

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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Introduction

PM_{2.5}, which is airborne particulate matter (PM) with sizes of less than or equal to 2.5 μm, is considered as to be one of serious air pollutants, and the PM_{2.5}-related air pollution is a big issue on a global scale.¹⁻⁴ Depending on the generation source, PM has different particle properties, such as size, shape and composition,^{5,6} which are related to diverse diseases.⁷ Especially, as for the size effect of PM on health risk, since PM_{2.5} was demonstrated the deeper penetration into the alveoli,⁸ PM_{2.5} present a higher risk than PM with sizes of over 2.5 μm. The size of PM is an important indicator for evaluating PM_{2.5} effects on human health.

Presently in Japan, air-floating PM_{2.5} is monitored in the unit of weight concentration as an indicator of air pollution. The gold standard for PM_{2.5} measurements is β-ray absorption which analyzes the PM_{2.5} concentration by measuring any β-ray intensity difference caused by the collection of air-floating

particles on a filter.⁹ Although the collected particles are clarified as PM_{2.5} in size, actually, the collected particles still have PM with larger than 2.5 μm. Since β-ray absorption only analyzes particles based on the weight concentration and PM with larger than 2.5 μm make a larger contribution on the weight concentration than PM_{2.5}, a methodology to satisfy the lacking size information is highly desired.

Here, we 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.^{10,11} In conventional ionic current sensing, the detection of fine PM_{2.5} particles requires the use of a micropore with a tailored size for fine particles which leads to frequent pore-clogging by particles due to the great diversity of PM_{2.5} particle sizes. Therefore, the application of conventional ionic current sensing is extremely difficult. Our methodology using the bridge circuit allows for the suppression of the background current and could detect a PM_{2.5} particle of 0.4 μm in size (0.2% pore volume), even if a relatively large micropore (height, 3.7 μm; width, 2.0 μm; length, 2.2 μm) is used. This is the first demonstration of PM_{2.5} particle detection *via* ionic current sensing; our method enables analyses of both the number concentration and size information.

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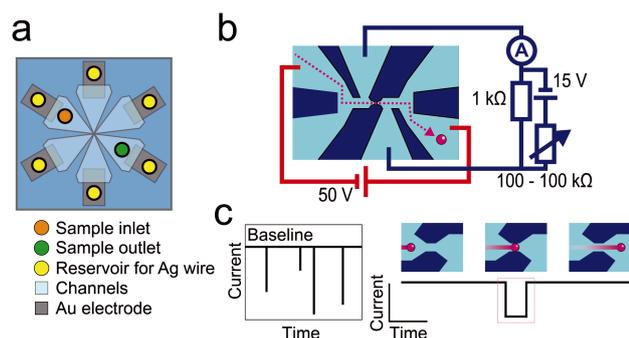


Fig. 1 Schematic illustrations of an ionic current sensor. (a) Design drawing of a micropore chip. (b) Circuit diagram of a bridge circuit and flow path of sample particles in a micropore chip. (c) Schematic diagram of a current signal due to translocation of a sample particle in a micropore.

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).^{10,11} The micropore chip was filled with conductive $5 \times$ 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-k Ω resistive element (E-Globaleedge Co.). The circuits were placed inside a shield box (Shield Room Co.) to reduce any high-frequency noise from other apparatuses. A voltage was applied to the 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-k Ω 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 k Ω 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 was applied through Au electrodes (Fig. 1a). At the center of the micropore chip, there was a micropore with a height of 3.7 μm , a width of 2.0 μm and a length of 2.2 μm . The micropore chip was filled with the $5 \times$ TBE buffer.

Sample preparation

The PM_{2.5} sample was prepared by aerosolizing purchased urban air dust (NIES CRM No.28, National Institute for

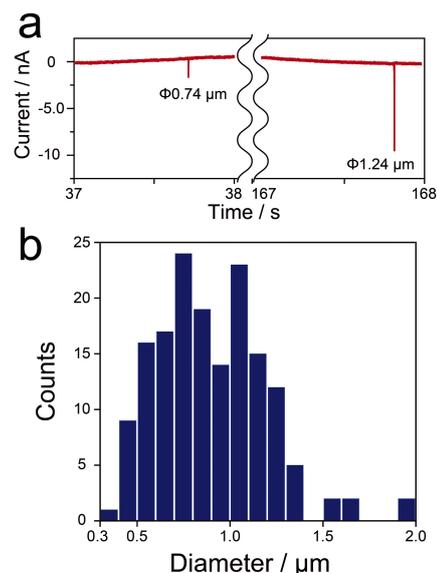


Fig. 2 Ionic current signals of PM_{2.5} particles and analyzed size distribution. (a) Ionic current signals due to passage of PM_{2.5} particles in the micropore. The calculated diameters of left and right signals were 0.73 and 1.24 μm , respectively. (b) Histogram of the diameters of detected PM_{2.5} particles. The number of detected PM_{2.5} particles in the 1500 s detection time was 161.

Environmental Studies (NIES)) in 15 L of air, and then collecting particles inside a liquid thin film of $5 \times$ TBE buffer of 300 μL .¹² 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 $\mu\text{L}/\text{min}$ (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 $\mu\text{L}/\text{min}$. Thus, we estimated the particle concentration in the solution at 1.3×10^4 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 PM_{2.5} 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,¹¹ 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 PM_{2.5} 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.¹² From these results, we successfully analyzed the particle size distribution of PM_{2.5}.

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 ($S/N \sim 3$) is that particle detection range should be 4.6% of pore volume (9.12 μm³) under the connection of a syringe.¹⁴ On the other hand, our bridge circuit enabled suppression of the background current flowing through the amplifier by balancing the potentials,^{10,11} 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 PM_{2.5} composition had a diversity: some particles were electrophoretically introduced but the others were not, accurate PM_{2.5} detection required connecting a syringe for pressure introduction, which generally upset the noise level and significantly degraded the S/N level, such as from 1.0 to 4.6% in the conventional circuit^{15,16} or from 0.01 to 0.2% in the bridge circuit.¹¹

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 PM_{2.5} particles due to the high S/N ratio. These advantages of our method allowed us to analyze PM_{2.5} 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 PM_{2.5} particles using ionic current sensing with a bridge circuit. Our sensing method enabled the detection of PM_{2.5} 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 PM_{2.5}.

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Supporting Information

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

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