Characterization of aerosol sources with potential post-emission particle-size transitions

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論 文 の 内 容 の 要 旨

論文題目　　　Characterization of aerosol sources with potential post-emission
　　　　　　　particle-size transitions
　　　　　　　（排出後に粒子径変化の可能性を持つエアロゾル発生源の特性評価）

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Particle size of aerosol plays an important role in its aerodynamic, optical and chemical properties which govern effects on health and environment. Generally, smaller particles tend to penetrate deeper into the respiratory tract where their adverse effect on health is stronger. From environmental point of view particle size, however, represents a more complex problem, where larger particles show stronger interaction with radiation and small particles down to the sub-micrometer range can reach higher number concentrations acting as cloud condensation nuclei. Transitions in particle size during or after emission can be caused by processes like particles breaking up or absorbing gaseous substances and are dependent on the particles nature and the way in which they are generated. This work aims at the characterization of aerosols with high potential of particle size changes during or after emission. Aerosols with high potential of particle size changes during or after emission have been characterized for two types of aerosol particles. Particles originating from biogenic sources which can be broken up during emission or re-suspension processes and aerosols produced by pyrotechnics which show a dramatic change in optical properties through hygroscopic growth at high humidity conditions have been investigated.

Proteins are found in almost all biogenic materials including aerosols and are also triggers for most allergic reactions. Amino acid composition of protein content in aerosol samples was analyzed for different size fractions in order to identify contributing biogenic sources. Ambient aerosol samples were collected on the rooftop of the three-story Komaba Communication Plaza building at the Komaba campus of the University of Tokyo near Shibuya. Sampling times from about one to two weeks were chosen to cover a variety of weather and pollution episodes during a sampling period of almost a whole year ranging from February 2009 to January 2010, providing insight into seasonal variations of protein content in urban ambient aerosol. Source samples were collected as bulk or dust samples and directly hydrolyzed or were sampled on filters with the high volume aerosol sampler at the respective aerosol source or from re-suspended dust samples. Bulk samples included leaves which play a role in re-suspended road dusts, and skin, scale and hair samples, which can accumulate in house dusts. Source samples which were directly sampled with the high-volume aerosol sampler from the aerosol sources included kitchen aerosols (exhaust) and pollen emissions from blooming Japanese cedar of the Kumodōri variety. For analysis, they were pulverized by grinding in a mortar or filing with a needle file except for the skin scrapings which were already sufficiently powdered at the time of collection. Analysis of constituent amino acids allowed source apportionment in a receptor-model to be applied using the

multi-dimensional amino acid profiles found in ambient aerosols and aerosol sources.

A high volume Anderson-type cascade impactor was used as aerosol sampler to be able to collect sufficient amounts of protein material from ambient aerosols for size-resolved analysis. Four impactor stages and a backup filter divided the aerosol into five size fractions of >7µm, 7-3.3µm, 3.3-2.0 µm, 2.0-1.1µm and <1.1µm. For sampling aerosol sources with high loads of large particles, which would break through the impactor stages, a cyclone separator was constructed in order to separate the particle fraction larger than 7 µm efficiently. A vacuum hydrolysis method with 6M HCl was applied to the aerosol samples collected on Pallflex Tissuquartz™ filters after which the solution was separated from the filter material and dried by rotary evaporation. Amino acids were then dissolved in distilled water and were reacted with 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (available as AccQ-Tag™ reagent kit from Waters, Milford) to yield fluorescent derivates. Derivatized amino acids were analyzed by high performance liquid chromatography (HPLC) with fluorescense and UV/VIS detectors in two gradient programs at 5.1pH to yield amino acid patterns. Quantification was performed with norleucine as internal standard.

Amino acids measured from hydrolysate of ambient aerosol were detected in the range of less than one to several tens of ng·m^{-3}. Figure 1 shows the amino acid concentrations for each size fraction in a sample collected in November 2009. When converted to protein content, that makes up around 1.5% of ambient aerosol mass and is present in the same order of magnitude in all size fractions including particles <1.1µm in diameter. Aerosols near sources occur at much higher concentrations of around 1000µg· m^{-1} with around 2-4% protein content. In samples prepared from bulk samples, combined amino acid made up to 66% of total mass. Amino acid profiles measured from the different aerosol sources displayed enough dissimilarity to be used in a chemical mass balance (CMB) model published by the US Envitonmental Protection Agency.

Source apportionment which was carried out separately for each size fraction showed, that some sources like kitchen aerosols and pollen are detected throughout the whole year, while others like leaves and house-dust related particles are present only occasionally. Kitchen aerosols which showed relatively high abundance of small particles <1.1µm in source samples were predominantly found in large fractions of >3.3µm or >7µm depending on the season, indicating growth of particles after emission. Pollen-like patterns were found in large particles >7µm and especially at high abundance for smaller fractions <1.1µm which shows, that pollen sources must also produce a significant amount of small particles either at the emission source, as analysis of source samples verify, or during re-suspension processes from e.g., roads.
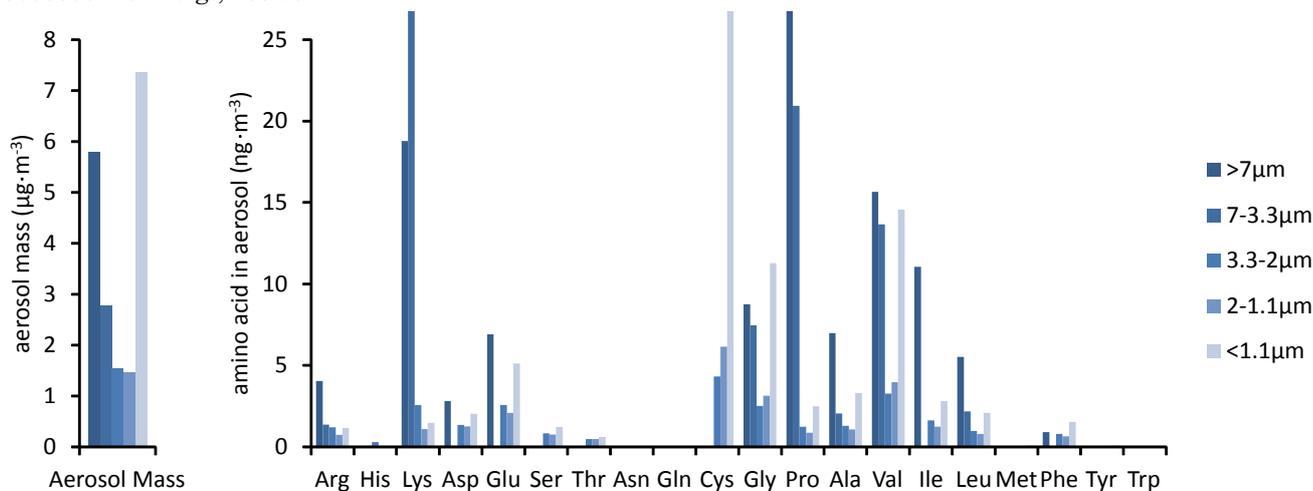

Figure 1. Amino acids profiles measured from hydrolysate of ambient aerosol samples (November 5th - 19th).

The second type of aerosol particles investigated in the course of this work is aerosols emitted by

pyrotechnics. Previous works mainly concentrate on inorganic pollutants like heavy metals and inorganic ions, which have also been found at elevated levels in ambient aerosols during periods in which pyrotechnics are used. Here, the main interest is the effect of those aerosol emissions on visibility. Aerosol particles emitted by pyrotechnics are reported in the range of a few 100 nm in diameter. At high humidity conditions, however these particles can grow in size by absorption of water vapors in which case they scatter light much more efficiently according to the MIE scattering theory. These aerosols can produce thick clouds and obscure firework scenes. Such conditions are often encountered during the warm season when most of the firework festivals are held, especially in the Asian region.

Visible aerosol development after combustion of pyrotechnics in ambient air of arbitrary relative humidity was simulated in chamber experiments. Gas and particulate emissions are quickly diluted and cooled in air and undergo nucleation, coagulation and condensation processes. In this work, a measurement method using a small-scale combustion-chamber is proposed for quantification of visual obstruction by aerosol. This allows comparison of visible aerosol development after combustion of different types of pyrotechnic compositions over a range of controlled humidity conditions. Humidity characteristics of the following three types of pyrotechnic compositions were measured in preliminary experiments: Ammonium and potassium perchlorate (AP, KP) based compositions which are widely used as a basis for pyrotechnic compositions (Kosanke & Kosanke, 2004). Black powder (BP) which is still the predominant composition used as lifting charge, although it is well known for producing relatively dense aerosols. Further measurements were performed with AP based compositions in order to investigate the effect of various additives commonly used to achieve color, light and sound effects in pyrotechnics.

A chamber consisting of a cubic steel frame covered with acrylic sheets at the top and three sides, a stainless steel floor and a detachable soft PVC sheet at the front side was constructed. Room temperature was controlled by air conditioning. After initial temperature and humidity conditions were applied with a humidity controllable type air-conditioning unit (Apiste PAU300S-HC), the chamber was sealed. Combustion experiments were mainly performed at 20°C, but measurements which were also made at 30°C and for BP also at 10°C showed that aerosol opacity is virtually independent of temperature. Samples were placed on a combustion platform in the middle of the chamber and ignited electrically using a nichrome wire embedded in a ceramic tube. Air in the chamber was mixed using an electric fan so that a sufficiently homogeneous aerosol was yielded within about ten seconds after combustion. Light extinction measurements were performed with two sets of laser sensors (Keyence LX-100, λ=670nm) installed at different transmission distances. A MIE scattering particle size distribution analyzer was modified to allow measurements of aerosols.

Measurements of light transmission showed that light attenuation (A) and maximum scattering (attenuation) coefficient (b) occurring in an experiment (b_{max}) show linear dependencies to transmission length (l) and sample mass (m), respectively, even at high humidity settings (90%RH).

$$A = \log_{10}\left(\frac{I_0}{I}\right) = b \cdot l = b^* \cdot m \cdot l \tag{1}$$

Based on Equation (1) analogous to the Lambert- Beer law they can be converted to sample-mass specific scattering coefficient values (b^*; b^*_{max}) which are independent of the two parameters. Only for scattering coefficients greater than 2m^{-1}, this relation shows a non-linear behavior and mass-specific scattering coefficients decrease. Processes like coagulation and deposition, which are dependent on aerosol concentration and particle size, reduce particle numbers and thereby overall light scattering.

After combustion under high humidity conditions, particle growth (mode diameter: ○) was observed for 4 to 6 minutes and b^* in phase I and reached a maximum after which b^* declined slowly (Figure 2a.). Continuing growth in mode diameter of the aerosol observed in phase II suggest coagulation processes, but increased losses due to particle deposition on wall and fan surfaces also possible with larger particles. Under dry conditions up to 50%RH, b^* reached it's a nearly constant value immediately after initial fluctuations due to fan circulation. The maximum of b^* denoted as b^*_{max} can be interpreted as the

maximum visual obscurrance the aerosol can achieve under the pre-set ambient conditions. A relative humidity curve of b^*_{max} accurately describes the visual impact over the whole humidity range in a single chart and can be used to choose the best performing low smoke products at given humidity conditions.

In order to analyze the effect of additives a base composition had to be chosen, which produces the least possible amount of visible aerosols while allowing the additives to fully develop their performance. KP based composites, which most of the classic firework compositions belong to, as well as BP have shown to produce high levels of visible aerosols throughout the whole humidity range and were not suitable for this kind of measurement. AP, on the other hand, shows excellent low-smoke performance below around 85%RH and also works very well with all of the common additives.

Mg, Magnalium (~50% alloy of Mg-Al), Al and Ti were analyzed as spark and sound generating metal additives and $Ba(NO_3)_2$ (green), CuO (blue), NaC_2O_4 (oxalate, yellow) and $SrCO_3$ (red), were analyzed as coloring agents and showed almost linear dependence on additive amount at a relative humidity of 80% (Figure 2b. for metals). For coloring agents, the slopes for each of the colorant metals which are converted to their respective volatile chlorides even coincided when plotted as metal chloride mass. Only Ba for the coloring agents and Al and Ti for the light effect metals showed low smoke development.
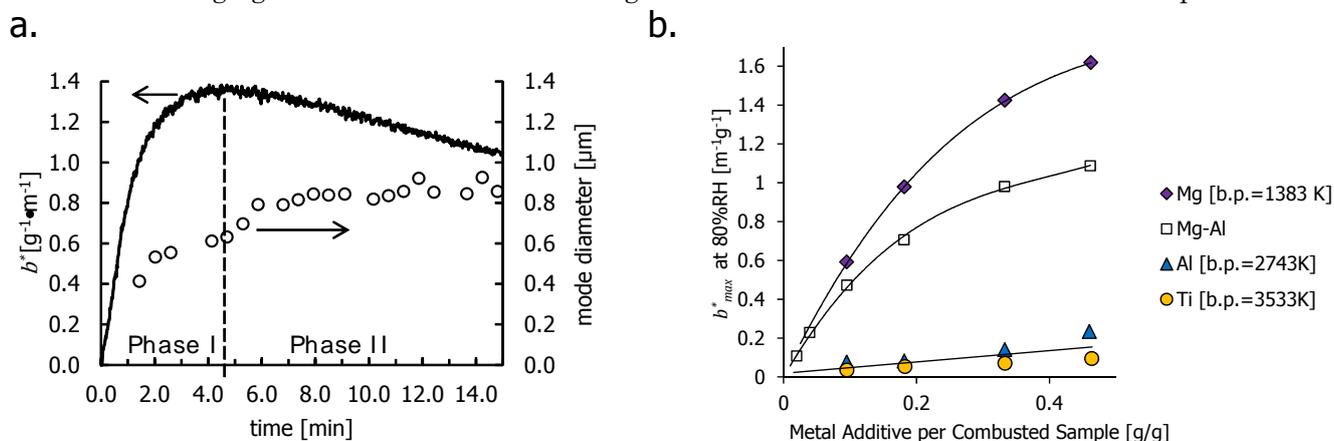
a.

b.

Figure 2. a. Change of sample-mass specific extinction coefficient b^* and mode diameter of aerosol from AP/HTPB composites with 10% CuO additive over time b. Dependence of maximum sample-mass specific extinction coefficient b^*_{max} at 80%RH on amount of metal additive added to the base composition.

Protein content in aerosols did not show high seasonal variability, but contributing sources like pollen were found to show slightly higher abundance in spring for large particles. A significant fraction of small particles seems to have been overlooked being already emitted at the point of generation for some sources like pollen, but other sources seem to undergo growth processes such as for kitchen aerosols. For aerosol emissions from pyrotechnics, a method for measuring and characterizing optical properties and humidity characteristics was developed, which allows comparison of different pyrotechnics. Also some additives were found to produce only low levels of visible smoke even at high humidity conditions.