

Determination of Arsenic in Airborne Particulate Matter by Inductively Coupled Plasma Mass Spectrometry

CHU-FANG WANG^{*a}, SU-LING JENG^a AND FANG-JIR SHIEH^b

^aDepartment of Nuclear Science, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

^bMaterial Science Division, Industrial Technology and Research Institute, Hsinchu, Taiwan, Republic of China

ilar papers at core.ac.uk

provided by National Ts

digestion procedure, entailing the digestion of airborne particulates with HNO₃-HClO₄ and then digestion with HClO₄-HF after the removal of the intact filter membrane, appears to be the most effective pre-treatment procedure for determining As by ICP-MS. The direct determination of As in airborne particulate matter by laser ablation ICP-MS was also investigated. Standard filters prepared in the laboratory and real samples were both analyzed, and the results agreed with the certified concentrations and data obtained from the conventional acid digestion-ICP-MS method. Finally, the capabilities of various analytical techniques applied to real sample analysis were compared.

Keywords: Arsenic determination; airborne particles; microwave digestion; high-pressure bomb digestion; inductively coupled plasma mass spectrometry

Arsenic, considered the major 'marker element' of air pollution emitted from coal combustion, has been increasingly released into the atmosphere in recent periods of industrial development. Arsenic is one of the most hazardous anthropogenic air pollutants affecting humans globally. The Environmental Protection Agency of Taiwan has recently rated it as a class 'A' substance to be determined in air.¹ The US National Institute of Occupational Safety and Health (NIOSH) has recommended a standard method, procedure P&CAM 139, for determining As in airborne particulate matter.² The method involves collecting a sample on a membrane filter for dissolution in a nitric acid-sulfuric acid mixture, in which As is determined by hydride generation in an argon-hydrogen flame. For a 301 air sample, the range of the method is from 0.002 to 0.06 mg m⁻³. However, a much lower concentration level of As is expected in ambient air.

Our previous experiments involved developing a two-step closed-vessel digestion procedure, first entailing the digestion of samples with HNO₃-HClO₄ followed by adding HF after removal from the intact filter membrane for multi-element analysis of the airborne particles.³⁻⁶ However, inherent problems arise with the As determination during the acid digestion process. It is known that As may be volatile in the halide form, e.g., as arsenic fluorides which are primarily formed by interaction with digestion agents such as hydrofluoric acid. Determining the formation and volatility of such compounds requires systematic studies under conditions associated with the decomposition of airborne particulate matter samples, but such studies are not available at present.

ICP-MS was selected in our previous work as the instrumental method of detection. Compared with other analytical

multi-elemental capability allows a large body of chemical data throughput, the detection limits are lower than those in most conventional techniques and most of the elements in the Periodic Table can be detected.⁷ However, interference problems due to the acid-derived background ions formed during the ion extraction process in ICP-MS significantly degrade the sensitivity of As determination.^{8,9} A survey of the literature¹⁰⁻²⁰ revealed that the chloride, introduced *via* reagents or samples, combining with argon from the plasma can give rise to the formation of ⁴⁰Ar³⁵Cl⁺, which may seriously inhibit the detection of ⁷⁵As⁺ (100%).

The introduction of a small amount of nitrogen into the plasma has been shown by Branch and co-workers^{17,18} to reduce ArCl formation. However, nitrogen addition was not effective in removing the ArCl interference for samples with a high chlorine content, which made the technique unsuitable for determining As in airborne particle samples. Anderson *et al.*¹¹ proposed the use of the hydride generation technique as a means of eliminating chloride interference for determining As in soils by ICP-MS. However, the chemistry is not straightforward and care must be taken to ensure that the analyte elements are in the optimum oxidation states for evolution of the hydrides.²¹ A mathematical correction method by measuring blank and sample signals at *m/z* 77, 78 or 82 to eliminate the chloride interference at *m/z* 75 has also been suggested by various workers.^{14,19,22,23}

Introducing a laser ablation (LA) technique, involving the removal of particulate matter directly from the filter media by ablation with laser pulses, in conjunction with ICP-MS (LA-ICP-MS), may help to avoid many of the problems associated with conventional As determination methods.^{24,25} The advantages of LA-ICP-MS for determining As over the conventional aqueous method are that almost no sample treatment is required, which means that losses due to the formation of volatile As compounds are negligible. Furthermore, no interference is caused by undesirable polyatomic ions from water and acids during ICP-MS measurement. However, the major problems that remain are the instability of the laser output and inhomogeneity of the filter matrix and the loaded particles.

The objectives of this work were two-fold. The first aim was to establish optimized sample digestion conditions for determining As in airborne particulate matters by ICP-MS, and the second was to investigate the feasibility of an LA-ICP-MS technique for the quantitative analysis of airborne particulate matter loaded on PTFE-membrane filters. In addition, the capabilities of various analytical techniques applied in real sample analysis were compared throughout the investigation.

EXPERIMENTAL

Sample Preparation

Between 1991 and 1993, airborne particulate samples were collected from different monitoring stations in Taiwan. Hi-Vol samplers, PM-10 samplers and dichotomous samplers were employed to collect samples on glass-fiber and PTFE-membrane filters. A total of 566 loaded filters were collected and analyzed. Detailed information regarding the sampling instruments and methods has been given elsewhere.⁵

Apparatus

A pressure bomb digestion system consisting of a 25 ml PTFE vessel and a thermostatically controlled heating block supplied by Berghof (Eningen, Germany) was used for sample digestion. The microwave digestion system was a Model MDS 2000 630 W instrument (CEM, Matthews, NC, USA) operating at a frequency of 2.455 GHz. Details of the instruments were given in a previous paper.⁴ The ICP-MS instrument employed was a Perkin-Elmer SCIEX (Thornhill, Ontario, Canada) ELAN 5000 and the LA instrument was a Perkin-Elmer SCIEX Model 320 sampler equipped with a Quanta-Ray GCR-11 pulsed Nd:YAG laser. Details of operating conditions for the LA and ICP-MS instruments are given in Table 1.

Containers and Reagents

PTFE, polyethylene and polypropylene containers were cleaned by immersion in concentrated HNO₃, heated in a microwave oven and then washed with de-ionized water. Two heating cycles of approximately 30 min each with concentrated nitric acid were performed in the microwave system to minimize the blank background. All chemicals employed were of analytical-reagent grade from Merck (Darmstadt, Germany), and high-purity water (resistance >16 MV cm) was produced by reverse osmosis and de-mineralization. Stock solutions of the elements of interest (1000 ng ml⁻¹) were prepared from Titrisol concentrates (Merck) by diluting to volume with de-ionized water.

Analysis

To determine As concentrations in loaded airborne particulate filters, two different techniques, namely ICP-MS after acid digestion and direct LA-ICP-MS, were employed. To determine the optimum digestion conditions, both the high-pressure

bomb and microwave closed-vessel digestion methods were tested with NIST SRM 1648 Urban Particulate Matter.

High-pressure bomb digestion (HPBD)

Glass-fiber or PTFE-membrane filters loaded with airborne particulate matter or around 10 mg of reference standard were placed in 25 ml PTFE containers and 10 ml of acid mixture, including HNO₃, HClO₄ and HF, in different combinations, were added. The sealed containers were transferred into a pressure bomb and heated on a heating block to facilitate complete dissolution. After digestion, the sample solution was transferred into a PTFE beaker and heated gently at about 80°C to allow the HF to evaporate. The residue was then diluted to 10 ml for measurement by ICP-MS.

Microwave digestion (MD)

Teflon filters loaded with airborne particulate matter and about 5 mg of reference standard were placed in closed PFA digestion vessels with 5 ml of acid mixture and digested in the microwave oven for a total digestion time of 27 min. Detailed programme settings for the digestion process were given in a previous paper⁴ and are described here in Fig. 1. An evaporation process was also performed to evaporate the HF before the ICP measurement.

ICP-MS and LA-ICP-MS measurements

After digestion, aliquots were analyzed directly using the ICP-MS instrument. A direct LA technique combined with ICP-MS was also tested, employing standard filter samples prepared in the laboratory. NIST SRM 1648 Urban Particulate Matter was deposited on the PTFE-membrane filter by a designed sampling box, and the certified As concentrations on each filter were verified by the conventional ICP-MS method after the LA-ICP-MS analysis.

Procedures

Fig. 1 shows the experimental flow chart for this investigation. Several alternatives, including sample preparation (A, B, C), two-step digestion (E, F, G, H, I, J), evaporation (K, L), instrument analysis (D, M) and data evaluation (N) were explored to accomplish the following objectives:

- (i) To study the influence of acid mixture on sample dissolution: Different digestion procedures, including (6)→(8)→(10)→(14)→(15)→(17)→(19)→(21), (6)→(8)→(12)→(19)→(21), (6)→(9)→(11)→(14)→(16)→(18)→(20)→(21), and (6)→(9)→(13)→(20)→(21), were performed to study the influence of acid mixtures in different proportions on sample dissolution and to determine the optimum digestion conditions. NIST SRM 1648 Urban Particulate Matter was utilized for the recovery test.
- (ii) To evaluate the two-step digestion procedure: A two-step HPBD digestion procedure [(1) or (4)→(8)→(10)→(14)→(15)→(17)→(19)→(21)] was used to determine the As content of airborne particulate samples in order to achieve complete digestion and minimize the blank contributions from the filter media. Real samples collected on PTFE-membrane filters and also NIST SRM 1648 were utilized to examine the applicability of the method.
- (iii) To investigate the feasibility of the LA-ICP-MS method: Prepared standard filters and real samples were directly analyzed by the LA-ICP-MS (D) by procedure [(2)→(23)] and the optimum experimental conditions were investigated. Following LA-ICP-MS measurement, samples were then analyzed by the conventional HPBD-ICP-MS method. A comparison between the results of the two

Table 1 LA-ICP-MS operating conditions

<i>ICP-MS—</i>	
Instrument	Perkin-Elmer SCIEX ELAN 5000
Power	1100 W
Coolant argon flow rate	14 l min ⁻¹
Auxiliary argon flow rate	0.8 l min ⁻¹
Carrier argon flow rate	0.8 l min ⁻¹
Dwell time	10 ms
Resolution	Normal
Readings/replicate	100
Sweeps/reading	1
Scanning mode	Peak hopping transient
Isotope	⁷⁵ As
<i>Laser ablation —</i>	
Instrument	Perkin-Elmer SCIEX Model 320 sampler
Operating mode	Free running
Ablation type	Single pulse
Laser flash lamp energy	35 J (laser beam energy # 140 mJ)
Defocus distance	5.5 mm

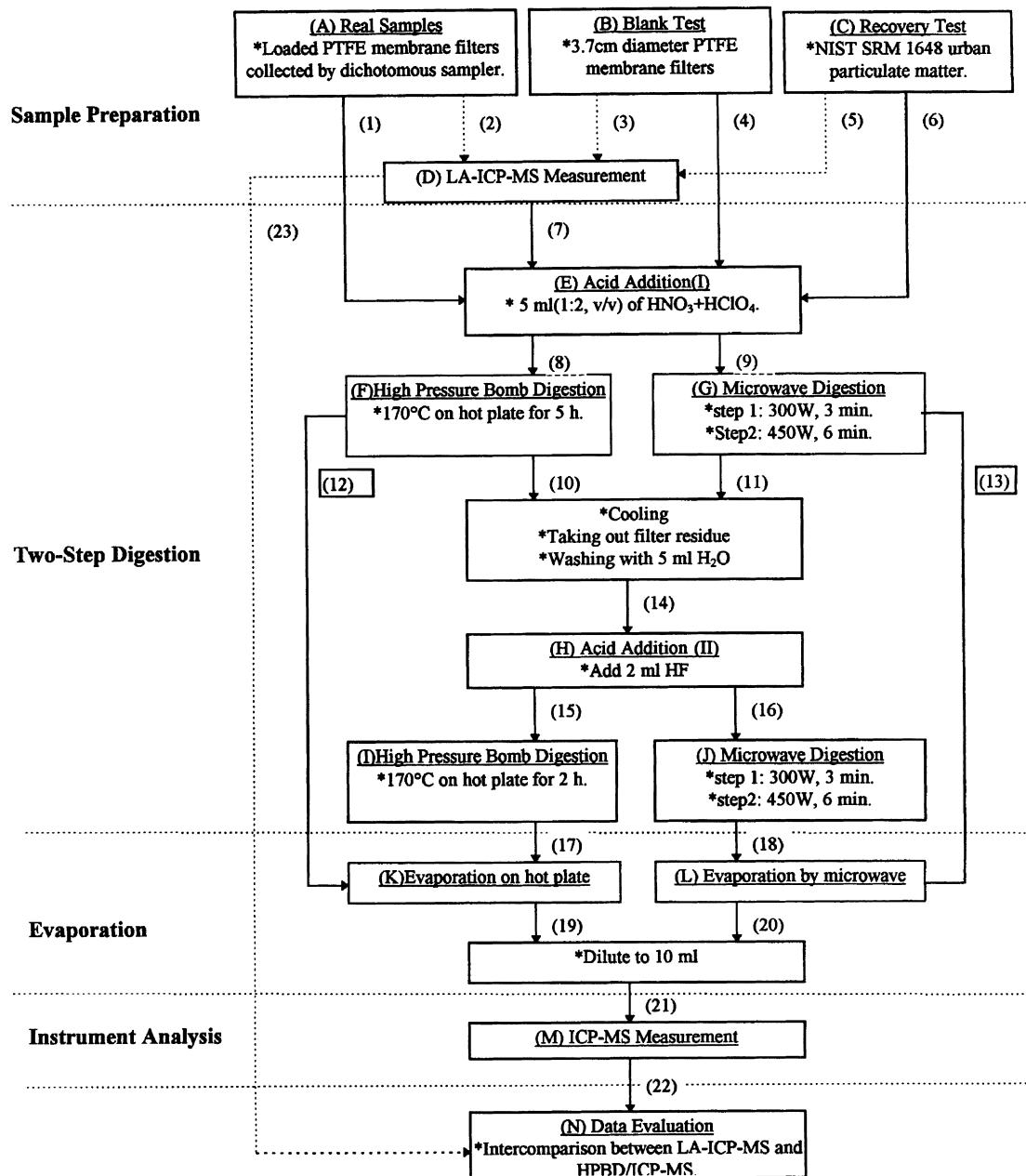


Fig. 1 Flow chart for the determination of As in suspended particulates collected on filters by ICP-MS.

methods (N) was performed to verify the capability of the proposed method.

RESULTS AND DISCUSSION

Optimized Digestion Conditions for ICP-MS Measurements

The data presented in Table 2 were obtained using the high-pressure bomb and microwave digestion methods with different combinations of acid mixture. These methods may suffer, to varying extents, from the losses of volatile As compounds, incomplete digestion and contamination of the reaction mixture by impurities from the filter matrix and from reagents leached from the walls of the digestion vessels.

Losses of volatile As, and also incomplete digestion during the digestion process, for airborne particulates can be minimized by the two-step digestion process proposed in our previous work.⁴ It was designed to accomplish the digestion first with a mixture of nitric and perchloric acids to dissolve and separate collected airborne particulates from filter media,

followed by treatment with hydrofluoric acid to destroy the difficult-to-digest silicates.^{26,27} As Table 2 illustrates, the lower recoveries of one-step high-pressure bomb digestion with HNO₃ and HNO₃-HClO₄ can be attributed to the incomplete dissolution of difficult-to-digest silicates in airborne particles. On the other hand, the high-pressure bomb method with two-step HNO₃-HClO₄/HF digestion, exhibited excellent precision and accuracy, which may indicate that complete digestion and far smaller losses of As were achieved with the addition of HF. In the digestion of airborne particulate matter with hydrofluoric acid, complete oxidation of As^{III} to As^V under the closed-system conditions is essential. Several previous studies have verified the volatilization of As^{III}, e.g., AsF₃, from non-oxidizing media of hydrofluoric acid.²⁸⁻³¹ Clearly, with digestion with HNO₃-HClO₄ at 170 °C for 5 h, only the oxidized As^V remained in the final solution from the high-pressure bomb method. To restate the position, the losses by evaporating AsF₃ can be avoided if complete digestion is achieved in a continuous low-temperature closed-vessel digestion system.

Arsenic in airborne particulates can also be determined by

Table 2 Comparison of As determinations in airborne particulate matter by closed-vessel digestion methods under different conditions ($n=10$)

Digestion method	Amount of acid mixture/ml	Digestion time	SRM recovery (%)
<i>High-pressure bomb digestion—</i>			
HNO ₃	10	5 h	74.5 ± 10.3
HNO ₃ -HClO ₄	10 (1+1)	5 h	82.0 ± 5.4
HNO ₃ -HClO ₄ /HF	10 (3+5/2)	7 h	96.4 ± 3.8
HNO ₃ -HClO ₄ /HClO ₄ -HF	10 (3+3/2+2)	7 h	101.3 ± 4.5
<i>Microwave digestion*—</i>			
HNO ₃ -HClO ₄ -HF	5 (3+5+2)	18 min	140.2 ± 10.0
HNO ₃ -HClO ₄ /HClO ₄ -HF	5 (3+3/2+2)	18 min	107.4 ± 10.5

* Only PTFE-membrane filter samples were digested by microwave methods.

the more rapid but vigorous microwave digestion method. Minimal blank values may be achieved in a closed vessel microwave digestion system, as the amount of acid is reduced and the contact of the reaction mixture with the laboratory atmosphere is eliminated. The largest and most difficult-to-determine blank contribution in the analysis of airborne particulates may be attributed to the filter matrix dissolving during the digestion process. However, this contribution may also be reduced by the above-suggested two-step acid mixture digestion method. To prevent dissolution of the filter media by hydrofluoric acid, the filter residue after the first digestion step with HNO₃-HClO₄ was removed from the vessel before adding HF.

Generally, complete evaporation of the acid residue cannot be performed by the microwave system. The relatively higher recovery of As during the microwave digestion, as indicated in Table 2, may be due to the interference of ArCl⁺ caused by the residual chloride in the treated sample solution. The magnitude of this interference was checked by measuring the reagent blank signal directly. It was estimated that almost one sixth of the measuring signal could be contributed by ArCl⁺ interference in the microwave digestion procedure.

It is doubtful whether incomplete oxidation of As^{III}, which exists in the silicates of airborne particles, occurs during the second step of digestion in the absence of sufficient oxidizing agent. Adding HClO₄ in the second digestion step may overcome this problem. It also appears that the presence of HClO₄ with HF offers the advantage of increasing the boiling temperature of the reaction mixture and of improving the efficiency of HF. An acid digestion employing the combination of HNO₃-HClO₄ with HClO₄-HF (3+3 and 2+2 v/v) in both the high-pressure bomb and microwave digestion procedures did indeed exhibit better recovery results in Table 2 for determining As in airborne particles.

Therefore, losses in As can be prevented by carefully controlling the temperature during both the closed digestion and the open-phase evaporation process. It was concluded that the highest recovery of As in airborne particulates is achieved if the evaporation temperature is maintained below 80 °C. In addition, the recovery data for NIST SRM 1648 listed in Table 2 indicate that the proposed two-step acid mixture digestion method adequately liberates As from particulate matter and achieves complete oxidization.

Feasibility Study of Direct LA-ICP-MS Analysis

Determination of trace contents of As in airborne particulate matter was also examined by LA-ICP-MS, although major obstacles arose. These included instability of the operating conditions, such as fluctuation of the laser beam intensity and signal delay, and the preparation of calibration standards. Fig. 2 depicts the response of As when a single laser pulse was fired at blank, standard and real PTFE-membrane filter samples. Several seconds after the shot, the integrated signals

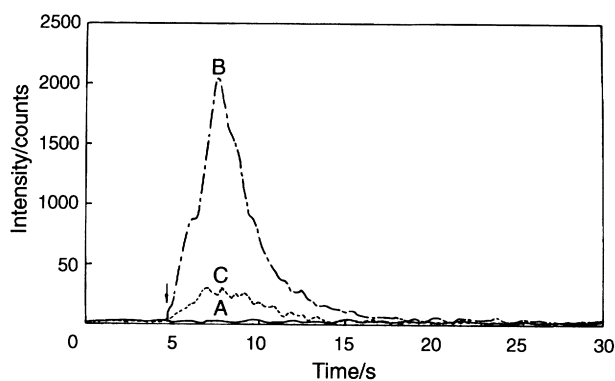


Fig. 2 Single laser pulse transit signal of As ablated from A, blank, B, standard and C, real PTFE-membrane filter samples. The mass loadings of standard and real filter samples are 0.38 and 0.13 mg cm⁻², respectively.

reached a maximum, then gradually decreased for around 20 s. In this investigation, the dwell time was 10 ms and scans were repeated 100 times, extending the total acquisition time to 1000 ms. Since a total of 22 elements were designed to be scanned in the measurement, a replicate time of 35 s for each element was allowed for. Spectra of standards with different As concentrations and real sample and blank filters were plotted to reveal the general variations produced during the measurement. The fluctuation of the laser beam intensity was reflected significantly in the signal peak. A delay of the signal peak, which was mainly affected by the transport time in addition to the operational shift from LA equipment to the ICP-MS, was also indicated. Fig. 2 confirms that the optimization of the laser energy and the time duration of the signal peaks could be maintained, and that an accurate analysis could therefore be achieved by appropriately integrating the signal peaks.

To minimize the inhomogeneous fluctuations of the As concentrations distributed on the real filter samples, ten randomly selected spots on the same filter were ablated and detected during the measurement. The RSD of the averaged intensities for As was <7% in all cases.

Standard filter samples with different As contents were prepared in the laboratory to assess the capability of LA-ICP-MS. NIST SRM 1648 Urban Particulate Matter was deposited on a PTFE-membrane filter by a designed sampling chamber, and the certified As concentrations on each filter were verified by the conventional ICP-MS method after LA-ICP-MS analysis. All the ablation processes were performed in a single-shot, free-running mode with a laser flash lamp energy of 35 J (laser beam energy # 140 mJ). Consecutive laser shots on the thick samples may have given improved precision but seemed an inappropriate approach for membrane filter samples which are usually thinner than 100 μm. A single

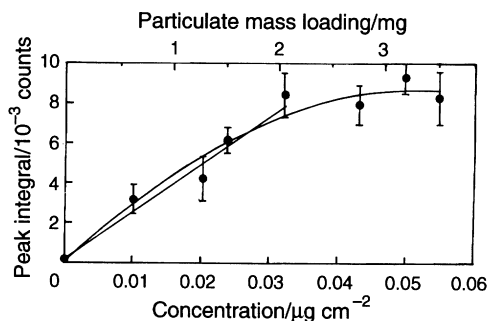


Fig. 3 Calibration curves for As obtained from NIST SRM 1648 Urban Particulate Matter mass loadings from 0 to 3.5 mg per filter.

laser shot was confirmed to provide sufficient energy to ablate samples on the filter, although preventing efficient burning of low-b.p. PTFE substrates.

A calibration curve was then generated from the integration of these transient signals. Fig. 3 demonstrates that the measured intensities are generally enhanced with increasing As concentration, and reach a plateau with greatly amplified fluctuations at higher concentrations. Possibly the incomplete ablation may be the cause of such 'saturation' in the excess mass loading of particulates on the filter media. The ablated particulate samples on the filter are apparently limited to the amount of energy propagated by each laser shot. As indicated in Fig. 3, efficient ablation can be performed by a single 140 mJ shot with a particulate mass loading in less than 2 mg on the filter. A slight increase in laser energy reveals a shift of saturation to higher concentrations but also increases the possibility of incinerating a shallow crater. During the ablation process, the focused laser beam induces a plasma of ionized argon, sample vapor and free electrons above the filter surface. In the Q-switched mode (at 240 ns delay) or in the higher energy free-running mode, much of the energy is propagated to the nearby region of the ablated surface, and affects the coupling efficiency of the energy to the sample. Because the filter sample is generally less than 100 mm thick, an inappropriate energy adjustment may easily burn through the membrane. Therefore, a free-running operation mode with a laser beam energy at 140 mJ was selected.

As depicted in Fig. 3, an excellent linear calibration curve was obtained with a mass loading of less than 2 mg, which is considered to be the limit of the loading capacity for collecting airborne particles of a PTFE-membrane filter. It was also found that the color of particulates deposited on the white filter membrane significantly influences the absorbed energy.

The amount of ablated particulates depends not only on the laser energy setting but also on the defocused distance of the samples. A large portion of filter area could be ablated by defocusing and rastering the laser beam over the sample surface. The integral intensities of As generally increase at a defocused distance of <6 mm, which may be attributed to the laser beam evaporating more particles on the filter. However, since only limited energy can be transferred with each laser setting, the amount of particulates ablated becomes limited at higher defocused distances. Therefore, a 5.5 mm defocused distance was selected for this investigation.

Consequently, in view of the above mentioned advantages of rapidity and sensitivity, non-destructive LA-ICP-MS is considered an appropriate analytical technique for determining As and other elements in airborne particulate matter on membrane filter samples.

Comparison of LA-ICP-MS and Conventional HPBD-ICP-MS methods

To examine the practicability of the proposed LA-ICP-MS method for real sample analysis, the HPBD-ICP-MS method

was also employed in a comparative exercise. Sets of airborne particulate-loaded filter samples collected from the heavily polluted metropolitan area of Kaoshiung, Taiwan, and standard filter samples prepared in the laboratory were analyzed. As Fig. 4 illustrates, LA-ICP-MS measurements in a sequence of 12 spot analyses with a crater diameter of 1.5 mm on the filter samples were carried out. The purpose was to minimize the fluctuations due to laser instability and to the inhomogeneity of the particles on the filter. The area of the Teflon filter for particle collection was calculated to be around 7 cm². An ablated area of about 70 mm² was cut away with care. The remainder of the filter was then digested by the high-pressure bomb method and analyzed by ICP-MS. Fig. 5 exhibits an excellent linear correlation for all the data between LA-ICP-MS and HPBD-ICP-MS. A total of 14 standard ($n=7$) and real filter ($n=7$) samples with different As concentrations were analyzed by both methods. The standard filters exhibited a larger scattering of data, which might be attributed to the loss of loosely attached particulates on the filters during the preparation process.

It is recognized that, in conventional ICP-MS analysis, As may be lost owing to the formation of volatile fluoride compounds, e.g., AsF₃, during the acid digestion process.³¹ Any remaining HF in the final solutions is liable to attack the glassware employed in ICP-MS nebulizers, spray chambers and injectors. Evaporation prior to analysis is suggested as an efficient method of removing all HF from the solutions. However, this may also contribute to the loss of As. Adding HClO₄ for complete oxidation may form ArCl⁺, which could introduce significant spectral interferences when determining As in airborne particulate matter by ICP-MS measurements.

A correction for ⁴⁰Ar³⁵Cl⁺ interference with ⁷⁵As can be performed by ICP-MS measurement to obtain more reliable data. Since chlorine has isotopes at both mass 35 and 37, the extent of ⁴⁰Ar³⁵Cl interference could then be corrected by using the following equation:

$$i(^{75}\text{As}) = i(75) - 3.08i(77) + 2.54i(82) \quad (1)$$

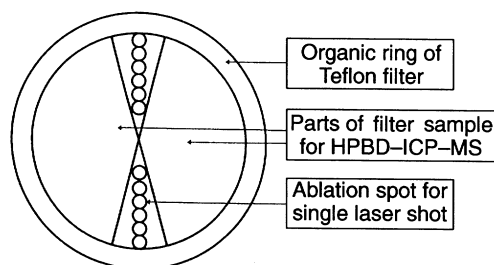


Fig. 4 Preparation of Teflon filter samples for the determination of As by LA-ICP-MS and HPBD-ICP-MS.

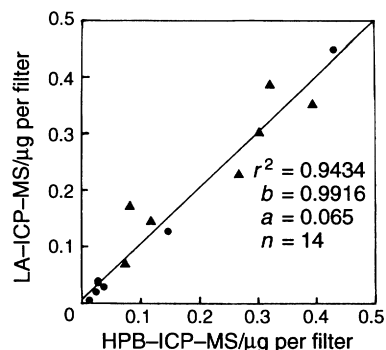


Fig. 5 Comparison of As concentrations of various standard (+) and real filter (\$) samples ($n=7$) measured by LA-ICP-MS and HPBD-ICP-MS.

Table 3 Quality assurance/quality control results for the determination of As in airborne particulate samples analyzed in the last 3 years

QA/QC parameter	MD-ICP-MS	HPBD-ICP-MS
SRM recovery (%)	107.4 ± 10.5	98.7 ± 8.2
Blank value (ng g ⁻¹)	11.5 ± 1.5	66.0 ± 64.0
Relative deviation of repeated analysis (%)	7.8	2.6

where $i(X)$ represents the integral counts at mass X and 3.08 is the isotopic ratio of ³⁵Cl/³⁷Cl. Because of the existence of appreciable concentrations of selenium in the airborne particles, further correction for Se at mass 77 should be considered. The coefficient 2.54 is therefore the product of isotopic ratios, ³⁵Cl/³⁷Cl and ⁷⁷Se/⁸²Se. However, Nixon and co-workers^{23,24} mentioned that these isobaric fractionation (IBF) methods may consistently underestimate the ⁴⁰Ar/³⁵Cl interference and potentially give rise to a large error in determining As in biological materials.

The above problems can also be easily resolved by applying LA-ICP-MS. This method allows direct sample analysis and therefore introduces little dilution of the sample. Eliminating sample dissolution shortens the sample analysis time markedly. Contamination from reagents is minimized since sample handling is minimal. In addition, diminishing the levels of H₂O entering the plasma reduces the levels of interfering polyatomic ions and allows for the low level determination of As. Consequently, LA-ICP-MS is appropriate for determining As in airborne particulate matter collected on thin membrane filters (approximately 100 nm thick).

Comparison of the Determination of As in Airborne Samples by Various Methods

In real sample analysis, both glass-fiber filters and PTFE-membrane filters were employed to collect suspended particulates. This aspect was reported in a previous paper which mentioned that the blank contribution for As from filters and also reagents could be negligible.⁶ Table 3 gives the quality control results obtained in a recent several year long investi-

gation of As concentrations in airborne particulate samples collected in Taiwan. They indicate that the high-pressure bomb digestion method may be superior to the microwave digestion method. Table 3 also indicates that the blank values of As in PTFE-membrane and glass-fiber filters were 11.5 ± 1.5 and 66.0 ± 64.0 ng g⁻¹, respectively. Clearly, major factors affecting the accurate and precise determination of As can only be attributed to the sensitivity of the selected analytical instrument. Restated, the applicabilities of the analytical methods depend mainly on the elemental content to be determined in airborne particulate matters.

Our laboratory has previously employed several analytical techniques, such as XRF, INAA, AAS, ICP-AES and ICP-MS, to analyze airborne particulate matter collected on membrane filters. A general comparison of the various techniques for As determination was therefore performed and the results are given in Table 4. The detection limits and other key elements of the methods were compared to examine their capabilities in real sample analysis.

ICP-MS in combination with the proposed two-step digestion method is certainly the most sensitive technique for the determination of As in airborne particulate matter. It offers the added advantage of determining many other elements within the same digestion procedure. ETAAS may be an apt choice for determining As, but only if As is the single element to be determined. XRF, ICP-AES and INAA should be ruled out either because of their insensitivity or their labor- and time-consuming procedures. In terms of convenience, rapidity and sensitivity, LA-ICP-MS has decided advantages over the other methods. Fig. 6 depicts the frequency distribution of the As content in the atmosphere of Taiwan from 1991 to 1993. It is estimated from the frequency curve that nearly 50% of the samples register As concentrations of less than 0.002 mg m⁻³ [in total suspended particulate (TSP) < 100 mg m⁻³ conditions], and 20% less than 0.001 mg m⁻³ (TSP < 50 mg m⁻³). LA-ICP-MS is recommended for the accurate As determination of airborne particulate matter in real sample analysis.

The authors thank the National Science Council, Republic of China for financially supporting this research under Contract

Table 4 Comparison of techniques for As determination in airborne particulate matter*

Technique	Type of analysis	Analysis time	Detection limit/mg g ⁻¹	Cost	Advantages	Limitations
FAAS	Atomization of analyte solution after digestion	~10 h	2 [†]	Medium	High sensitivity Low interferences	Single-element analysis High chemical loss
ICP-AES	Excitation of analyte solution after digestion	~10 h	350 [†]	Medium	Low interferences	Poor sensitivity High chemical loss
ICP-MS	Excitation of analyte solution after digestion	~10 h	0.4 [†]	High	High sensitivity	High interference High chemical loss
LA-ICP-MS	Direct evaporation and/or excitation by laser	~10 min	3.2	High	High sensitivity Low interferences Excellent mapping	Inhomogeneity Poor reproducibility
INAA	Direct activation by neutron source	2-3 d	400	High	High sensitivity Low interferences	Time consuming Poor sensitivity
XRF	Direct excitation by X-ray source	~10 min	—	Medium	Qualitative screening	Very poor sensitivity

* A 12 h particulate loading of 1 mg per filter on the PTFE-membrane filter was assumed.

[†] The digested solution, which contains less than 0.1% dissolved particulate material, was diluted to 10 ml for spectrometric measurement.

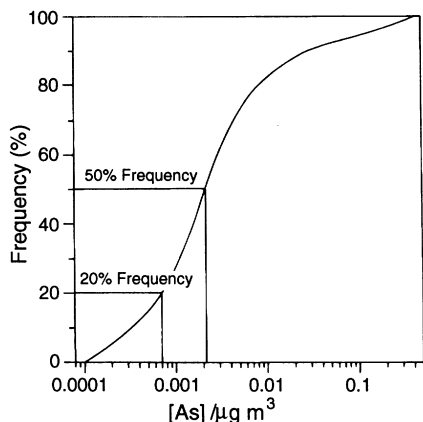


Fig. 6 Frequency distribution of As content in the atmosphere of Taiwan from 1991 to 1993 ($n=566$).

Number NSC84-2621-M007-008EA. Professor M. H. Yang, Department of Nuclear Science, National Tsing Hua University, and Professor P. C. Chiang, Institute of Environmental Engineering, National Taiwan University, are appreciated for their valuable help and discussions. The authors also gratefully acknowledge the assistance with the ICP-MS measurements given by Mr. W. F. Chang of the National Science Council's Regional Instrument Center at Hsinchu.

REFERENCES

- 1 *The Annual Assessment Report of the Air Pollution Control in Taiwan Area for 1994*, Environmental Protection Agency, Taiwan, 1995.
- 2 NIOSH, *Manual of Analytical Methods*, National Institute of Occupational Health and Safety, Washington, DC, 1979.
- 3 Wang, C. F., Miau, T. T., Perng, J. Y., Yeh, S. J., Chiang, P. C., Tsai, H. T., and Yang, M. H., *Analyst*, 1989, **114**, 1067.
- 4 Wang, C. F., Chen, W. H., Yang, M. H., and Chiang, P. C., *Analyst*, 1995, **120**, 1681.
- 5 Wang, C. F., Chang, E. E., Chiang, P. C., and Aras, N. K., *Analyst*, 1995, **120**, 2521.

- 6 Wang, C. F., Yang, J. Y., and Ke, C. H., *Anal. Chim. Acta*, 1996, **320**, 207.
- 7 Kuss, H.-M., *Fresenius' J. Anal. Chem.*, 1992, **343**, 788.
- 8 Kawaguchi, H., Tanaka, T., Nakamura, T., Morishita, M., and Mizuike, A., *Anal. Sci.*, 1987, **3**, 205.
- 9 Olivares, J. A., and Houk, R. S., *Anal. Chem.*, 1986, **58**, 20.
- 10 Larsen, E. H., and Sturup, S., *J. Anal. At. Spectrom.*, 1994, **9**, 1099.
- 11 Anderson, S. T. G., Rob ert, R. V. D., and Farrer, H. N., *J. Anal. At. Spectrom.*, 1994, **9**, 1107.
- 12 Coedo, A. G., and Dorado, M. T., *J. Anal. At. Spectrom.*, 1994, **9**, 1111.
- 13 Cleland, S. L., Olson, L. K., Caruso, J. A., and Carey, J. M., *J. Anal. At. Spectrom.*, 1994, **9**, 975.
- 14 Jiang, S. J., Lu, P. L., and Huang, M. F., *J. Chin. Chem. Soc.*, 1994, **41**, 139.
- 15 Sheppard, B. S., Heitkemper, D. T., and Gaston, C. M., *Analyst*, 1994, **119**, 1683.
- 16 Ebdon, L., Fisher, A. S., and Worsfold, P. J., *J. Anal. At. Spectrom.*, 1994, **9**, 611.
- 17 Branch, S., Ebdon, L., and O'Neill, P., *J. Anal. At. Spectrom.*, 1994, **9**, 33.
- 18 Branch, S., Ebdon, L., Ford, M., Foulkes, M., and O'Neill, P., *J. Anal. At. Spectrom.*, 1991, **6**, 151.
- 19 L szity, A., Krushevska, A., Kotrebai, M., Barnes, R. M., and Amarasiriwardena, D., *J. Anal. At. Spectrom.*, 1995, **10**, 505.
- 20 Campbell, M. J., Demesmay, C., and Oll , M., *J. Anal. At. Spectrom.*, 1994, **9**, 1379.
- 21 Imai, N., *Anal. Chim. Acta*, 1989, **235**, 381.
- 22 Nakahara, T., *Spectrochim. Acta Rev.*, 1991, **14**, 95.
- 23 Nixon, D. E., and Moyer, T. P., *Spectrochim. Acta, Part B*, 1996, **51**, 13.
- 24 Kershishni, N. M., Kalamegham, R., Ash, K. O., Nixon, D. E., and Ashwood, E. R., *Clin. Chem.*, 1992, **28**, 2197.
- 25 Durrant, S. F., and Ward, N. I., *Food Chem.*, 1994, **49**, 317.
- 26 Maher, W. A., *Chem. Geol.*, 1984, **45**, 173.
- 27 Bajo, S., *Anal. Chem.*, 1978, **50**, 649.
- 28 Stock, L. W., *Fresenius' Z. Anal. Chem.*, 1934, **99**, 321.
- 29 Portmann, J. E., and Riley, J. P., *Anal. Chim. Acta*, 1964, **31**, 509.
- 30 Lounamaa, K., *Fresenius' Z. Anal. Chem.*, 1955, **146**, 422.
- 31 Sulcek, Z., and Povondra, P., *Methods of Decomposition in Inorganic Analysis*, CRC Press, Boca Raton, FL, 1989.

Paper 6/05658J

Received August 13, 1996

Accepted September 24, 1996