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Preparation of airborne particulate standards on PTFE-membrane filter for laser ablation inductively coupled plasma mass spectrometry

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Abstract

This study presents a feasible means of preparing simulated membrane-filter standards from SRM materials for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The homogeneity of the prepared standards and the accuracy and precision of determination of various elements in the prepared standards analyzed by LA-ICP-MS were also investigated. Results compared with those of X-ray fluorescence (XRF) spectrometry and ICP-MS after sample digestion in a high pressure bomb indicated that a standard filter prepared by the developed technique can be used to analyze for trace elements in airborne particulates by LA-ICP-MS with a high degree of sensitivity and convenience. In addition, up to sixteen elements on a single filter sample can be determined within 10 min. © 1998 Elsevier Science B.V.

Keywords: Multielement determination; Airborne particles; High-pressure bomb digestion; ICP-MS; LA-ICP-MS; XRF

1. Introduction

Several methods of performing inductively coupled plasma mass spectrometry (ICP-MS) on airborne particulate samples were developed in our previous research work [1,2]. Many analytical problems have been encountered in airborne particulate analysis; samples are difficult to digest, trace elements may be lost or contaminated in the course of the digestion process and spectrometric interference may be serious due to the acid-derived background ions having formed during the ion extraction process of ICP-MS [3–7].

By using a laser ablation (LA) technique, particulates are directly removed from the filter media by ablation with laser pulses and incorporated with ICP-MS spectrometry (LA-ICP-MS), thereby averting many of the problems associated with conventional particle analysis methods [8–11]. LA-ICP-MS is superior to the conventional aqueous ICP-MS method in that, nearly no sample pre-treatment is required for determining elements, therefore, the losses due to the formation of volatile compounds and presence of contaminants could be negligible. Furthermore, only a slight amount of interference arises during ICP-MS measurement originating from undesirable polyatomic ions from water and acids. However, some difficulties still persist with respect to unstable laser output and the inhomogeneity of filter matrix as

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well as particulates loaded during the sampling process.

Preparing standards for calibration is a prerequisite for analysis by LA-ICP-MS since it is probably the limiting factor for a quantitative analysis of airborne particles collected on membrane filters. Several types of thin deposited standards have been employed to determine airborne particles by nondestructive analytical methods, such as X-ray fluorescence (XRF) spectrometry [12,13]. Among those standards include filter deposits of materials obtained from vacuum-evaporated elements and compounds, from solutions after solvent evaporation, or from liquid suspension. However, none of those standards can simulate the matrix of real samples collected by membrane filtration.

Based on the above considerations, this work presents a simple means of preparing simulated membrane-filter standards from standard reference materials for LA-ICP-MS measurement. The homogeneity of the prepared standards and the accuracy and precision of various elements in the prepared standards were closely examined.

2. Materials and methods

2.1. Sample preparation

Real samples were collected from an ambient air quality monitoring station in the Kaohsiung metropolitan area of Taiwan during the summer of 1996. A dichotomous sampler was employed to collect samples on polytetrafluoroethylene (PTFE)-membrane filters (Gelman Teflo, 37 mm diameter, 2 μm pore size). Detailed information regarding the sampling instrument was reported in our previous paper [13]. Standard filters were prepared by a sample preparation chamber comprising three parts: an upper collection tube (I), a mixing chamber (II) and a lower blowing tube (III) (Fig. 1). The parts are made of acrylic plexiglass or poly (vinyl chloride) (PVC) to permit observation during experiments as well as to prevent contamination during the process. A weighted blank PTFE-membrane filter was assembled in the collection tube as well as the blowing tube. The collection tube consists of a filter assembly in which the PTFE-membrane filter is mounted directly on a glass-fiber filter. The same assembly, but in reverse order, was also arranged for the blowing tube. An extra glass fiber filter was added between the supporting stainless steel screen (Gelmen, steel 316 screen) and the membrane filter, thereby allowing for a more homogeneous collection.

Urban Particulate Matter from the National Institute of Standards and Technology (NIST SRM 1648) and City Waste Inceration Ash from the Community of Bureau of Reference, Commission of the European Communities (BCR No. 176), were placed on the filter of the blowing tube and purged by the N_2 gas into the mixing chamber. The N_2 gas purge rate was accurately controlled by the needle valve (A) and flow meter (B). The suspended particulates were distributed by two 3000 rpm mini-fans (F) inside the mixing chamber and collected on the preweighed filter in the collection tube through vacuum suction action (G). To maintain the size distribution of loaded particles on the filter similar to those of the standard reference materials, the flow rate of N_2 gas was gradually increased from 0.1 to 15.0 l min^{-1}. The adjusted flow rates caused the particulates of various sizes to float into the chamber. Next the gas flow through the pump was regulated by the needle valve (C) according to the N_2 gas flow. To ensure the flow of particulates, a vibrator (E) controlled by a motor with a 1500~5000 rpm vibration rate was installed beside the blowing tube. The vibration rate for various sizes of particles was experimentally determined so that the particulates could effectively be floated into the chamber.

Notably, the purging N_2 gas caused the particulate plume to float from the blowing tube and was then distributed in the chamber at each preset flow rate. Similar procedures were repeated until the particulates were collected. After preparing the sample, the loaded filters were put on the dichotomous sampler, which was located in a clean room, for 5 min air sampling to ensure firm adhesion of particles to the filter medium.

To examine the matrix effects of standard material on the LA-ICP-MS analysis, standard filters of BCR No. 176 were also prepared.

2.2. Verification of the prepared standard filters

Different analytical techniques, including XRF spectrometry, ICP-MS after high pressure bomb acid digestion (HPBD/ICP-MS), and LA-ICP-MS, were

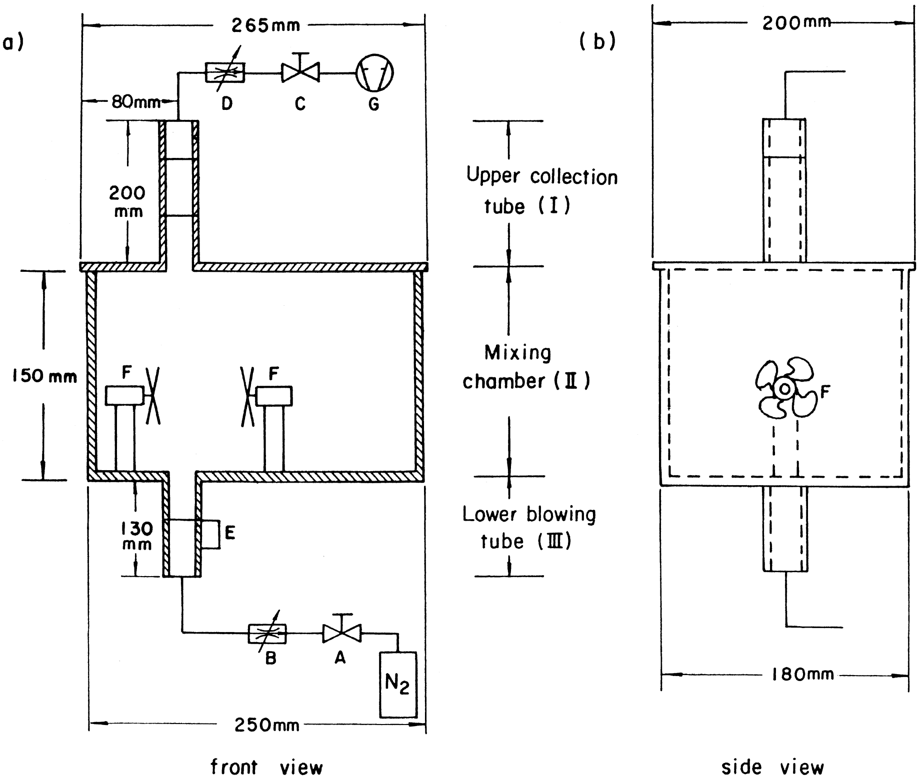


Fig. 1. Assembly of the chamber used for standard filter preparation; (A) and (C): needle valve; (B) and (D): flow meter; (E): vibrator; (F): mini-fan; (G): sampling pump.

used to measure the elemental concentrations in prepared PTFE-membrane filter standards. Detailed information regarding these methods can be found elsewhere[1,2,11,13]. Fig. 2 schematically depicts the multiple elemental analysis procedure including sample preparation (A and B), elemental analysis (C, D and E) and data evaluation (F) for samples prepared on PTFE-membrane filters.

The prepared standard or real filter sample was initially measured by XRF to determine the concentration of the most abundant element in the sample, Si, on the filter (step 1a or 1b). LA-ICP-MS was then used directly to measure the multi-elements by seven consecutive random ablation processes on the same filter (step 2). Calibration results for different elements were established by use of a set of prepared standard filters (step 1b and 2). After LA-ICP-MS, the filter was dissolved by high pressure bomb digestion for ICP-MS measurement (step 3). Finally, the analytical results were compared with the standards on the basis of accuracy and precision (step 4a and 4b).

3. Results and discussion

3.1. Homogeneity of prepared PTFE-membrane filter standards

Fig. 3 displays the enlarged photographs (×2.7) of a blank PTFE-membrane filter (A), a standard filter (B) prepared from NIST SRM 1648 and real coarse (C; 2.5∼10 µm) and fine particle samples (D; <2.5 µm) used for the LA-ICP-MS analysis. The fact that the sample color heavily influences the ablation efficiency by the laser explain why large amounts of energy are reflected by the white blank filter membrane, thereby explaining the insignificant crater formation in Fig. 3(A). The color of the prepared

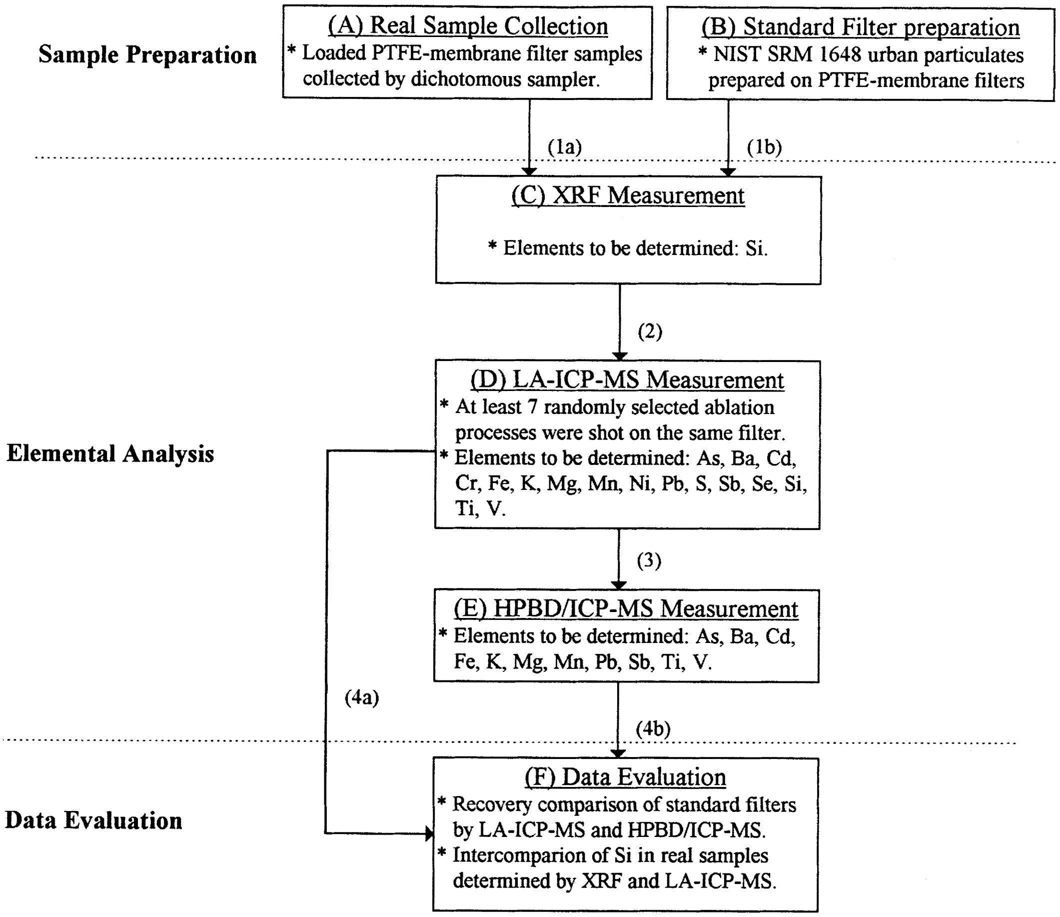
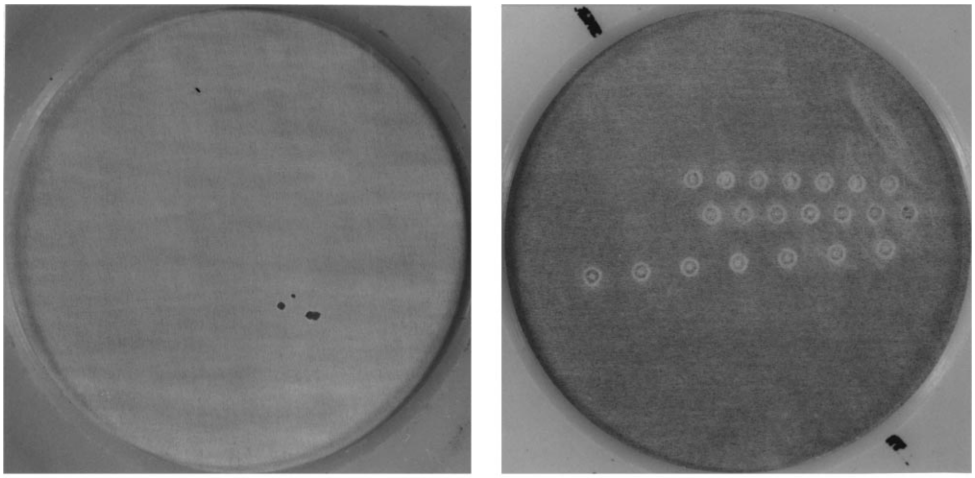


Fig. 2. Flow chart of multiple elemental analysis procedure for prepared standard filters.

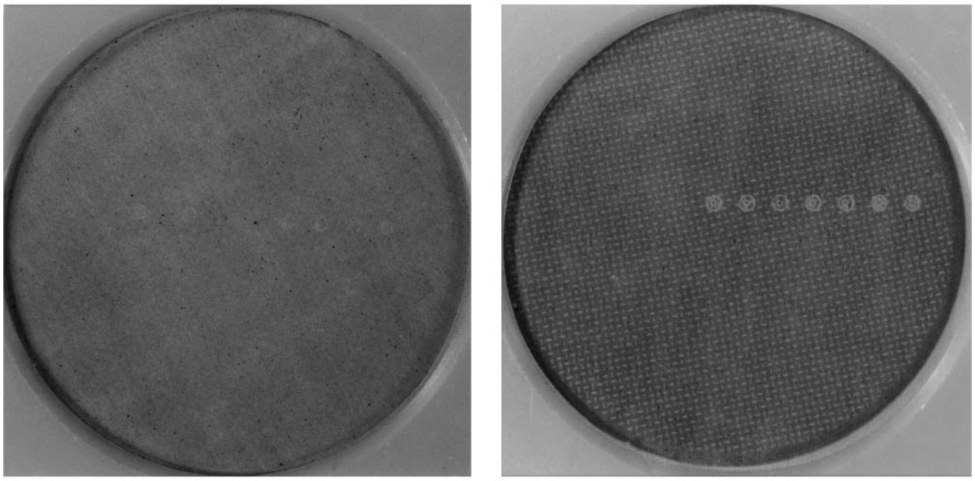
standard filter closely resembles that of the real ambient air sample collected on a coarse filter. However, the deposited particles on the filter surface may absorb sufficient laser energy and be evaporated completely during LA-ICP-MS [10,11]. As Fig. 3(B, C and D) reveal, each shot causes a nearly 1 mm diameter round crater to form on the 37 mm diameter filter surface. Therefore, repetitive multiple analysis of the filter samples at random locations should minimize variations due to the inhomogeneity of deposited particles.

In this study, a number of standard filters with varying amounts of loaded SRM particulates were introduced to evaluate their respective homogeneity by LA-ICP-MS. Several randomly selected shots (seven in this study) are made at different locations on each prepared standard filter. Notably, the measured values do not correlate with the shot sequence. Table 1 indicates that, except for Al, Ti and Sr, the relative standard deviations (RSDs) of measured values from seven repeated shots are less than 15% for most investigated elements. Fluctuations may be induced not only by the inhomogeneity of loaded particulates on the filter, but also by the instability of the LA-ICP-MS instrument. However, both the inhomogeneity and instability problems can be minimized by averaging the multiple measurements at random locations. Larger fluctuations of ^{48}Ti may be attributed to spectroscopic interference since a significant improvement is achieved by choosing ^{49}Ti as the isotope to be determined. Poor reproducibility of Sr analysis is likely ascribed to its low concentration in the sample. Table 1 also reveals that



(A) Blank PTFE-membrane filter

(B) Standard filter prepared from NIST SRM 1648



(C) Real samples in coarse (2.5 ~10μm) part

(D) Real samples in fine(<2.5μm) part

Fig. 3. Enlarged photographs (×2.7) of a blank PTFE-membrane filter (A) a standard filters (B) prepared from NIST SRM 1648 and real samples in coarse (C; 2.5∼10 μm) and fine part (D; <2.5 μm) for LA-ICP-MS analysis.

the laser shots in the Q-switch mode have a smaller deviation than those measured by the free running mode.

3.2. Calibration graphs for LA-ICP-MS analysis

The prepared standard filters serve as a control while measuring elements in airborne particulate samples by direct analytical methods such as XRF spectrometry and LA-ICP-MS. By using LA-ICP-MS, calibration graphs for all elements were established from standard samples of various loading on the filters. Fig. 4 demonstrates that the calibration graphs for the elements, at different concentration levels and atomic numbers, all exhibit similar trends. This finding further suggests that the measured intensities (i.e.

Table 1
Relative standard deviations (%) of elements on a prepared standard filter by seven consecutively random shots in Q-switch and free running laser ablation modes with 160 mJ laser beam energy.

Element	Q-switch mode	Free running mode
Na-23	1.6	2.0
Mg-24	10.6	12.4
Al-27	18.1	17.6
Si-29	10.4	8.9
Cl-35	2.3	4.5
K-39	3.7	5.8
Ca-44	11.0	11.4
Ti-48	20.4	26.5
V-51	5.6	13.4
Cr-52	6.2	11.6
Mn-55	3.9	12.5
Fe-57	6.5	11.2
Ni-60	4.9	13.0
Cu-63	6.9	10.9
Zn-66	7.5	13.6
As-75	6.2	11.3
Se-77	9.6	10.8
Sr-88	18.7	18.9
Cd-114	7.9	8.5
Sb-121	8.3	10.4
Ba-138	11.0	14.4
Pb-208	18.3	14.1

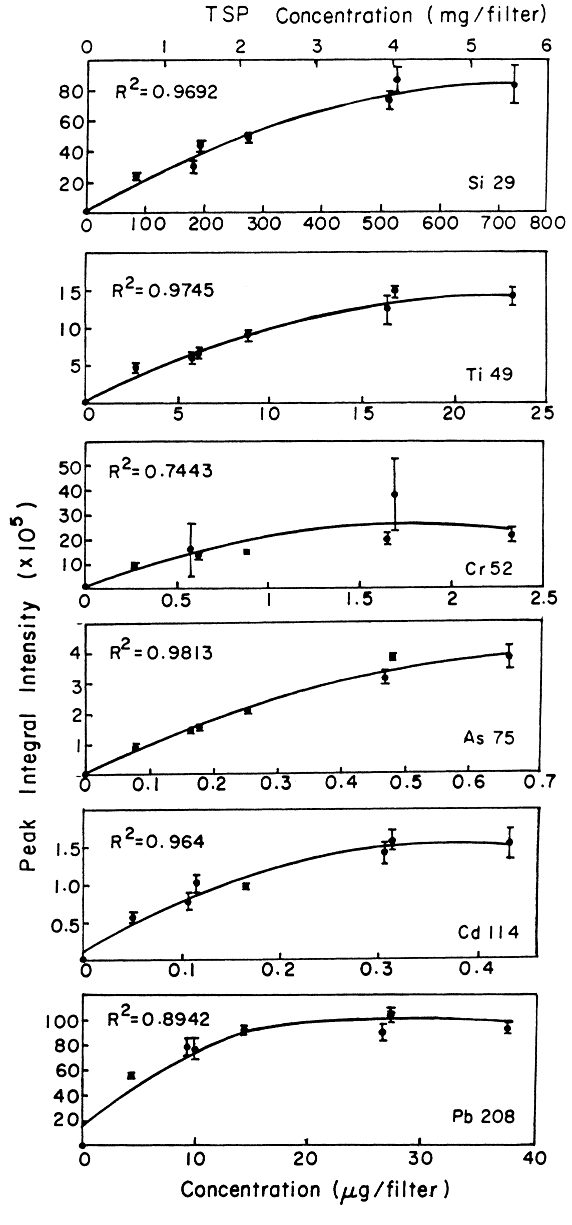


Fig. 4. Calibration graphs of ^{29}Si, ^{49}Ti, ^{52}Cr, ^{75}As, ^{114}Cd and ^{208}Pb for the NIST SRM 1648 urban particulate standard on PTFE-membrane filters. Data presented herein and in the rest of the figures are the average of seven random shots. The corresponding total amounts of suspended particulate deposited on the standard filters are given above the fig.

peak integral counts) generally increase with increasing concentrations and, ultimately, reach a plateau with significantly larger fluctuation at higher concentrations. We believe that with fixed laser energy dissipated on the sample, the amount of particulate matter ablated from the filter surface may be limited. Incomplete ablation might therefore occur with excess mass loading of particulates on the filter. Notably, a higher plateau was observed in a separate run with a slight increase in laser energy.

Different crystal structures and chemical composition of the particles may affect the laser ablation efficiency at a lower energy. Fig. 5 presents the calibration graphs for the various elements obtained from BCR 176 standards. Totally different characteristics of these curves from those for NIST SRM 1648 are observed. Instead of reaching a saturation plateau, the integral intensities of the filter samples measured by LA-ICP-MS rapidly increase at a higher mass loading of particulates on the filter media. The exact reason for such an obvious difference remains unclear. This phenomenon may possibly be caused by the airborne standard particles being

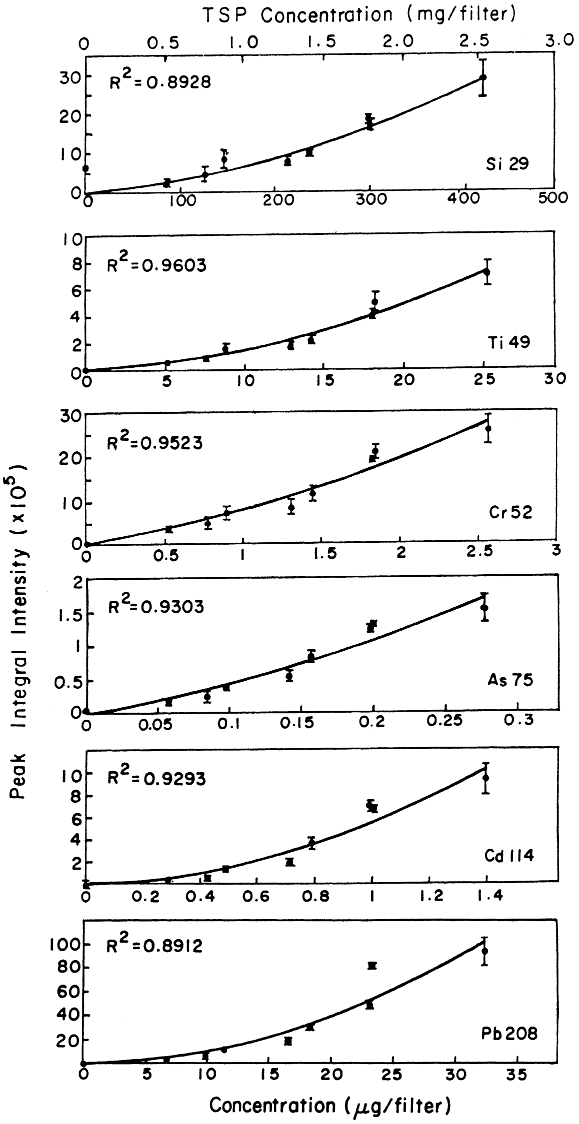


Fig. 5. Calibration graphs of ^{29}Si, ^{49}Ti, ^{52}Cr, ^{75}As, ^{114}Cd and ^{208}Pb for the reference material BCR No.176 city waste incineration ashes standard on PTFE-membrane filters.

more crystallized with Si as a major component, whereas the ashes are more porous. With more stronger bonds in the crystal structure, evaporation of elements by laser energy may be limited to the surface of a large particle.

Nevertheless, a linear calibration relationship is achieved at the lower concentration levels for most elements. Fig. 6 presents a typical example of As calibration graphs with two standard particulates at a mass loading of <2 mg/filter. We believe that achieving a better calibration and analysis relies on limiting the PTFE-membrane filter's loading capacity for collecting airborne particles to ca. 2 mg/filter.

3.3. Validation of certified values by different analytical methods

Herein, the concentrations of elements on standard filters obtained by LA-ICP-MS are compared with the results from the HPBD/ICP-MS method. Table 2 summarizes the percent recoveries of certified concentrations for the various elements obtained by both methods from three different simulated samples prepared from NIST SRM 1648. The fact that the same sample filter is initially laser-ablated and then dissolved accounts for why a small correction for the HPBD/ICP-MS results is applied in each case. In this study, sixteen elements certified in the NIST SRM 1648 standard are compared. As is well known, the acid mixture digestion method is an effective means of determining trace elements in suspended particulate

Table 2
Recovery (%) for prepared standard filters determined by HPBD/ICP-MS and LA-ICP-MS (mean±RSD)

Element	HPBD/ICP-MS	LA-ICP-MS
Mg	73.1±17.6	90.4±11.0[a]
Si	–	90.0±1.1
S	–	105.7±19.0
K	78.8±15.0	97.7±17.9
Ti	95.6±12.5	98.8±17.5
V	62.5±20.3	85.7±15.4
Cr	–	96.0±11.6
Mn	76.4±23.8	90.3±7.7
Fe	71.8±12.2	103.1±17.0
Ni	–	101.8±25.5
As	80.8±22.8	100.9±16.7
Se	–	103.8±14.7
Cd	93.6±11.6	86.3±8.0
Sb	140.0±22.6	78.8±12.4
Ba	103.5±8.0	106.2±23.4
Pb	111.7±11.8	107.5±19.4

[a] For LA-ICP-MS, RSDS were determined by analyzing for each of 3 filters 7 times; for HPBD/ICP-MS RSDS were calculated on the basis of 3 measurements.

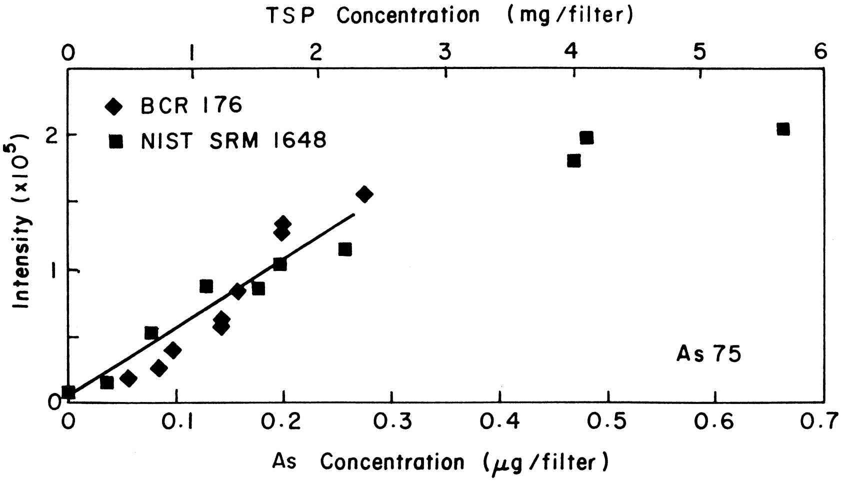


Fig. 6. A comparison of calibration graphs of ^{75}As in NIST SRM 1648 and BCR 176 standard filters. The corresponding total amounts of suspended particulate deposited on the standard filters are given above the fig.

matter [14]. However, interference problems due to the formation of background ions during the ICP-MS ion extraction process significantly degrades the sensitivity for some elements. For example, since $HClO_4$ is utilized in the digestion procedure, the $^{35}Cl^{16}O^+$ ion may seriously interfere with vanadium at m/z 51, $^{35}Cl^{16}OH^+$ with chromium at m/z 52, $^{40}Ar^{35}Cl^+$ with arsenic at m/z 75 and $^{40}Ar^{37}Cl^+$ with selenium at m/z 77. Table 2 suggests that LA-ICP-MS is more sensitive for many low level elements, therefore, the data measured by the LA-ICP-MS are more accurate than that by the HPBD/ICP-MS.

Different elemental concentrations in standard reference materials should be varied with different size distributions.. According to Table 2, except for V, Cd and Sb, average recoveries of most elements in prepared filters determined by LA-ICP-MS are within 100±10%. This finding clearly demonstrates that the size distribution of particles remains constant on the filters in the same manner as for the standard reference materials. In addition, poor recoveries of V, Cd and Sb are attributed to the low concentration of these elements in the standard filters.

As is generally known, Si is a rich element in airborne particles and its concentration may significantly vary in various size distributions of the particles [15]. Analysis results presented herein have demonstrated that Si can be determined quite accurately by LA-ICP-MS. Therefore, direct XRF spectrometric and LA-ICP-MS methods were employed to analyze Si concentrations in real air filter samples. Fig. 7 summarizes those results. Fourteen air samples in fine fractions and nine air samples in coarse fractions confirm a reasonable correlation between the two methods.

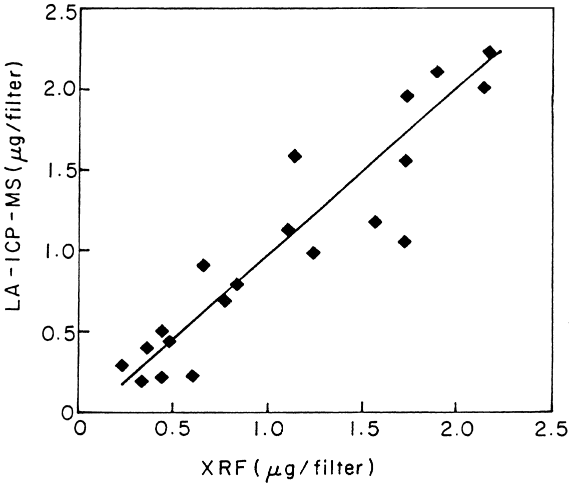


Fig. 7. A comparison of Si concentrations of loaded PTFE-membrane filter samples collected by a dichotomous sampler and determined by both XRF spectrometry and LA-ICP-MS.

4. Conclusions

A standard filter prepared by the proposed method can aptly determine trace elements in airborne particulates collected on PTFE-membrane filters by LA-ICP-MS. In using this technique, as many as sixteen elements on a single filter sample can be determined within 10 min with convenience and high sensitivity (in the sub-μg range per filter). Furthermore, the technique proposed herein can minimize matrix-matching problems that may occur in most airborne particulate matter analysis.

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