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Quantitative real-time monitoring of multi-elements in airborne particulates by direct introduction into an inductively coupled plasma mass spectrometer☆

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ABSTRACT

A new calibration system for real-time determination of trace elements in airborne particulates was developed. Airborne particulates were directly introduced into an inductively coupled plasma mass spectrometer, and the concentrations of 15 trace elements were determined by means of an external calibration method. External standard solutions were nebulized by an ultrasonic nebulizer (USN) coupled with a desolvation system, and the resulting aerosol was introduced into the plasma. The efficiency of sample introduction via the USN was calculated by two methods: (1) the introduction of a Cr standard solution via the USN was compared with introduction of a $Cr(CO)_6$ standard gas via a standard gas generator and (2) the aerosol generated by the USN was trapped on filters and then analyzed. The Cr introduction efficiencies obtained by the two methods were the same, and the introduction efficiencies of the other elements were equal to the introduction efficiency of Cr. Our results indicated that our calibration method for introduction efficiency worked well for the 15 elements (Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Sn, Sb, Ba, Tl and Pb). The real-time data and the filter-collection data agreed well for elements with low-melting oxides (V, Co, As, Mo, Sb, Tl, and Pb). In contrast, the real-time data were smaller than the filter-collection data for elements with high-melting oxides (Ti, Cr, Mn, Ni, Cu, Zn, Sn, and Ba). This result implies that the oxides of these 8 elements were not completely fused, vaporized, atomized, and ionized in the initial radiation zone of the inductively coupled plasma. However, quantitative real-time monitoring can be realized after correction for the element recoveries which can be calculated from the ratio of real-time data/filter-collection data.

1. Introduction

Multi-element analysis of airborne particulate matter is generally performed by means of inductively coupled plasma mass spectrometry (ICP-MS) or optical emission spectrometry after airborne particulates (APs) are collected on a filter and then dissolved by acid digestion [1–3]. However, obtaining enough APs for ICP-MS requires several hours or days, and thus the results provide average concentrations of elements in APs from various sources during the sampling period.

Trace elements in APs have been also measured online in real time by direct introduction of air samples into the spectrometer via a nebulizer [4–7]. However, the volume of the air sample is limited with this method. To increase the air sample volume, a differential mobility analyzer has been used as a gas-exchange device [8]. In addition, Nishiguchi et al. recently reported a gas-exchange device for ICP-MS that exchanges the gas molecules from air to Ar without any loss of particulate matter, and the resulting gas-converted air sample can be introduced directly into the ICP-MS instrument [9]. However, the multi-element data obtained by these investigators were only qualitative, although semi-quantitative data were obtained for Sn. In previous work, we reported the quantification of Pb in a single nanoparticle (diameter, 90 nm; mass, 0.458 fg) calibrated by an external standard introduced with an ultrasonic nebulizer (USN) coupled with a desolvator system [10], but this method has not yet been validated.

In this study, we evaluated the efficiency of sample introduction via the USN by collecting aerosols generated by the USN on filters and then analyzing the aerosols. Then, we calibrated real-time data by nebulizing an external multi-element standard solution and using the sample introduction efficiency of the USN. During real-time analysis, we also simultaneously collected APs on a filter, and we validated the real-time data by comparison with the filter-collection data.

2. Experimental

2.1. Reagents

A custom multi-element standard solution (Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb Th, and U) (XSTC-384, SPEX CertiPrep Inc., Metuchen, NJ) and Ti (PLTL9-2Y, SPEX CertiPrep Inc.) and Sn (PLSN2-2X, SPEX CertiPrep Inc.) standard solutions were used as an external standard for real-time analysis. A $Cr(CO)_6$

☆ This paper is dedicated to Gary M. Hieftje, on the occasion of his 70th birthday, in recognition of his boundless contributions to spectroscopy and analytical chemistry.

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gas, which was generated by standard gas generator (J-Science Lab Co., Kyoto, Japan), was used for the determination of the sample introduction efficiency of the USN. Nitric acid (70%, electronic laboratory grade, Kanto), HF (50%, semiconductor grade, Daikin Industries Co., Tokyo, Japan), H_2O_2 (30%, electronic laboratory grade, Kanto), and ultrapure water (Milli-Q Element, Millipore, Tokyo, Japan) were used for sample digestion and preparation of standard solutions.

2.2. System for real-time determination of elements in APs

A schematic diagram of the analytical apparatus is shown in Fig. 1. Outdoor air samples were collected from the rooftop (30 m high) of building no. 5 of Chuo University (Kasuga, Bunkyo-ku, Tokyo) through an 80-m-long Tygon tube (inside diameter is 7.94 mm) by means of a diaphragm pump equipped with a mass flow controller. The sampling dates are listed in Table 1. Additionally, a blank air sample was collected from a clean bench (class 100) equipped with HEPA filters. Each air sample was introduced to a multinozzle cascade impactor (inline type with NL-1-1A (<1.0 μm) or NL-1-2.5A (<2.5 μm), Tokyo Dylec Corp., Tokyo, Japan) at a flow rate of 1.0 L min^{-1}. A portion of the sample was vacuumed from the impactor at 0.75 L min^{-1} by means of a diaphragm pump equipped with a mass flow controller, and the APs from this portion were collected on a cellulose nitrate filter (VSWP04700; pore size, 0.025 μm; Millipore, Tokyo). The remaining portion of the flow (0.25 L min^{-1}) was introduced to a gas-exchange device (J-Science Lab Co., Kyoto, Japan), which replaced the air with Ar. This portion of the air sample was introduced to the ICP-MS (HP4500, Agilent Technologies, Tokyo, Japan) by means of a micro diaphragm gas-sampling pump (NMP05L, KNF Neuberger AG, Balterswil, Switzerland).

Standard $Cr(CO)_6$ gas was introduced to the ICP-MS via an Ar flow at 0.05 L min^{-1}. The multi-element standard solution was introduced to the ICP-MS via a USN coupled with a desolvation system (U6000AT+, CETAC, Omaha, NE, USA). Milli-Q water was continuously introduced via the USN/desolvation system during analysis of the $Cr(CO)_6$ standard gas as well as during tuning of the ICP-MS instrument and analysis of the air samples. The ICP-MS operating conditions are summarized in Table 1.

2.3. Calculation of USN sample introduction efficiency by comparison with introduction of $Cr(CO)_6$ by a standard gas generator

We calculated the sample introduction efficiency of the USN daily by comparing ^{53}Cr intensities measured by the ICP-MS for a standard $Cr(CO)_6$ gas with intensities measured for a Cr standard solution. A 5.0 ng mL^{-1} Cr standard solution was prepared by diluting 1000 μg mL^{-1} Cr with 0.1 mol L^{-1} nitric acid. The standard Cr solution was introduced to the USN at an uptake rate of 1.56 mL min^{-1}, and the resulting nebulized mist was dewatered by the desolvation system. The signal intensities of ^{53}Cr were measured 5 times over a sampling period of 9 s. When standard gases and solutions were analyzed, air samples were obtained from the clean bench. The introduction efficiency (E_g) of the Cr standard solution was calculated by means of the following equation:

$$E_g = \frac{F_g \times (I_s - I_b)}{C \times F_s (I_g - I_b)} \times 100\% \qquad (1)$$

where F_g is the mass flow rate of the Cr as $Cr(CO)_6$ standard gas (ng min^{-1}) determined previously [10]; C is the Cr concentration (ng mL^{-1}) in the standard solution introduced into the USN; F_s is the uptake rate (mL min^{-1}) of the Cr standard solution into the USN; and I_s, I_g, and I_b are the ^{53}Cr intensities of the standard solution, the standard gas, and the blank, respectively.

2.4. Calculation of USN sample introduction efficiency by comparison with filter-collection data

A 200 ng mL^{-1} multi-element external standard for 15 elements (Cr, Ti, V, Mn, Co, Ni, Cu, Zn, As, Mo, Sn, Sb, Ba, Tl and Pb) was prepared by mixing 10 μg mL^{-1} custom multi-element standard, 1000 μg mL^{-1}Ti, and 1000 μg mL^{-1} Sn and then diluting with 0.1 mol L^{-1} nitric acid. Aerosols of the multi-element external standard generated by the USN were trapped on tandem nitro cellulose filters (pore size, 0.22 μm; MILLEX-LG for ion chromatography, FOS1S0017, Dionex, Japan) for 15 min. Trapped elements were extracted with four 2.5-mL portions of 0.1 mol L^{-1} HNO_3, and then the element concentrations were determined by ICP-MS. We

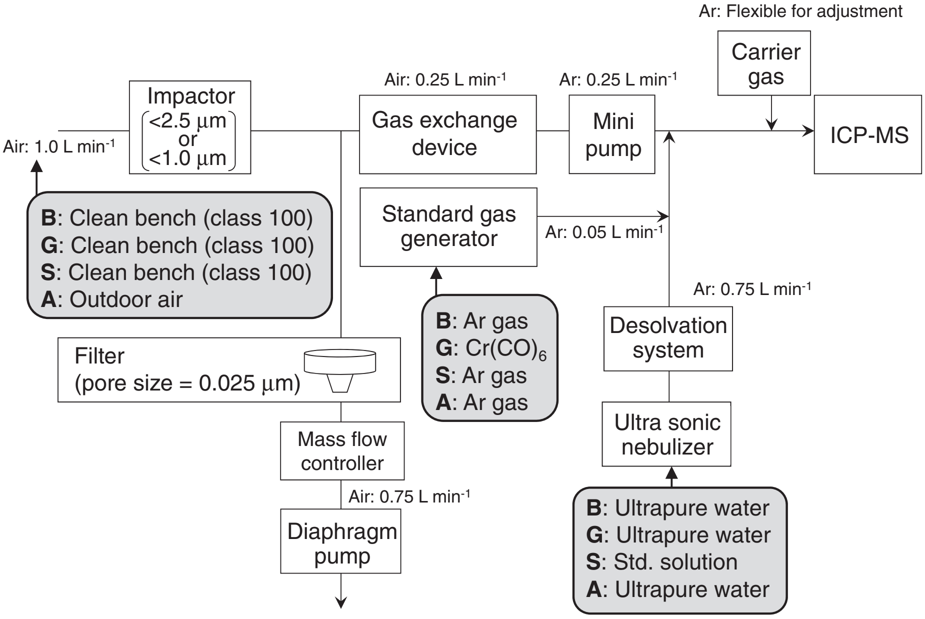

Fig. 1. Schematic diagram of apparatus for real-time analysis. B: blank; G: $Cr(CO)_6$ gas; S: standard solution; and A: outdoor air.