On the Number Size Distribution of Aitken Particles in the Urban Atmosphere — With Regard to Sulfate Particles —

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(Manuscript received 14 June 1983, in revised form 13 August 1983)

Abstract

Collections of aerosol particles were carried out with an electrostatic aerosol sampler in the summertime at Nagoya and Yokkaichi which are heavily polluted areas in Japan. By electron microscopic examination 21 number size distributions of all particles and those of sulfate particles, including those in the Aitken size range, were obtained. Method for the detection of sulfate ions by electron microscopy, proposed by Bigg *et al.* (1974), was applied to the individual particles. Sulfate particles were found to be predominant in the range of 0.016 to 0.28 μm radius and they were detected with high number fractions of particles, 55 to 75% on the average. It is considered that the distributions of aerosol particles in the Aitken size range were closely related to the behavior of sulfate particles formed by gas-to-particle conversion influenced by the amount of pre-existing particles.

1. Introduction

Number concentration and chemical composition of aerosol particles are fundamental knowledge to assess the effect of aerosols on the atmospheric environment. Measurements of size distribution of aerosol particles, including those in the Aitken size range, have been performed in the atmosphere (e.g., Junge, 1953; Whitby *et al.*, 1972). However, a knowledge of chemical composition of particles especially in the Aitken size range is still meager up to the present. Sulfate particles are one of the most important aerosols in the atmosphere. The mass concentration of sulfate ions in aerosol particles in the urban atmosphere has been measured in various size ranges by a bulk analysis (Roesler *et al.*, 1965; Wagmann *et al.*, 1967; Mészáros, 1970; Kadowaki, 1976; Ahlberg *et al.*, 1978; Hering and Friedlander, 1982). Their results showed that about 50% of sulfate ions in mass existed in the Aitken size range. However, a little is known concerning the number size distribution of sulfate particles with radii less than 0.1 μm . The number size distribution of sulfate particles in the Aitken size range was obtained only by

morphological identification (Mészáros and Vissy, 1974; Mészáros, 1977 and 1978). Although the morphological identification by electron microscopy is one of the useful methods to obtain the knowledge on the composition of individual particles (Frank and Lodge, 1967; Heard and Wiffen, 1969), only the morphological identification may not provide a unique identification of sulfate particles. The method using a vapor-deposited thin film of barium chloride proposed by Bigg *et al.* (1974) is adequate one to detect sulfate ions in individual submicron particles (Ayers, 1978; Mamane and de Pena, 1978; Ono *et al.*, 1981).

The purpose of this paper is to indicate the number size distribution of sulfate particles together with that of all particles, including those in the Aitken size range, in the urban atmosphere of Nagoya and Yokkaichi by the single particle method proposed by Bigg *et al.* (1974).

2. Method

The collections of aerosol particles were carried out in the urban atmosphere of Nagoya (Nagoya University) and Yokkaichi (The Environmental Science Institute of Mie Prefecture),

which are heavily polluted areas in Japan (Fig. 1). Some collections of particles were also carried out in the summertime at Mt. Gozaisho (Gozaisho Youth Hostel) having an altitude of 1210 m and located about 20 km away from Yokkaichi. Number size distributions of all and sulfate particles in the present study were obtained by electron microscopic examination in the range of 0.005 to $0.28\mu\text{m}$ and of 0.016 to $0.28\mu\text{m}$ radius, respectively. An electron microscope used in the present study is a transmission one (Hitachi HS-9).

Aerosol particles were collected directly on a carbon-covered nitrocellulose film supported on an electron-microscopic grid by using an electrostatic aerosol sampler (Thermo-system, Inc., Model 3100). The sampler was operated in the intermittent collection mode with a flow rate of air, 5 l/min . After the collection the specimen was kept in the air of relative humidity less than 50%.

The shape and apparent diameter of individual particles on a carbon film were investigated with the electron microscope (Fig. 2a). The same specimen was placed in vacuum evaporator and coated with a vapor-deposited thin film of

Sampling places; Nagoya and Yokkaichi (X), Mt. Gozaisho (▲). Residential area (⋯), industrial area (⊗), ≥200 meters altitude (⊙).

Fig. 1 Location of site.

Fig. 2a Electron micrograph of aerosol particles collected at Yokkaichi with the electrostatic aerosol sampler during the period from 17:51 LST on 6 to 00:00 LST on 7 August in 1982.

Fig. 2b Electron micrograph of aerosol particles shown in Fig. 2a which was taken after the evaporation of barium chloride.

Fig. 2c Electron micrograph of reaction product of barium chloride with aerosol particles shown in Fig. 2a which was taken after the exposure to octanol vapor for 24 hours.

barium chloride ($20 \text{ \AA}$ in thickness) with shadowing angle of $\arctan 0.5$ in high-vacuum of about 4×10^{-6} torr. The specimen was taken out of the evaporator after the evaporation and kept in the air of relative humidity less than 50%. This specimen was investigated with the electron microscope in order to estimate the shadow length of particles (Fig. 2b). In the procedures mentioned above the specimen was irradiated by the electron beam of weak intensity to avoid the destruction of particles. Then, specimen was placed in an atmosphere saturated with octanol vapor for 24 hours at a room temperature. Subsequently, it was investigated with the electron microscope (Fig. 2c). If the Liesegang's rings of reaction product can be seen clearly around the individual particle, it is identified to be sulfate-containing particle. Although individual particles are expected to be present as the mixture of various material, particles which gave a positive sulfate reaction by this method are termed sulfate particles. The lower detection limit of sulfate particles was evaluated to be $0.016 \mu\text{m}$ radius in the present study. It is to be noted that the number of particles on the collecting surface hardly changed during the electron microscopic examination as shown in Figs. 2a to 2c.

Volume of each particle was calculated on the basis of the measurements of apparent diameter d and shadow length l on the collecting surface. If the particle reveals the ratio l/d less than $4/5$, the volume of particle was calculated on the basis of assumption that the particle exists as a spherical cap with the ratio l/d equal to 0.1. If the particle reveals the ratio more than $4/5$, the volume was evaluated by assuming that the size of particles is equal to apparent diameter on the collecting surface. As shadow length of particles with radii less than $0.015 \mu\text{m}$ cannot be evaluated owing to the grain structure of vapor-deposited thin film of barium chloride, it was assumed that such small particles exist as the spherical cap. The volume of sulfate particles which contain sulfuric acid was obtained by the method proposed by Gras and Ayers (1979). Then, the radii of these particles were obtained by assuming that the particles had been spherical prior to collection. The areas of the electron micrograph used for the counting of particles were from 420 to $2520 \mu\text{m}^2$ for obtaining each distribution.

The number concentration of aerosol particles

was obtained by using the collection efficiency of the electrostatic aerosol sampler (Liu *et al.*, 1967). The collection efficiency for particles with radii between 0.014 to $0.005 \mu\text{m}$ was estimated by the extrapolation of this collection efficiency. Recently, Yamada (1983) reassessed the collection efficiency of this instrument by electron microscopy, and showed that the collection efficiency for particles with radii less than $0.025 \mu\text{m}$ was large (90%) as compared with that (60%) by Liu *et al.* (1967). Then, the number concentration of particles obtained in the present study has a possibility that the concentration of particles with radii less than $0.025 \mu\text{m}$ are overestimated by a factor of 1.5. In order to assess the validity of the number size distribution obtained in the present study by electron microscopic examination, measurements of aerosol number size distribution were also performed with an electrical aerosol analyzer EAA (Thermo-system, Inc., Model 3030) on some occasions, keeping the relative humidity of the air less than 65%. Their results indicated that the difference in the number concentrations of aerosol particles measured by electron microscopy and with the EAA was within a factor of 2.5 in the range of 0.005 to $0.28 \mu\text{m}$ radius.

3. Results

In July and August 1978, 1980 and 1981 21 samples were taken at Nagoya and Yokkaichi. The collection time of about 5 hours was adopted in order to collect the particles enough to the electron microscopic examination. In Figs. 3a and 3b 21 number size distributions of all particles and those of sulfate particles measured in the urban atmosphere of Nagoya and Yokkaichi are indicated respectively. The radius intervals dr used for the counting of particles in the present study are indicated in the lower part of Fig. 3. Most of distributions of all and sulfate particles indicate that particles with radii more than $0.08 \mu\text{m}$ have a tendency to decrease in number concentration with radius in a similar manner to Junge's power law (Junge, 1953). Whereas, particles in the Aitken size range have some types of number size distribution. As shown in Fig. 3a, the ranges of number concentration of Aitken particles tend to increase with decreasing radius and most of distributions exhibit high number concentrations of smaller particles than $0.01 \mu\text{m}$ radius, more than 10^4 cm^{-3} in $dN/d\log r$. Some number size distribu-

Fig. 3 Number size distributions of all particles in the urban atmosphere of Nagoya and Yokkaichi (a). The distributions indicated by dotted lines were those obtained at Mt. Gozaisho. Number size distributions of sulfate particles in the urban atmosphere of Nagoya and Yokkaichi (b).

tions of all particles at Mt. Gozaisho are also indicated in Fig. 3a by dotted lines. The distributions at Mt. Gozaisho which is considered to be relatively clean area have a maximum number concentration in the range of 0.02 to 0.04 μm radius and they imply a low number concentration of small particles with radii less than 0.01 μm . Then, high number concentrations of particles especially in the range of less than 0.01 μm radius would be one of characteristics of number size distribution of particles in the urban atmosphere.

Fig. 4a shows the averaged number size distribution of all and sulfate particles in the urban atmosphere which were shown in Fig. 3. Averaged distribution reveals that the number concentration of all particles increases with decreasing radius and it is more than 10^4 cm^{-3} in $dN/d\log r$ in the range below 0.07 μm radius. It is found clearly that the distribution of sulfate particles is similar in shape to that of all particles. Fig. 4b shows the mean radii of number concentration of sulfate particles N_{sulfate} to that of all particles N_{all} in the range of 0.016 to 0.28 μm radius. Ranges of the ratios for whole cases are indicated by bars. Fig. 4b shows that

sulfate particles occupied 55 to 75% of all particles of 0.016 to 0.28 μm radius. Morphological examination indicated that most of particles with radii less than 0.016 μm seemed to have the features similar to water-soluble particles. Then, it is considered that most of small particles with radii less than 0.016 μm , which are unable to detect sulfate ions owing to the detection limit of the method used in the present study, would be also sulfate particles. It is to be noted that particles made up of the aggregation of electron-dense spherules, which are similar in morphological features to carbon particles, dominated the particles other than sulfate particles.

As shown previously in Fig. 3, the number concentrations were present in wide range. Then, we will show the distributions of all particles in the daytime and night, separately, as shown in Fig. 5. Surface area of aerosol particles is an important value to indicate the amount of particles together with the number and volume concentrations (Whitby, 1978), and it ranged widely from 101 to 1872 $\mu\text{m}^2 \text{ cm}^{-3}$ in the range of 0.005 to 0.28 μm radius in the urban atmosphere of Nagoya and Yokkaichi. A surface area of

Fig. 4 Averaged number size distributions of all particles and those of sulfate particles in the urban atmosphere of Nagoya and Yokkaichi (a). Averaged ratio of number concentration of sulfate particles N_{sulfate} to that of all particles N_{all} (b). Ranges of the ratios for whole cases are indicated by bars.

particles, $600\mu\text{m}^2\text{cm}^{-3}$, was employed as a criterion for the classification of distributions. Solid and chain lines represent the distributions for cases of surface areas more than and less than $600\mu\text{m}^2\text{cm}^{-3}$, respectively. It is found from Fig. 5a that number concentrations of aerosol particles in the Aitken size range increase strongly with decreasing radius in the daytime in the cases of surface area less than $600\mu\text{m}^2\text{cm}^{-3}$ and concentrations of particles with radii less than $0.01\mu\text{m}$ are usually higher than those measured in the cases of larger surface area than $600\mu\text{m}^2\text{cm}^{-3}$. On the other hand, the distributions, which have larger surface area than $600\mu\text{m}^2\text{cm}^{-3}$, reveal high number concentrations of particles in the range of 0.02 to $0.07\mu\text{m}$, more than 10^4cm^{-3} in $dN/d\log r$. Fig. 5b shows the distributions of all particles in the night. Although, the pronounced difference in

the distributions between daytime and night was not recognized in the distributions with the surface areas more than $600\mu\text{m}^2\text{cm}^{-3}$, the difference was measured strongly in the cases of surface area less than $600\mu\text{m}^2\text{cm}^{-3}$. This tendency was identical with that found in the distributions measured with the electrical aerosol analyzer (Okada, 1982).

4. Discussion

Sulfate particles were usually found to be large number fractions of aerosol particles in the range of 0.016 to $0.28\mu\text{m}$ radius and they comprised 55 to 75% of particles on the average. Then, it can be said that sulfate particles control strongly the number size distribution of aerosol particles in the urban atmosphere of Nagoya and Yokkaichi. The difference in number size distribution of particles between daytime and night was found clearly for small particles with radii less than $0.01\mu\text{m}$ in the cases of surface area of particles less than $600\mu\text{m}^2\text{cm}^{-3}$. Moreover, the difference was present in the number size distributions of particles in the Aitken size range increased strongly with decreasing radius in the cases of surface area less than $600\mu\text{m}^2\text{cm}^{-3}$ and concentrations of small particles with radii less than $0.01\mu\text{m}$ are usually higher than those measured in the cases of larger surface area than $600\mu\text{m}^2\text{cm}^{-3}$.

Although Aitken particles are emitted primarily by the combustion of fossil fuels, most of Aitken particles in the urban atmosphere are expected to be formed by gas-to-particle conversion as stated by Gartrell and Friedlander (1975). It is considered that photochemical formation of sulfate particles would occur in the daytime. Condensable molecules such as sulfuric acid vapor, which were generated photochemically, form new particles by gas phase reactions or condense on pre-existing particles, and the amount of pre-existing particles has an effect of depressing the formation of new particles owing to the consumption of condensable molecules by heterogeneous condensation (e.g., Friedlander, 1977). Okada (1982) measured the number concentration of particles with the EAA in Nagoya and found out that the number concentration of particles with radii less than $0.01\mu\text{m}$ changed with time in the similar way as the intensity of solar radiation in the presence of a small

Fig. 5 Number size distributions of all particles in the daytime (a) and night (b). Solid and chain lines represent the distributions for cases of particle surface area more and less than $600 \mu\text{m}^2 \text{cm}^{-3}$, respectively.

amount of existing particles. Then, it is suggested that photochemical formation of new particles occurred strongly in the daytime in the presence of a small amount of pre-existing particles, and that the formation of new particles was suppressed in the presence of a large amount of pre-existing particles. Together with the behavior of small particles, it is worth noting that number size distributions of particles, which have larger surface area of particles than $600 \mu\text{m}^2 \text{cm}^{-3}$, often exhibited high number concentrations of particles in the range of 0.01 to $0.07 \mu\text{m}$, more than 10^4cm^{-3} in $dN/d\log r$. Okada (1983) pointed out that hygroscopic particles with single water-insoluble inclusion were present in high number fractions of particles of 0.03 to $0.1 \mu\text{m}$ radius, more than 45% in the cases of larger surface area than $10^3 \mu\text{m}^2 \text{cm}^{-3}$. Then, it is considered that relatively large particles in the Aitken size range were produced by gas-to-particle conversion mostly through heterogeneous processes on pre-existing particles. Although more detailed study should be performed in association with their formation processes, it is considered that gas-to-particle conversion influenced by the amount of pre-existing particles acted an important role to form the number

size distribution of sulfate particles especially in the Aitken size range.

In order to clarify the cause of the difference in the number size distribution between daytime and night, the time change in the distribution should be studied in detail in relation to the formation and modification of aerosol particles. Moreover, the detection of sulfate ions in particles with radii less than $0.015 \mu\text{m}$ should be carried out in future.

5. Conclusion

The collections of aerosol particles were performed in the summertime at Nagoya and Yokkaichi. By the method for the detection of sulfate ions in individual particles 21 number size distributions of all particles and those of sulfate particles, including those in the Aitken size range, were obtained. Sulfate particles were found to be large in number fractions of particles of 0.016 to $0.28 \mu\text{m}$ radius and they occupied 55 to 75% of particles on the average. Most of distributions of all particles and those of sulfate particles with radii more than $0.08 \mu\text{m}$ have a tendency to decrease in the number concentration with radius in a similar manner to Junge's power law. On the other hand, Aitken

particles have some types of number size distribution which are considered to be closely related to the formation processes of sulfate particles by gas-to-particle conversion influenced by the amount of pre-existing particles.

Acknowledgement

The authors are deeply grateful to Prof. A. Ono, Water Research Institute, for useful advice related to the electron microscopic examination and useful comments throughout this study and to Prof. K. Isono, Nagoya University, for encouragement throughout this study. They express their hearty thanks to Miss S. Hayashida, Mr. M. Horiguchi and Mr. M. Ikeyama, Water Research Institute, for their hearty supports during the observations at Yokkaichi and Mt. Gozaisho. They wish to express their thanks to the staff members of The Environmental Science Institute of Mie Prefecture, including Director and Dr. T. Maekawa, for their kind helps for the observation at Yokkaichi and to staff members of Gozaisho Youth Hostel for their kind helps for the observation at Mt. Gozaisho. This study was supported in part by Grant-in-Aid for Scientific Research, the Ministry of Education and Culture.

References

- Ahlberg, M. S., A. C. D. Leslie, and J. W. Winchester, 1978: Characteristics of sulfur aerosol in Florida as determined by PIXE analysis. *Atmos. Envir.*, **12**, 773-777.
- Ayers, G. P., 1978: Quantitative determination of sulphate in individual particles. *Atmos. Envir.*, **12**, 1613-1621.
- Bigg, E. K., A. Ono, and J. Williams, 1974: Chemical tests for individual submicron aerosol particles. *Atmos. Envir.*, **8**, 1-13.
- Frank, E. R., and J. P. Lodge, Jr., 1967: Morphological identification of airborne particles with the electron microscopy. *J. Microscopie*, **6**, 449-456.
- Friedlander, S. K., 1977: *Smoke, Dust and Haze: Fundamentals of Aerosol Behavior*. John Wiley and Sons, New York, 317 pp.
- Gartrell, G. Jr., and S. K. Friedlander, 1975: Relating particulate pollution to sources: The 1972 California Aerosol Characterization Study. *Atmos. Envir.*, **9**, 279-299.
- Gras, J. L., and G. P. Ayers, 1979: On sizing impacted sulfuric acid particles. *J. Appl. Meteor.*, **18**, 634-638.
- Heard, M. J., and R. P. Wiffen, 1969: Electron microscopy of natural aerosols and the identification of particulate ammonium sulfate. *Atmos. Envir.*, **3**, 337-340.
- Hering, S. V., and S. K. Friedlander, 1982: Origins of aerosol sulfur size distributions in the Los Angeles basin. *Atmos. Envir.*, **16**, 2647-2656.
- Junge, C. E., 1953: Die Rolle der Aerosole und der gasförmigen Beimengungen der Luft im Spurenstoffhaushalt der Troposphäre. *Tellus*, **5**, 1-26.
- Kadowaki, S., 1976: Size distribution of atmospheric total aerosols, sulfate, ammonium and nitrate particulates in the Nagoya area. *Atmos. Envir.*, **10**, 39-43.
- Liu, B. Y. H., K. T. Whitby, and H. H. S. Yu, 1967: Electrostatic aerosol sampler for light and electron microscopy. *Rev. Sci. Instr.*, **38**, 100-102.
- Mamane, Y., and R. G. de Pena, 1978: A quantitative method for the detection of individual submicrometer size sulfate particles. *Atmos. Envir.*, **12**, 68-82.
- Mészáros, A., 1977: On the size distribution of atmospheric aerosol particles of different composition. *Atmos. Envir.*, **11**, 1075-1081.
- , 1978: On the concentration and size distribution of atmospheric sulfate particles under the rural conditions. *Atmos. Envir.*, **12**, 2425-2428.
- , and K. Vissy, 1974: Concentrations, size distribution and chemical nature of atmospheric aerosol particles in remote oceanic area. *J. Aerosol Sci.*, **5**, 101-109.
- Mészáros, E., 1970: Seasonal and diurnal variations of the size distribution of atmospheric sulfate particles. *Tellus*, **22**, 235-238.
- Okada, K., 1982: Size distribution of aerosols in the urban atmosphere. *Features and Behavior of Aerosols in the Urban Atmosphere* (edited by T. Takeda and Y. Iwasaka), 57-79, Water Research Institute, Nagoya University.
- , 1983: Two characteristic types of number size distribution of Aitken particles in the urban atmosphere of Nagoya—in relation to the formation process of sulfate particles. Submitted to *Atmos. Envir.*
- Ono, A., K. Okada, and K. Akaeda, 1981: On the validity of the vapor-deposited thin film of barium chloride for the detection of sulfate in individual atmospheric particles. *J. Meteor. Soc. Japan*, **59**, 419-424.
- Roesler, J. F., H. J. R. Stevenson, and J. S. Nader, 1965: Size distribution of sulfate aerosols in the ambient air. *J. Air Pollut. Control Ass.*, **15**, 576-579.
- Wagmann, J., R. E. Lee, and C. L. Axt, 1967: Influence of some atmospheric variables on the concentration and size distribution of sulfate in urban air. *Atmos. Envir.*, **1**, 479-489.
- Whitby, K. T., 1978: The physical characteristics of sulfur aerosols. *Atmos. Envir.*, **12**, 135-159.

- , R. B. Husar, and B. Y. H. Liu, 1972: The aerosol size distribution of the Los Angeles smog. *J. Colloid Interface Sci.*, **39**, 177-204.
- Yamada, Y., 1983: A new method for the determination of collection efficiency of an aerosol sampler by electron microscopy. *Atmos. Envir.*, **17**, 369-372.

都市大気中のエイトケン粒子の個数粒径分布について

——サルフェイト粒子に注目して——

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名古屋及び四日市における都市大気中のエアロゾル粒子の採集を夏期に electrostatic aerosol sampler により実施し、エイトケン粒子領域を含む粒子個数粒径分布を電子顕微鏡観察により 21 個得た。Bigg *et al.* (1974) の方法により個々の粒子に含まれる SO_4^{2-} イオンの検出も併せて行なった。その結果、サルフェイト粒子は、半径 $0.016 \sim 0.28 \mu\text{m}$ において平均でエアロゾル粒子個数濃度の 55~75% を占めていた。エイトケン粒子の個数粒径分布が、既存粒子の存在量の違いに影響されたガス-粒子変換過程により生成されたサルフェイト粒子の挙動と密接に関係していることが示唆された。