Atmospheric Environment xxx (2014) 1–4

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Improved methods for elemental analysis of atmospheric aerosols for evaluating human health impacts of aerosols in East Asia

Tomoaki Okuda [a,*], James J. Schauer [b], Martin M. Shafer [b]

[a] *Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan*
[b] *Environmental Chemistry and Technology Program, University of Wisconsin-Madison, 660 North Park Street, Madison, WI 53706-1413, USA*

HIGHLIGHTS

- Comprehensive trace element analysis of PM was carried out using SF-ICP-MS.
- A rapid and simple element analysis was carried out using EDXRF.
- The analytic results obtained by these two methods agreed well.
- The concentrations of 44 elements in PM were obtained by SF-ICP-MS.
- EDXRF can analyze each sample as fast as 900 s (15 min) for 16 elements.

ARTICLE INFO

Article history:
Received 30 September 2013
Received in revised form
23 January 2014
Accepted 27 January 2014

Keywords:
EDXRF
Microvolume microwave-assisted acid digestion
Particulate matter
SF-ICP-MS
Trace elements

ABSTRACT

This paper provides improved elemental analysis methods for the characterization of atmospheric particulate matter (PM) samples. With the aim of developing an approach for comprehensive trace element analysis of small mass of PM samples, we coupled an enhanced microwave-assisted acid digestion method with high-resolution magnetic sector inductively coupled plasma-mass spectrometry (SF-ICP-MS). We also propose a rapid and simple method using energy dispersive X-ray fluorescence spectrometry (EDXRF) that has secondary targets and three-dimensional polarization optics for screening elemental composition of PM. We obtained the concentrations of 44 elements ranged from 10^{-3} to 10^{5} μg/g by SF-ICP-MS, and 16 elements ranged from 10^{1} to 10^{5} μg/g by EDXRF. The analytic results obtained by these two methods agreed well. Comprehensive analysis for a large set of elements was demonstrated by using the improved SF-ICP-MS method, while EDXRF coupled with fundamental parameter (FP) quantification method can analyze several selected elements as fast as 900 s (15 min) per sample with only minimal sample pretreatment. We provide two possible choices of analysis methods for elucidating elemental composition of PM according to the number of samples, target elements, sample amounts, time and cost for analysis required.

1. Introduction

A large number of health studies are currently being conducted, or are planned for the future, that are directed toward understanding the effects on human health of exposure to atmospheric particulate matter (PM). Many of these efforts would be greatly enhanced if cost-effective analytic methods were available that could provide detailed elemental composition of PM. There is still much to learn about the role of chemical composition of PM in environmental health perspectives (Schauer et al., 2010), and improved robust cost-effective methods for analyzing elements in PM are needed more than ever. Recently, Schauer et al. (2010) have reported that the optimization of sampling and inductively coupled plasma-mass spectrometry (ICP-MS) analysis techniques for the measurement of trace metals and selected trace element-isotope signatures in PM samples collected with personal exposure samplers. The proposed methods will enable advanced characterization of PM from low-volume personal exposure samples, and thereby provide data for improved exposure assessments and source apportionment of elemental components of atmospheric PM. However, ICP-MS analysis essentially requires destructive acid digestion that needs a time-consuming, complex pretreatment. Alternatively, X-ray fluorescence spectrometry (XRF) has been used for measuring major elements in aerosols with only minimal sample pretreatment. Traditionally, it is thought that the bench-top type energy-dispersive XRF (EDXRF) is unsuitable for trace element

---

* Corresponding author.
E-mail address: okuda@applc.keio.ac.jp (T. Okuda).

1352-2310/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.atmosenv.2014.01.043

analysis because of its relatively low sensitivity; however, it has increasingly been applied to aerosol multi-element measurements because of the improvements in sensitivity associated with the utilization of many new techniques such as secondary targets and three-dimensional polarization optics (Okuda et al., 2013a, b, c, d, e; Okuda and Hatoya, 2013; Spolnik et al., 2005; Yatkin et al., 2012; Zhang et al., 2012). Okuda et al. (2014) have even tried to analyze sub-milligrams of PM collected with personal exposure samplers using EDXRF, and they have successfully shown that EDXRF would be suitable for applying to epidemiological studies since it could analyze enormous number of samples for obtaining chemical compositions of aerosols. Note that XRF is generally described as nondestructive, and it's true for nonvolatile elements; however, some lighter elements and semivolatile compounds have the potential to decomposition or volatilize by X-ray radiation and/or from being in a vacuum generated to prevent air from attenuating X-rays (Baron and Willeke, 2001). For example, XRF analysis under vacuum (20 Pa) for 12 h caused 12.3–23.5% reduction of several methoxyphenols in ambient PM samples collected on PTFE filters (Simpson et al., 2005).

There have been a few published studies that address the comparability of EDXRF and ICP-MS data in the context of PM analysis. For example, Yatkin et al. (2012) have concluded that EDXRF could be considered as an alternative method to ICP-MS for measurements of selected elements in PM. Reasonably good agreement is observed between the methods when PM filter loading is adequate for EDXRF quantification (Herner et al., 2006; Niu et al., 2010; Steinhoff et al., 2000). Consequently, ICP-MS and EDXRF techniques have their own merits when considering elemental analysis for aerosol samples; however, there is still room for improvement in the methods, such as analytical time and the level of detection limits.

This paper provides a comparison of the improved elemental analysis methods for the characterization of atmospheric PM samples. With the aim of developing an approach for comprehensive trace element analysis of a few milligrams of PM samples, we coupled an enhanced microwave-assisted acid digestion method with high-resolution magnetic sector inductively coupled plasma-mass spectrometry (SF-ICP-MS). We also propose a rapid and simple method using energy dispersive X-ray fluorescence spectrometry (EDXRF) that has secondary targets and three-dimensional polarization optics for screening elemental composition of PM.

2. Experimental

2.1. Improved SF-ICP-MS method

The basic analytical method for elemental analysis used in this study has been previously reported (Hamad et al., 2012; Schauer et al., 2010; Zhang et al., 2008). In this study, several significant analytical improvements are presented. We have listed a few important considerations/improvements to standard ICP-MS methods below:

a. Very few published reports/methods incorporate magnetic sector ICP-MS, instead relying on quadrupole instrumentation. Dramatic improvements in both background noise and sensitivity are characteristic of magnetic sector ICP-MS, resulting in orders-of-magnitude gains in signal to noise.
b. The magnetic-sector ICP-MS also very importantly effectively isolates and removes from consideration (by high mass resolution) many spectral interferences that still plague the quantification of many elements by quadrupole ICP-MS. This allows the magnetic-sector method to quantify not only at much lower concentrations, but also a much larger number of elements.
c. We employed a unique microwave assisted acid digestion method that uses less than 2 mL of a mix of ultra-high purity acids. Not only does this enable the quantitative recovery of all elements from the PM, but significantly lowers the acid matrix blank.
d. The low-volume, high sensitivity methods enable the quantification of nearly 50 elements in PM masses as low as 50 μg and at a reasonable throughput of 25–30 samples per day.
e. All analyses were carried-out in a clean-room, specifically built and dedicated to trace element research.

Detailed analytical procedure has been described below. Elemental analysis by mass spectrometry was performed in the trace metals clean room at the University of Wisconsin–Madison's Wisconsin State Laboratory of Hygiene (Madison, WI). A Thermo-Finnigan, Element 2, double-focusing, magnetic sector (high-resolution) ICP-MS (SF-ICP-MS) was used to acquire elemental data for over 50 elements in the PM samples. The sample introduction system consisted of an ESI FAST (SC-E2-DXS) nebulizer/autosampler (with enclosure) with a PEEK switching valve and 2 mL sample loop. The complete analytical system is located within a dedicated trace metal clean room. This approach enables accurate and precise quantification of low levels of elements in complex PM sample digests and extracts. The signal-to-noise of SF-ICP-MS is far superior to that of quadrupole ICP-MS for most elements, and when operated in medium ($R = 4000$) or high ($R = 10{,}000$) resolution modes, spectral interferences (e.g. polyatomic ions or elemental isobars) that compromise quantification of many elements by traditional quadrupole ICP-MS, are eliminated.

Samples are typically diluted with 2% (v/v) ultra-high purity 16 M nitric acid to a final volume of 5 mL and introduced into the plasma at a flow rate of 0.4 mL/min with a PFA ST nebulizer, quartz cyclonic spray chamber, and quartz torch with 1.5 mm injector. Standard nickel sampler and skimmer cones are used. Fifty-four isotopes are acquired in Low resolution ($R = 300$); 32 isotopes in Medium resolution, and 9 isotopes in High resolution. A sample acquisition consists of 4 runs × 4 passes, with 10 samples per peak, for a total analysis time of 4 min per sample. With the ESI autosampler system, carry-over between samples can virtually be eliminated with quite short equilibration/rinse times (18 s each for sample uptake and rinsing). Plasma conditions (16.0 L min^{-1} cool gas, 0.90 L min^{-1} aux gas, 1.00 L min^{-1} nebulizer gas, 1350 W Rf power) are optimized for our acid digest matrix.

The analytical sequence is based on EPA 200.8, with an initial calibration, 2nd source check standards and continuing calibration check blanks and standards at 12 sample intervals. The typical SF-ICP-MS batch includes 25 participant samples, 2 sample matrix spikes, 2 blank spikes, 4 certified reference materials (CRMs), 4-5 matrix blanks, 2 method blanks, and 2 sample duplicates in addition to the check blanks and calibration verification checks. CRMs included are: NIST SRMs San Joaquin Soil (2709), Urban Particulate Matter (1648a), Used Autocatalyst (2556), and Marine Sediment (2702).

Instrumental detection limits (3-sigma) were in the range of 0.01–2 ng/L for most trace elements and in the range of 5–50 ng/L for major elements. Extraction spike recoveries at the 40 and 80 ng level (equivalent to 2 and 4 μg/L) were, with only minor exceptions, all within our acceptance window (85–115%). Sample spike recoveries were also well within our acceptance window (85–115%). The mean analytical instrument precision for total trace elements at typical environmental levels was 4.8% and for the major metals 1.6%.

2.2. EDXRF method

Filter samples were analyzed by EDXRF without any pretreatment using an EDXL300 spectrometer manufactured by Rigaku