

Validation of a Simple Microwave-Assisted Acid Digestion Method Using Microvessels for Analysis of Trace Elements in Atmospheric PM_{2.5} in Monitoring and Fingerprinting Studies

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Abstract: Two microwave-assisted digestion procedures, followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis, were evaluated for the determination of trace elements in fine atmospheric aerosols (PM_{2.5}) for air monitoring purposes. The first procedure used 40%(v/v) HNO₃ and a digestion program with a maximum temperature of 175°C. The second digestion procedure provided the dissolution of silicate matrix through the use of a mixture of HNO₃/HF/H₃BO₃ at 200°C. Both digestion procedures employed microvessels (MicroVessel™), which significantly reduced the amount of reagents needed, and increased the sample throughput by two-fold.

The effectiveness of both digestion procedures was studied through the analysis of NIST standard reference materials (SRM), namely SRM 2783 (PM_{2.5} Air Particulate Matter deposited on a polycarbonate filter membrane), and SRM 1648 (Urban Particulate Matter). The accuracy was also checked through the analysis of co-located ambient PM_{2.5} samples collected within the Canadian National Air Pollution Surveillance (NAPS) network. Comparison of analytical results for PM_{2.5} samples showed that 40% (v/v) HNO₃ could dissolve most of the metals of interest to the same degree as the HNO₃/HF/H₃BO₃ mixture. Good agreement was also obtained by comparison with Energy Dispersive X-ray Fluorescence Spectrometry (ED-XRF). The efficiency of the simple microwave digestion procedure (no HF) was not dependent on the origin, mass loading, or elemental composition of the analyzed samples, thus it is quite suitable for monitoring purposes. However, the total dissolution of several trace elements such as Ti, Cr and U in PM_{2.5}, and Ti, Cr, Al, lanthanides, and Sb in coarse fractions of PM (PM_{10-2.5}) would require digestion in the presence of HF.

Keywords: Trace elements, atmospheric aerosols, microwave-assisted digestion, ICP-MS.

1. INTRODUCTION

Concern over the adverse health effects associated with exposure to particulate matter (PM), specifically those fractions that are less than 10 µm (PM_{10-2.5}) and more recently, less than 2.5 µm (PM_{2.5}) is growing [1, 2]. Although there is no evidence to pinpoint any single feature or component of PM as the cause for the observed epidemiological effects, it does seem apparent that metals contribute, at least in part, to the toxic and carcinogenic effects associated with exposure to airborne PM [3-5]. Besides epidemiological studies, trace elements in airborne particulate matter are extensively used to identify emission sources and the region of their origin in source apportionment studies that are necessary in developing emission reduction strategies [6-9].

Analytical methods which are traditionally used for the measurement of elemental composition of particles, such as Proton Induced X-ray Emission (PIXE), Energy Dispersive X-ray Fluorescence Spectrometry (ED-XRF) and Instrumental Neutron Activation Analysis (INAA) have been applied quite often to trace element analysis of filter

collected aerosols [8, 10-12]. These methods have the advantage of minimal sample manipulations, which reduces the risk of sample loss and contamination and increases the sample throughput. However, these methods suffer from relatively high limits of detection and erroneous results due to the non-uniformity of sample distribution on the filters.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) combined with microwave assisted digestion has become the preferred methodology for the analysis of metals in environmental samples including PM [13-21]. This technique offers low detection limits, wide linear dynamic range, multi-element capability, ability to measure isotope ratios and high sample throughput. However, the traditional ICP-MS systems are equipped with liquid sample introduction systems which require the dissolution of solid samples prior to measurements. Depending on the sample matrix and elements of interest, a large number of different combinations of mineral acids and oxidizing agents such as HNO₃, HNO₃/HCl, HNO₃/HCl/HF, HNO₃/HF/H₃BO₃, HNO₃/HClO₄, HNO₃/H₂O₂ have been used for microwave assisted acid digestions. For example, determination of platinum group elements in atmospheric aerosols requires the presence of HCl in the digestion mixture, or hydrofluoric acid is required to completely release the trace elements from the aluminosilicate matrix of PM [15, 22-24]. However, the presence of some digestion acids in the sample matrix aggravates the spectroscopic interferences in ICP-MS

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analysis by formation of species with m/z ratio that can not be resolved from that of the analyte of interest, and non-spectroscopic interferences related to the increased total dissolved solid (TDS) content in the solution [13, 14, 23]. Although recent developments, such as reaction/collision cell or high resolution sector field ICP-MS offer the analyst effective tools for suppressing matrix-induced interferences [16, 25], selecting a suitable combination of the mineral acids and using the minimum amount of reagents remains critically important for achieving low detection limits and interference-free measurements in trace element analysis by ICP-MS.

Compared to other environmental samples, the analysis of aerosols collected on filters present the challenge of handling samples of very limited mass ($\ll 1$ mg) and low concentrations of analytes. Despite the low detection limits of ICP-MS, a minimum dilution of digested samples is desirable for quantification of several trace elements. This leads to solutions that have elevated levels of TDS and high acid concentrations which render the matrix-related interferences more significant and accelerate corrosion of conventional ICP-MS interface components, especially the sampler and skimmer cones [26]. Consequently, decreasing the amount and concentration of digesting acids is essential for PM analysis. Furthermore, the necessity of monitoring trace elements in PM involves analysis of a great number of samples on a day-to-day basis, which in turn adds the need for developing easy, fast and reliable methods with reduced amounts of toxic acids used.

The aim of this work was, therefore, to establish a simple and fast microwave-assisted digestion procedure suitable for routine analysis of a large number of airborne $PM_{2.5}$ samples prior to ICP-MS measurements. The main focus was to minimize the amount and concentration of digestion acids and to investigate the possibility of avoiding HF for the analysis of metals that are often present at very low concentration in $PM_{2.5}$. These include metals such as Ni, V, Zn, Co, Cd, Cu, Mn, Pb, As, Se, which are often used in fingerprinting of specific pollution sources. For example, Ni and V are good indicators of emissions from heavy fuel oil combustion [8, 27, 28]; Zn, Cu and Pb signify emissions from non-ferrous metallurgy [29, 30] or As and Se are tracers of coal burning [28, 31, 32]. In this paper we compare two microwave assisted acid digestion procedures utilizing microvessels (MicroVesselsTM). The first digestion procedure used 40% (v/v) HNO_3 , and was based on our previous studies [19, 33, 34]. The second digestion procedure, based on the work of Kulkarni *et al.* [17] used a HNO_3 /HF mixture for the first stage of microwave digestion, followed by a second stage in the presence of H_3BO_3 . The efficiency of the tested procedures was evaluated by: (i) analyzing standard reference materials, (ii) analysis of co-located $PM_{2.5}$ samples treated with two different digestion procedures and (iii) comparison of the results obtained by ICP-MS and ED-XRF analysis.

2. MATERIALS AND METHODOLOGY

2.1. Reagents, Standards and Reference Materials

Double-deionized water (DDI) with resistance higher than 18 $M\Omega$ cm (Millipore, Milli RO-15 and Super-Q systems, Bedford, MA, and Barnstead, Nanopure

DiamondTM, Dubuque, IA) was used throughout this work. Concentrated HNO_3 (68-70% w/v, Fisher, ACS Plus) was purified prior to analysis using a duoPUR Subboiling Distillation System (Milestone, Sorisole, BG, Italy), whereas HF (48% wt in water, Sigma-Aldrich, 99.99+%) and H_3BO_3 (Sigma-Aldrich, 99.99+%) were used without further purification.

The ICP-MS calibration standards and sample spikes were prepared from premixed multi-element solutions CLARITAS PPT[®] Instrument Calibration Standard 2 and CLARITAS PPT[®] Spike Sample Standard 1, respectively (SPEX CertiPrep, Metuchen, NJ, USA). The tuning solution and the internal standard solution were prepared from *PlasmaCal* single element standards and *PlasmaCal* Internal Standard Stock solutions (SCP Science, Baie D'Urfé, QC, Canada), respectively.

NIST standard reference materials (SRMs) (National Institute for Science and Technology, Gaithersburg, MD, USA) 2783 (Air Particulate on Filter Media) and 1648 (Urban Particulate Matter) used in this study were stored and handled as instructed, unless otherwise stated.

2.2. $PM_{2.5}$ Samples

All $PM_{2.5}$ samples were collected within the Canadian National Air Pollution Surveillance (NAPS) $PM_{2.5}$ Speciation monitoring program. Particles were collected over 24 hours on Teflon filters (PTFE, 47-mm diameter) with a polyethylene support ring (PALL Corporation, NY, USA) using R&P Partisol-Plus Model 2025-D sequential dichotomous and R&P Partisol Model 2300 Speciation samplers. The sequential dichotomous sampler collected simultaneously coarse and fine PM, with flow rates of 1.7 $L\ min^{-1}$ and 15 $L\ min^{-1}$, respectively. The speciation sampler was operated at a total flow rate of 10.0 $L\ min^{-1}$.

The Teflon filters were weighed before and after sample collection using a Mettler Microbalance (MT-5, Mettler-Toledo Inc., Highstown, NJ) under controlled relative humidity ($45 \pm 5\%$) and temperature ($23 \pm 3\ ^\circ C$) conditions. Subsequent to filter weighing, the Teflon filters from dichotomous samplers were analyzed by ED-XRF followed by ICP-MS after digestion with 40% (v/v) HNO_3 , whereas the co-located filters from speciation samplers were digested using the HF/ HNO_3 / H_3BO_3 procedure prior to ICP-MS measurements.

Digestion efficiency was validated for a wide range of matrix compositions by analyzing 250 (125 from each sampler) $PM_{2.5}$ samples collected at various sites that featured urban-commercial, urban-residential and agricultural settings.

2.3. Microwave Digestion Procedures

A closed vessel microwave assisted reaction system (MARS 5, CEM Corporation, Matthews, NC) was used. The oven is equipped with a 2450 MHz microwave power supply of 0-1200 W output, a 14-position turntable and 100-mL Teflon liners (HP-500 Plus, CEM Corporation, Matthews, NC) with 355° rotatable pressure release valves, resistant up to 350 psi and 210 °C. All digestions were performed in 7-mL Teflon digestion microvessels (MicroVesselTM, CEM Corporation, Matthews, NC, USA) accommodated inside the

standard liners (two per each vessel) (Fig. 1). The pressure inside the liners and the internal temperature of the microvessels were monitored in a control vessel assembly, which is equipped with pressure and temperature sensor units.

For the analysis of standard reference materials, the SRM 2783 filters (loaded and blanks) were cut in half and digested separately, whereas ~10 mg of SRM 1648 was accurately weighed directly into the digestion microvessels. Although this sample size was much smaller than ~100 mg recommended by NIST, it has been shown that it provides good analytical reproducibility [13, 15, 17, 35].



Fig. (1). Control MicroVessel™ (7 mL) assembly inserted inside an HP-500 Plus control vessel.

PM_{2.5} laden Teflon filters, after cutting off the polyethylene support rings, were transferred to digestion microvessels using cleaned plastic forceps. They were first wetted with 50 µL of isopropanol followed by the addition of the appropriate acid(s) listed in Table 1. The microvessels were then left inside the PURIFIER® trace element work station (Class-100 air, Labconco Corporation, Kansas City, MO, USA) for about 15 min, with the caps put loose on them. Meanwhile, the HP-500 Plus liners were prepared by placing the spacers in the bottom and adding 7.5 mL of deionized water. The microvessels were then tightly closed

in the capping station using a 20-inch lb torque wrench, and arranged two in each liner. Finally, liners were tightened by a torque wrench at 60-inch lb and placed in the microwave oven for digestion. After digestion and cooling down to room temperature, sample solutions were quantitatively transferred into 50 mL graduated tubes (Fisher Scientific, Ottawa, ON, Canada) and diluted to 20 mL with DDI. Reagent blanks, filter blanks and other QA/QC samples were prepared in the same manner.

In Procedure 1, samples were treated with 2 mL of 40% (v/v) HNO₃ and heated in the microwave oven following a two-step digestion program (Table 1). During the first step the temperature was ramped within 1 min to 165°C. After 5 min dwell time, the temperature was ramped to 175°C and samples were digested at this temperature for 15 min. Procedure 2 had two digestion stages separated by a cooling period (Table 1). In the first stage, samples were treated with 1.5 mL of concentrated HNO₃ and 3 µL HF. Temperature was ramped to 200°C within 15 min and kept at this level for 20 min. The vessels were cooled down to room temperature inside the oven, vented and opened. Then, 24 µL of 5% H₃BO₃ solution was added and samples were digested following the same temperature program. SRM 1648 was digested with 1.5 mL concentrated HNO₃ and 30 µL HF in the first step followed by addition of 240 µL H₃BO₃ during the second digestion step. After dilution to 20 mL, the digestate was further diluted 10-fold prior to ICP-MS analysis.

2.4. ICP-MS Analysis

All measurements were performed using an Agilent Technologies 7500c ICP-MS system (Agilent Technologies, Wilmington, DE, USA), equipped with an octopole collision/reaction system (ORS), a Babington nebulizer, a Peltier cooled (2°C) quartz Scott-type double pass spray chamber and an Agilent I-AS integrated autosampler. The ICP-MS ChemStation software (Agilent Technologies, Inc., 1989) was used to control all instrument operations including tuning, data acquisition and data analysis.

The instrument was tuned in both normal and reaction cell mode before the daily analysis in terms of sensitivity, interference levels and resolution, using a tuning solution that contains 10 µg L⁻¹ of Li, Y, Tl, Ce and Co in 2% (v/v) HNO₃. The doubly charged ratio (⁷⁰Ce⁺⁺/¹⁴⁰Ce⁺) was kept at 0.50 ± 0.02% and the oxide ratio (¹⁵⁶CeO/¹⁴⁰Ce) was 1.5 ± 0.2%. Quantification was performed using a 100 µg L⁻¹ multi-element matrix-matched calibration standard solution

Table 1. Summary of the Microwave Digestion Procedures

Procedure	Digestion Solution	Digestion Program				
		Step	Power (W)	Ramp Time (min)	Temp. (°C)	Hold Time (min)
Procedure 1	2 mL 40% (v/v) HNO ₃	1	600	1	165	6
		2	1200	5	175	15
Procedure 2 ^a	1.5 mL HNO ₃ + 3 µL HF	1	1200	15	200	20
		2	Cooling to room temperature venting and opening the vessels			
	24 µL of 5% H ₃ BO ₃ solution	3	1200	15	200	20

Note: ^a For the total digestion of SRM 1648, 30 µL HF and 240 µL H₃BO₃ were added to ca. 10 mg sample. After digestion and dilution to 20 mL, the digestates were further diluted 10-fold prior to ICP-MS measurements.

[36]. The matrix induced interferences were corrected by using matrix matched blank subtraction. Spectral interferences were minimized or eliminated either by choosing a non-interfering isotope or by using the octopole reaction system (ORS) with H₂ as the reaction gas [37]. Thus ²⁷Al, ⁴⁷Ti, ⁵¹V, ⁵⁵Mn, ⁵⁹Co, ⁶⁰Ni, ⁶⁵Cu, ⁶⁶Zn, ⁷⁵As, ⁸⁸Sr, ⁹⁵Mo, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁸Sn, ¹²¹Sb, ¹³³Cs, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ²⁰⁵Tl, ²⁰⁸Pb and ²³⁸U isotopes were measured in normal mode and ⁵²Cr, ⁷⁸Se, and ⁵⁶Fe in reaction cell mode. Internal standardization with 1 mg L⁻¹ solution of ⁴⁵Sc, ⁸⁹Y, ¹¹⁵In, and ¹⁶⁵Ho was used to correct for instrumental drifts and nonspectral interferences. The internal standard was added on line and was automatically mixed with the sample solution before being introduced into the nebulizer. The optimized operating conditions are listed in Table 2.

The precision and accuracy of the ICP-MS measurements were checked by analyzing CRM's prepared in the same matrix as the digested samples, spikes and duplicates. The 95% expanded relative analytical uncertainties [38] above limits of quantitation (3 times limits of detection) ranged from 10 to 25%. Generally, uncertainties were higher in the HF/HNO₃/H₃BO₃ matrix.

Table 2. Typical Parameters for the Agilent 7500c ICP-MS Operation

Sample Introduction and Plasma	
RF power	1390 - 1550 W
Plasma gas flow	15 L min ⁻¹
Auxiliary gas flow	1 L min ⁻¹
Nebulizer gas flow	1.04 - 1.22 L min ⁻¹
Sampling depth	6.2 - 8.8 mm
Interface	Nickel sampling cone and Platinum skimmer cone
Ion lens voltages	Optimized for sensitivity in 10 µg L ⁻¹ tuning solution (Li, Y, Ce, Tl, Co)
Sample uptake rate	0.35 mL min ⁻¹
Data Acquisition	
Acquisition mode	Peak hopping
Integration time	0.1–0.3 s/point
Peak pattern	6 points/peak
Repetition	3
Collision/Reaction Cell Parameters	
Cell gas flow	4.0 mL min ⁻¹ H ₂
Octopole bias	-14 V
Quadrupole bias	3 – 5 more positive than Octopole bias

2.5. ED-XRF Analysis

A KeveX EDX-771 x-ray spectrometer (KeveX Instruments, Valencia, CA, USA) with 200-watt rhodium target tube as excitation source, was used for the analysis of 22 elements (Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zn, Se,

Br, Rb, Sr, Cd, Sn, Ni, Cs, Ba, Pb). Micromatter[®] standard reference samples were used for the quantitative calibration of the system. Calibration was checked by analyzing NIST standards (SRM 1832 and SRM 1833). Blank filters were used for background subtraction. Typical analytical uncertainties above limits of quantitation [38] were estimated to be in the range of 5-15% for Si, Fe, Ca, K, Ti, S, and 5-25% for the remaining elements analyzed.

2.6. Limits of Detection and Contamination Control

The limits of detection (LOD) of the ICP-MS analysis were established from at least seven replicate analysis of reagent blanks fortified at a concentration no greater than 5-10 times the expected detection limit and treated the same way as samples. The standard deviation value was then multiplied by the one-tailed Student's test value for 99% confidence level.

In order to minimize the risk of contamination, all sample manipulations were performed inside the trace element work station. After each digestion, liners and microvessels were soaked for at least 16 h in 5% (v/v) Citranox solution (Alconox, Inc.) prepared in deionized water followed by thoroughly rinsing with DDI. After drying, the microvessels were filled with 3 mL of 15% (v/v) HNO₃ solution and treated in the microwave oven for 20 min at 175°C. Finally, all vessels were rinsed with DDI, dried inside the trace element work station, capped and stored in closed plastic boxes. The safety membranes were changed between each digestion batch. Filter handling was cautious, using clean forceps and disposable gloves. Reagent and filter blanks were analyzed to monitor the cleanliness of the microwave digestion vessels and to account for possible contaminations during sample handling procedures.

2.7. Statistical Analysis

STATISTICA ver. 8 software (StatSoft Inc., Tulsa, OK, USA) was used for statistical analyses. Comparability between the results was evaluated by regression analysis and outliers were identified by standard residual analysis. Cases that fell outside of the ± 2s limits were excluded and the analysis were run over to make sure that key results were not biased by the outliers.

3. RESULTS AND DISCUSSION

As stated in the Introduction, the main goal of this work was to establish a fast and simple microwave-assisted acid digestion method for ICP-MS analysis of trace elements that often are not detectable by ED-XRF analysis of PM_{2.5}. Using microvessels, two digestion procedures (Table 1) were compared by taking into account the LOD, digestion efficiency, total time of analysis, operational difficulties, amount of acids used and safety requirements.

The usage of microvessels has several advantages as compared to digestions performed with standard 100-mL vessels which are commonly used in similar studies. Firstly, the microvessels can be used with as little as 1 mL of digestion solution which reduces significantly the amount of digestion acids. This feature is especially important for analysis of samples with very small mass, such as atmospheric aerosols collected on Teflon filters, for which a

minimum dilution of digested samples is desirable. In this study, PM_{2.5} samples were digested with 2 mL or less of the digestion mixture, whereas in previous methods, 3 to 10 mL or more were used. Secondly, using the microvessels 27 samples can be digested simultaneously thus, doubling sample throughput. However, the microvessels cannot be used with reactive compounds such as H₂O₂ or for samples that contain high concentrations of organic material.

3.1. Blanks and Limits of Detection

Maintaining low and stable blanks and limits of detection (LOD) are crucial in the analysis of trace elements in PM_{2.5} samples. The presence of metals in blank samples is highly affected by several factors such as cleaning procedures, purity of reagents/filter media, and conditions of sample manipulations during digestion and dilution. All these

factors, in addition to instrumental noise (electronics, flow rates, etc.) and interferences, affect the LOD, and consequently were carefully controlled.

The LOD and average filter blank concentrations of ICP-MS analysis after both digestion procedures are shown in Table 3.

Most of the elements of interest in both matrices had LOD below 1 ng m⁻³. The only exceptions were Zn, Fe and Al with LOD of *ca.* 4 to 8 ng m⁻³. Nevertheless, this was not a problem for analysis of atmospheric PM_{2.5} samples, as the concentrations of these elements were usually well above these concentrations.

As expected, the lowest LOD values were obtained after digestion with 40% (v/v) HNO₃. Due to spectral interferences and high total dissolved solid caused by the

Table 3. LOD and Average Concentration of Trace Elements in Filter Blanks in ng m⁻³

Element	ICP-MS ^a				ED-XRF ^b	
	Procedure 1 N = 75		Procedure 2 N = 25		N = 118	
	LOD	Average Filter Blank	LOD	Average Filter Blank	LOD	Average Filter Blank
Be	0.05	0.005	0.1	0.04	ND	ND
Al	2	2	7	3	1	9
Ti	0.5	0.1	1	1	15	4
V	0.1	0.01	0.1	0.03	11	3
Cr	0.5	0.2	1	0.2	9	3
Mn	0.1	0.1	0.2	0.05	7	2
Fe	4	3	10	4	6	6
Co	0.05	0.01	0.1	0.04	4	1
Ni	0.3	0.2	0.8	0.2	3	1
Cu	0.5	0.3	2	0.4	4	6
Zn	4	1	9	5	2	1
As	0.1	0.01	0.1	0.1	1	0.1
Se	0.2	0.02	0.1	0.04	1	0.4
Sr	0.1	0.02	0.2	0.1	1	0.3
Mo	0.1	0.01	0.1	0.03	1	0.4
Ag ^c	0.1	0.01	0.2	0.08	1	0.1
Cd ^c	0.02	0.004	0.1	0.05	1	0.1
Sn ^c	0.1	0.03	0.2	0.08	1	0.2
Sb ^c	0.1	0.01	0.4	0.2	1	0.2
Cs ^c	0.01	0.01	0.05	0.02	3	3
Ba ^c	0.1	0.05	0.2	0.1	3	5
La ^c	0.03	0.01	0.06	0.02	3	6
Ce ^c	0.1	0.01	0.08	0.02	3	5
Tl	0.05	0.01	0.1	0.04	ND	ND
Pb	0.2	0.1	0.6	0.1	3	1
U	0.05	0.02	0.12	0.01	ND	ND

Note: LOD are calculated as: ^a measured LOD in ng mL⁻¹ x 20 mL/ 21.6 m³; ^b measured LOD in µg cm⁻² x 11.641 cm² x 1000/ 21.6 m³; ^c Semi-quantitative results by ED-XRF.

presence of HF and H_3BO_3 [14], the LOD of all elements determined after HF digestion were up to 5 times higher. Also, compared to ED-XRF analysis for most of the elements, the LOD values for digestion with 40% (v/v) HNO_3 were up to 100 times lower. The only exceptions were Al and Zn which showed lower LOD when analysed by ED-XRF.

The elemental concentrations of filter blanks digested by both digestion procedures were below LOD for all metals.

3.2. Analysis of Spiked Filters and SRMs

Analysis of spiked blank filters at concentration levels similar to samples were used to monitor for either loss of analytes or sample contamination during digestion. The elemental recoveries for spiked blank filters digested by both procedures ranged from 85% to 110% indicating that no significant loss or contamination was associated with any of the digestion procedures and ICP-MS measurements.

The most common approach for validation of the efficiency digestion procedures is the estimation of recoveries of metals from SRMs with composition and structure similar to that of the samples. In our preliminary studies using microvessels for analysis of SRM 1648 we used US EPA method 3051 [39], US EPA Compendium Method IO-3.1 [40] with few modifications [19], and the digestion procedure with 40% (v/v) HNO_3 based on the work of Lee *et al.* [41] and optimized for our laboratory conditions [33, 34]. Our results (Table 4) showed that compared to digestion with concentrated HNO_3 , the digestion with 40% (v/v) HNO_3 provided similar recoveries for most of the elements. Using the mixture of 16.7% $\text{HCl}/5.56\%$ (v/v) HNO_3 improved the digestion efficiency of Sb by *ca.* 10%. In this case, elements like ^{75}As and ^{51}V suffered severe spectral interferences by the Cl-containing species formed in the plasma ($^{40}\text{Ar}^{35}\text{Cl}$ and $^{35}\text{Cl}^{16}\text{O}$, respectively) and were acquired using the octopole collision cell system with He as the collision gas, which lowered the sensitivity and precision by 10% or more [19]. Thus the digestion procedure using 40% (v/v) HNO_3 was further investigated and validated by comparison with the HF-digestion procedure.

Elemental recoveries obtained for analysis of SRM 1648 showed that the digestion with 40% (v/v) HNO_3 provided recoveries of 80% or better for most of the elements of interest, such as Ni, V, Zn, Co, Cd, Cu, Mn, Pb, As and Se (Table 4). As expected, the total digestion procedure improved the dissolution of elements that are known to be associated with siliceous materials and/or refractory compounds of airborne PM such as Al, Cr and Ti. Recoveries of Cs, Ce, La, and U in the HF-digested samples were also increased by $\sim 30\%$ compared to HNO_3 digestion, probably due to formation of fluoride compounds that are soluble in H_3BO_3 . Also, the complexation properties of HF may explain better dissolution of Sb after HF digestion of the sample.

However, the presence of HF decreased the recovery of Se from 107% to 90%. Similar results were reported by Swami *et al.* [13] who suggested that formation and volatilization of SeF_4 may account for some loss of Se during digestion. The results of the total digestion procedure used in our study (Procedure 2) were generally in good agreement with results published by other groups. The

precision of measurements, expressed as standard deviation of repeated analysis, was comparable for both digestion procedures (Table 4).

Whilst SRM 1648 exemplifies the composition of the fraction of air particulate matter with particle size up to 53 μm , SRM 2783 (PM_{2.5} air particulate matter deposited on a polycarbonate filter membrane) resembles the fine atmospheric aerosols collected on filters and for this reason, it can give a better indication of the digestion efficiency of PM_{2.5} samples used in monitoring and fingerprinting studies. The digestion of SRM 2783 using 40% (v/v) HNO_3 provided recoveries that ranged for 90% to 114% for most of the elements except for Cr, Ti and U for which the recoveries were 55%, 44% and 76%, respectively (Table 5). As expected, the a higher microwave extraction efficiency for Ti and U was obtained in the presence of HF reaching values of 70% and 92% respectively, whereas Cr results were well above the certified values, probably due to matrix-induced interferences. The concentration values obtained with both digestion procedures for non-certified elements were not significantly different (t-paired test, $p < 0.05$), suggesting that unlike for SRM 1648, the simple digestion procedure (no HF) studied in this work, yielded a complete dissolution of most of elements present in SRM 2783.

3.3. Analysis of Ambient PM_{2.5} Samples

Although the analysis of the SRMs provide a good assessment of the digestion efficiency they cannot fully reveal the efficacy of the digestion of aerosol samples, mainly because of differences in sample mass, particle size and matrix composition. In order to overcome these uncertainties, the results of ICP-MS analysis of fine atmospheric aerosols digested with 40% (v/v) HNO_3 were firstly compared to total digestion (Procedure 2) prior to ICP-MS analysis of co-located samples.

The concentration range for most elements present in samples analyzed in this study covers one to two orders of magnitude. The major elements were Fe and Al with average concentrations of 74 ng m^{-3} and 47 ng m^{-3} , respectively. Average concentrations of Cd, Mo, Ag, Co, Ce and La were below 1 ng m^{-3} , whereas Be, Cs, Tl and U were below LOD for all analyzed samples. Concentrations of other elements ranged from 1 to 25 ng m^{-3} . It is worth noting that the higher LOD of HF/ HNO_3 / H_3BO_3 digestion in comparison to simple nitric acid digestion caused a significant decrease in the number of samples with detectable concentrations. For example, the percentage of samples quantified after nitric acid digestion (no HF) for the presence of Cd and Cr dropped from 67% and 21% to 3% and 2%, respectively. Also, the frequency of detection for Ni, Cu, Zn, Sn, and Sb was decreased by 2 to 5-fold.

Although the co-located samples inherent concentration differences that are related to collection, handling and storage of samples prior to ICP-MS analysis, they have been shown to be useful for comparisons similar to this study [43, 44]. Linear regression analysis of PM_{2.5} mass collected by both co-located samplers showed a strong correlation (Pearson correlation coefficients $r = 0.92$; $N = 125$) with slope 0.95 ± 0.02 , which indicates that both samplers provided consistent sampling efficiency.

Table 4. Elemental Recoveries in SRM 1648 Determined by ICP-MS After Microwave-Assisted Acid Digestion^a

Element	Concentration (mg kg ⁻¹) Unless Noted as (%)	Celo <i>et al.</i> [33, 34]		This study		Swami <i>et al.</i> [13]	Karthikyeen <i>et al.</i> [15]	Wu <i>et al.</i> [42]	Kulkarni <i>et al.</i> [17]	Toscano <i>et al.</i> [21]
		Conc. HNO ₃	5.56% (v/v) HNO ₃ /16.7% (v/v) HCl	40% (v/v) HNO ₃	HF/HNO ₃ /H ₃ BO ₃	HNO ₃ /H ₂ O ₂ /HF/H ₃ BO ₃	HNO ₃ /H ₂ O ₂ /HF	HNO ₃ /H ₂ O ₂ /HF/H ₃ BO ₃	HNO ₃ /HF/H ₃ BO ₃	HNO ₃ /HF
Al	3.42%	26 (8.3)	49(8.4)	50 (1)	86 (10)	NR	NR	NR	104 (8)	91 (2)
Ti ^b	0.40%	17 (15)	53(12)	28 (2)	73 (10)	NR	NR	97 (1)	107 (4)	NR
V	127	70 (2)	91(5.7)	83 (7)	96 (6)	86 (42.0)	105 (4)	105 (1)	101 (6)	87 (3)
Cr	403	23 (9)	32(8.3)	30 (5)	56 (14)	85 (9.6)	82 (7)	94 (1)	81 (8)	79 (7)
Mn	786	84 (2)	93(7.7)	94 (8)	99 (7)	109 (3.3)	99 (3)	99 (1)	96 (5)	97 (5)
Fe	3.91	72 (1)	80(5.8)	82 (11)	92 (10)	107 (5.0)	86 (2)	NR	98 (4)	102 (10)
Co ^b	18	70 (3)	80(3.5)	81 (5)	90 (6)	109 (12.0)	87 (1)	108 (2)	98 (8)	NR
Ni	82	76 (2)	80(4.2)	89 (7)	93 (10)	103 (10.3)	109 (3)	99 (1)	99 (4)	83 (4)
Cu	609	83 (1)	80(7.7)	97 (6)	91 (5)	96(4.6)	90 (3)	89 (1)	91 (7)	97 (5)
Zn	0.48%	94 (2)	90(6.0)	116 (9)	94 (4)	108 (7.0)	109 (14)	93.3 (0.2)	101 (9)	120 (4)
As	115	91 (1)	99(4.3)	104 (8)	102 (4)	101 (1.9)	94 (2)	120 (1)	109 (7)	91 (3)
Se	27	NR	NR	107 (10)	90 (3)	NR	NR	100 (7)	107 (10)	NR
Cd	75	91 (1)	92(7.0)	107 (7)	99 (5)	100 (3.5)	98 (3)	98 (1)	112 (4)	89 (3)
Sb ^b	45	16 (11)	86(8.6)	74 (7)	101 (9)	105 (2.5)	NR	98 (1)	86 (3)	NR
Ba ^b	737	74 (6)	91(6.6)	82 (8)	102 (10)	NR	NR	102 (1)	110 (3)	NR
La ^b	42	NR	NR	57 (7)	89 (7)	NR	NR	NR	98 (6)	NR
Ce ^b	55	NR	NR	62 (7)	91 (9)	NR	NR	NR	107 (2)	NR
Pb	0.66%	94 (1)	90(4.8)	101 (9)	98 (4)	110 (4.5)	77 (3)	NR	108 (5)	96 (2)
U	5.5	NR	NR	71 (5)	90 (7)	NR	NR	99 (1)	88 (6)	NR

Note: ^aValues in parenthesis are standard deviations of repeated analysis; ^bNon certified values; NR- non reported.

Table 5. Elemental Recoveries in SRM 2783 Determined by ICP-MS After Microwave-Assisted Acid Digestion

Element	Certified/Non Certified ^a (ng)	Near-Total Digestion ^b		Total Digestion ^b		Recovery (%) [17]
		Measured (ng)	Recovery (%)	Measured (ng)	Recovery (%)	
Be	NR	0.54 (0.08)	—	0.6 (0.2)	—	—
Al	23210 (530)	21064 (196)	91 (1)	20889 (372)	90 (2)	96 (4)
Ti	1490 (240)	651 (4)	44 (1)	1036 (30)	70 (12)	111 (16)
V	48.5 (6.0)	46 (1)	95 (2)	45.8 (0.1)	94 (1)	107 (29)
Cr	135 (25)	62 (1)	46 (1)	NR	NR	NR
Mn	320 (12)	319 (1)	100 (1)	304 (4)	95 (1)	117 (0)
Fe	26500 (1600)	26420 (18)	100 (1)	24600 (664)	93 (3)	111 (4)
Co	7.7 (1.2)	7.1 (0.1)	92 (1)	7.4 (0.2)	96 (3)	94 (8)
Ni	68 (12)	66 (1)	97 (2)	67 (1)	100 (2)	101 (9)
Cu	404 (42)	406 (5)	101 (1)	345 (30)	85 (7)	112 (6)
Zn	1790 (130)	2036 (39)	114 (2)	1680 (35)	94 (2)	92 (1)
As	11.8 (1.2)	12.0 (0.1)	102 (1)	10.7(0.3)	91 (2)	92 (8)
Se	NR	2.9 (0.7)	—	<LOD	—	—
Sr	NR	40.7 (0.3)	—	40.0 (0.5)	—	—
Mo	NR	16.9 (0.3)	—	18.2 (0.4)	—	—
Ag	NR	<LOD	—	<LOD	—	—
Cd	NR	<LOD	—	<LOD	—	—
Sn	NR	22.2 (0.6)	—	20 (1)	—	—
Sb	71.8 (2.6)	68 (1)	95 (1)	65 (2)	91 (2)	107 (6)
Cs	NR	2.4 (0.2)	—	2.4 (0.1)	—	—
Ba	335 (50)	310 (3)	92 (1)	302 (5)	90 (2)	104 (9)
La	NR	10.2 (0.1)	—	10.4 (0.1)	—	—
Ce ^c	23.4 (3.5)	21.2 (0.4)	91 (2)	21.6 (0.2)	92 (1)	91 (5)
Tl	NR	0.14 (0.04)	—	0.10 (0.07)	—	—
Pb	317 (54)	342 (1)	108 (1)	291 (2)	92 (2)	104 (7)
U ^c	1.234 (0.024)	0.94 (0.01)	76 (1)	1.13 (0.09)	92 (7)	97 (8)

Note: ^a Values in parenthesis are uncertainties at the 95% confidence level, reported by NIST; ^b Values in parenthesis are standard deviations of two replicates (the same filter, split in half and analyzed separately). Concentrations are blank subtracted using the blank filters provided by NIST and analyzed together with samples; ^c Non certified values.

Table 6. Comparison of the Analytical Results for Analysis of PM_{2.5} Samples by ICP-MS and ED-XRF

Element	Procedure 1 vs Procedure 2				ICP-MS (Procedure 1) vs ED-XRF			
	N ^a	Slope ^b	Intercept ^c	Pearson Correlation Coefficient	N ^a	Slope ^b	Intercept ^c	Pearson Correlation Coefficient
				(p < 0.05)				(p < 0.05)
Al	41	0.92 ± 0.09	0.067 (0.08)	0.75	Semi quantitative ED-XRF results			
Ti	19	0.45 ± 0.12	-0.011 (0.77)	0.75	N < 3	NA	NA	NA
V	109	0.88 ± 0.05	0.016 (0.28)	0.89	21	0.81 ± 0.09	-0.43 (0.76)	0.95
Mn	95	0.94 ± 0.19	0.007 (0.75)	0.9	31	0.73 ± 0.04	-5.10 (0.09)	0.85
Fe	69	0.98 ± 0.17	-0.247 (0.74)	0.78	1032	0.86 ± 0.05	3.04 (0.08)	0.97
Ni	9	0.91 ± 0.22	0.001 (0.76)	0.93	19	0.93 ± 0.14	-0.43 (0.76)	0.86
Cu	10	1.15 ± 0.26	-0.252 (0.21)	0.86	Semi quantitative ED-XRF results			
Zn	10	0.85 ± 0.28	0.140 (0.56)	0.87	439	0.97 ± 0.02	3.63 (0.05)	0.97
As	63	0.85 ± 0.06	0.001 (0.98)	0.83	14	0.89 ± 0.09	-0.88 (0.03)	0.89
Se	33	1.21 ± 0.11	0.017 (0.19)	0.81	47	1.03 ± 0.09	-0.43 (0.09)	0.95
Sr	18	0.83 ± 0.22	0.002 (0.79)	0.85	22	1.00 ± 0.07	-0.88 (0.02)	0.98
Mo	13	0.82 ± 0.08	0.004 (0.27)	0.83	N < 3	NA	NA	NA
Cd	8	0.96 ± 0.28	0.003 (0.15)	0.98	N < 3	NA	NA	NA
Sn	12	1.15 ± 0.12	-0.010 (0.25)	0.98	73	0.79 ± 0.04	0.08 (0.67)	0.88
Sb	13	0.87 ± 0.16	0.013 (0.53)	0.76	N < 3	NA	NA	NA
Ba	68	1.02 ± 0.16	0.026 (0.16)	0.81	Semi quantitative ED-XRF results			
La	50	0.85 ± 0.17	0.004 (0.42)	0.78	Semi quantitative ED-XRF results			
Ce	13	1.00 ± 0.26	-0.003 (0.52)	0.78	Semi quantitative ED-XRF results			
Pb	62	1.09 ± 0.16	0.010 (0.73)	0.78	92	1.12 ± 0.03	-2.01 (0.03)	0.98

Note: ^aNumber of samples above quantitation limit; ^bValues reported as slope ± 95% confidence interval; ^cValues in parenthesis are the 95% significance level.

Results from the analysis of co-located samples digested with two different procedures were compared by linear regression analysis. Pearson regression coefficients were above 0.75 (p < 0.05), demonstrating that both procedures provided comparable results (Table 6).

For most of the elements, the slopes were not significantly different from 1.00 (± 95% confidence interval). One notable exception was Ti, with a slope of 0.45 ± 0.12, indicative of a poor extraction efficiency using nitric acid digestion. Also the results for Se analysis (slope of 1.21 ± 0.11) suggested that the presence of HF in the digestion solution may cause some loss of Se during digestion [13].

The accuracy of Procedure 1 (no HF) was also checked by comparing results of analysis of over 1500 PM_{2.5} samples by both ED-XRF and ICP-MS methods. Due to poorer LOD of the ED-XRF method, the number of samples with elemental concentrations quantified by this technique was much lower than ICP-MS. Hence, the comparison was only possible for 10 elements (Ni, V, Fe, Zn, Mn, Pb, As, Se, Sr, Sn). As illustrated in Fig. (2), the results obtained by both methods were in very good agreement, with slopes of linear regression lines ranging from 0.86 to 1.12 and Pearson correlation coefficients better than 0.95. This suggests that, the simple microwave digestion (no HF) procedure using microvessels is an optimum method for estimating trace metal concentrations in PM_{2.5} for monitoring purposes.

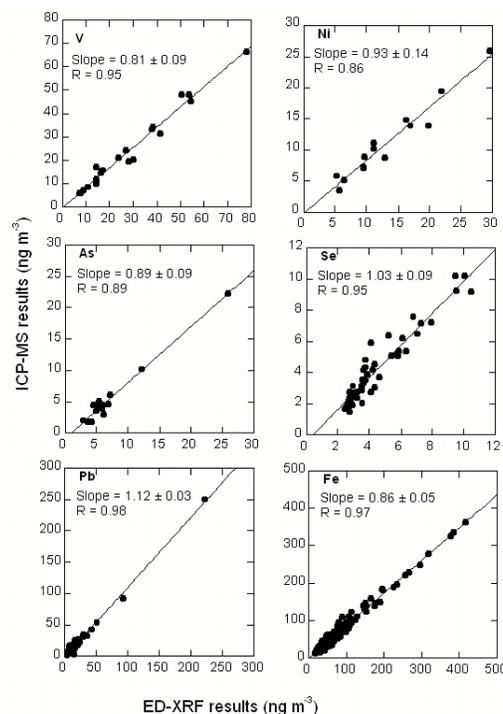


Fig. (2). Examples of correlation between concentrations obtained via ED-XRF and ICP-MS using a simple digestion method (no HF).

CONCLUSIONS

The microwave assisted digestion procedure, using 40% (v/v) HNO₃ prior to ICP-MS analysis, has proved to be an effective and simple method to measure trace elements in PM_{2.5}, often not detectable by ED-XRF. The digestion efficiency validated by analyzing SRM 2783 and co-located PM_{2.5} samples showed that the recovery of most of the trace elements of interest (e.g. Ni, V, Zn, Co, Cd, Cu, Mn, Pb As, and Se) was higher than 80%. By the use of microvessels, the amount of acids used for digestion was significantly reduced, and the sample throughput was increased by two-fold. Compared to the digestion using a HNO₃/HF/H₃BO₃ mixture, this method provides lower LOD for most elements, requires fewer manipulations, is safer, and requires smaller amounts of reagents. These factors make it quite preferable for routine analysis of the large number of samples commonly generated in air quality monitoring and fingerprinting studies. However, the total dissolution of several trace elements such as Ti, Cr and U in PM_{2.5} and Ti, Cr, Al, lanthanides, and Sb in coarse fractions of PM would require digestion in the presence of HF.

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