Measurements of Ammonium and Sodium salt Aerosol Particles Using a Laser-ionization Single-particle Aerosol Mass Spectrometer

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Using a laser-ionization single-particle aerosol mass spectrometer (LISPA-MS), mass spectra of ammonium and sodium salt particles were obtained. In the negative-ion mass spectra, HSO_4^-, and NO_2^- and NO_3^- were dominant ions for $(NH_4)_2SO_4$ and NH_4NO_3 particles, respectively, while ions with sodium were also dominant for Na_2SO_4 and $NaNO_3$ particles. The chemical compositions of such salt aerosol particles can be inferred from the distribution of ions in those negative-ion mass spectra obtained using the LISPA-MS.

Understanding the chemical compositions of aerosol particles in the atmosphere is important for evaluating the effect of the particles on visibility, climate, and human health. The compositions of the particles have been measured by off-line techniques, which have provided important information about the compositions. However, the off-line techniques tend to have sampling artifacts.[1] In addition, filters and impactors only provide the compositions of an ensemble of the particles, and thus it is difficult to measure individual particles.

For the last decade, real-time aerosol mass spectrometry has been remarkably developed. Those instruments can size, count, and mass-analyze individual particles with high time-resolution. Reviews of real-time aerosol mass spectrometry are available in the literature.[2,3] We have recently developed a laser-ionization single-particle aerosol mass spectrometer (LISPA-MS) for real-time single-particle measurements. Using the LISPA-MS, apparent changes in the compositions of Asian dust particles were captured,[4] and measurements of dicarboxylic acid particles and secondary organic aerosol particles revealed that those negative-ion mass spectra provide information about the compositions of those particles.[5]

Here, we arrange and present standard mass spectra of ammonium and sodium salt aerosol particles, obtained using the LISPA-MS. Such standard mass spectra are necessary to understand the compositions of ambient aerosol particles. The purpose of this study is to evaluate whether the compositions of such salt aerosol particles can be identified from those mass spectra obtained using the LISPA-MS.

The details of the LISPA-MS are described in the literature.[5] Briefly, aerosol particles are focused into a narrow particle beam by an aerodynamic lens.[6] After exiting the lens, the particle beam is transmitted into the ion source region. For detecting the particles introduced into the ion source region, a continuous-wave laser beam, produced by a frequency-doubled Nd:YAG laser at 532 nm, crosses the particle beam. The scattered light from the individual particles at 532 nm is detected by a photomultiplier tube (PMT). The intensity of the scattered light is approximately proportional to the particle size, and is utilized for roughly determining the particle size.

The signals from the PMT are amplified, and those above a selectable threshold level trigger a pulsed laser beam. A pulsed KrF excimer laser at 248 nm is used as a light source for the desorption/ionization of particles. The resultant ions are measured by a time-of-flight mass spectrometer with a microchannel plate (MCP) detector. The signals from the MCP are amplified linearly, digitized, and recorded as mass spectra with a high time-resolution (less than 2 s). Either the positive- or negative-ion mass spectra are obtained by changing the voltage polarity of the instrument.

Standard compounds, $(NH_4)_2SO_4$, NH_4NO_3, Na_2SO_4, $NaNO_3$, NaF, and NaCl (>98% purity, Wako Pure Chemical Industries) were used without further purification. Synthetic sea-salt, which was commercially available from Nihon Pharmaceutical Corporation, was also used. Each compound was dissolved in distilled water ($\approx$1%). For generating aerosol particles, the solutions were atomized using a compressed air nebulizer ($\approx$3 L min^{-1}). The generated particles passed through a homebuilt diffusion drier, which was filled with silica gel. The resultant dried particles were directly introduced to the LISPA-MS. The mass spectra described in this study were obtained by averaging a minimum of 50 spectra from 50 single particles.

Figure 1 shows the negative-ion mass spectra of $(NH_4)_2SO_4$ and NH_4NO_3 particles. For the $(NH_4)_2SO_4$ particle, the dominant ion was HSO_4^- at m/z 97. For the NH_4NO_3 particle, those were NO_2^- and NO_3^- at m/z 46 and 62, respectively. Those ions were also observed in the negative-ion spectra of Asian dust particles using the LISPA-MS[4] and an aerosol time-of-flight mass spectrometer,[7] which is a real-time aerosol mass spectrometer based on desorption/ionization by the 266-nm light from an Nd:YAG laser. In the positive-ion spectra of those particles, none of the dominant ions were observed.

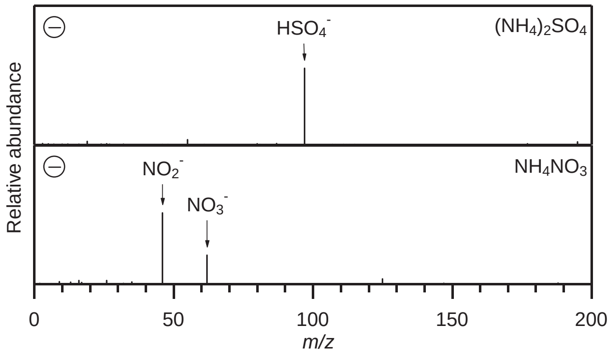

Figure 1. Averaged negative-ion mass spectra of $(NH_4)_2SO_4$ and NH_4NO_3 particles.

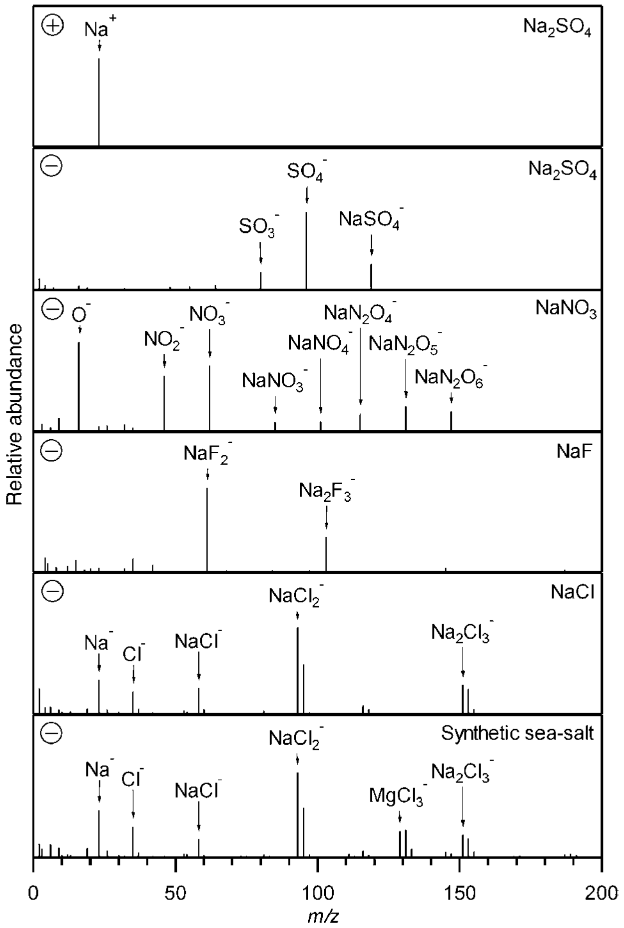

Figure 2. Averaged positive-ion mass spectrum of Na_2SO_4 particle, and negative-ion mass spectra of Na_2SO_4, $NaNO_3$, NaF, NaCl, and synthetic sea-salt particles.

As shown in Figure 2, Na^+ at m/z 23 was a single strong ion in the positive-ion spectrum of the Na_2SO_4 particle. The positive-ion spectra of other sodium salt (including synthetic sea-salt) particles were similar to that of the Na_2SO_4 particle.

The negative-ion spectra of Na_2SO_4, $NaNO_3$, NaF, NaCl, and synthetic sea salt particles are also shown in Figure 2. The negative-ion spectra of the sodium salt (Na_2SO_4 and $NaNO_3$) particles were obviously different from those of the ammonium salt ($(NH_4)_2SO_4$ and NH_4NO_3) particles. For the Na_2SO_4 particle, dominant ions were not only SO_4^- but also SO_3^- and $NaSO_4^-$ at m/z 80 and 119, respectively. Similar results were obtained for the Na_2SO_4 particle using RSMS (rapid single-particle mass spectrometry),[8] which is a real-time aerosol mass spectrometer based on desorption/ionization of particles by the 248-nm light from an excimer laser as well. For the $NaNO_3$ particle, dominant ions were not only NO_2^- and NO_3^- but also $NaNO_3^-$, $NaNO_4^-$, $NaN_2O_4^-$, $NaN_2O_5^-$, and $NaN_2O_6^-$ at m/z 85, 101, 115, 131, and 147, respectively. Oxygen ion (O^-) was also a dominant ion for the $NaNO_3$ particle. Therefore, it is possible to distinguish ammonium and sodium salt particles in the atmosphere by examining the negative-ion spectra of ambient aerosol particles, because the ions with sodium were only observed from the sodium salt particles, as shown in Figure 2.

For the NaF and NaCl particles, dominant ions in those negative-ion spectra included ions with sodium as well, as shown in Figure 2. For the NaF particle, dominant ions were NaF_2^- and $Na_2F_3^-$ at m/z 61 and 103, respectively. For the NaCl particle, those were Na^-, Cl^-, $NaCl^-$, $NaCl_2^-$, and $Na_2Cl_3^-$ at m/z 23, 35, 58, 93, and 151, respectively. Because chlorine has two isotopes (^{35}Cl and ^{37}Cl), some twin peaks were observed for the NaCl particle. Some characteristic ions of the NaCl particle were also observed for ambient particles using the LISPA-MS[4] and for NaCl particle using the RSMS.[9]

Distinctive ions ($MgCl_3^-$ at m/z 129 and 131), which were not observed for the NaCl particle, were observed in the negative-ion spectrum of synthetic sea salt particle, as shown in Figure 2, because the synthetic sea salt solution contained $MgCl_2$ (about $2\,g\,L^{-1}$). Although, the synthetic sea salt solution also contained Na_2SO_4 (about $1\,g\,L^{-1}$) and NaF (about $1\,mg\,L^{-1}$), the ions derived from Na_2SO_4 and NaF were not observed as significant peaks for synthetic sea salt particle. Aged sea salt particles in the atmosphere can contain Na_2SO_4 and $NaNO_3$ via reactions with sulfuric and nitric acids, which are major anthropogenic pollutants in the atmosphere. The characteristic ions of the $NaNO_3$ particle were observed for NaCl particle exposed to nitric acid and ammonia vapor using RSMS,[9] and for marine aerosols using laser microprobe mass analysis, which is an off-line technique.[10] Therefore, searching the characteristic ions of $NaNO_3$ in the negative-ion spectra of ambient sea salt particles makes it possible to identify fresh and aged sea salt particles.[11,12]

In conclusion, using the LISPA-MS, the chemical compositions of ammonium and sodium salt aerosol particles can be more easily identified from the distribution of ions in the negative-ion spectra than the positive-ion spectra, because the ions with sodium were only observed from the negative-ion spectra of the sodium salt particles. The real-time single-particle analysis by the LISPA-MS is useful to examine ambient aerosol particles.

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References

1 X. Q. Zhang, P. H. McMurry, *Atmos. Environ.* **1992**, *26A*, 3305.
2 D. G. Nash, T. Baer, M. V. Johnston, *Int. J. Mass Spectrom.* **2006**, *258*, 2.
3 D. M. Murphy, *Mass Spectrom. Rev.* **2007**, *26*, 150.
4 J. Matsumoto, K. Takahashi, Y. Matsumi, A. Yabushita, A. Shimizu, I. Matsui, N. Sugimoto, *Geophys. Res. Lett.* **2006**, *33*, L07816.
5 M. Narukawa, Y. Matsumi, J. Matsumoto, K. Takahashi, A. Yabushita, K. Sato, T. Imamura, *Anal. Sci.* **2007**, *23*, 507.
6 X. Zhang, K. A. Smith, D. R. Worsnop, J. Jimenez, J. T. Jayne, C. E. Kolb, *Aerosol Sci. Technol.* **2002**, *36*, 617.
7 R. C. Sullivan, S. A. Guazzotti, D. A. Sodeman, K. A. Prather, *Atmos. Chem. Phys.* **2007**, *7*, 1213.
8 K. R. Neubauer, S. T. Sum, M. V. Johnston, A. S. Wexler, *J. Geophys. Res.* **1996**, *101*, 18701.
9 P. G. Carson, K. R. Neubauer, M. V. Johnston, A. S. Wexler, *J. Aerosol Sci.* **1995**, *26*, 535.
10 F. Bruynseels, R. Van Grieken, *Atmos. Environ.* **1985**, *19*, 1969.
11 D. M. Murphy, D. S. Thomson, A. M. Middlebrook, M. E. Schein, *J. Geophys. Res.* **1998**, *103*, 16485.
12 E. E. Gard, M. J. Kleeman, D. S. Gross, L. S. Hughes, J. O. Allen, B. D. Morrical, D. P. Fergenson, T. Dienes, M. E. Gälli, R. J. Johnson, G. R. Cass, K. A. Prather, *Science* **1998**, *279*, 1184.