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Individual shape and composition analysis of urban atmospheric aerosols using FIB-TOF-SIMS

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Minute solid or liquid particles suspended in air are called aerosols. Aerosols can be of natural origin, such as yellow sand, or of anthropogenic origin, such as railroad wear dust. Bulk analysis has been used for the chemical analysis of aerosols with such various sources. However, bulk analysis can only determine the average chemical composition of a group of particles and cannot, in principle, analyze the chemical composition of individual particles [1]. In our group, we have developed an FIB-TOF-SIMS (Focused Ion Beam Time-of-Flight Secondary Ion Mass Spectrometer) to analyze the compositional distribution of individual particles [2]. Our investigations have revealed that there is a certain correlation between particle composition (source) and particle shape. In addition, it is important to understand the composition and shape of particles originating from urban areas because the traffic volume is relatively high in urban areas and there is concern about the emission of large amounts of aerosols and their health effects on human health [3,4]. In this study, we sampled aerosols in Shinjuku area and analyzed them using FIB-TOF-SIMS. In this presentation, we will report the component analysis of urban atmospheric aerosols and the shape characteristics of the particles.

I. Introduction

In the environment where we live, there are many particles of invisible size. These minute solids and liquids suspended in the atmosphere are called aerosols. The sources of aerosols range from natural sources such as pollen and yellow sand to anthropogenic sources such as automobile exhaust and railroad dust. In addition, with the economic development of Asia in recent years, a large number of aerosols have been emitted from industrial areas and have become a factor in air pollution. For chemical analysis of aerosols, bulk analysis has been performed after filter collection. Bulk analysis can obtain quantitative data with high accuracy. However, it can only determine the average chemical composition of a group of collected particles and cannot in principle identify the source of individual particles or analyze their chemical composition [1].

In our research group, we have developed an FIB-TOF-SIMS (Focused Ion Beam Time-of-Flight Secondary Ion Mass Spectrometer), which enables to analyze individual particles of aerosols. We have been analyzing the distribution of components from the surface structure to the internal structure of individual particles [2]. From previous studies, it has been found that there is some correlation between particle composition (source) and particle shape observed with the FIB-TOF-SIMS. In addition, in urban areas, there is a

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relatively large amount of traffic such as automobiles and railroads, and there are concerns about the emission of large amounts of aerosols and the health effects of these aerosols on human health [3,4]. Therefore, it is important to understand the composition and shape of urban-derived particles.

In this study, we sampled aerosols in Shinjuku and analyzed them using FIB- TOF-SIMS. As a result of the analysis, it was confirmed that the aerosols suspended in the urban city have a unique structure. In this paper, we report the component analysis of urban atmospheric aerosols by FIB-TOF-SIMS and the shape characteristics of these particles.

II. Experimental

Sampling was done on two days, July 21, 2021, and November 3, 2021. Table 1 shows the details of each sampling date. Figure 1 shows the details of the sampling sites. The sampling sites were located in the Shinjuku campus of Kogakuin University. The sampling point was located facing the road, with Shinjuku station about 450 m away.

Table 1: Sampling details

Sampling dates	Sampling time	Flow rate (L/min)
2021/7/21	1：13:25～13:55 2：13:55～14:25 3：14:25～14:55 4：14:55～15:25 5：15:25～15:55 6：15:55～16:25	1.5
2021/11/3	1：12:15～14:15 2：14:25～15:25 3：15:35～17:15	

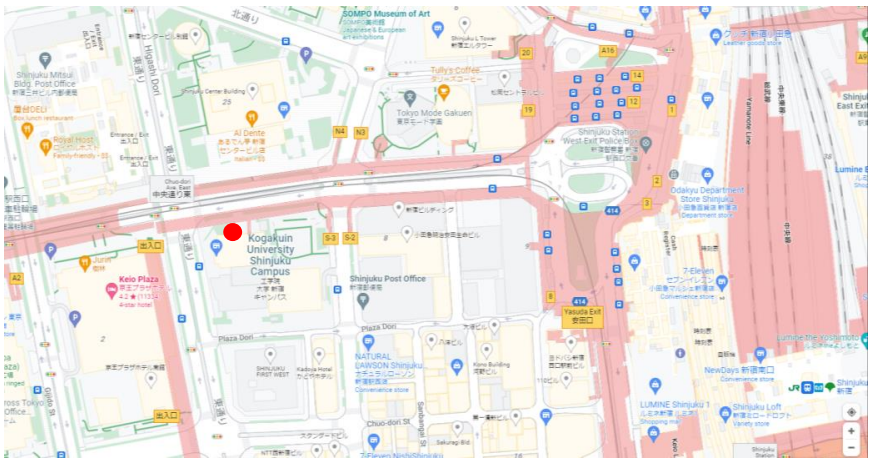

Fig.2 Location of the sampling (red solid circle)

The collected samples were analyzed by using the FIB-TOF-SIMS apparatus, and the shapes of the particles were observed from the images obtained by FIB-TOF-SIMS analysis. Aerosol source data and particle shape characteristics were used to identify the single particle source.

III. Results and Discussion

The results of the FIB-TOF-SIMS analysis of Fe-containing particles-a) and -b). The particle-a) contained Cr and Fe, and a small amount of Cu. It is said that particles from muffler of automobiles contain Mn, Cr, and Fe originated from engine wear and/or engine oil [5]. As for Cu and Ca, they are the markers for brake dust [6]. From these information, the particle-a) was assumed to be automobile origin.

As for the particle-b), the particle contained Li, Na, Al, K and Fe. And SiO_2 and PO_2 were detected as negative ions. The particle containing these components are considered to be of coal combustion origin [7]. However, particles of combustion origin generally exist in a spherical shape. Therefore, the particle-b) is considered to be soil origin because the chemical composition of soil-origin particles containing iron is similar to that of coal combustion-origin particles.

Table 2 shows the source profiles of aerosols surveyed by the Ministry of the Environment in 2015[8]. The existence ratios of the elements constituting the single particle-a) and -b) were compared with those calculated from the source profile. Source data are expressed by weight ratio, and existing ratio was calculated by the ion counts of the TOF-

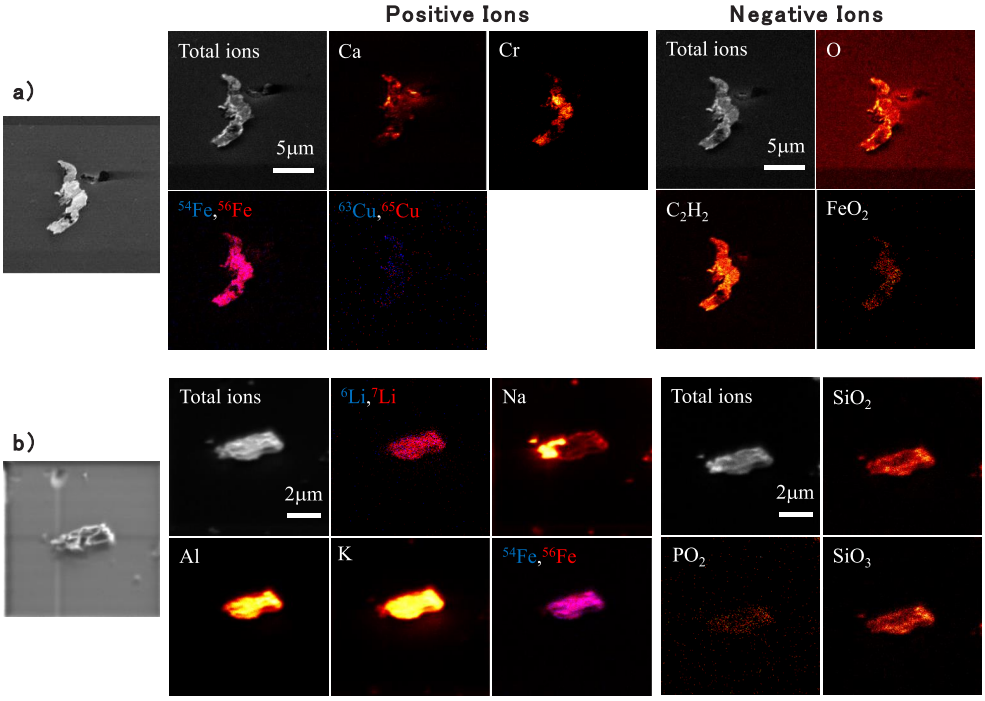

Figure 2: TOF-SIMS images of each elements of collected iron-containing particles.

Table2: Source Data[8]

Elements	Source data			
	Brake dust		Soil and road dust	
	Concentration (g/g)	existence ratio (%)	Concentration (g/g)	existence ratio (%)
Na	7.6E-03	4.8	1.3E-02	6.6
Al	1.9E-02	12	6.1E-02	31
K	3.5E-03	2.2	1.3E-02	6.6
Ca	3.2E-02	20	5.5E-02	28
V	5.9E-05	0.037	1.1E-04	0.056
Cr	4.2E-04	0.26	2.8E-04	0.14
Mn	7.2E-04	0.45	1.1E-03	0.56
Fe	9.1E-02	57	5.3E-02	27
Zn	3.3E-03	2.1	1.3E-03	0.66
Sb	2.1E-03	1.3	1.3E-05	0.0066

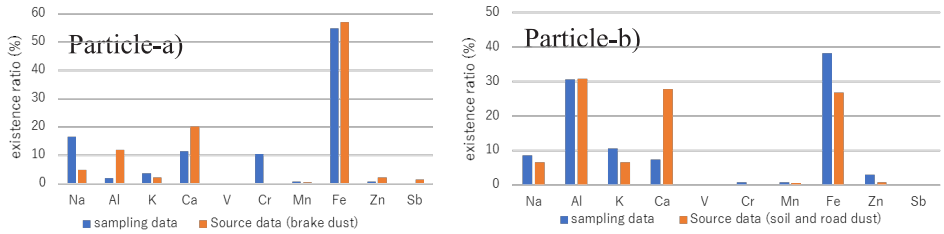

Figure 3: Comparison of elemental abundance ratios between sampled particles and source profiles.

SIMS analysis. In essence, they cannot be compared exactly. However the similarity or correlation can be estimated by this expression.

Figure 3 compares the chemical composition estimated by TOF-SIMS of the particle-a) with the source data of brake dust. Calcium and Fe are the similarity. However, Sb, which is the most characteristic element in brake dust was too small in the TOF-SIMS result. Therefore we cannot confirm it to be brake dust. As for the particle-b), as shown in Fig.3b, it has a certain similarity with the source data of soil and road dust.

In this study, it was confirmed that most of the collected Fe-containing particles were in a state of mixing with salts. Figure 4 shows the FE-SEM image and FIB-TOF-SIMS analysis results of the Fe-containing particles in the same area. It is thought that the primary particles of metallic Fe-containing particles emitted, and were rapidly oxidized in atmosphere, and a liquid coating was formed by the condensed water on the cooled particle surface which resulted in the salts [9].

IV. Conclusions

The Fe-containing particles collected in Shinjuku were analyzed for their composition and evaluated for their shape characteristics. The observed Fe-containing particles were confirmed to be of automobile origin and soil origin, respectively. In addition, it was

confirmed that salts were attached around the Fe-containing particles. As a future prospect, we would like to perform internal structure analysis by taking advantage of the surface sensitivity of FIB-TOF-SIMS. We also plan to quantitatively show the source of the iron-containing particles.

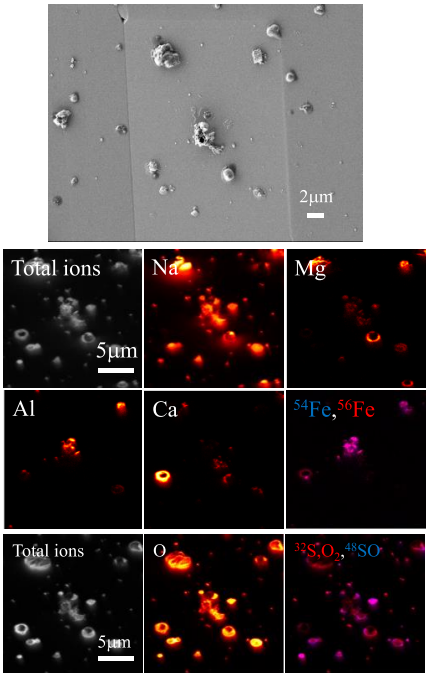

Figure 4: Examples of iron particles with salts around them (right: FE-SEM image, middle: positive, left: negative). The FE-SEM image shows the traces of FIB scraping.

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