PM$_{2.5}$ Particle Detection in a Microfluidic Device by Using Ionic Current Sensing

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We have demonstrated a PM$_{2.5}$ analysis method that adds information on the number concentration and size by using microfluidic-based ionic current sensing with a bridge circuit. The bridge circuit allows for suppression of the background current and the detection of small PM$_{2.5}$ particles, even if a relatively large micropore is used. This is the first demonstration of the detection of PM$_{2.5}$ particles via ionic current sensing; our method enables analyses of both the number concentration and size.

Keywords PM$_{2.5}$, size analysis, ionic current sensing, bridge circuit, micropore

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Sample preparation

Micropore chip was filled with the TBE buffer (0.45 M Tris, 0.45 M boric acid, 0.01 M EDTA). The red circuit in Fig. 1b is a circuit for voltage application and the blue one is a circuit for balancing potentials between both ends of the micropore, and that of a 1-kΩ resistive element could be adjusted by a variable resistor (7270, BI Technologies). The current flowing through an amplifier (low-noise current amplifier DLPCA-200, FEMTO) was output to a recorder composed of a signal converter (NI USB-6259, National Instruments) and a PC equipped with LabVIEW software (National Instruments). In ionic current sensing, the potential difference at both ends of the micropore and that of the 1-kΩ resistive element were used for the output signal. As a PM$_{2.5}$ particle passed through the micropore, the potential difference at both ends of the micropore increased and the balanced potential was lost. Losing the balanced potential led to current flow through the amplifier, and passage of the particle through the micropore was detected as a signal (Fig. 1c).

**Experimental**

**Construction of the ionic current sensing circuit**

Ionic current sensing was performed by using an ionic current sensor composed of a micropore chip and two electric circuits (Figs. 1a and 1b). The micropore chip was filled with conductive 5×TBE buffer (0.45 M Tris, 0.45 M boric acid, 0.01 M EDTA). The red circuit in Fig. 1b is a circuit for voltage application and the blue one is a circuit for balancing potentials between both ends of the micropore, and that of a 1-kΩ resistive element could be adjusted by a variable resistor (7270, BI Technologies). The current flowing through an amplifier (low-noise current amplifier DLPCA-200, FEMTO) was output to a recorder composed of a signal converter (NI USB-6259, National Instruments) and a PC equipped with LabVIEW software (National Instruments). In ionic current sensing, the potential difference at both ends of the micropore and that of the 1-kΩ resistive element were used for the output signal. As a PM$_{2.5}$ particle passed through the micropore, the potential difference at both ends of the micropore increased and the balanced potential was lost. Losing the balanced potential led to current flow through the amplifier, and passage of the particle through the micropore was detected as a signal (Fig. 1c).

**Fabrication of the micropore chip**

The micropore chip was fabricated by pouring polydimethylsiloxane (PDMS; SILPOT184, Dow Corning Toray Co., Ltd.) into a SU-8 mold (SU-8 3005, Kayaku Co., Ltd.) formed by conventional photolithography. Au electrodes having a thickness of 40 nm were deposited onto a slide glass using a sputtering apparatus (MSP-mini, Vacuum Device), and a voltage-applying circuit using a battery (6LR 61 YXJ/1 S, Panasonic) connected through Ag wires (FTVS-408, Oyaide). In a balancing circuit, the potential difference at both sides of the 1-kΩ resistive element could be adjusted by a variable resistor (7270, BI Technologies). The current flowing through an amplifier (low-noise current amplifier DLPCA-200, FEMTO) was output to a recorder composed of a signal converter (NI USB-6259, National Instruments) and a PC equipped with LabVIEW software (National Instruments). In ionic current sensing, the potential difference at both ends of the micropore and that of the 1-kΩ resistive element were used for the output signal. As a PM$_{2.5}$ particle passed through the micropore, the potential difference at both ends of the micropore increased and the balanced potential was lost. Losing the balanced potential led to current flow through the amplifier, and passage of the particle through the micropore was detected as a signal (Fig. 1c).

**Sample preparation**

The PM$_{2.5}$ sample was prepared by aerosolizing purchased urban air dust (NIES CRM No.28, National Institute for Environmental Studies (NIES)) in 15 L of air, and then collecting particles inside a liquid thin film of 5×TBE buffer of 300 μL. We observed PM$_{2.5}$ particles which were sampled on a solid filter membrane having 100 nm pores (Merck & Co.) by a scanning electron microscope (SEM), and confirmed that the some of the particles were close to having a ball shape (Fig. S1; Supporting Information). According to the product data sheet, urban air dust contains many particles with 1 μm diameter, which was confirmed by the NIES using optical microscopy measurements.

**Scheme of measurements**

A voltage of 50 V was applied to the micropore chip. A solution containing the PM$_{2.5}$ particles was introduced to the sample inlet and pulled using a syringe pump with a flow rate value of 0.5 μL/min (Fig. S2). We measured the current signals derived from passage of the sample particles through the micropore.

**Results and Discussion**

PM$_{2.5}$ particles in a sample solution were introduced to the micropore and detected as ionic current signals without clogging inside of the micropore (Fig. 2a). For example, when 12.5 μL of the sample solution containing PM$_{2.5}$ flowed through the micropore, 161 particles were detected in 1500 s at a flow rate of 0.5 μL/min. Thus, we estimated the particle concentration in the solution at 1.3×10$^6$ particles/mL.

It is considered that large particles were not introduced into the micropore within the experimental time because the PM$_{2.5}$ sample had a small abundance ratio of large particles compared with the micropore width, based on information from the product data sheet.$^{13}$ From a proportional relationship between the signal amplitude and particle volume,$^{10}$ we calculated the...
diameter of PM2.5 particles by assuming that the particles had a ball shape. For example, a particle detected at 37.3 s in Fig. 2a showed a signal amplitude of 1.9 nA. From the calibration curve in our previous research, this signal was derived from a particle having a volume of 0.21 fL, which was 0.74 μm in size. The largest signal from among the detected particles indicated a particle diameter of 1.95 μm (Fig. S3). Particles over 2 μm in diameter were not detected. The size distribution of the calculated diameter of PM2.5 particles showed the number of particles with size less than 1 μm was predominant (Fig. 2b), which agreed with our previous result measured by SEM. From these results, we successfully analyzed the particle size distribution of PM2.5.

Conventionally, ionic current sensing using a circuit with a direct connection between the micropore and an amplifier is not sensitive enough to detect particles with a diameter of 0.74 μm in the micropore (height, 1.2 μm; width, 2.6 - 1.4 μm; length, 4.0 μm); the inherent limitation (S/N ~3) is that particle detection range should be 4.6% of pore volume (9.12 μm³) under the connection of a syringe. On the other hand, our bridge circuit enabled suppression of the background current flowing through the amplifier by balancing the potentials, and therefore, our bridge circuit could detect particles with a diameter of 0.4 μm (0.2% of the pore volume) in the micropore (height, 3.7 μm; width, 2.0 μm; length, 2.2 μm; pore volume, 16.3 μm³), which meant that our method could detect 54% smaller particles compared to conventional method, even if the same micropore was used. Since the PM2.5 composition had a diversity: some particles were electrophoretically introduced but the others were not, accurate PM2.5 detection required connecting a syringe for pressure introduction, which generally upset the noise level and significantly degraded the S/N level, as from 1.0 to 4.6% in the conventional circuit or from 0.01 to 0.2% in the bridge circuit. A relatively large micropore has a lower frequency of pore-clogging than a smaller one; however, utilizing the larger micropore in the conventional ionic current sensing lowers the detection sensitivity which makes it difficult to detect small particles. On the other hands, our method allows to use relatively large micropores without losing any sensitivity to small PM2.5 particles due to the high S/N ratio. These advantages of our method allowed us to analyze PM2.5 properties, size and number, even if a relatively large micropore was used.

Conclusions
From the presented results, we successfully demonstrated the first detailed analysis of PM2.5 particles using ionic current sensing with a bridge circuit. Our sensing method enabled the detection of PM2.5 particles with relatively smaller size compared to the micropore size, and the number concentration and sizes of individual particles were analyzed. We believe that the presented demonstration provides a new method for detailed analyses of PM2.5.

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Supporting Information
This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/

References