

# Real-time monitoring and determination of Pb in a single airborne nanoparticle

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We used a differential mobility analyzer, an aerosol particle mass analyzer, and a gas exchange device to continuously introduce airborne nanoparticles (ANPs) to an inductively coupled plasma mass spectrometer. Pb concentrations in single ANPs with a diameter of 90 nm and a mass of 0.458 fg (density is 1.20 g cm<sup>-3</sup>) were determined. The developed method enabled us to determine Pb in ANPs having a Pb content of more than 10%.

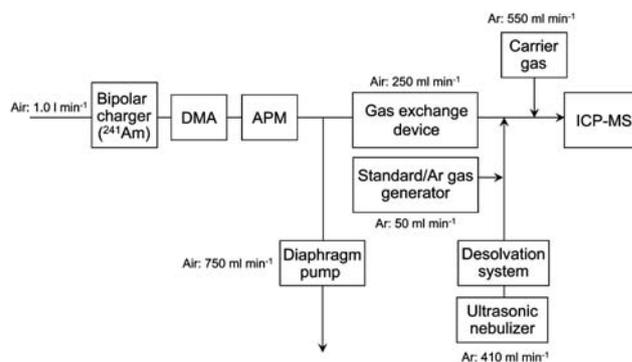
Though the field of nanotechnology is rapidly expanding and the number of new products containing nanomaterials continuously increases, the toxicity of such nanomaterials to humans still remains unknown. This potential toxicity is of great concern owing to the specific characteristics of nanomaterials. Nanomaterials' large specific-surface area allows them to activate biological reactions in human bodies. Studies using human subjects have clearly shown that inhaled airborne nanoparticles (ANPs) can pass into blood circulation and can be found in organs such as the liver, kidneys, and colon.<sup>1</sup> ANPs may also be inhaled unknowingly by humans. The elemental composition of a single ANP can provide useful information about the origin of the ANP. Generally, multi-element analysis for airborne particulate matter is performed with an inductively coupled plasma mass spectrometry (ICP-MS) after airborne particulate matter is collected on a filter and then acid digested to convert to a solution. This method requires several days to obtain a sufficient amount of airborne particulate matter for ICP-MS analysis, and the results can provide us with an average concentration of elements in various airborne particulates during a sampling time period. It has been reported that various particles containing heavy metals could be identified in aerosol samples by means of scanning electron microscope-energy dispersive X-ray spectrometer (SEM-EDX) or electron probe X-ray microanalysis (EPXMA), as a single-particle analysis technique.<sup>2,3</sup> However, obtaining time-dependent changes in elemental concentrations in air samples by SEM-EDX or EPXMA is difficult. In addition to the single-particle analysis of elements, real-time monitoring of elements is expected to be useful for elucidating the dynamic behavior of ANPs in the atmosphere and identifying their emission sources.

The combination of a differential mobility analyzer (DMA), which can separate particles depending on the diameter-to-charge ratio, and an aerosol particle mass analyzer (APM), which can separate particles depending on the mass-to-charge ratio, has enabled us to obtain

particle density information for ANPs.<sup>4</sup> Moreover, a recently developed gas exchange device for ICP-MS has enabled us to exchange gas molecules from air to Ar without any loss of particulate matter and to directly introduce gas-converted air samples into the ICP-MS instrument.<sup>5</sup> We utilized these three instruments (*i.e.*, the DMA, APM, and gas exchange device) to determine the Pb concentration in single ANPs in units of  $\mu\text{g g}^{-1}$ .

## Instrument setting for analysis of single ANPs in air

A schematic diagram of the instrument used in the present experiments is shown in Fig. 1. Outdoor air samples were collected from a location at Kasuga, Bunkyo-ku, Tokyo, near our laboratory. The sampling was carried out in December, 2009. A long tygon<sup>®</sup> tube was used to collect the outdoor air samples. Additionally, a blank air sample was collected from a clean bench (class 100) equipped with HEPA filters. Each air sample was introduced to the bipolar charger, DMA (Model 3081 (Long DMA), Tokyo Dylec Corp., Tokyo, Japan), and APM (APM 3600, Kanomax, Osaka, Japan) at a flow rate of 1.0 l min<sup>-1</sup>. After determination of the diameter and mass of the sampled particles, 0.75 l min<sup>-1</sup> of each air sample was vacuumed by a diaphragm pump with a mass flow controller. Then the remaining 0.25 l min<sup>-1</sup> was subjected to a gas exchange device (Sumitomo Seika Chemicals Co. Ltd., Osaka, Japan) that replaced the air with Ar. The reason why only 0.25 l min<sup>-1</sup> was introduced to the gas exchange device is its maximum gas exchange capacity is 0.25 l min<sup>-1</sup>. After being introduced to the gas exchange device, this portion of the air sample was introduced to the ICP-MS (HP4500, Agilent Technologies, Tokyo, Japan) *via* an aspirator consisting of a pneumatic concentric nebulizer. Standard gases of Cr, Mo, and W



**Fig. 1** Schematic diagram of real-time element determination in a single airborne nanoparticle by means of ICP-MS coupled with DMA (differential mobility analyzer), APM (aerosol particle mass analyzer), and gas exchange device.

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carbonyl complexes were introduced to the ICP-MS *via* Ar flow at 50 ml min<sup>-1</sup>. The signal intensities of <sup>208</sup>Pb were measured every 10 ms for a sampling period of 30 s. We continually introduced Milli-Q water *via* an ultrasonic nebulizer (U5000AT+, CETAC, Omaha, USA) coupled with a desolvation system (Aero membrane dryer unit, Elemental Scientific Inc., Omaha, USA) during tuning of the ICP-MS instrument as well as during analysis of the air samples and of the standard gas. We describe our rationale for using the ultrasonic nebulizer below.

### Calibration using the ultrasonic nebulizer

The mass flow rate (ng min<sup>-1</sup>) of standard gases of Cr, Mo, and W carbonyl complexes was determined by following steps. A standard gas generator aerated with Ar at 50 ml min<sup>-1</sup> was placed in a thermostatic chamber at 10, 15, 20, and 25 °C, then Cr, Mo, and W carbonyl complexes were trapped by passing the gases through methyl isobutyl ketone (MIBK) in serially arranged three impingers, after that concentrations of these elements trapped in MIBK solutions were measured by ICP-MS. As a result, Cr, Mo, and W amounts per unit time could be acquired under different temperature. Finally, the relational expressions between a mass flow rate and temperature were obtained for three elements. We externally calibrated the Cr, Mo, and W mass flow rates using standard gases but were unable to do so for other elements, in this case for Pb. We used an ultrasonic nebulizer to introduce elemental standard solutions into the ICP-MS as aerosols. We determined the introduction efficiency *via* an ultrasonic nebulizer daily by comparing <sup>53</sup>Cr intensities measured by the ICP-MS for the standard gas with those measured for the standard solutions. Cr and Pb standard solutions were prepared by diluting 1000 µg ml<sup>-1</sup> Cr and Pb standards (chemical analysis grade, Kanto Chemical Co., Inc., Tokyo, Japan) with 0.1 mol l<sup>-1</sup> nitric acid (70%, electronic laboratory grade, Kanto Chemical Co., Inc.). Standard solutions of 1.0 and 2.0 ng ml<sup>-1</sup> Cr and of 20, 50, and 100 pg ml<sup>-1</sup> Pb were introduced to the ultrasonic nebulizer at an uptake rate of 1.56 ml min<sup>-1</sup>, and the resulting nebulized mist was dewatered by the desolvation system. The signal intensities of <sup>208</sup>Pb or <sup>53</sup>Cr were measured every 10 ms for a sampling period of 30 s. When standard gases and solutions were analyzed, air samples were obtained from the clean bench. The introduction efficiency (*E*) of Cr standard solution was calculated from the following equation:

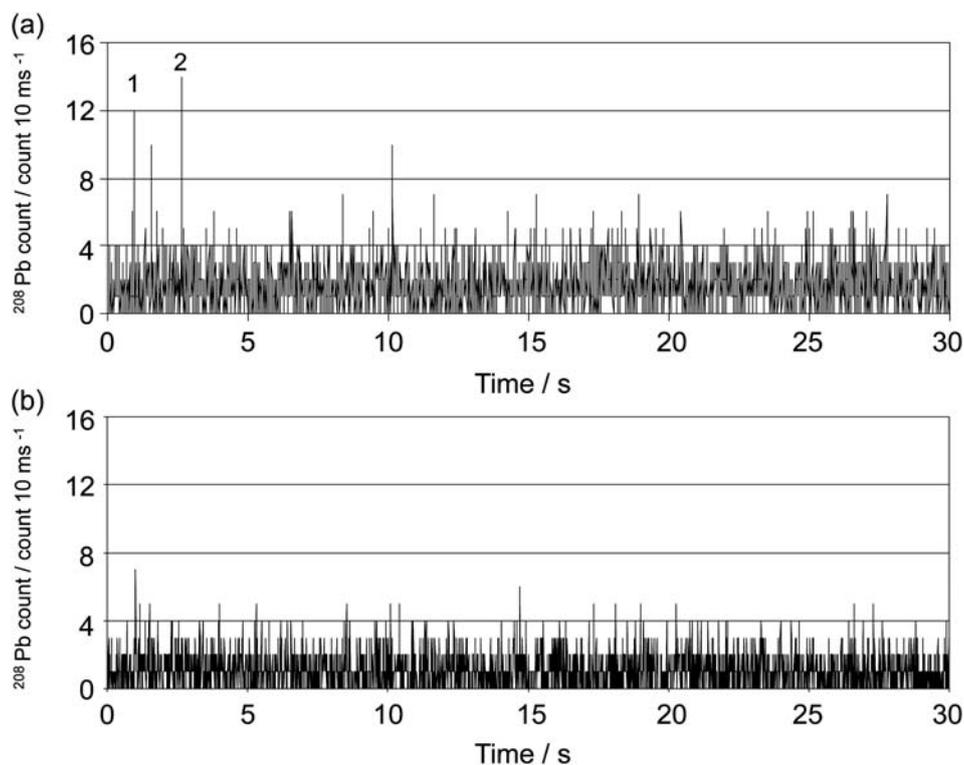
$$E = \frac{F_g \times (I_s - I_b)}{C \times F_s \times (I_g - I_b)} \quad (1)$$

$F_g$  is the mass flow rate of Cr carbonyl complex standard gas (ng min<sup>-1</sup>).  $C$  is the Cr concentration (ng ml<sup>-1</sup>) in the standard solution introduced into the ultrasonic nebulizer; for this calculation we used the 1.0 ng ml<sup>-1</sup> Cr standard solution.  $F_s$  is the uptake rate (ml min<sup>-1</sup>) of the Cr standard solution into the ultrasonic nebulizer.  $I_s$ ,  $I_g$ , and  $I_b$  are the <sup>53</sup>Cr intensities of the standard solution, the standard gas, and the blank, respectively. In this study,  $F_g$ ,  $F_s$ ,  $I_s$ ,  $I_g$ , and  $I_b$  were 0.145 ng min<sup>-1</sup>, 1.56 ml min<sup>-1</sup>, 104 counts, 269 counts, and 3.77 counts, respectively. By substituting these values into eqn (1), we calculated an introduction efficiency of 1.70%. Introduction efficiencies obtained from Mo and W carbonyl complexes were 1.90 and 0.03%, respectively. The difference of the introduction efficiency between W and the other two elements was owing to the difference of their matrix. The matrixes of Cr, Mo and Pb standard

solutions were 0.1 mol l<sup>-1</sup> HNO<sub>3</sub> but that of W was deionized water. In this study, using Cr introduction efficiency along with the uptake rate of 1.56 ml min<sup>-1</sup>, we converted the Pb concentrations (pg ml<sup>-1</sup>) in the Pb standard solutions to Pb mass flow rates (ag ms<sup>-1</sup>). The correlation coefficient of the Pb calibration curve was 0.9993, and the detection limit was 2.8 ag ms<sup>-1</sup>. During ICP-MS measurements of air samples containing <sup>208</sup>Pb, Milli-Q water was introduced into the ICP-MS *via* the ultrasonic nebulizer to maintain constant plasma conditions.

### Real-time monitoring of Pb in a single ANP

The results of real-time monitoring of single ANPs with a diameter of 90.0 nm and a mass of 0.458 fg (density is 1.20 g cm<sup>-3</sup>) are shown in Fig. 2 for the air sample collected in Tokyo (Fig. 2a) and for the blank air sample obtained from the clean bench (Fig. 2b). The average ion count for the blank was 1.1 ± 1.1. Therefore, we determined the detection limit for Pb to be 4.2 counts (3σ) and the quantitation limit to be 11.7 counts (10σ) including the blank value (1.1 counts). During the 30-s sampling period, we observed 27 detectable peaks (*i.e.*, 27 peaks with an intensity equal to or greater than 4.2 counts), and we noticed that in rare instances more than two particles were detected in a sampling time of 10 ms simultaneously. In contrast, only two quantifiable peaks were detected during the 30-s sampling period. Real time monitoring was repeated three times, and one quantifiable peak was detected for the other two 30-s sampling period. The amounts of Pb detected in these two peaks (Peaks 1 and 2 in Fig. 2a) were 65 and 76 ag, respectively, corresponding to Pb concentrations of 14.1 and 16.7%, respectively, in a single ANP (Table 1). These percentages corresponded to about 2 × 10<sup>5</sup> atoms of Pb. Normally, 1 count per 10 ms of an ICP-MS signal corresponds to about 2 × 10<sup>4</sup> atoms of an ion introduced from a sampling cone,<sup>6</sup> so it is reasonable to conclude that the 12 and 14 counts of <sup>208</sup>Pb signal detected by ICP-MS in the two peaks labeled in Fig. 2a corresponded to about 2 × 10<sup>5</sup> atoms of Pb, in which approximately 1 × 10<sup>5</sup> atoms of <sup>208</sup>Pb (natural abundance of <sup>208</sup>Pb is 52.4%) would have been present. We collected airborne particulates in January, 2010 by separating by size with aerodynamic diameter  $D_p < 0.06$ , 0.06–0.12, 0.12–0.20, 0.20–0.30, 0.30–0.50, 0.50–0.70, 0.70–1.2, 1.2–2.1, 2.1–3.6, 3.6–5.2, 5.2–7.9, 7.9–11, and > 11 µm on cellulose acetate membrane filters (ToyoRoshi Kaisha Ltd, Tokyo, Japan) using an Andersen-type Low Pressure Impactor (LPI) air sampler (LP-20; Tokyo Dylec Co., Tokyo, Japan), and then determined Pb after acid digestion. The measurement of weight of airborne particulates collected on each filter was difficult because the amounts of airborne particles were small, then we calculated the concentration in units of pg m<sup>-3</sup>. Pb concentration in the fraction with aerodynamic diameter of 0.06–0.12 µm was 420 pg m<sup>-3</sup>, and this concentration was comparable to that collected from road side of Tatebayashi, Gunma, Japan.<sup>7</sup> Considering the sampling flow rate of 0.25 l min<sup>-1</sup> and the ionization efficiency of 24.1% by a bipolar charger, Pb concentration of 420 pg m<sup>-3</sup> is converted to Pb mass flow of 25.3 fg min<sup>-1</sup>. If we assume that the Pb concentration of ANPs in every 1 nm is the same from 60 to 120 nm, Pb mass flow of ANPs with a diameter of 90 nm is estimated to 421 ag min<sup>-1</sup>. In this study, we obtained two Pb contained particles for 30 s in which Pb amount was 65 and 76 ag, respectively, therefore, it is calculated that Pb mass flow is 282 ag min<sup>-1</sup>. This value is reasonably comparable with the Pb mass flow of 421 ag min<sup>-1</sup> determined by an ordinary method of the 13 size-classified impactor.



**Fig. 2** Real-time profiles for  $^{208}\text{Pb}$  in a single airborne nanoparticle with a diameter of 90 nm and with a mass of 0.458 fg (density is  $1.20\text{ g cm}^{-3}$ ) in (a) outdoor air and (b) blank air collected from a clean bench.

**Table 1** Pb concentrations in a single airborne nanoparticle

Peak No.	Slope/ count $\text{fg}^{-1}$	$^{208}\text{Pb}$ count/ count $10\text{ ms}^{-1}$	Size/ nm	Mass/ fg	Concentration/%
1	168.8	10.9	90.0	0.458	14.1
2	168.8	12.9	90.0	0.458	16.7

However, in order to quantify the detectable small 25 Pb peaks, the sensitivity of analytical instruments must be improved by a factor of 10 or more relative to the sensitivity afforded by the current experimental setup.

## Conclusions and future directions

Pb concentrations in single ANPs having Pb content of more than 10% were determined. As the amounts of elements in particles decrease with decreasing particle mass, the determination of elemental concentrations by means of a mass-dependent detection method such as ICP-MS becomes more difficult. To quantify the detectable small 25 Pb peaks, it is necessary to improve the sensitivity of such analytical instrumentation by a factor of 10 relative to a current instrument. Sb and Cd concentrations in airborne particulate matter were 10 and 33 times lower than Pb concentration, respectively.<sup>8</sup> For the determination of Sb and Cd in a single ANP, the sensitivity should be improved by a factor of 100 or more relative to a current instrument. To determine multiple elements in a single ANP, simultaneous multi-element analysis is required. And for that reason, a time-of-flight mass spectrometer or a Mattauch-Herzog sector field mass spectrometer is preferred over a quadrupole mass spectrometer. When a quadrupole mass spectrometer is replaced with

the above-mentioned types of mass spectrometers, the most important parameter is the sensitivity improvement for the determination of Pb, Sb, and Cd in a single ANP.

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