser and to initiate data acquisition were controlled by a delay/pulse generator (Stanford Research Systems, DG645) driven by the detection of a scattering signal exceeding a set threshold. The irradiation of the pulsed 263 nm laser was delayed by 1.2 μ s after the generation of the trigger pulse. Fluorescence from individual particles in the 335–379 nm (Channel 1), 420–500 nm

(Channel 2), and 500–600 nm (Channel 3) bands was selected using three optical filters (Semrock, FF01-357/44-25, FF02-460/80-25, and FF01-550/88-25) and then simultaneously detected by three PMTs (Hamamatsu, R374).

In order to select fluorescent particles in each wavelength region using the LIF module, thresholds of $\langle S_i \rangle + 3\sigma_i$ (i = Channel 1, Channel 2, and Channel 3) were employed.⁴² The average background signal for each wavelength region $\langle S_i \rangle$ and its standard deviation σ_i were measured in the absence of particles by measuring filtered ambient air while operating the UV laser in internal trigger mode. The fluorescent particles were defined as those producing fluorescence signals exceeding $\langle S_i \rangle + 3\sigma_i$ at one or more channels.

On the LII detection module, we employed same module to Figure 1 in Moteki et al., (2011). An intracavity Nd:YVO₄ laser, operating at 1064 nm and with a diameter beam of ~1 mm, resonated below the injected nozzle. The alignment of the laser and injected nozzle on the LII module was almost identical to that on the LIF module. The particle stream, surrounded by coaxial sheath airflow, passed vertically through the laser beam. Particles introduced into the optical chamber were detected by scattering of the 1064 nm laser. Scattering light intensity was detected using two Si-avalanche photodiodes (Hamamatsu, S8890-30) installed in mutually orthogonal

directions. Laser-induced incandescence (420–550 nm) from the particles was measured using two PMTs (Hamamatsu, H6779) through the optical band-pass filters installed against the photodiodes. Particle-size calibration was performed using PSL particles of known sizes in the range of 0.15–2.0 μm (Duke Scientific). Particle-size calibration of BC (D_{BC}) was also conducted based on measurement of LII signal intensities from fullerene particles. Particles in the range of 0.15–0.6 μm generated by an atomizer were selected using a differential mobility analyzer (TSI, DMA3080) and then introduced to the LII module instrument. During calibration of LII signals, we ensured that no fluorescence signals from the fullerene particles were detected.

After measurement of LIF, the particles were led to the outlet nozzle, whose entrance was located 5 mm below the injector nozzle, and then introduced to the LII detection module using a straight tube (0.2 mm internal diameter and 20 cm length). The flow rate in the LIF and LII modules was controlled using mass flow controllers. The total injected flow rate to the optical chamber in the LIF module was 0.3 L/min, of which 0.25 L/min was the filtered sheath air. Approximately 43% (0.13 L/min) of the total injected flow to the LIF module was introduced to the LII module, with additional filtered sheath air of 0.8 L/min. Exhaust flow was also maintained at 1.0 L/min. To keep the flow rates balanced, purge airflow of 0.07 L/min was introduced into the LII optical chamber.

3. Results and Discussion

3.1 Identification of detections of the same single particle in the tandem system

To identify detections of the same particles by the LIF and LII modules, we employed the time intervals between light scattering detections by the two modules. We characterized the time intervals for the detection of scattered light of PSL particles of known size. During this experiment, particle concentrations were kept low such that the arrival rates of the particles were as low as 1 Hz to facilitate individual particle identification.

The histogram in **Figure 3** indicates the time intervals recorded with several sizes of PSL particles. We employed a mixed suspension consisting of 0.4, 0.5, 0.7, and 1.0 μm PSL particles to identify detections of the same particle by both modules. For each particle size, approximately 70% of particles were detected by the LII module between 0.25 and 0.7 s after they were detected by the LIF module. The estimated time interval between detections based on the inner diameter, length, and volumetric flow rate of the tube connecting the LIF and LII detection modules was approximately 0.35 s, indicating good agreement with the values measured in this study. Therefore, we assumed that particles detected by the LII detection module between 0.25 and 0.7 s after

detection by the LIF module were identical. Scattering light intensities in both modules were also employed to crosscheck the same-particle detection. It should be noted that scattering light intensity for BC-containing particles should be lower when measured by the LII detection module than when measured by the LIF detection module due to evaporation of their coatings.

We also checked the performance of the tandem detection system with LIF and LII signals using a mixture solution consisting of fullerene and tryptophan. This could generate particles including (i) only tryptophan, (ii) only fullerene, or (iii) both of them. It is well known that fluorescence produced from tryptophan particles upon excitation at 263 nm is strong at 300–400 nm, producing signals in Channel 1 (Taketani et al., 2013). As expected, all three types of particles were successfully classified, suggesting that this module could be used to similarly categorize atmospheric fluorescence materials and black carbon on the single-particle basis.

3.2 Measurement of ambient particles

3.2.1 Size distribution of ambient particles

Ambient particle measurement was performed at the University of Tokyo (35.66°N, 139.66°E) during October 26–29, 2012 using the tandem instrument system. The University of Tokyo is located approximately 10 km west of the Tokyo Bay coastline near the southeastern edge

of the Kanto Plain. Ambient air was collected at 20 m above ground level and introduced into the instrument through a diffusion dryer using a conductive tube, aided by supporting bypass flow to minimize deposition of particles. Also, the sampled air was diluted with filtered air to keep the arrival rate of particles low (approx. $< 2\text{Hz}$). Over the course of this experiment, approximately 620,000 particles were detected. Of these, 43,881 particles in the range of $0.4 - 2.5\text{ }\mu\text{m}$ were employed for analysis. Smaller-sized particles ($D_p < 0.4\text{ }\mu\text{m}$) were so abundant that they were difficult to identify individually. Therefore, in this study we focused on analysis of $> 0.4\text{ }\mu\text{m}$ particles (D_p).

The system can identify four classes of particles (Table 1): (i) those with a detected fluorescence signal but no incandescence signal (defined as “FL”), (ii) those with an incandescence signal but no fluorescence signal (defined as “BC”), (iii) those with both fluorescence and incandescence signals (defined as “MIX”), and (iv) those with no fluorescence or incandescence signals (defined as “NON”). The numbers of “FL”, “BC”, and “MIX” particles were 6213 (14.2%), 1010 (2.3%), and 122 (0.3%), respectively, indicating that 16.8% of the particles greater than $0.4\text{ }\mu\text{m}$ contained fluorescent materials and/or black carbon. This is the first report on classification for fluorescence and incandescence from individual particles and to indicate the presence of “MIX”

particles in the atmosphere. **Figure 4** presents the size distribution of the classified particles measured based on scattering light intensity by the LIF detection module. “NON” and “BC” particles populated the smaller size range, whereas “FL” and “MIX” particles resided in the larger size range, suggesting a tendency for fluorescent materials are favorably found in a larger size range, when compared with “BC” particles.

3.2.2 Mixing state of BC

During the measurement period, LII signals (for both “BC” and “MIX” particles) were detected for 1232 particles. **Figure 5** shows the ratios of particle size (D_p) estimated by scattering light intensity in the LIF instrument to BC size (D_{BC}) estimated based on LII signals for “BC” and “MIX” particles. This result was applied for comparative shell/core analysis using the two instruments. Shell/core analysis is generally achieved with the SP2 instrument, where the leading edge of the time profile of scattering light was only employed (leading edge-only (LEO) fit) to avoid the influence of the evaporation of the particles in the detection process (Moteki et al., 2009; Gao et al., 2007). In contrast, our tandem analysis system allowed full use of the scattering data measured on the LIF instrument determining D_p , to be combined with the incandescence signals determining D_{BC} ; shell/core analysis could thus be carried out more reliably without any fitting. In

Figure 5, the D_p/D_{BC} ratios ranged from 0.7–5. Ratios less than 1 were observed, indicating that D_p was smaller than D_{BC} . This likely corresponds to cases where uncoated BC particles were detected due to a difference in the respective refractive indices of uncoated BC and PSL particles. BC particles with ratios larger than 2 should be densely coated, whereas those with ratios near 1 should be thinly coated or uncoated. In this study, over 50% of particles were present in the internal mixture state of “BC” particles, while almost all particles were present in the internal mixture of “MIX” particles in the $D_p > 0.4\mu\text{m}$. Shiraiwa et al., (2007) reported the mixing state of black carbon in the Tokyo area and estimated the fraction of the internal mixture of BC particles with a diameter of 180 nm based on the delay between occurrence of peaks of light scattering and LII signals using an SP2 instrument. The results indicated that 6–50% of particles were present in the internal mixture. This result may seem inconsistent with our results. However, this could be explained by the difference in the detected particle sizes. In our system, analyzed D_p were $>0.4\mu\text{m}$. Normally, the dominant D_{BC} is in the range of 0.1–0.2 μm (Shiraiwa et al., 2007), suggesting that our analyzed D_p is larger than normal D_{BC} . Particles detected based on incandescence signals should therefore be present in the internal mixture state within our system. Over 90% of “MIX” particles were present in the internal mixture state, as determined by comparison of D_p with D_{BC} . This result would reasonably indicate that there are different compounds within the same particle.

3.2.3 Fluorescence from BC-containing and non-BC-containing particles

Fluorescent signals were detected from 6335 particles (14.5%) (sum of “FL” and “MIX” particles) during the measurement period. The fractions reported by previous studies for detection of ambient fluorescent particles using ~270 nm laser were 5–50%, 25.3%, and 26% for diameters of >3 μm (Pan et al., 2007), 1–10 μm (Pan et al., 2009), and >0.7 μm (Taketai et al., 2013), respectively. The proportion of the combined “FL” and “MIX” particles to the total number of detected particles in this study was relatively lower. This may be partially caused by different size ranges in the analyses. As shown in **Figure 4**, the size distributions of “FL” and “MIX” particles exhibited similar tendencies toward larger size ranges, suggesting that inclusion of small particles down to 0.4 μm in this study could reduce the overall fluorescent fraction. For particles with sizes > 0.7 μm , the combined proportion of “FL” and “MIX” particles was 34%. This analysis suggested that fluorescent-material-containing particles make a significant contribution to ambient particles.

In this study, fluorescence signals from individual particles were detected with three channels within 330–370 nm, 420–500 nm, and 500–600 nm ranges. The fluorescent particles are subdivided into seven different categories, namely, FL1, FL2, FL3, FL12, FL23, FL13, and FL123, in which fluorescence signal(s) were detected at the designated channel number(s). The fractions of

individual categories to the total number of “FL” and “MIX” particles are listed in **Table 2**. First, we regard FL123 as corresponding to fluorescent biological aerosol particles (FBAPs) based on the likely co-presence of tryptophan and NADH (nicotinamide-adenine dinucleotide), which should emit fluorescence in Channel 1 (300–400 nm) and Channels 2 and 3 (400–600 nm). The contributions of FBAPs to total “FL” and “MIX” particles were only 3% and 2%, respectively, indicating that over 95% of “FL” and “MIX” particles were not categorized as FBAPs. The remaining part might be polycyclic aromatic hydrocarbons (PAHs), considering their ubiquity in ambient particles of the Tokyo region(Okuda et al.,2004), or humic-like substances (HULIS) and secondary organic aerosols (SOAs) (Pöhlker et al., 2012). More studies are needed to reliably relate each category to specific compound types.

The contribution of FBAPs to total detected particles in the measurement period was approximately 0.4 %. This is near the lower end of the range (0.26–42%) reported by a previous study⁴⁶ using the flash-lamp-induced fluorescence technique. These different levels might arise from different local emission rates; the rate in Tokyo under more urban conditions might be lower. It should be noted that the fractions of FBAPs to total “FL” and “MIX” particles had size dependence; they increased to 17% in the 1–2 μm size range (**Figure 6**). In **Table 2**, the relative

contributions from the seven FL categories to the “FL” and “MIX” particles were almost identical, suggesting that particles with BC and fluorescent composition might be formed by aggregation in ambient air. Although the contribution of internal mixture particles of BC and of biological materials to total detected particles was less than 0.01%, this is the first report of the presence of single particles in the ambient atmosphere in which BC and biological species are internally mixed.

To summarize this study, we reported the development of an instrument using laser-induced fluorescence and incandescence techniques to specify single particle mixing states. We first demonstrated, using model particles, that the same particles could be diagnosed on LIF and LII modules when the arrival rates of particles were carefully controlled by dilution. Then, we performed ambient measurements in Tokyo to explore single particles containing BC and/or fluorescence species. We analyzed 43,881 particles with diameters larger than 0.4 μm . Individual particles with fluorescent composition, BC, and both were successfully detected. This is the first report on the presence of particles in which BC and fluorescent species are internally mixed in ambient air. From particles' fluorescence properties, internal mixtures of biological materials and BC were also suggested. From the similarity of the fluorescence patterns of “FL” and “MIX” particles, the mixing process between fluorescent materials and BC in Tokyo ambient air may be

aggregation agglutination. The measurement system employed in this study can provide new insights on the mixing states of biological materials and BC.

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Figure captions

Figure 1. Schematic diagram of the instrument used in this study for detection of laser-induced fluorescence (LIF) and incandescence (LII) from single particles. Instruments for detection of LIF and LII are connected in series. Single particles are delivered to the LII detection instrument after analysis by the LIF detection instrument.

Figure 2. Schematic diagram of LIF detection module. The particles pass vertically through the intersection point of the two laser beams. After measurement of LIF, the particles introduced to the LII detection module. ADC: analog to digital converter; PMT: photomultiplier tube; PC: personal computer.

Figure 3. Histogram of time differences between the detection of light scattering at the LII instrument and that at the LIF instrument for 0.4, 0.5, 0.6, and 1.0 μm PSL particles.

Figure 4. Size distribution of particles obtained during the measurement period, classified into four particle categories. Particle sizes were measured based on scattering light intensity at the LIF detection instrument (D_p). The total number of analyzed particles $>0.4 \mu\text{m}$ was 43,811.

Figure 5. Normalized frequency of D_p/D_{BC} . D_{BC} was estimated based on the laser-induced incandescence signal. The solid line denotes the particles detected only by LII. The gray line denotes particles for which both FL and LII signals were detected.

Figure 6. Size dependence contribution of detected FBAPs in FL and MIX particles. The gray area represents the contribution of FBAPs.

Figure 1. Schematic diagram of the instrument used in this study for detection of laser-induced fluorescence (LIF) and incandescence (LII) from single particles. Instruments for detection of LIF and LII are connected in series. Single particles are delivered to the LII detection instrument after analysis on the LIF detection instrument. The flow rates of sample air, sheath air and pump out in the LIF detection instrument are 0.05, 0.25, and 0.17 L/min, respectively, whereas those of sheath air, purge air, and pump out are 0.8, 0.07, and 1.0 L/min, respectively.

Figure 2. Schematic diagram of LIF detection module. The particles pass vertically through the intersection point of the two laser beams. After measurement of LIF, the particles introduced to the LII detection module. ADC: analog to digital converter; PMT: photomultiplier tube; PC: personal computer.

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Figure 6. Size dependence of detected FBAPs contribution in “FL” and “MIX” particles. The gray area represents the contribution of FBAPs.

Table 1 Summary of the four classes of particles categorized by this system.

	LIF module	LII module
"FL"	<i>X</i>	-
"BC"	-	<i>X</i>
"MIX"	<i>X</i>	<i>X</i>
"NON"	-	-

X: signal detected

Table 2 Summary of quantitative contributions to the total number of detected FL and MIX

particles measured by the tandem analysis system using the LIF and LII techniques.

	FL particles	MIX particles
FL1	1%	0%
FL2	36%	30%
FL3	18%	24%
FL12	1%	4%
FL23	41%	39%
FL13	0%	0%
FL123	3%	2%

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