Divisive Refinement of Metal Fiber at the PM$_{0.1}$ Classification Stage for PM$_{0.5-0.1}$ Sampling with Nanosampler

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ABSTRACT

Multi-component analysis of PM$_{0.5-0.1}$ collected by Nanosampler II metal (Steel Use Stainless: SUS) wool fiber at the PM$_{0.1}$ classification stage is challenging owing to difficulties in SUS wool fiber separation after collection. A 4-division (4D) cartridge was developed to enable quantitative analysis of multiple components by dividing the SUS wool fibers into four sections. The performance of the 4D cartridge was evaluated using sulfate ion concentrations of actual atmospheric particulate matter (PM). Observations using the 4D cartridge revealed that the relative standard deviation (RSD) of sulfate ions was lower for mesh with a large open area. In the case of the mesh with a large opening area, the partition did not block too much of the cross-sectional area of the SUS wool fiber, thus minimizing its effect on the airflow and possibly suppressing particle adhesion on the stainless-steel mesh. The PM$_{0.1}$ classification efficiency test was conducted, and a linear analysis of the total filling mass of SUS wool fiber along with classifying efficiency of 100 nm PM was performed. In the 4D cartridge, it was estimated that 8.7 mg of SUS wool fiber was required to achieve a classification efficiency of 100 nm at 50% cutoff diameter because the apparent volume fraction of SUS wool fiber increases with the introduction of the partition. Using optimal mesh and amount of SUS wool fiber, the average RSD of sulfate ions was 5.6%, which was within the acceptable range ($\pm$ 15%) for reanalysis of the Ministry of the Environment in Japan due to changes in analytical sensitivity of ionic components, confirming that PM was evenly collected from the four pieces of SUS wool fiber. This enabled multi-component analysis of all particle sizes including PM$_{0.5-0.1}$ through the classified collection of PM using Nanosampler II.

Keywords: 4-division cartridge, Particulate matter, Multi-component analysis, Nanosampler

1 INTRODUCTION

Air pollution caused by particulate matter (PM) has become a major environmental problem that can potentially lead to adverse health effects, such as respiratory diseases and cancer (Bhargava et al., 2019; WHO, 2021; Lian et al., 2022). PM is divided into coarse (PM$_{10}$), fine (PM$_{2.5}$), and ultrafine (PM$_{0.1}$) particle sizes. The mass concentration of PM$_{0.1}$ is as small as 10–20% of the total suspended particles, whereas the number concentration accounts for approximately 90% (Vu et al., 2015; Inerb et al., 2022). For the same mass, smaller particles tend to cover larger surface areas and exhibit higher toxicity (Oberdörster et al., 2005). PM$_{0.1}$ penetrates deep into the alveoli and is easily absorbed by blood vessels and cells (Koullapis et al., 2020; Schraufnagel, 2020), raising concerns about its greater health effects compared to larger particles (Kumar et al., 2014). Therefore, it is necessary to properly classify and collect PM$_{0.1}$ and characterize its chemical components.

One instrument that samples PM$_{0.1}$ is Nanosampler II (NS) (Model 3182, KANOMAX, Osaka, Japan) (Otani et al., 2007; Furuuchi et al., 2010b); it consists of six classification stages (> 10 µm, 10–2.5 µm, 2.5–1.0 µm, 1.0–0.5 µm, 0.5–0.1 µm, < 0.1 µm), with the upper four stages classifying
and collecting particles > 0.5 µm through the impaction method, and the fifth stage of the inertial filter (IF) simultaneously promoting the inertial collection and suppression of diffusive collection by passing particles at a high filtration velocity (20–30 m s\(^{-1}\)) through an IF cartridge filled with metal (Steel Use Stainless: SUS) wool fiber, thereby cutting particles > 100 nm (Otani et al., 2007; Furuuchi et al., 2010a; Kim et al., 2010). This eventually allows PM\(_{0.1}\) to be classified and collected in a backup filter. Therefore, PM with particle sizes of 0.5–0.1 µm (PM\(_{0.5\text{-}0.1}\)) are collected on SUS wool fiber. The NS has the advantage of having a lower pressure drop than other PM\(_{0.1}\) collection devices such as low-pressure impactors, which allows for accurate analysis of semi-volatile chemical components, such as polycyclic aromatic hydrocarbons in PM (Hata et al., 2012; Shibata et al., 2012).

The NS has been used for PM\(_{0.1}\) observations not only in Japan but also in Vietnam, Thailand, Indonesia, Malaysia, and other countries (Kudo et al., 2012; Kim et al., 2016; Thuy et al., 2018; Hongtieab et al., 2020; Nghiem et al., 2020; Amin et al., 2021; Boongla et al., 2021; Huyen et al., 2021; Putri et al., 2021; Inerb et al., 2022; Phairuang et al., 2022). However, most of these studies did not analyze the composition of the PM\(_{0.5\text{-}0.1}\) component. Only a few cases have been reported on the analysis of ionic components, water-soluble organic carbon, and polycyclic aromatics (Jamhari et al., 2022; Kurotsuchi et al., 2022; Kakimoto et al., 2017). In particular, there have been no reports of the simultaneous analysis of components with different chemical properties (e.g., water-soluble and non-water-soluble) in PM\(_{0.5\text{-}0.1}\). In general, PM samplers use filter paper samples as the collection material. Filter paper samples can be cut, punched, or otherwise divided into fixed areas after collection, and different pretreatments, such as water and organic solvent extraction, can be used to quantify multiple components. PM collected on SUS wool fiber is unevenly collected on the inlet side of the IF cartridge owing to the structure of the sampler. In contrast to a filter paper sample, PM cannot be evenly divided into multiple components after collection. Therefore, when analyzing a single sample for components that use different extraction solvents for equipment and pretreatment, such as ionic components and PAHs, uniform division of the collected sample is necessary for quantitation. In wet chemical analysis of ionic components and water-soluble organic carbon, it is possible to extract and quantify the entire sample regardless of the unevenness of the collection. However, previously, current NS did not have a method for evenly dividing the SUS wool fiber after collection, and therefore, for both PM\(_{0.5\text{-}0.1}\) collected on SUS wool fiber and other particle sizes, multiple compositions could not be obtained through measurement using different pretreatment methods. Therefore, many studies excluded them from chemical composition analysis and only measured particle mass. Thus, while NS as a classification collector for all PM is capable of accurate classification collection of PM\(_{0.1}\), analyzing the components of PM\(_{0.5\text{-}0.1}\) collected on SUS wool fiber remains a problem.

Understanding the behavior of PM constituents in the atmosphere requires the simultaneous analysis of multiple constituents, such as carbon components, water-soluble ionic constituents, and organic indicators, using analytical methods with different pretreatments and measurements. PM\(_{0.5\text{-}0.1}\) is the region where PM is generated and accumulates, and a detailed analysis of the chemical composition of PM\(_{0.5\text{-}0.1}\) will aid the understanding of the dynamic behavior of PM in the atmosphere. To analyze PM components collected on SUS wool fiber, research has been conducted to improve the classification stage and increase the number of IF cartridges to three (Kumsanlas et al., 2019). However, the improved device has a different shape from that of the NS, making it difficult to use.

In this study, as a refined method of the PM\(_{0.1}\) classification stage without changing the shape of the existing NS body for multiple chemical component analysis of all PM particle sizes, we aimed to introduce a 4-division (4D) partition into the IF cartridge, developing a 4D cartridge that can separate SUS wool fiber prior to PM collection. Quantitative resolution of PM\(_{0.5\text{-}0.1}\) collected on SUS wool fiber and the possibility of simultaneous analysis of multiple components were investigated.

### 2 METHODS

#### 2.1 Atmospheric PM Collection for 4D Cartridge Performance Evaluation

The IF cartridge (Fig. 1(a)) of the NS is a 9 mm long Teflon cylinder with an outer diameter of
10 mm and a hollow inner diameter of 5 mm. A 4D cartridge was made by machining 0.2 mm grooves in the IF cartridge and inserting stainless-steel mesh partitions there. Several stainless-steel mesh partitions with different wire diameters and mesh counts were used (Table 1). Two 6 mm long and 5 mm wide partitions were centered together and introduced into the cross groove. Four SUS wool fiber pieces (SUS316L, 8 µm), each weighing 2.45 ± 0.05 mg, were individually inserted into the divisions of the 4D cartridge. All components were sealed inside the cylinder with a stainless-steel retainer, rubber O-ring, and Teflon ring (Fig. 1(b)).

During the ambient PM collection, the NS, equipped with the 4D cartridge, was used and a quartz fiber filter (2500 QAT-UP, Pallflex, CT, USA) was attached to the upper impactor’s collection section and a PM0.3, backup filter. The collection flow volume was 40 L min⁻¹ and the sampling time was 23.5 h. The sampling sites were the 4th floor rooftop of the lecture hall and the 10th floor balcony of the Research and Project Building on the Saitama University campus (35.867°N, 139.65°E); three to four observations were made for each stainless mesh. These buildings are located 150–300 m away from National Road 463. Therefore, direct sources of PM, such as automobile exhaust and soil particles, are mitigated by distance from the road and ground (Kuwabara et al., 2016). The observation periods are shown in Table S1.

Fig. 1. Experiment components: (a) Nanosampler II (NS) and IF Cartridge, (b) 4-division (4D) Cartridge and Assembly parts of the 4D Cartridge.
Table 1. Details of the stainless-steel mesh partitions.

<table>
<thead>
<tr>
<th>Type</th>
<th>Wire Diameter (mm)</th>
<th>Mesh Count a</th>
<th>Mesh Opening b (mm)</th>
<th>Opening Area c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.08</td>
<td>120</td>
<td>0.132</td>
<td>38.7</td>
</tr>
<tr>
<td>B</td>
<td>0.14</td>
<td>80</td>
<td>0.18</td>
<td>31.3</td>
</tr>
<tr>
<td>C</td>
<td>0.14</td>
<td>60</td>
<td>0.28</td>
<td>44.8</td>
</tr>
<tr>
<td>D</td>
<td>0.14</td>
<td>50</td>
<td>0.37</td>
<td>52.5</td>
</tr>
<tr>
<td>E</td>
<td>0.14</td>
<td>40</td>
<td>0.49</td>
<td>60.8</td>
</tr>
<tr>
<td>F</td>
<td>0.1</td>
<td>80</td>
<td>0.218</td>
<td>46.9</td>
</tr>
<tr>
<td>G</td>
<td>0.12</td>
<td>80</td>
<td>0.198</td>
<td>38.7</td>
</tr>
</tbody>
</table>

a Mesh Count: Number of Wires per inch
b Mesh Opening = (25.400 mm /Mesh Count) – Wire Diameter
\[ (1) \]
c Opening Area = Opening^2/(Opening + Wire Diameter)^2
\[ (2) \]

The sulfate ion concentrations of the PM collected from each of the four introduced SUS wool fibers were measured. Each SUS wool fiber was placed in 20 mL ultrapure water, subjected to ultrasonic extraction for 20 minutes, filtered (0.2 µm pore size), and measured using an ion chromatograph (ICS-1600; Dionex Corp., CA, USA) (Kurotsuchi et al., 2022). The lower limit of sulfate ion quantification in the instrument was 0.003 mg mL⁻¹. The relative standard deviation (RSD) was calculated from the mean and standard deviation of the sulfate ion concentrations from the four SUS wool fiber pieces introduced into the 4D cartridge of each stainless mesh. The observation period was from summer to winter (February–November 2020), and ammonium nitrate, whose gas particle distribution changes with temperature, was considered unsuitable for evaluating the stability of the four divisions of SUS wool fiber. The concentration variations of the PM components in each SUS wool fiber piece were evaluated.

2.2 Classification Efficiency Test of PM0.1

The PM0.1 classification efficiency test was conducted on a 4D cartridge with a stainless-steel mesh. A schematic of the experimental setup used in this study is shown in Fig. 2. NaCl particles with a peak particle size of 100 nm were generated using a particle generator (ATM-226, TOPAS, Germany, 5 L min⁻¹), dried using a diffusion dryer, and introduced into a SUS mixing tube (inner diameter: 10 mm, length 200 mm). They were then introduced into the NS and passed through the classification stage up to PM0.1 using a vacuum pump at a flow volume of 40 L min⁻¹. The PM before and after the NS was classified into eight segments in the range of 60–200 nm using a differential mobility analyzer (Model 3081, TSI, MN, USA) under a 3 L min⁻¹ sheath flow volume and a 0.7 L min⁻¹ aerosol flow volume. Then, the particle number concentration was measured using a handheld condensation particle counter (Model 3800, KANOMAX, Osaka, Japan) with a 0.7 L min⁻¹ flow volume. A classification curve was determined from the number concentrations before and after NS to evaluate the classification efficiency of PM0.1.

IF cartridges used to classify PM0.1 in NS can classify PM with 50% cutoff diameter (d50) of approximately 50–200 nm by appropriately selecting the structure and filtration conditions (filtration speed, SUS fiber diameter, wool fiber volume fraction) (Furuuchi et al., 2010a). In this study, the IF cartridge structure, filtration rate, and SUS wool fiber diameter were the same as those of normal IF cartridges, and the classification efficiency of particles was controlled by changing the volume fraction of the SUS wool fiber through altering the total mass of the wool fiber. To investigate the filling mass of SUS wool fiber at d50 of 100 nm, four SUS wool fiber pieces were introduced into the 4D cartridge, with SUS wool fiber amounts of 6, 7, 8, 9, 9.8, 11, and 12 mg. The mass of each introduced SUS wool fiber piece was weighed to keep within ±0.1 mg (e.g., 8 mg, 2 ± 0.1 mg × 4).

3 RESULTS AND DISCUSSION

3.1 Evaluation of the Performance of a 4D Cartridge in Atmospheric PM Collection

The mean, standard deviation, and RSD of the PM sulfate ion concentrations collected from
the SUS wool fiber pieces of the 4D cartridges with different stainless-steel mesh partitions are presented in Table S2. The RSD of the sulfate ion concentration in each stainless mesh plotted by wire diameter and open area of stainless-steel mesh is shown in Fig. 3. The open area was calculated from the wire diameter and mesh count according to Eq. (2) in Table 1. From the results in Fig. 3(a), it is evident that the RSD tended to be lower with increasing wire diameter. However, there was no significant dependence because it was 10–15 times thicker than the SUS wool fiber diameter (8 µm). Additionally, because the stainless-steel mesh was placed parallel to the flow, the PM classification was not significantly affected. A comparison of the meshes with a 0.14 mm wire diameter (B–E) showed that the lesser the number of meshes, the lower the RSD. The plot with the opening area (Fig. 3(b)) shows a tendency to depend on the opening area of the introduced stainless-steel mesh. The larger the opening area and the wider the gap between the meshes, the smaller the RSD tended to be and the more evenly it was divided into four parts. IF suppressed smaller size PM diffusion due to its high filtration velocity. The 4D cartridge with a mesh with a small opening area may have altered the airflow, resulting in more particles hitting the partitions without sufficiently suppressing the diffusion effect. However, in the case of the mesh with a large opening area, the partition did not block too much of the cross-sectional area of the SUS wool fiber, thus minimizing its effect on the airflow and possibly suppressing particle adhesion on the stainless-steel mesh. Based on these results, mesh E, which had the greatest opening area (60.8%) that could reduce particle adhesion to the partition due to diffusion, was used for the classification efficiency tests.

3.2 Classification Efficiency Test of PM0.1 in the 4D Cartridge

To confirm the classification efficiency of PM0.1, a test was conducted using mesh E, which had the smallest concentration variation (Section 3.1). Fig. 4 illustrates the results of classification efficiency tests when SUS wool fiber was introduced into a normal IF cartridge without grooves. The normal IF cartridge achieved a sharp-cut classification curve with a d50 of 100 nm when filled with 9.8 ± 0.5 mg of SUS wool fiber. The sharper the classification curve, the higher the response of the classifier to the particle size and the more sensitive the classification.

The filling mass of SUS wool fiber with d50 of 100 nm when using the 4D cartridge with mesh E was investigated. The mean classification efficiency results for the 4D cartridge using mesh E filled with four SUS wool fiber pieces and the total amount of SUS wool fiber of 6–12 mg are shown in Fig. 5. At a SUS wool fiber amount of 9.8 mg, which showed a d50 of 100 nm for the normal IF cartridge without grooves, the d50 of the 4D cartridge shifted to the smaller diameter side, close to 95 nm. The d50 of each filling mass of SUS wool fiber was 120 nm for 6–7 mg, 110 nm for 8 mg,
Fig. 3. Relative standard deviation (RSD) of the sulfate ion concentration by the (a) wire diameter and (b) open area of each stainless mesh (A–G_Wire Diameter/Mesh Count).

Fig. 4. Classification curve of a normal IF cartridge without grooves for different amounts of SUS wool fiber (9.3 mg, 9.8 mg, and 10.3 mg).
Fig. 5. Mean classification curve of a 4D cartridge of mesh E (0.14/40) for different amounts of SUS wool fiber (6–7 mg, 8 mg, 9 mg, 10 mg, 11 mg, and 12 mg).

100 nm for 9 mg, 90 nm for 10–11 mg, and 70–80 nm for 12 mg, indicating a clear tendency to shift toward smaller particle sizes as the amount of SUS wool fiber increased. This decrease in cutoff diameter with increasing SUS wool fiber filling mass was also observed by Furuuchi *et al.* (2010a). As the total amount of SUS wool fiber increased, the wool fiber volume fraction of the IF cartridge increased. Then, the $d_{50}$ may have shifted to the small diameter side owing to the stronger effect of inertia collection. The effect of diffusion collection is more significant for smaller particle sizes. When the amount of introduced SUS wool fiber was 12 mg, diffusion collection could not be sufficiently suppressed and the amount of PM collected below 100 nm tended to increase, resulting in a sharp-cut classification curve. Fig. 5 shows a sharp classification curve at approximately 100 nm for 8–9.5 mg of SUS wool fiber.

To evaluate the optimum total amount of SUS wool fiber for a $d_{50}$ of 100 nm, a linear analysis was performed by plotting the amount of SUS wool fiber and the classification efficiency of PM at 100 nm (Fig. 6). Regression lines are shown as solid red lines and 95% confidence intervals as dashed blue lines, with a Pearson correlation coefficient of 0.94 ($p < 0.05$). From these results, it was estimated that 8.7 mg of SUS wool fiber were required to obtain a classification efficiency with a $d_{50}$ of 100 nm. The apparent SUS wool fiber volume fraction increased in the 4D cartridge compared to the normal IF cartridge without grooves due to the introduction of the partition, which resulted in a classification curve with a $d_{50}$ of 100 nm at a filling mass of SUS wool fiber lower than the 9.8 mg of the normal IF cartridge.

3.3 Atmospheric PM Observations under Optimum Conditions for the 4D Cartridge

The atmospheric observation was conducted using the conditions under which the optimum classification efficiency was obtained with the 4D cartridge using mesh E (0.14/40) and total SUS wool fiber mass (8.7 mg), while the 4D performance was evaluated from the sulfate ion concentration RSD of the SUS wool fiber pieces. Information on the samples is presented in Table S1 and the sulfate ion concentration of each SUS wool fiber piece is shown in Fig. 7. The RSD of ambient PM averaged 5.6% for S1–S4, which was within the acceptable range ($\pm 15\%$) for reanalysis of the MOEJ (2019) due to changes in analytical sensitivity of ionic components. It was also lower than the RSD (PM: 9%, total carbon: 5.9%) obtained by Kumsanlas *et al.* (2019) for the improvement of the PM$_{0.1}$ classification stage. Thus, PM was sufficiently and evenly collected among the four SUS wool fiber pieces through PM collection using the 4D cartridge. As such, classifying PM collection
Fig. 6. Evaluation of optimum amount of SUS wool fiber with $d_{50}$ of 100 nm.

Fig. 7. Sulfate ion concentration observed using the 4D cartridge of mesh E (0.14/40).

using the NS with a 4D cartridge enabled the simultaneous analysis of multiple chemical components for all particle sizes, including PM$_{0.5-0.1}$.

4 CONCLUSIONS

The NS PM$_{0.1}$ classification stage was refined to enable multi-component analysis of the classified collected particles. As a method that does not modify the shape of the existing NS body, a 4D partition was introduced into the IF cartridge to investigate the possibility of PM$_{0.5-0.1}$ quantitative partitioning using SUS wool fiber, allowing the simultaneous analysis of multiple components. Several stainless meshes were introduced into the 4D cartridge to collect PM; based on the concentration variations of PM sulfate ions on the SUS wool fiber pieces, the mesh with the most stable 4D collection was investigated as a partition. The larger the mesh opening area and the wider the gap, the smaller the RSD and the more evenly the PM tended to be divided into four parts. In the case of the mesh with a large opening area, the partition did not block too much of the cross-sectional area of the SUS wool fiber, thus minimizing its effect on the airflow and possibly suppressing particle adhesion on the stainless-steel mesh. Mesh E (0.14/40), which had the largest opening area (60.8%), was the best partition for the 4D cartridge. In the classification efficiency test of PM$_{0.1}$ on mesh E, the classification curve with a $d_{50}$ of 100 nm was obtained with
8.7 mg of SUS wool fiber filling the 4D cartridge. Under optimal conditions (mesh E, 8.7 mg of SUS wool fiber), the RSD of sulfate ions averaged 5.6%, confirming that PM was evenly collected from the four pieces of SUS wool fiber. This allows the analysis of multiple chemical components for all particle sizes by PM classification and collection using NS. Therefore, taking advantage of the NS' ability to classify semi-volatile components down to PM$_{0.1}$ with reduced loss from a classification principle that does not use a low-pressure process, the 4D cartridge can be applied to the analysis of the size-segregated chemical composition of various PM in observations. In actual PM observations in the atmosphere, it is expected that more detailed information on the emission sources and particle dynamics in the atmosphere, such as the growth process of PM, can be obtained by acquiring multi-component data of PM$_{0.5-0.1}$ using the 4D cartridge.

**ADDITIONAL INFORMATION**

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**Supplementary Material**
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